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Synthesis, Macroscopic and Local Probe Characterization of AgCrO_2 and CdCr_2S_4

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Abstract

The search of new materials with new and/or enhanced physical properties has, nowadays, a strict relation with the evolution of technology. The hunt for systems exhibiting simultaneous (anti)ferroelectric and (anti)ferromagnetic orders has re-started in the last years, and remains as one of the hot topics for Physic, Chemistry and Materials Science scientific communities. This is triggered by the possibility to apply these materials into, *e.g.*, new multiferroic memories that could be written electrically and read magnetically (or vice-versa).

This thesis presents an experimental study on two of these so-called multiferroic materials, the AgCrO_2 delafossite and CdCr_2S_4 spinel type compounds. Different methods have been tested for the synthesis of delafossite silver chromium oxide AgCrO_2 , namely, solid state reaction (SSR) and sol-gel combustion. The processes were optimized regarding complexing/combusting agents, temperature and duration of the heat treatments, as well as the processing atmospheres. The solid state reaction method yielded single phase samples of AgCrO_2 structure whereas in the sol-gel method almost single phase samples were produced but traces of secondary phases were found. The formation of the AgCrO_2 phase was followed at each synthesis step through x-ray powder diffraction analysis.

Magnetic and electric characterization allowed to show that the produced samples have the expected behavior near the ordering temperature (ferroelectric and antiferromagnetic). The magnetic susceptibility above T_N (21 K) has shown a peculiar behavior, generally attributed to the development of 2D short-range magnetic correlations due to strong frustration coming from antiferromagnetic exchange interactions in a triangular lattice. However, correlating our magnetization results with our PAC data, a slightly different picture emerges. In fact, we have evidence that a second local environment emerges below 100 K, possibly due to Ag lattice displacements. Our results suggest that these are precursor effects of the ferroelectric/antiferromagnetic phase transition.

In parallel we have developed a system to perform the synthesis of sulfide compounds. In particular, in this work we prepared the CdCr_2S_4 compound with spinel structure and performed a thorough study of its physical properties.

High quality polycrystalline samples were prepared using a double evacuated quartz ampoule, which is a branch of the solid state reaction method. Powder x-ray diffraction analysis allowed to follow the formation of the phase at each step of the synthesis. At the end we were able to produce a high quality single phase sample. We have performed the structural refining using Rietveld analysis which allowed verify the excellent agreement with those reported in the literature.

The magnetic characterization of the CdCr_2S_4 sample was performed showing that besides the good agreement of the T_C and μ_{eff} , short-range magnetic correlations (SRMC) (or spin-cluster) in the PM phase were observed and it was possible to define a new temperature scale $T_G \sim 116$ K where these clusters start to form.

Local probe studies were performed using the ^{111}In probe, and a systematic study allowed to

verify the evolution in temperature of the EFG's detected by the probe. In fact we show that below 120 K time dependent interactions set in which can be connected with the onset of local distortions triggered by the magnetic short-range correlations observed in the magnetization data.

Resumo

A procura de novos materiais com propriedades novas e/ou melhoradas, possui hoje em dia, uma estreita relação com a evolução da tecnologia. Desencadeada pela possibilidade de aplicação destes materiais, *p.e.*, em memórias multiferróicas que demonstram a possibilidade de serem gravadas electricamente e lidas magneticamente (e vice-versa), uma demanda por sistemas que exibem simultaneamente ordens (anti)ferroeléctrica e (anti)ferromagnéticas, renasceu nos últimos anos, e continua a ser um dos tópicos mais discutido nas comunidades de Física, Química e Ciências dos Materiais.

Neste trabalho é apresentado um estudo experimental em dois destes materiais, AgCrO_2 do tipo delafossite e CdCr_2S_4 do tipo espinela, reivindicados como multiferróicos. Diferentes métodos de síntese foram testados para a preparação do composto AgCrO_2 , nomeadamente, reacção de estado sólido e combustão de sol-gel. Os processos foram otimizados, tendo em consideração os agentes complexantes/combustão, temperatura e duração dos tratamentos térmicos bem como as atmosferas de síntese. Pelo método de reacção por estado sólido foi possível a produção de amostras puras (uma única fase cristalográfica), ao passo que pelo método de sol-gel além do composto desejado, pequenas contaminações foram encontradas. A formação da fase AgCrO_2 foi acompanhada entre cada passo de síntese através da análise por difracção de raios-x.

A caracterização magnética e eléctrica permitiu observar que as amostras produzidas apresentam o comportamento esperado junto à temperatura de ordenamento (ferroeléctrico e antiferromagnético). A susceptibilidade magnética acima de T_N (21 K) mostrou possuir um comportamento peculiar, geralmente atribuído ao desenvolvimento de correlações magnéticas de curto alcance 2D devido à forte frustração que emerge das interacções de troca antiferromagnéticas numa rede triangular.

Contudo, correlacionando os nossos resultados de magnetização e de PAC (Correlações Angulares Perturbadas), um cenário ligeiramente diferente surge. Na verdade, possuímos evidências do aparecimento de um segundo ambiente local abaixo de 100 K, possivelmente devido a deslocamentos do átomo de Ag na rede. Os nossos resultados sugerem que estes são precursores da transição ferroeléctrica/antiferromagnética.

Em paralelo, foi desenvolvido um sistema para efectuar a síntese de compostos de enxofre. Em particular, neste trabalho foi preparado o composto CdCr_2S_4 pertencente à família das espinelas e um estudo pormenorizado das suas propriedades físicas foi realizado.

Amostras policristalinas foram produzidas utilizando um sistema de dupla ampola de quartzo fechada em vácuo, que é uma variante do método por reacção de estado sólido. A análise por difracção de raios-x de pós, permitiu um acompanhamento da formação da fase desejada ao longo de cada passo da síntese. No final conseguimos produzir uma amostra de alta qualidade (uma única fase cristalográfica). O refinamento estrutural foi realizado, recorrendo a uma análise de Rietveld, o que permitiu verificar a boa concordância das suas propriedades com as reportadas na literatura.

A caracterização magnética da amostra de CdCr_2S_4 realizada, mostra que além de uma boa concordância com T_C e μ_{eff} , correlações magnéticas de curto alcance (SRMC) (ou clusters de spin) estão presentes na fase PM. Sendo assim possível definir uma nova escala de temperatura $T_G \sim 116$ K onde se inicia a formação destes clusters.

Estudos de sonda local foram realizados com a utilização de ^{111}In como sonda, e um estudo sistemático permitiu verificar a evolução na temperatura dos EFG's detectados pela sonda. De facto, mostramos que abaixo de 120 K interações dependentes do tempo estabelecem-se e podem ser relacionadas com o começo de distorções locais activadas pelas correlações magnéticas de curto alcance observadas nos dados de magnetização.

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List Of Abbreviations

- AFM, Antiferromagnetic
- BSE, Backscattered Electrons
- CEMUP, Centro de Materiais da Universidade do Porto
- ESCA, Electron Spectroscopy for Chemical Analysis
- EDS, Energy Dispersive X-ray Spectroscopy
- EDX, Energy Dispersive X-ray Spectroscopy
- EFG, Electric Field Gradient
- FE, Ferroelectric
- FEP, Ferroelectric Polarization
- FM, Ferromagnetic
- FC, Field-Cool
- FWHM, Full Width at Half Measurement
- H , Magnetic Field
- HI, Hyperfine Interactions
- IFIMUP-IN, Instituto de Física dos Materiais da Universidade do Porto
- LRMI, Long Range Magnetic Interactions
- M , Magnetization
- ME, Magnetoelectric
- MES, Mössbauer Effect Spectroscopy
- MHF, B_{hf} , Magnetic Hyperfine Field
- NMR, Nuclear Magnetic Resonance
- NO, Nuclear Orientation
- PAC, Perturbed Angular Correlations
- PAD, Perturbed Angular Distribution
- PCM, Point Charge Model
- PXRD, Powder X-ray Diffraction
- RT, Room Temperature
- SE, Secondary Electrons
- SSR, Solid State Reaction
- SGM, Sol-Gel Method
- SQUID, Superconducting Quantum Interference Device
- SRMC, Short Range Magnetic Correlations
- SRMI, Short Range Magnetic Interactions
- T , Temperature
- T_C , Curie Temperature
- T_N , Néel Temperature
- TSL, Triangular Spin Lattice
- TGA, Thermogravimetric Analysis
- XRD, X-ray Diffraction
- XPS, X-ray Photoelectron Spectroscopy
- ZFC, Zero Field Cooling

Introduction

Since the beginning of ceramic pottery, the development, synthesis and use of new materials with desired properties has changed considerably the developing society. The use of these materials in a vast field of applications has marked entire civilizations and sometimes even categorizes periods in human history.

Nowadays the use of new inorganic ceramic materials, shapes the way of life as they are incorporated into modern technology, and we become more and more dependent of them. Microelectronics is a recent field in modern science. The understanding of the properties of these materials is a must, in order to improve them, making them smaller and more efficient^[1]. In this field, the flow of electric charges was exploited in microprocessors, transistors and a vast set of other domestic appliances. However, with the objective to improve the existing materials and to go forward in the multi-functionality of devices (for example, carrying out data processing and storage on the same device)^[1], researchers are exploring another intrinsic property of electrons - the spin. It was discovered that spin could carry information among devices, as it is accomplished by the charge flow. Spin has advantages in comparison with charge, because it can be manipulated by external magnetic field and possess a long relaxation time that enable processing of information. These characteristics put forward the possibility to develop new and more efficient devices than those using the charge paradigm^[2-5].

Therefore, using materials like semiconductor with magnetic properties, gives the possibility to use spin-related phenomena that emerge from exchange interactions. The electric control of ferromagnetic ordering, gave birth to a new field in electronics, involving the use of spin-states inside semiconductor materials, the so called semiconductor spintronics^[1,6].

Physical, Chemical and Materials Science scientific communities set on a meticulous search for new solid state materials where these properties could be exploited. This search lead to systems that exhibit simultaneous (anti)ferroelectric and (anti)ferromagnetic orders, the so-called multiferroic materials. Researchers went beyond searching the simultaneous electric and magnetic orders, but also having in mind the maximization of its coupling, so they could have the possibility to manipulate the magnetic degrees of freedom by electric field or vice-versa. The high potential of use present in new non volatile memories for computers and cellular phones has brought a technological interest in these multiferroic materials.

In the last years, the search for ferroelectric properties in materials where magnetic properties are known, already have shown results, namely in manganites (RMnO_3 , $\text{R}=\text{Gd, Tb, Lu, Y, Er} \dots$) with perovskite or hexagonal structure and more recently in chromites with spinel (DCr_2X_4 , $\text{D}=\text{Cd, Hg, Co Fe, Mn}$ e $\text{X}=\text{O, S, Se}$) or delafossite (ACrX_2 , $\text{A}=\text{Ag, Cu}$ e $\text{X}=\text{O}$) structure^[7-11].

In this kind of compounds there still exists some controversy about the mechanisms that drive the coupling between the dielectric and magnetic properties. Its known that lattice local distortions

have a fundamental influence in the ferroelectric and ferromagnetic proprieties and the understanding of these phenomena requires an adequate description of the structural, magnetic and charge degrees of freedom.

With this work we hope to contribute to clarify some issues about two of those systems, the AgCrO_2 and the CdCr_2S_4 . For that, the synthesis of sulphur chalcogenide spinel and silver chromium oxide with high degree of purity is required. Since in most cases the mechanisms associated to the macroscopic properties have origin at an atomic level, a study of the distortions at a local level using the perturbed angular correlation technique is also an important source of information.

In this way, this work presents a contribution for the experimental study of multiferroic semiconductor materials with magnetoelectric coupling. The thesis organization can be summarized as follows: a brief introduction to the materials under study, and in particular to the AgCrO_2 and CdCr_2S_4 , where the crystal structure and studies of magnetic and dielectric properties are presented; the techniques used to prepare and characterize the systems; Our studies on the delafossite system are presented followed by the spinel one; At the end general conclusions to the work are presented.

Chapter 1

General Aspects

1.1 Multiferroic and Magnetoelectric Materials

Ferromagnetic materials possess spontaneous magnetization which can be switched hysteretically by the influence of a magnetic field. In the same way, ferroelectric materials present spontaneous electric polarization which can be switched by an electric field. Ferroelectricity and ferromagnetism are on the top of the list of properties researched in solid state materials.

Interestingly, there are materials where electric and magnetic order degrees of freedom coexist. Within this scope it is important to distinguish between multiferroic and magnetoelectric materials. According to *Eerenstein et al*^[12] multiferroic materials are those exhibiting two or even three ferroic properties, namely ferroelectricity, ferromagnetism and ferroelasticity, in the same phase (see figure 1.1.1 from *Hill et al*^[13]). On the other hand magnetoelectric materials belong to the group of compounds that are electrically and magnetically polarizable and in addition develop polarization when under a magnetic field and magnetization in the presence of an electric field^[12]. However, in current literature is often found that the definition of multiferroic materials is extended to include non-primary order parameters, like antiferromagnetism and ferrimagnetism.

Multiferroic and magnetoelectric materials allow the opportunity to efficiently develop control of magnetization and/or polarization by an electric field and/or magnetic field (see figure 1.1.1), and in this way to develop new multifunctional applications^[14].

After the prediction of a magnetoelectric effect in Cr_2O_3 by Dzyaloshinskii^[15] and its measurement^[16,17], many new multiferroic and/or magnetoelectric materials were reported during the 1960s and 1970s. Recently, special attention was given to materials where a strong coupling between the magnetic and dielectric degrees of freedom is present, since they would have the possibility to tune electrically the magnetization or magnetically the electric polarization. This opened the prospect for new applications and triggered the revival of the interest on the magnetoelectric effect. In fact, materials exhibiting strong magnetoelectric coupling allow additional degrees of freedom in device design and thus they are very promising in magnetic data storage, high-frequency magnetic devices, spintronics and micro-electro-mechanical systems^[18], among other multiple applications^[12]. As an example of the highest importance of new prototype systems based in the magnetoelectric coupling, are devices able to read the spin states and to write the polarization states, to reverse the spin states by electric field and with this overcome the high writing energy in magnetic random access memories (MRAMs).

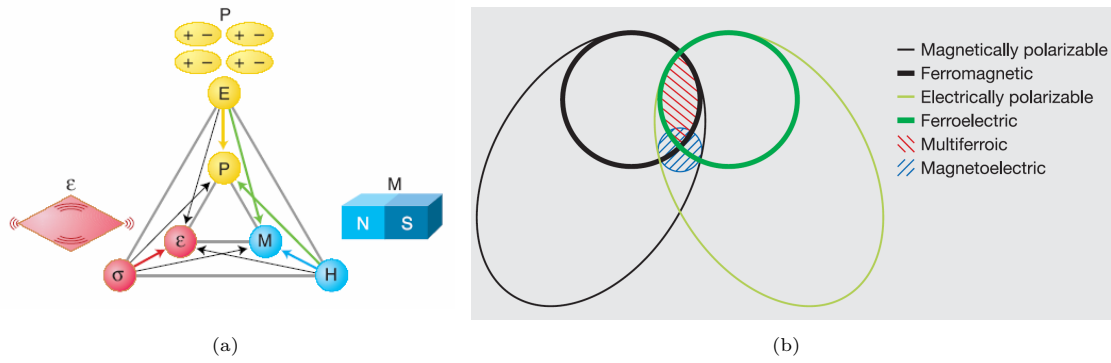


Figure 1.1.1: The electric field E , magnetic field H , and stress σ control the electric polarization P , magnetization M , and strain ε , respectively. In a ferroic material, P , M , or ε are spontaneously formed to produce ferromagnetism, ferroelectricity, or ferroelasticity, respectively. In a multiferroic material, the coexistence of at least two ferroic ordering forms leads to additional interactions a). The relationship between multiferroic and magnetoelectric materials b).

Of all magnetically and electrically polarizable materials only a smaller group are ferromagnetic or ferroelectric. Materials exhibiting simultaneous both ferroic properties appear rarely.

Despite the fact that materials can exhibit the presence of ferroelectricity and (anti)ferromagnetism, the relation between the two orders is not a sufficient conditions for a strong magnetoelectric coupling and so achieve a good mutual control among them. Luckily, recent works in this area managed to create and find more materials exhibiting such properties, especially in frustrated magnets, where a strong and intrinsic magnetoelectric coupling is present. In this respect AgCrO_2 and CdCr_2S_4 were recently claimed to be strong magnetoelectric materials. In this work we will focus our attention in these two compounds.

The range of applicability of the magnetoelectric effect in single phase compounds is still narrow because this effect is most of the times very small. However in cases like multilayered structures where piezoelectric and ferromagnetic layers are put together, this effect can be extremely enhanced and a giant magnetoelectric effect is accomplished^[19–21].

For a review of multiferroic and magnetoelectric materials the works from *M. Fiebig*^[20], *Li et al.*^[21] and more recently *Wang et al.*^[14] present a large insight and are recommended.

1.2 Antiferromagnetic Delafossite - AgCrO_2

Due to their peculiar magnetic and electric properties, systems with delafossite structure are now under special examination for the understanding of the microscopic origin of the coupling between the magnetic and electric degrees of freedom.

1.2.1 Crystal structure

The first compound observed to exhibit the delafossite structure $\text{A}^{1+}\text{B}^{3+}\text{O}_2$ was CuFeO_2 ^[22]. Here the Fe^{3+} ions were found to be localized at the B site surrounded by six oxygen atoms forming a regularly inclined octahedra, and connected to the monovalent atoms in the A site, which have a twofold linear coordination parallel to the c-axis. Many compounds with the general formula ABO_2

belonging to the delafossite family can be encountered where A is Pd, Pt, Cu, or Ag and B is Al, Ga, In, Sc, Y, Cr, Fe, rare earths, etc.

The delafossite structure can crystallize into two polymorphic forms^[23] (3R and 2H), one belonging to the space group $R\bar{3}m$ (3R) and a less common stacking variant of R phase the $P6_3/mmc$ (2H).

Within the rhombohedral description the crystal has three ABO_2 molecules per unit cell and, typically, lattice constants range from $a, b=2.8$ to 3.8 Å and $c=17$ to 19 Å. The other variant of the delafossite phase (2H) have the lattice constants range from $a=2.8$ to 3.5 Å and $c=11.2$ to 12.3 Å and only two ABO_2 formulas in the unit cell.

In this work we will focus our attention in the system with $\text{A}=\text{Ag}^+(\text{d}^{10})$ and $\text{B}=\text{Cr}^{3+}(\text{d}^3)$ which crystalizes in the space group $R\bar{3}m$.

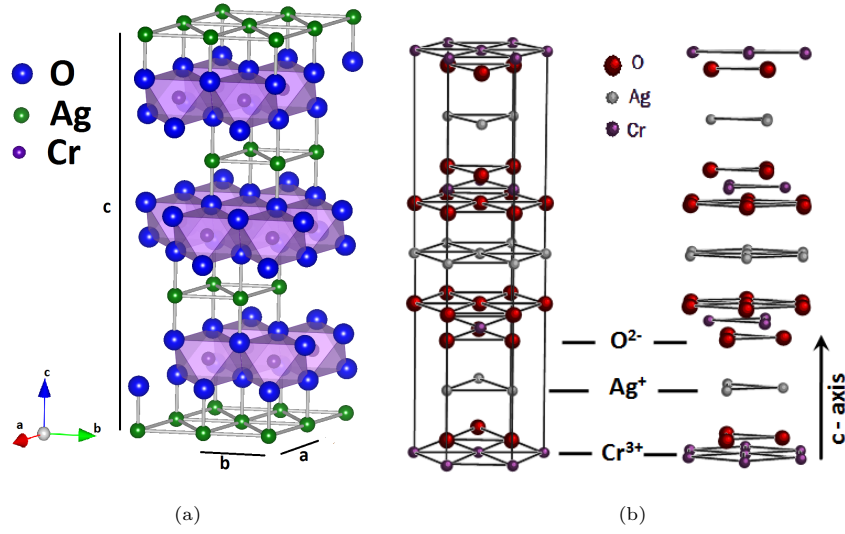


Figure 1.2.1: Polyhedron model of AgCrO_2 (a) and ball and stick model of AgCrO_2 (b).

We can describe this system (see figure 1.2.1) as being composed by edge-shared CrO_2 trigonal layers forming CrO_6 octahedrons with Cr^{3+} ^[24]. In each unit cell three successive CrO_2 layers are stacked along the c-direction with diamagnetic Ag^+ ions in the middle of these layers forming $\text{O} - \text{Ag} - \text{O}$ bridges. The triangular lattice planes formed by the B site atoms are stacked along the $[001]$ axis rhombohedrically^[25].

The hexagonal arrangement of the delafossite structure promote another perspective of the structure, where instead of oxygen octahedra arrangement a set of planes formed with the different ions is found in the form of $\text{O}^{2-} - \text{Cr}^{3+} - \text{O}^{2-} - \text{Ag}^+ - \text{O}^{2-} - \text{Cr}^{3+}$.

In the AgCrO_2 crystal, the CrO_6 octahedra connect each other in ab -plane to form a layer by sharing edges where each oxygen is coordinated by four cations (one A^+ and three B^{3+}) in a pseudotetrahedral arrangement^[26] and between those layers are silver atom layers.

1.2.2 Magnetic and Electric Properties

The physical properties of numerous delafossites were first reported as part of a large study on the synthesis, structure, and electrical transport properties of such systems by *Rogers, Shannon*, and

Prewitt.^[27–29]

The delafossite compounds are semiconductors when the A site is occupied by Cu or Ag and conductors when the A-site is occupied by Pd or Pt. In both kinds of compounds the conductivity is highly anisotropic^[22,30].

The ACrO_2 ($\text{A}=\text{Ag}, \text{Cu}$) delafossite system, which has a triangular-lattice antiferromagnetic structure, is one of the interesting class of chromium-based oxides that many people are investigating the magnetoelectric properties. Powder neutron diffraction studies^[7] proposed that the ground state of CuCrO_2 exhibits a spin chiral out-of-plane 120° spin structure in which three spins on a triangle form a 120° angle to each other and the spiral plane is normal to the triangular lattice plane (TLP) (see figure 1.2.2 a)). Thus, the spin system can be described as a highly isotropic one (namely, Heisenberg type) with a weak easy axis type of single ion anisotropy^[31]. Due to the similarities between the copper and silver delafossite systems, the same description is in order to the silver chromium oxide delafossite. *Kadowaki et al*^[32] describe the crystal structure of the Cr^{3+} triangular lattices stacking sequence as ABCABC... as illustrated in figure 1.2.2 c). In this way, the delafossite magnetic structure in the antiferromagnetically ordered phase (see figure 1.2.2) can be represented using nine sublattices of magnetic structures by ABC, $\text{A}'\text{B}'\text{C}'$ and $\text{A}''\text{B}''\text{C}''$ in $z=0$, $\frac{1}{3}c$, $\frac{2}{3}c$ planes, respectively (see figure 1.2.2 c)). In fact, *S.Seki et al*^[33] confirmed recently that the geometrical frustration of the antiferromagnetic interaction in ACrO_2 ($\text{A}=\text{Ag}, \text{Cu}$) favors a 120° spiral spin structure characterized by the modulation vector $(0.327\ 0.327\ 0)$ ^[34] and antiferroelectricity emerges upon that spin order^[33], that is, below the Néel temperature. Furthermore, they predicted that many trigonal materials with the same magnetic arrangement can be magnetoelectric multiferroic.

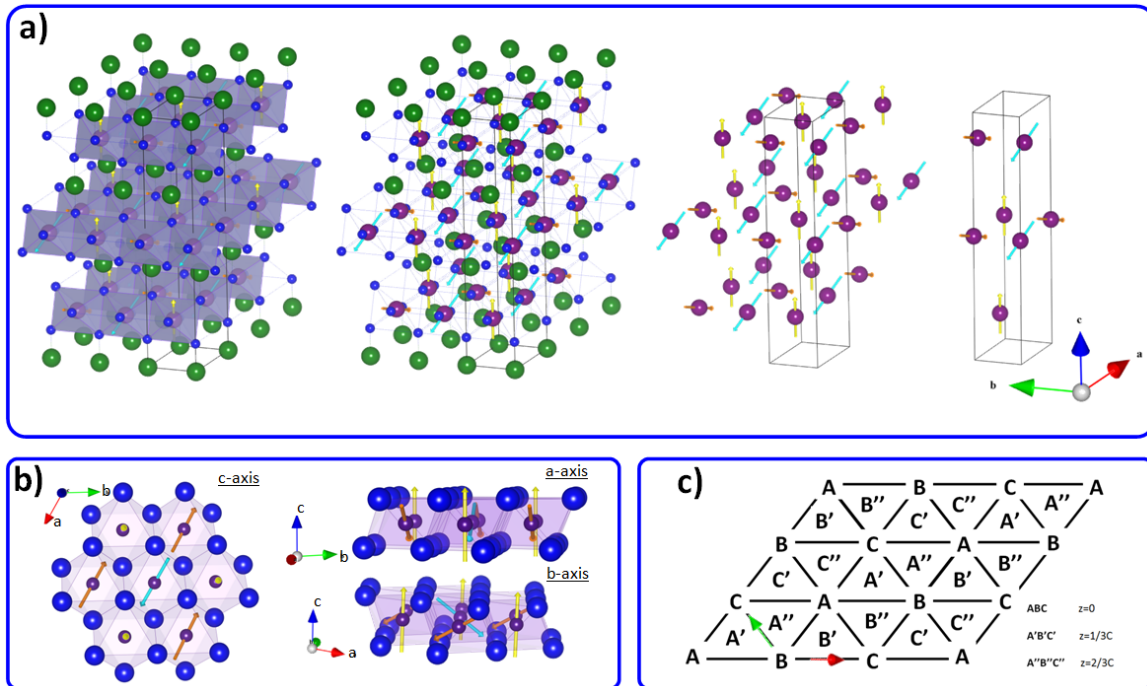


Figure 1.2.2: Model of the AgCrO_2 magnetic structure in the antiferromagnetically ordered phase. Simplification of the model into a single unit cell a). Spin orientation along the crystallographic axes b). *Kadowaki's* model of the magnetic structure c).

Given that multiferroism was found in ACrO_2 compounds, much research has to be done to shed light on the origin of the multiferroic behavior in these materials. As a matter of fact and as referred by the same authors the existence and possible direction of spontaneous polarization can be inferred by symmetry analysis of spin structure [35,36] but a comprehensive understanding of the microscopic origin of the coupling between ferroelectricity and magnetic order is still missing.

The AgCrO_2 delafossite in study exhibits a magnetic ordering below the Néel temperature of 21 K. At the same temperature occurs the dielectric ordering.

As recently reported by *Kan et al* [37] symmetry arguments imply that the ferroelectric polarization (FEP) can emerge not only along two fold rotational axis but also along a mirror plane. The authors also use *ab initio* calculations and show that these theoretical calculations for the ferroelectric polarization are in agreement with those obtained experimentally [24].

1.3 Ferromagnetic Spinel - CdCr_2S_4

Recent studies claim that a ferroelectric order can also be found in chromium-based magnetic systems with spinel structures [3,10]. In this work we have selected the CdCr_2S_4 spinel as it can be considered a model system to study the mechanism that drives the dielectric order in spinels, still under strong debate among the scientific community.

1.3.1 Crystal Structure

Compounds with the general formula $\text{A}^{2+}\text{B}_2^{3+}\text{X}_4^{2-}$ form the so called spinel family, that had their name due to the mineral spinel oxide MgAl_2O_4 . The crystal structure is characterized by a face-centered cubic (*fcc*) arrangement with a large unit cell, containing eight formula units (8 A-cations, 16 B-cations and 32-anions) [38], in a cubic close-packed arrangement of the anions, with the cations located in the interstitial positions. In the spinel crystal two different interstitial positions are present, one called the A-site position where the anions are in the vertices of a tetrahedron having the divalent cation (Cd^{2+}) at the center and a B-site with the divalent anions in the vertices, of an octahedron having the trivalent cation (Cr^{3+}) in the center.

The spinel structure crystallizes in the cubic $Fd\bar{3}m$ space group [38,39] with the following lattice parameters $a, b, c = 10.244 \text{ \AA}$ and $\alpha, \beta, \gamma = 90^\circ$. A polyhedron model of the structure can be visualized in figure 1.3.1.

Another structure related with the previous one, is the so-called inversed spinel. Here the tetrahedral sites are occupied by trivalent cations whereas the octahedral sites by divalent cations. A random distribution of the divalent and trivalent cations, in the octahedral B-site is also possible to be formed in the inverse structure. In this work only the normal spinel structure will be considered.

For many purposes, as in the study of electric quadrupole interactions, the atomic point symmetry is crucial. In this way the A-site can be described as a cubic environment, and thus it possess four threefold axes resulting in a null electric field gradient. On the other hand the atoms at B and X sites have a axial symmetric field gradients due to an unique threefold axis.

1.3.2 Magnetic and Electric Properties

The CdCr_2S_4 compound is characterized as being a ferromagnetic material with a Curie temperature of $T_C = 84.5 \text{ K}$ [38]. Moreover, it as a paramagnetic Curie-Weiss temperature of $\Theta_{CW} = 152 \text{ K}$ [38].

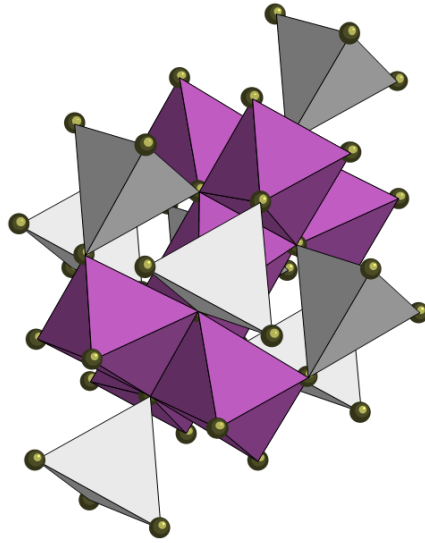


Figure 1.3.1: Polyhedron model of CdCr₂S₄ structure. The cadmium tetrahedron (grey) and the chromium octahedron (purple) with the sulphur atoms in the vertices.

Recently, this compound has received special attention^[9], since it was claimed the coexistence of ferromagnetism and relaxor ferroelectricity together with colossal magnetocapacitance. It was also claimed that there is a radical change of the dielectric relaxational dynamics driven by the onset of magnetization that leads to the observed strong increase of the dielectric permittivity in these compounds^[40]. However these findings were followed by some debate^[7,41].

In figure 1.3.2 we present a model of the CdCr₂S₄ magnetic structure in the ferromagnetically ordered phase. In this way a better understanding of the magnetic moments alignment can be accomplished.

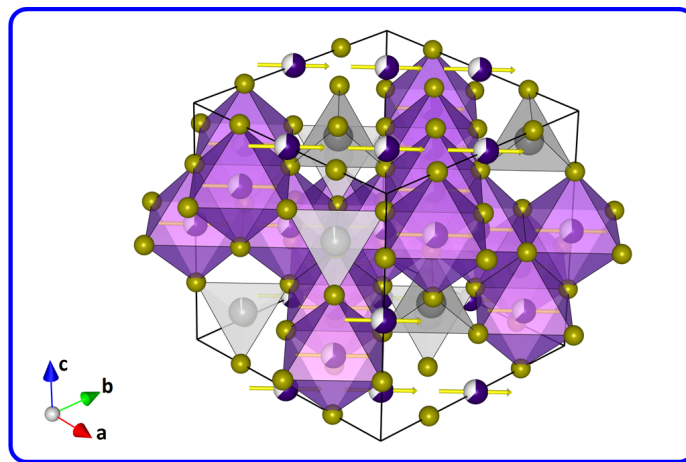


Figure 1.3.2: Model of the CdCr₂S₄ magnetic structure in the ferromagnetically ordered phase.

The microscopic origin of the spin driven polar moments in CdCr₂S₄ was associated to ferroelectric distortions resulting from an off-center position of the Cr³⁺ ions. The off-centering of Cr ions gives the system a local polar character with a macroscopic isotropic ferroelectric cluster

state^[42,43]. Geometric frustration within a room temperature highly symmetric cubic lattice may drive the relaxor-like freezing^[44] observed at low temperatures.

Still undisclosed is the origin of the strong coupling of magnetization and dielectric permittivity in this compound. As pointed out, the relaxation dynamics of the polar moments is accelerated below T_C ^[40], but it remains to be clarified what is the microscopic origin of the detected relaxation dynamics and why the dynamics couples so strongly to the magnetic order parameter. A coupling via exchange-striction, *i.e.*, volume changes arising from the magnetic exchange energy seems possible^[40]. The onset of spin order leads to a softening of the lattice thereby reducing the energy barriers against dipolar reorientation and thus enhancing the mean relaxation rate. As an alternative explanation one could also consider a magnetic-field-induced variation of charge-carrier mobility or density. Though much scientific effort has been dedicated to unveil the nature of such effects and to settle multiferroism in this system the understanding of these phenomena requires an adequate description of the structural, magnetic and charge degrees of freedom.

Chapter 2

Experimental Techniques

In this chapter, an overview of the experimental techniques used in this work is presented. First the techniques used for sample preparation will be approached, followed by the techniques for their structural and morphological, magnetic and electric characterization. Finally technical information on the Local Probe technique is provided. For completeness we will give reference to previous works (thesis, books, articles, etc.) where the techniques are described in more detail, if an in depth knowledge is required.

2.1 Sample Preparation

Nowadays solid-state chemistry continues to have a grand and expanding role in an enormous set of disciplines. Given that the discovery of new physical phenomena greatly depends on the development of new materials, the synthesis of novel stable solid-state materials having the desired properties is of great importance. The synthesis processes utilized to prepare inorganic materials are different from those used by organic chemists. The former has to work with complete lattices, either building or modifying them which is necessarily a complex task^[45]. In fact the preparation of solids with the desired structure, composition and properties is still a challenge to chemists, material scientists and engineers.

Historically, the preparation of solid-state materials has been accomplished with the use of high temperature solid-state diffusion reactions, generally yielding the most thermodynamically stable phases. A variety of techniques have been developed to overcome the limitations inherent to this traditional approach. As an example of other methods now available, the AgCrO_2 system has been already prepared by, *e.g.*, the sol-gel combustion method^[46] and hydrothermal synthesis^[47].

2.1.1 Sol-Gel Method

The interest on sol-gel processing can be followed back to the mid-1880s when hydrolysis of tetraethyl orthosilicate (TEOS) under acidic conditions led to the formation of SiO_2 in the form of fibers and monoliths. The sol-gel method for sample preparation used in research gained, in the last years, such importance that in the 1990's more than 35,000 papers were published worldwide referring this process^[48].

The sol-gel method can be described as a wet-chemical technique (chemical solution deposition) that is widely used nowadays in a great number of fields such as materials science and

ceramic engineering, to name just a few examples. Initially the method was used for the fabrication/preparation/invention of materials (typically metal oxides) having a chemical solution as the starting point (sol, short for solution) which acts as the precursor for an integrated network (or gel) of either separate particles or network polymers. Metal alkoxides and/or metal chlorides are used as typical precursors, which undergo hydrolysis and polycondensation reactions to form either a network "elastic solid" or a colloidal suspension (or dispersion) - "*a system composed of discrete (often amorphous) sub-micrometer particles dispersed to various degrees in a host fluid*"^[48]. The formation of a metal oxide is achieved by the connection between the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, and in this way generating metal-oxo or metal-hydroxo polymers in solution. Therefore, the evolution of the solution is towards the formation of a gel-like diphasic system containing both a liquid and solid phases. In the gel-like phase we can encounter different morphologies, ranging from discrete particles to continuous polymer networks.

Typically, in order to observe gel-like properties, in the case of colloids, a significant amount of fluid may need to be removed, since the volume fraction of particles (or particle density) is, in many cases, very low. Centrifugation can also be used to accelerate the process of phase separation.

A drying process is generally performed to remove the remaining liquid (solvent) phase. The drying is typically accompanied by a significant amount of shrinkage and densification. The distribution of porosity in the gel sets up the rate at which the solvent can be removed. The obtained microstructure of the final component is strongly influenced by changes implemented during this phase of processing. Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

The sol-gel precursor phase can be either deposited on a substrate to form a film (*e.g.*, by dip-coating or spin-coating), assigned into a suitable container with the desired shape (*e.g.*, to obtain monolithic ceramics, glasses, fibbers, membranes, aerogels)^[48], or used to synthesize powders (*e.g.*, nanospheres, nanotubes). The sol-gel approach can be a cheap and low-temperature technique allowing a fine control of the product's chemical composition, and in this way it has become a desirable and very used technique to prepare many organic and inorganic compounds^[49,50]. Even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the solution and end up in uniformly dispersed in the final product. It can be used in ceramics processing and manufacturing as an investment casting material, or as a mean of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine (*e.g.*, controlled drug release) and separation (*e.g.*, chromatography) technology^[48].

Among the the sol-gel technique many variations and conditions can be encountered, from urea sol-gel process^[49], glycine nitrate process, ethylene glycol process^[51], sol-gel microwave combustion to solution combustion synthesis.

Despite the many advantages of the sol-gel based method, it exhibits some difficulties. One of those difficulties is the laborious process of pH adjustment. Usually in sol-gel we aim to achieve the the maximum pH value without letting precipitation to occur. So a rigorous and precise control of the adjustment with the acid/base must be present in the mind of the experimentalist.

A more detailed description of the method and reaction evolution is described in section 3.1 for the case of AgCrO₂ preparation.

2.1.2 Solid State Reaction

In a solid state reaction the reactants chemically react or diffuse without the use of a solvent. It can be also called a dry media reaction. A standard chemical reaction is typically accomplished by placing the reacting agents in a solvent before the reaction take place. These reactants react to form a new substance. After the reaction is completed, it's possible to remove the new product from the solvent.

Solid state reactions happen through solid state diffusion, *i.e.*, the movement and transport of atoms without leaving the solid phase. The diffusion process takes place preferentially through defects in solids. Point defects, *e.g.* vacancies and interstitial ions, are responsible for lattice diffusion. Diffusion can also occur along line and surface defects which include grain boundaries, dislocations, inner and outer surfaces, etc. Notice that diffusion along linear, planar and surface defects is most of the times faster than in the lattice, they are also termed high diffusivity or easy diffusion paths.

The relative contribution of the different types of diffusion in oxides and other inorganic compounds is dependent of the temperature, partial pressures or activities of the constituents of the compounds, the microstructure, grain size, porosity, etc.

The method used to prepare the solid reactant, and the pretreatment it receives prior to reaction, can influence profoundly its reactivity. Crystal nucleation is controlled by the area and the perfection of available surfaces, and the sizes and shapes of the constituent particles of a powder exert an obvious control over the rates and geometry of interface development. Where reaction happens in a sequence of successive steps, the reactant of each later stage is the product of the preceding reaction and has probably undergone lattice reorganization, with changes in the size, shapes and perfection of the component crystallites. These changes are of particular significance where dehydration (or loss of other ligand) precedes the reaction of interest. In many cases, product crystallinity is seriously dependent on the prevailing availability of water vapor during the dehydration process. Grinding and other forms of mechanical pretreatment, exposure to diverse forms of radiation and ageing of the reactant during storage may all influence the course of subsequent decomposition. We further remark that impurities, present in the reactants, can be positive used as dopants^[52].

Though there are many benefits to developing solid state reactions, there are also many drawbacks. The ideal procedure should result in a homogeneous, or uniform substance, and some solid state reactions do not. In addition, these reactions are, for obvious reasons, useless for reactions requiring solvents.

In addition reactions are usually performed in different atmospheres like: Air, O₂ rich atmosphere, inert atmosphere (Ar, N₂) or vacuum (*e.g.* evacuated ampoule).

In summary, formation of solids by the solid state reaction method is controlled by the diffusion of atoms and ionic species through reactants and products and thus requires repeated grinding, pelletizing and calcination of reactants (oxides, carbonates and nitrates) for longer durations (than soft chemical routes) at high-temperatures^[46].

2.2 Structural and Morphological Characterization

2.2.1 X-Ray Diffraction

The most common tool for phase identification of polycrystalline solids is powder x-ray diffraction ("PXRD or XRD")¹.

Each crystalline solid produces a characteristic "fingerprint" diffraction pattern which can be used for phase identification or, if sufficiently high-quality data is collected, for structural refinement. The theory of diffraction is well established and the experimental setup of a modern laboratory diffractometer is described at length in many textbooks and it can be reviewed, in the references [54–58] and will be covered next only briefly.

To generate x-rays, electrons are accelerated by an electric field and directed against a metal target (*e.g.* copper metal (Cu) being the most common choice). The beam is made monochromatic ($\lambda_{CuK\alpha} = 1.5418 \text{ \AA}$) by using a Ni filter that selectively removes the K_{β} , with a relatively much smaller loss of K_{α} .

In a powder sample, the various lattice planes are found in every possible orientation. Thus, a convergent x-ray beam focused on a polycrystalline sample is diffracted in cones of radiation whose pattern is determined by the internal architecture of the sample, see figure 2.2.1. The powder diffractometer has a detector, which scans a range of 2θ values (*e.g.*, $10 < 2\theta < 90$) at a constant angular velocity. A collection can take from minutes to hours depending on the desired quality of the data and on the specific instrument properties.

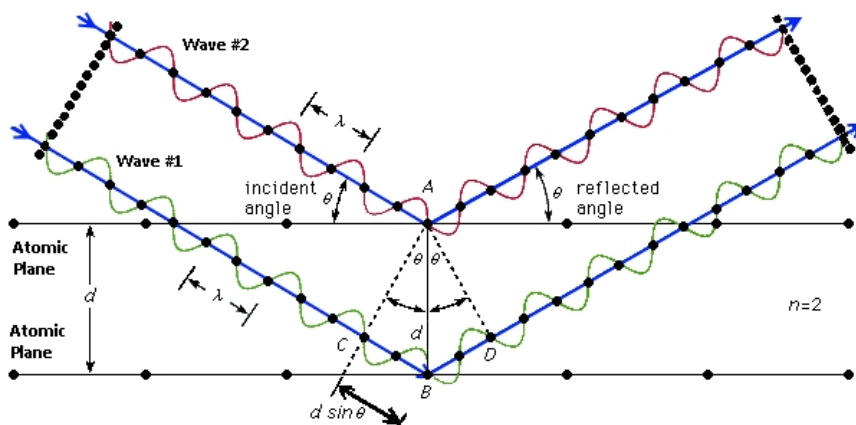


Figure 2.2.1: Braggs radiation reflection.

After a pattern is collected, it can be quickly compared to known powder diffraction patterns of that sample or to other patterns of compounds containing some or all the elements of the sample under examination. x-Ray diffraction patterns are most often used for qualitative phase identification,

¹"X-ray was the name given by *W. C. Roentgen* to the highly penetrating rays, which emanated when high energy electrons struck a metal target. On 8 November 1895, he noted for the first time this phenomenon and on 28 December 1895, he astonished the scientific world with his preliminary report *Ueber Eine Neue Art von Strahlen* (along with experimental radiographs and by the X-ray image of his wife's hand) given to the president of the *Wurzburg Physical-Medical Society*. A few weeks later, *C.H.F. Muller* was able to construct on his Hamburg factory the first commercial X-ray tube for one of the local hospitals. This was a milestone of what was to become a major technical industry. X-ray technology is one of the most important inventions of the nineteenth century. It plays a major role in our daily life. X-ray is nowadays one of the most powerful tools to investigate hard and soft matter, hence the necessity to develop new sources to achieve more high-intensity beams." [53]

however, if the sample is unknown, the data can also be used to determine the structure.

Structural characterization of the samples studied in the present work were performed mainly by means of x-ray diffraction (XRD) technique. The diffraction of short wavelength particles as x-ray photons, electrons and thermal neutrons is the most accurate tool in order to determine crystallographic structures and lattice parameters. The wavelength of the above mentioned particles has values of the order of 1 Å, which is the typical value of the lattice parameters in crystalline solids. Therefore, the coherent interference of the scattered particles in these solids will form a diffraction pattern with constructive and destructive interferences.

Taking into account only elastic scattering, the maximum intensity will appear for scattering directions that results from the addition of the moment of the incident particle (in units of $\hbar$) and any vector belonging to the reciprocal lattice of the solid (in units of the Bravais lattice parameters). These directions are called **Bragg positions** or **Bragg peaks**, and a set of Miller indexes can be assigned to them. The diffraction experiments provide a picture of the reciprocal lattice, and therefore the lattice in the real space can be obtained as the Fourier transform of the reciprocal space. Every Bragg position satisfies the Bragg's law:

$$\lambda = 2d_{hkl} \sin(\theta) \quad (2.2.1)$$

where λ is the wavelength of the incident wave, d_{hkl}^2 is the distance between planes with Miller indexes (hkl) , and $\phi_{hkl} = 2\theta$ is the angle formed by the propagation vectors of the incident and scattered waves. It can be shown that θ is the angle formed by the crystallographic plane and the momentum of the incident wave.

Diffraction patterns are usually represented as the number of diffracted particles counts versus 2θ or d_{hkl} . The Bragg's law (equation 2.2.1) can be used to associate inter-plane distances to each Bragg peak.

In non-textured polycrystalline solids, the grains have their crystallographic axes randomly oriented. The diffraction theory sets that the Bragg peaks are then substituted for maximal intensity at the **Scherrer cones**, which have axial symmetry around the incident momentum direction. The diffraction profiles in this work will always result as the intersection of the plane of the detectors with the Scherrer cones, giving rise to the powder diffraction profiles.

The x-ray diffraction measurements were performed at the Spectroscopy Laboratory in the *Institute of Nanoscience and Nanotechnology* (IFIMUP-IN) and at the Electronic Microscopy Unit in the *University of Trás-os-Montes e Alto-Douro* (UTAD). The diffractometer Siemens Bruker AXS D5000 theta-2 theta goniometer with a copper ($K_{\alpha 1;2}$ radiation ($\lambda = 1.540598$ and 1.544418 Å)) anode x-ray tube operated at 40 kV and 30mA and PAN'alytical, X'Pert Pro x-ray diffraction with detector X'Celerator and secondary monochromator operated at 50 kV and 40mA, respectively.

The XRD pattern can be collected in two different ways, using sample pellets fixed to the sample holder with the help of a small piece of plasticine or using sample powders where a liquid with some viscosity was used to fix the powder into the sample holder. Liquids like ethanol or isopropanol, were used in the set of XRD patterns presented in this work. When powder patterns are presented, a background contribution is, most of the times visible. Nevertheless such background intensity is not so important when compared with the attenuation created by the much higher relative intensities of some peaks when a preferential growth of the polycrystalline samples occur. Whenever it was possible PXRD patterns were collected to have a better understanding of the crystallographic phases

²($d_{hkl} = \frac{d}{n}$, where d is the distance between atomic planes and n is the diffraction order.)

present in the samples.

There are several refinement analysis methods and tools available for studying XRD patterns. *Rodriguez-Carvajal et al.* developed a library of programs that apply the Le Baile and Rietveld method to any X-ray or neutron diffraction pattern^[59–61]. These libraries are known by the name of **fullprof**. The FULLPROF software has been used to analyze diffraction profiles presented in this work.

The **Rietveld method** was designed to analyze powder diffraction profiles and extract accurate quantitative information. Its role is twofold: first, according to the diffraction laws, the Bragg positions must be indexed within an hypothetical crystallographic space group. This analysis provides the lattice parameters and the actual atomic positions (**Le Baile method**). Once the space group is determined, the shape of the peaks and the relative intensities must be fitted, which requires the assumption of a precise shape for the peak. This analysis provides the atomic occupancy as well as microstructural information such as internal strain and the shape of the grains. Making use of all the input information, the Rietveld method aims to minimize the difference between the calculated intensity and the observed one by means of the least squares criteria^[62,63].

It must be noted that only when a thorough analysis of the sample was desired (usually at the end of the annealing's set), data with considerable statistics was collected in order to perform a Rietveld refinement. Otherwise, standard data was collected and a Le Baile pattern matching was performed to determine the phases present and their corresponding lattice parameters. The Le Baile analysis provides all the information necessary to characterize the crystallographic phases present in a sample. When a deeper analysis is desired extra information (as indicated before) can be obtained from the Rietveld refinement.

2.2.2 Scanning Electron Microscopy

The scanning electron microscope (SEM) allows the observation and characterization on a nanometer (nm) to micrometer (μm) scale of heterogeneous organic and inorganic materials. The popularity of the SEM arises from its capability of obtaining three-dimensional-like images of the surfaces of a very wide range of materials. SEM images are used to characterize a wide range of materials, from pellets to insects. Its popularity is patent in the use of SEM images among scientific journals, popular magazines and, more recently, in the movies. Although the major use of SEM is to obtain topographic images in the magnification range 10 - 10000 $\times$, the SEM is much more versatile.

In the SEM analysis, the area to be examined or the microvolume to be analyzed is irradiated with a finely focused electron beam, see figure 2.2.2 (Adapted from ^[64]), which may be swept across the surface of the specimen to form images or may be static to obtain an analysis at one position. The type of signals produced from the interaction of the electron beam with the sample include secondary electrons³, backscattered electrons⁴, characteristic x-rays, and other photons of various energies. These signals are obtained from specific emission volumes within the sample and can be used to examine many characteristics of the sample (surface topography, morphology, composition, etc.).

³Secondary electrons (SE) are those electrons emitted by the specimen, under irradiation by the beam, which have energies between 0 and 50 eV. Because of their low energy the SE only travel relatively short distances in the specimen (3 – 10nm) and thus they emerge from a shallow 'escape' region beneath the surface.

⁴Backscattered electrons (BSE) are defined as being those electrons emitted from the specimen which have energies between 50eV and the incident beam energy E_0 . Unlike the secondary electrons which are produced as the result of the incident electron irradiation, backscattered electrons are incident electrons which have been scattered through angles approaching 180° within the sample and consequently leave the sample again.

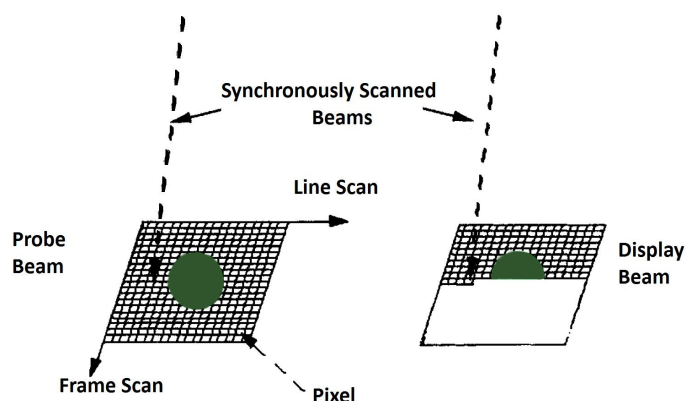


Figure 2.2.2: Schematic illustration of the basic mapping principle of the scanning electron microscope.

The imaging signals of greatest interest are the secondary and backscattered electrons because these vary primarily as a result of differences in surface topography. The secondary electron emission, confined to a very small volume near the beam impact area for certain choices of the beam energy, permits images to be obtained at a resolution approximating the size of the focused electron beam. The three-dimensional (3D) appearance of images has its origin due to the large depth of the field as well as to the shadow relief effect of the secondary and backscattered electron contrast.

In the SEM, as a result of electron bombardment, characteristic x-rays are also emitted. The analysis of the characteristic x-ray radiation emitted from samples can supply both quantitative elemental information and qualitative identification from regions of a specimen nominally $1\ \mu\text{m}$ in diameter and $1\ \mu\text{m}$ in depth under normal operating conditions, see section 2.2.3.

The SEM measurements presented in this work were performed at the "Centro de Materiais da Universidade do Porto (CEMUP)" with a FEI Quanta 400FEG SEM. Before the measurements the samples pellet surface was gently polished and was mounted into the SEM sample holder with carbon tape.

For a detailed description of the experimental apparatus, technical specifications and measurement principles see reference^[65].

2.2.3 Energy Dispersive X-ray Spectroscopy

Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is a microanalysis technique used together with scanning electron microscopy (SEM) for the chemical elemental analysis, chemical characterization of a sample, etc.⁵.

EDS is a spectroscopic technique that gathers information about a sample through interaction between electromagnetic radiation and matter, mainly by analyzing x-rays emitted as a response of an initial beam charged particles⁶ that hits the sample. Its characterization capabilities⁷ are due in large part to the fundamental principle that each chemical element has a unique electronic structure thus producing x-rays that are characteristic of the element in question allowing its identification.

⁵Foreign material analysis, corrosion evaluation, coating composition analysis, rapid material alloy identification, small component material analysis, phase identification and distribution.

⁶To stimulate the emission of characteristic x-rays from a specimen, a high energy beam of charged particles such as electrons or protons, or a beam of x-rays, is focused into the sample in study.

⁷Features or phases as small as $1\ \mu\text{m}$ or less can be analyzed.

At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell and this way creating an electron hole. Because an hole in a lower level of the electron shell doesn't correspond to a stable configuration, an electron from an outer shell will then fill the hole. The difference in energy between the higher energy shell and the lower energy shell may be released in the form of x-ray radiation, see figure 2.2.3 (Adapted from [66]). The number and energy of the x-rays emitted from a sample can be measured by an energy dispersive spectrometer. Because the energy of the x-rays are characteristic of the difference in energy between the two shells, and of the electronic structure of the element from which they were emitted, it is possible to determine the elemental composition of the sample to be measured.

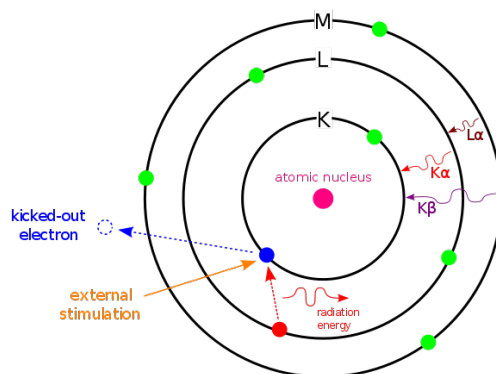


Figure 2.2.3: Electron shell model with different type of radiation emitted when an electron from the inner shell is removed.

The EDS x-ray detector measures the relative abundance of emitted x-rays versus their energy. The detector is typically a lithium-drifted silicon, solid-state device. When an incident x-ray hits the detector, a charge pulse proportional to the energy of the x-ray is created. The charge pulse is converted to a voltage pulse (which remains proportional to the x-ray energy) by a charge-sensitive preamplifier. The signal is then transmitted to a multichannel analyzer where the pulses are sorted by voltage. The energy, as determined from the voltage measurement, for each incident x-ray is sent to a computer for display and further data evaluation. The spectrum of x-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume.

The obtained EDS spectrum is compared with spectra of individual elements allowing to quantify the relative amount of an element in the sample.

The minimum detection limits of the EDS vary from approximately 0.1 to a few atomic percent, depending on the element and the sample matrix. Elements with atomic numbers above that of beryllium and up to uranium can be detected.

Samples up to 200 mm in diameter can be readily analyzed in the EDS. Larger samples, up to approximately 300 mm in diameter, can be loaded with limited stage movement. A maximum sample height of approximately 50 mm can be accommodated. Samples must also be compatible with a moderate vacuum atmosphere (pressures of 2 Torr or less).

When performing a microanalysis by EDS several considerations have to be taken into account. Changing the over-voltage of the EDS will result in different peak sizes - Raising over-voltage on the EDS will shift the spectrum to the larger energies making higher-energy peaks larger while making lower energy peaks smaller and also overlapping peaks can appear for some elements. x-ray escaping

the specimen, and thus being available to detect and measure, depend on the energy of the x-ray and the amount and density of material it has to pass through. This can result in reduced accuracy in inhomogeneous or rough samples.

To evaluate at the micrometer scale the chemical homogeneity of the sample (SEM-EDS) measurements were performed. The measurements presented in this work were performed at the "Centro de Materiais da Universidade do Porto (CEMUP)" with a FEI Quanta 400FEG ESEM/EDAX Genesis X4M.

For a detailed description of the experimental apparatus, technical specifications and measurement principles see reference [64].

2.2.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS)⁸ is used to study the chemical composition of the surface and its information depth is limited to a few atomic layers.

The XPS technique used the photoelectric process, where an electron is emitted from a solid when the latter is irradiated with x-rays. In the emitting atom an electron hole is created and charge rearrangement will occur. A charge rearrangement will take place in the electronic shell to eliminate the positive hole, thereby lowering the total energy of the system. Because the charge rearrangement generally occurs in a time interval that is comparable with the time of the photoemission process, the total energy is reduced, when compared to the frozen orbital situation, leading to an increase of the kinetic energy of the emitted photoelectron.

Since the binding energy of an electron is defined as the difference between the kinetic energy of the incoming photon and the kinetic energy of the outgoing photoelectron, that is,

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi) \quad (2.2.2)$$

and where ϕ is the work function of the spectrometer.

The detected electron has an increase of its kinetic energy resulting in a reduction, of the order of a few eV, of the effectively experimentally observed binding energy. These electronic screening effects occur in free atoms as well as in the condensed phase. As a result of the extra-atomic relaxation, screening will normally be larger for the condensed phase than for free atoms. Consequently, in the discussion of chemical shifts, it should be taken into consideration that these are not only determined by initial state charge transfer phenomena, but also by final state electronic screening effects.

When measuring the kinetic energy of the photoelectron with an analyzer, the work function, ϕ , of the latter must be taken into account, binding energies being referred towards the Fermi-level:

$$E_{Kin} = h\nu - E_b - \phi \quad (2.2.3)$$

For photoelectrons, a notation based on a x-ray notation, using the spectroscopic level (*e.g.*, C1s, Si2p_{1/2}, Si2p_{3/2}, etc.) is adopted. To a first approximation, the initial states before photoemission are characterized by completely filled shells, while after photoemission one electron hole is present. Consequently one only expects the corresponding spin-orbit splitting spectroscopic terms,

⁸XPS was developed in the mid 1960s by K. Siegbahn and his research group. K. Siegbahn was awarded the Nobel Prize for Physics in 1981 for his work in XPS. The phenomenon is based on the photoelectric effect outlined by Einstein in 1905 where the concept of the photon was used to describe the ejection of electrons from a surface when photons impinge upon it". [64]

explaining the notation used above. If, however, the electron hole thus created can couple with other holes already present, multiplet splitting occurs and the photoline becomes much more complex than the single lines just described. Since the measurement of the Full Width at Half Maximum (FWHM) value of the photoline is determined, among other factors, by the width of the exciting x-ray photon, narrow monoenergetic soft x-ray lines such as Al K_{α} (1486.6 eV) or Mg K_{α} (1253.6 keV) are used as primary excitation. The kinetic energies of the photolines are consequently limited to these values.

In an XPS spectrum, one notices the presence of core level photolines next to the valence band structure. In such a spectrum one normally can also clearly distinguish the presence of Auger lines^[64]. Indeed, upon creation of the core holes, deexcitation readily occurs, giving rise to the emission of Auger electrons, which are measured in the spectrometer, see figure 2.2.4 (Adapted from ^[67]). Determining binding energies and consequently identifying the chemical composition of a surface layer is the main subject of XPS. It is also known under the popular acronym ESCA (electron spectroscopy for chemical analysis).

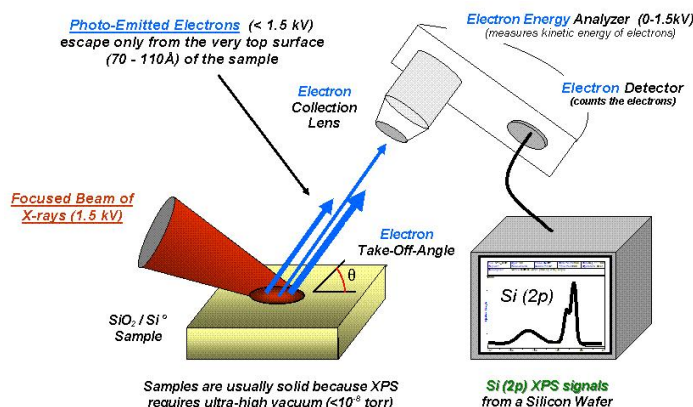


Figure 2.2.4: Basic structure of a X-ray photoelectron spectroscopy system.

Analysis is based on the fact that each element/chemical environment has a unique spectrum and can therefore be used as a kind of fingerprint. It is also straightforward that a mixture of elements gives rise to a mixture of these unique spectra and, to a first approximation, quantitative data can be obtained from the peak areas. In general, the identification of the peaks poses no severe problems, providing that one is aware of the fact that satellites such as plasmon losses, shake-up, and shake-off satellites may be present.

The XPS spectra were collected at CEMUP using a VG Scientific ESCALAB 200A spectrometer non-monochromatised Al K_{α} radiation (1486.6 eV)). The binding energies of the high resolution XPS spectra determined by curve deconvolution using non-linear least squares fitting routine after a Shirley-type background subtraction and compared to values reported in literature^[68].

For a more detailed description of the experimental apparatus, technical specifications and measurement principles, see reference ^[64].

2.3 Magnetic and Electric Characterization

2.3.1 SQUID Magnetometry

Superconducting Quantum Interference Device (SQUID), see figure 2.3.1 (Taken from ^[69]), are very sensitive magnetometers used to measure extremely small magnetic fields. It is a flux-voltage converter. It turns a small, hardly detectable, flux variation into a measurable voltage variation. The output voltage is a periodic function of the applied flux, with period ϕ_0 (the magnetic flux quantum) one can detect an output signal which corresponds to a flux much smaller than ϕ_0 . SQUIDS can thus measure any physical quantity which can be transformed into a flux, such as a magnetic field or its gradient, a current, a voltage, a displacement or a magnetic susceptibility. SQUIDS combine two physical phenomena, flux quantization in a superconducting ring, and the Josephson effect⁹.

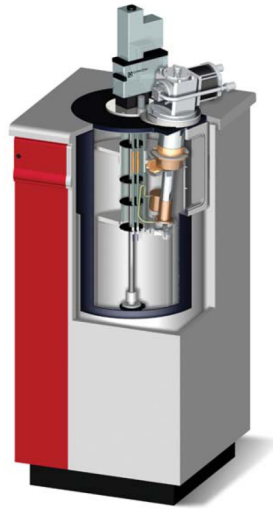


Figure 2.3.1: Figure of MPMS SQUID apparatus system, with dewar and Evercool system.

SQUIDS are usually made of either a lead alloy (with 10% gold or indium) and/or niobium, often consisting of the tunnel barrier sandwiched between a base electrode of niobium and the top electrode of lead alloy.

There exist two types of SQUIDS: A radio frequency (RF) SQUID that is made up of one Josephson junction, which is mounted on a superconducting ring. An oscillating current is applied to an external circuit, whose voltage changes as an effect of the interaction between it and the ring. The magnetic flux is then measured; A direct current (DC) SQUID, which is much more sensitive, consists of two Josephson junctions employed in parallel so that electrons tunneling through the junctions demonstrate quantum interference, dependent upon the strength of the magnetic field within a loop. DC SQUIDS demonstrate resistance in response to even tiny variations in a magnetic field, which is the capacity that enables detection of such minute changes

Although RF SQUID are more common on the market, DC SQUIDS are more sensitive. They are sensitive enough to measure fields as low as 5 aT (5×10^{-18} T) within a few days of averaged measurements. Their noise levels are as low as $3 \text{ fTHz}^{-1/2}$. For comparison, a typical refrigerator

⁹A Josephson junction is made up of two superconductors, separated by an insulating layer so thin that electrons can pass through.

magnet produces 0.01 Tesla (10^{-2} T), and some processes in animals produce very small magnetic fields between 1 fT and 1 μ T.

The magnetic measurements with a SQUID, should be performed with a magnetically virgin superconducting coil, in order to avoid remanent fields and field inhomogeneities. When that is not possible and a remanent field is present, the sample magnetization in the paramagnetic phase can be used to determine this remanent field, and perform a correction to the applied field. In magnetic measurements one defines the susceptibility as:

$$\chi = \frac{M}{H} \quad (2.3.1)$$

where M is the sample magnetization and H the magnetic applied field. This expression is valid only in the paramagnetic phase, although sometimes we also use it in the ordered phase.

The origin of the magnetic moments arises from the orbital motion and spin of unpaired electrons. The way atomic magnetic moments order in a material can be inferred by the behavior of the magnetic susceptibility of the sample, see figure 2.3.2 (From^[6]). Materials can be paramagnetic so that when an magnetic field is applied a magnetization appears which aligns parallel with it (unpaired electrons are present), and diamagnetic when a magnetic field induces a magnetic moment which opposes the applied magnetic field that cause it (all electrons are paired)^[70].

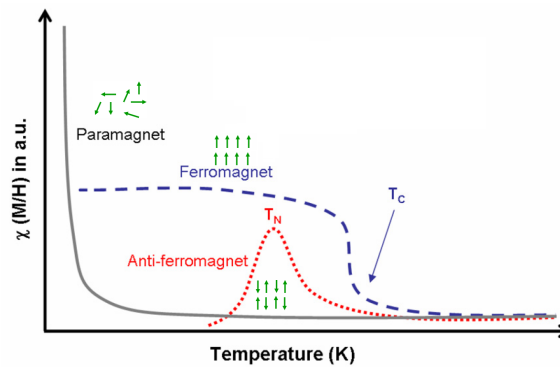


Figure 2.3.2: Generalized magnetic susceptibility response of a paramagnet, ferromagnet and antiferromagnet. The latter two are paramagnetic above their ordering temperatures, T_C and T_N , respectively..

Ferromagnetic materials possess spontaneous magnetization (*i.e.*, the magnetic polarization of all magnetic ions make a positive contribution to the net magnetization direction) when they are below a certain critical temperature, called the Curie temperature (T_C). Here the direction of the external applied magnetic field can change the direction of the magnetic alignment. This property make these materials to concentrate magnetic flux density, and therefore be used in applications where high magnetic fields are necessary.

On the other hand the antiferromagnetic materials, have the spins of neighbor magnetic atoms aligned in opposite directions. The temperature below which an antiferromagnetic material orders occur is called the Néel temperature (T_N). In the paramagnetic phase the temperature dependence of the susceptibility is given by the well-known Curie-Weiss law:

$$\chi = \frac{C}{T - \Theta_P} \quad (2.3.2)$$

where Θ_P is the Curie-Weiss temperature and is related with the exchange interaction between atomic magnetic moments, T is absolute temperature measured in kelvins and C is a material-specific Curie constant.

Notice that Curie's law is only valid in the low field regime and does not apply in the high-field regime where saturation of magnetization occurs and the magnetic moments are aligned with the external applied field. When the spins are aligned, increasing the external field will not increase the total magnetization.

For a paramagnetic ion with spin quantum number S (and quenched angular momentum, $\langle L \rangle = 0$), the Curie constant can be related to the individual ions magnetic moment:

$$C = \frac{N_A}{3k_B} \mu_{eff}^2 \quad \text{where} \quad \mu_{eff} = 2\sqrt{S(S+1)}\mu_B \quad (2.3.3)$$

where k_B is the Boltzman constant and N_A the Avogadro's number.

All of the magnetization measurements necessary to this work were performed at Instituto de Física de Materiais da Universidade do Porto (IFIMUP-IN) in a SQUID magnetometer (MPMS Quantum design, see figure 2.3.1). This magnetometer has a 10^{-7} emu resolution and is equipped with 5.5 Tesla superconducting coil. This system allows accurate magnetization measurements in low applied Fields in a 5 to 380 K temperature range. To perform the necessary measurements samples with needle shape were used¹⁰. These samples were mounted in plastic straws either glued with a special low temperature tape (Kapton tape) or inside a gelatine capsule with cotton.

For a detailed description of the experimental apparatus, technical specifications and measurement principles, see references [71,72].

2.3.2 Dielectric Constant

For understanding the dynamics of dielectric systems, measurements of the complex dielectric constant as a function of temperature play an important role. This can be obtained by making a parallel face capacitor, in which the sample in study is the dielectric, see figure 2.3.3.

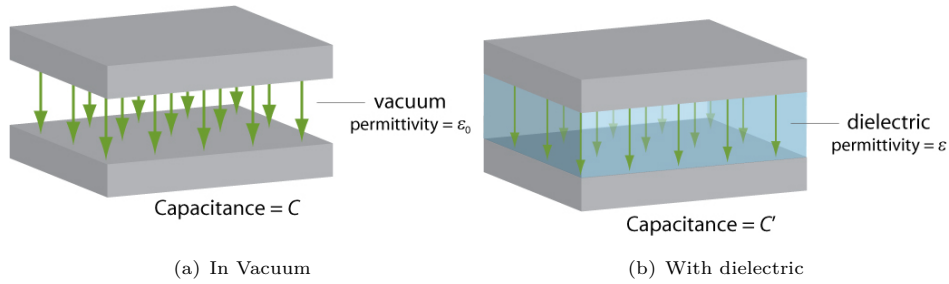


Figure 2.3.3: Scheme of a Capacitor.

The experimental method used consists in the analysis of the impedance of the system in study. Once the samples are not perfect insulators, the dielectric constant (ε) is a complex quantity having in this way a relationship between the electric current and the alternate electric voltage in the following way:

¹⁰Needle-like samples were used in order to reduce demagnetization effects.

$$I = i\omega\varepsilon^*(\omega) C_0 V = \omega\varepsilon''(\omega) C_0 V + i\omega\varepsilon'(\omega) C_0 V \quad (2.3.4)$$

where C_0 is the capacitor capacitance. The initial part of the equation 2.3.4 represents the resistive part of the circuit, with a equivalent resistance $R_P = \frac{1}{\omega\varepsilon''(\omega)C_0}$, connected in parallel with an ideal capacitor, of reactance $\frac{1}{\omega\varepsilon'(\omega)C_0}$. The current intensity that passes through the circuit in the assembly can be defined as:

$$I = \left(\frac{1}{R_P} + i\omega C \right) V \quad (2.3.5)$$

Comparing with the equations described above, is possible to write:

$$\varepsilon' = \frac{C}{C_0} \quad (2.3.6)$$

and

$$\varepsilon'' = \frac{1}{\omega R_P C_0} \quad (2.3.7)$$

The tangent of the angle that measures the phase difference between the current and the potential is given by:

$$\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \quad (2.3.8)$$

The experimental technique is based on the measurement of the capacity and the dielectric losses (*e.g.* conduction, relaxation phenomena, molecular resonances) as a function of temperature. The measurements presented in this work were performed at IFIMUP-IN, in Faculty of Sciences of Porto University.

The complex dielectric constant was measured with an impedance analyzer (for the frequency of 1 MHz), that is connected to a cryogenic refrigerator (≈ 10 K to 300 K) equipped with a temperature controller and meter, that has the ability to change the rate of the heating/cooling process. The experimental data are collected with a software that allows a direct acquisition of the capacity and dielectric losses.

2.4 Perturbed Angular Correlation - PAC

Hyperfine methods form a group of techniques that can probe a material at a nuclear level. Among them we can find Perturbed Angular Correlation (PAC) spectroscopy, Perturbed Angular Distribution (PAD), Nuclear Magnetic Resonance (NMR), Mössbauer Effect spectroscopy (MES), Nuclear Orientation (NO) among others.

The techniques collect information through the electric and magnetic hyperfine interaction between the nuclear moments of a specific probe nuclei and the magnetic or electric fields induced by the surroundings of the used probes (valence electrons, conduction electrons, neighbor atoms or ions, neighboring defects). These techniques working at the atomic scale, have many advantages for studying structural, electronic and dynamical properties of the host atoms, single impurities, and impurity-defect complexes because they probe only a small sample volume and they have a high sensitivity.

Perturbed angular correlation technique has a special place when compared with the other

hyperfine techniques. This is due to several aspects that make it an election technique. The amount of the material under study can be very small (normally small quantities as 1-100 mg can be used), sensitivity is temperature independent (contrary to what happens in MES and in NMR), mechanical vibrations do not interfere with the results (same does not happen in ME), can be measured with no external magnetic field and no high-frequency equipment is required (in opposition to NMR), normally can resolve weaker nuclear quadrupole interaction (than MES), uses small quantities of radioactive nuclei probes (around $10^{10} - 10^{13}$, that are orders of magnitude lower than for MES and NMR) [1,73,74].

The ^{111}In isotopes used in this work to perform the local probe measurements by PAC technique were produce in the Isotope Separator On-Line (ISOLDE) CERN Genebra. ISOLDE produce the isotopes by irradiating an appropriated target with a 1 GeV proton beam delivered by the CERN PS-Booster (PSB). Then isotope ions are accelerated and mass separated to a chamber where the samples are implanted. During the implantation the beam is swept in order to obtain a homogeneous implanted area. The current that emerges from the sample during the implantation process is measured and integrated to keep up with the dose of isotopes implanted. After implantation the samples are submitted to a high temperature treatment to recover any damage created by the implantation. For the AgCrO_2 samples a 20 minutes in O_2 flow at 700°C and for CdCr_2S_4 20 minutes in evacuated quartz ampoule at a temperature of 500°C are enough.

The decay scheme of the ^{111}In isotope is presented in figure 2.4.1 (From *Lopes* [73]).

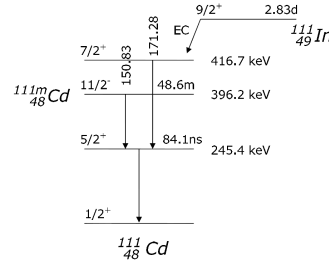


Figure 2.4.1: Simplified decay schemes for ^{111}In and $^{111\text{m}}\text{Cd}$ cascade. Intermediate PAC probe state with energy $E = 245.4$ keV, half life $\tau_{1/2} = 84.1$ ns and angular momentum $I=5/2$.

The ^{111}In probe decays with a half-life $T_{1/2}$ of 2.83 days by electron capture to the excited $+\frac{7}{2}$ state of ^{111}Cd . This state decays by the emission of the 171 (γ_1)-245 (γ_2) keV $\gamma - \gamma$ cascade to the $+\frac{1}{2}$ ground state of ^{111}Cd . The intermediate level $+\frac{5}{2}$ is characterized by the quadrupole moment $Q = 0.83$ b, the magnetic moment $\mu = 0.766 \mu_N$ and the mean life $\tau_{1/2} = 84.1$ ns (Adapted from [75]).

$\mu (\mu_N)$	$Q(b)$
0.766(3)	0.83(13)

Table 2.4.1: Magnetic dipole, μ , and electrical quadropole, Q , moments for the 245.4 keV state (intermediate state of the $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ cascade).

The PAC experiments were carried out using a normal slow-fast setup with six detector PAC spectrometer equipped with BaF_2 scintillators which have a 650 ps time resolution disposed in an 90° and 180° geometry. The experimental set-up for PAC experiments allows us to measure the time dependence of the $\gamma - \gamma$ cascade emitted when the probe decays from from the excited state

to ground state. With the six detectors and a set-up of electronic gadgets is possible to obtain 30 spectra carrying information about their provenance, in the form of counts/versus time.

A correlation between the emission of γ_1 and γ_2 exists, because conservation of the angular momentum, I , occurs. Usually, in an assembly of nuclei the spins are randomly oriented in space, therefore the radiation is emitted isotropically. When the nucleus is surrounded by other atoms interactions will occur. These interactions can be due to fields created by the atomic vicinity. In the presence of external fields an interaction with the nucleus magnetic and quadrupole moments appears. When that is the case a time dependent perturbation in the angular correlation function of the emitted gammas is present.

The nuclear magnetic sublevels can be splitted when the nuclear quadrupole moment couples with an Electric Field Gradient and/or the nuclear magnetic moment couples with a Magnetic Hyperfine Field occurs. If that is the case, during the time τ that the probe remains at the intermediate state, the nucleus is under the effect of a hyperfine interaction that promotes the different magnetic sublevels to be occupied in a different way. Thus, the emission probability of γ_2 , in a certain direction, becomes time dependent.

The perturbed time differential angular correlation in polycrystalline materials is expressed by:

$$W(\theta, t) = \sum_{k=0}^{k=k_{max}} A_k(\gamma_1) A_k(\gamma_2) G_{kk}(t) P_k(\cos(\theta)) \quad (2.4.1)$$

where θ is the angle between the detectors, A_{kk} is the anisotropy coefficient of the $\gamma - \gamma$ cascade, $P_k(\cos(\theta))$ Legendre polynomial of order k , and $G_{kk}(t)$ the perturbation factor, containing all the information on the hyperfine interaction.

Static Interactions - In the case of a static axial symmetric electric quadrupole interaction in polycrystalline samples $G_{kk}(t)$ is defined as:

$$G_{kk}(t) = \sum_{n=0}^{n_{max}} S_{kn} \cos(n\omega_0 t) \quad (2.4.2)$$

where S_{kn} are the frequency amplitudes, $n = |m^2 - m'^2|/2$ for I half integer and $n = |m^2 - m'^2|$ for I integer¹¹.

Dynamic Interactions - In the case that the diffusion of impurities or defects in the crystal lattice occurs or a slow lattice dynamics, a correction to the perturbed time differential angular correlation function has to be considered. Because these dynamic interactions can have different time-scales, three possible cases have to be defined. They can be grouped considering the mean fluctuation time of a given interaction, τ_c , and its relation to the life time of the probe in the intermediate state, τ .

$\tau_c \gg \tau$ - When τ_c is much greater than the perturbation measuring time, there is a great probability of no fluctuations during the measurement time. In this case static interactions will be observed due to the different positions of the defects or impurities during each jump in the diffusion process.

$\tau_c \ll \tau$ - When the time in which the defect or impurity remains at a determined position is much smaller than the measuring time, the anisotropy present in the creation of the intermediate state tends to zero, because the random transition between the substates tend to equal the respective

¹¹ m and m' are the spin angular momentum of the initial and final state of the probe

populations. In this case, the perturbation of the angular correlation can be described simply by an exponential attenuation:

$$G_{kk}(t) = e^{-\lambda_k t} \quad (2.4.3)$$

in which $\lambda_k \propto \tau \overline{w_0^2}$, with $\overline{w_0^2}$ being the mean quadratic frequency of the interactions verified in the case of static interactions.

$\tau_c \simeq \tau$ - When the time of the fluctuation is of the same order of magnitude of the time of the measurement, the model of random phase approximation is adopted, which is valid for many cases where we have a variation of the EFG's, including the lattice vibration effects and the diffusion of defects. In a first approach we can consider that the perturbed angular correlation oscillations amplitude due to these interactions is attenuated by a time decreasing exponential factor:

$$G_{22}(t) = e^{-\lambda t} \sum_{n=0} s_{2n} \cos(nw_0 t) \quad (2.4.4)$$

for $k = 2$ and for a single EFG of $\eta = 0$ (see equation 2.4.6).

The thirty time spectra obtained for all possible combinations of the six detectors are used to calculate the experimental perturbation function $R(t)$ given by:

$$R(t) = 2 \frac{N(180^\circ, t) - N(90^\circ, t)}{N(180^\circ, t) + 2N(90^\circ, t)} = A_{kk} \sum_{n=1}^{n_{max}} f_n G'_{kk}(t) \quad (2.4.5)$$

where f are the relative fractions for different EFG's contributing to the PAC spectrum and $G'_{kk}(t)$ the corresponding perturbation factors.

A scheme summarizing the perturbed angular technique is presented in figure 2.4.2.

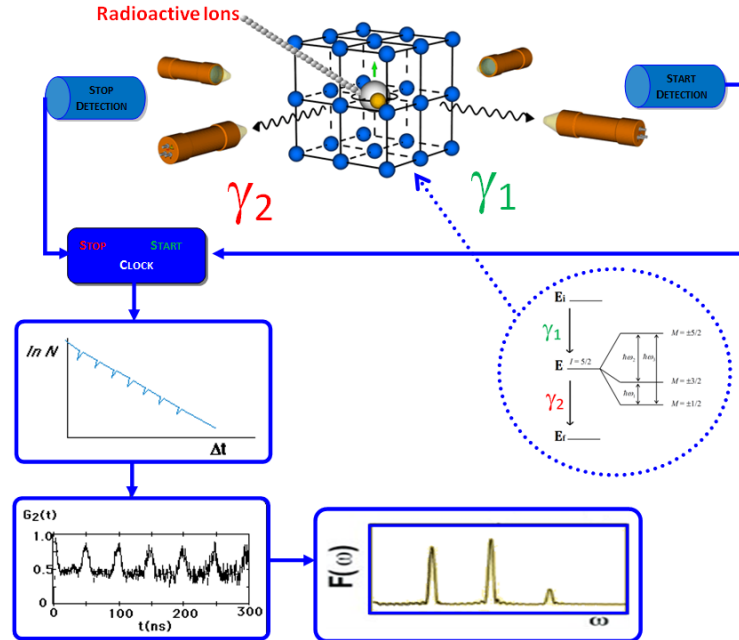


Figure 2.4.2: Perturbed angular correlation technique illustration.

Using PAC technique the electric field gradient (EFG) around the nuclear probe on a lattice site can be asserted. The EFG tensor V_{ij} is composed by three diagonal components V_{xx} , V_{yy} and V_{zz} that are by definition sorted in descending order of magnitude *i.e.* $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. The EFG tensor is fully described by the largest of the three components V_{zz} and the asymmetry parameter η ,

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad \text{with } 0 \leq \eta \leq 1 \quad (2.4.6)$$

where it represents the deviation of the EFG tensor from axial symmetry ($\eta = 0$).

The electric field gradient strength is represented by the quadrupole frequency constant ν_Q , defined by

$$\nu_Q = \frac{eQV_{zz}}{h} \quad (2.4.7)$$

In a similar way as the electric quadrupole interaction energy, the magnetic dipolar energy E_m can be introduced from a classical description and the following expression be obtained:

$$E_m = -\mu \cdot B \quad (2.4.8)$$

where μ is the nuclear magnetic moment. The splitting between any two adjacent sublevels is

$$E_m = \hbar\omega_L \quad (2.4.9)$$

where $\omega_L = \gamma B$ is the Larmor frequency.

For a more in-depth knowledge about these techniques many sources are available, from previous works ^[1,73] to dedicated books about the the hyperfine techniques ^[74].

Electric Field gradient point charge model calculations - Point charge model (PCM) calculations are extremely useful in order to obtain an estimative on the value of the efg around a determined nucleus probe. For this calculations the ions cores are treated as point charges, $Z_i e$, that are located at the ions lattice sites, giving in this way an approximation to the real lattice contribution to the EFG, V_{ij}^{latt} . In order to calculate the EFG, the second partial derivates of potential ϕ , at the probe site due to the influence of external charges z_i that are at a position r_i in relation to the origin, must be calculated. The contributions of all lattice atoms, normally within the distance of a few tens of angstroms and with the exception of the probe itself, have to be added, resulting in:

$$V_{ij}^{PCM} = \sum_i \frac{z_i e}{4\pi\epsilon_0 r_i^5} \begin{pmatrix} 3x_i^2 - r_i^2 & 3x_i y_i & 3x_i z_i \\ 3y_i x_i & 3y_i^2 - r_i^2 & 3y_i z_i \\ 3z_i x_i & 3z_i y_i & 3z_i^2 - r_i^2 \end{pmatrix} \quad (2.4.10)$$

After a diagonalization of the matrix the eigenvalues are obtained, corresponding to the EFG tensor and are chosen considering that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ and thus η the asymmetry parameter can be obtained.

In the case of ionic solids this model gives an good approximation to the observable EFG. However for covalent solids only poor agreement is obtained. In this work the PCM was used to obtain information about expected EFG for the ^{111}In probes in the A and B site in the AgCrO_2 delafossite structure. Also these values were compared with the ones obtained in the work of *Attili et al.* ^[22,30].

The experimental results of electric field major tensor V_{zz}^{exp} components were compared with the ones calculated theoretically V_{zz}^{PCM} using the Point Charge Model calculation.

Chapter 3

Synthesis and Characterization of the AgCrO_2 Delafossite

The delafossite family of minerals received its name in honor of the French mineralogist and crystallographer Gabriel Delafosse^[76]. His work contributed to share some insight to the interrelationships between crystal symmetry and physical properties. Many years later of the discovery of this mineral many studies on its properties became possible. Applications of delafossites go from transparent pn-junctions^[76] to non volatile memories^[77,78] and very recently the discovery of ferroelectricity driven by the magnetic order prompts these ACrO_2 systems to the forefront of the scientific research. Along with this discovery, the question of the microscopic origin of magneto-electric coupling in antiferromagnet triangular-lattice was raised. Thus, the aim of this work is to shed some light on the microscopic nature of this system.

In this chapter, the sample preparation procedures are described followed by the results obtained with the different techniques used to characterize/study it. At the end the general conclusions are presented.

3.1 Sample Preparation

The synthesis of the silver chromium oxide delafossite AgCrO_2 was tested using different methods, solid-state reaction and sol-gel combustion synthesis. Despite the fact that most of inorganic materials in solid state chemistry are produced by solid state reaction, a method that requires higher temperatures on its synthesis, different approaches are now being used to produce these compounds with characteristics suitable for other applications. One of those methods, is the sol-gel combustion synthesis that allows the preparation of these structures at nanoscale size^[46], making them suitable for an entire new world of applications, namely for medicine (biosensors, photocatalysts) and energy storage (solar cells)^[79,80], among others. The sol-gel combustion and microwave mixed method also presents itself as a promising, relative easy and fast way, to prepare this system.

In literature we can find different references in which the delafossite system is prepared. References to solid state reaction where chromium oxide and silver nitrate are used^[28,81] or LiCrO_2 , AgNO_3 and KNO_3 ^[82] (for solid-state reaction by cation exchange method), to hydrothermal synthesis^[47] passing by metathetical reactions, oxidizing flux^[76] and sol-gel combustion synthesis^[82]. The high temperature synthesis is still the method of election for the preparation of the delafossite

AgCrO_2 . However it is reported that with this method sometimes the formation of secondary phases^[81] (*e.g.* spinel Ag_2CrO_4) occurs even after annealings at temperatures as high as 900 °C. Also the presence of the initial reactants, chromium oxides or even of metallic silver at the surface is also reported^[81]. Several measurements reported in the literature using different analysis techniques, namely infra red fourier transform (FTIR), thermogravimetric analysis (TGA)^[81] and x-ray diffraction^[30,81], that after a treatment at 700 °C in air atmosphere the delafossite compound decomposes, but repeating the process in an O_2 flow the structure is synthesized again, showing that an oxygen rich atmosphere is necessary for the sintering process^[22,30].

Sol-Gel Combustion Synthesis

• SOL-GEL COMBUSTION METHOD

The AgCrO_2 delafossite was prepared by sol-gel combustion synthesis. Several experiments were conducted. Different complexing agents/combustion initiators were tested in order to prepare materials suitable for nanoscale applications, namely in the form of nanotubes, nanorods and even nanodots. In table 3.1.1 is presented a summary of the sintering stages.

Process	TAG	Complexing Agent		pH	Calc.	Anneal. #1 700 °C	Anneal. #2 900 °C
Sol-gel +	SG1	Urea	(NH ₂) ₂ CO	4.2	X	24h Air	24h Air
Microwave	SG2			4.7		48h O ₂	48h O ₂
	SG3.0			3.5		24h Air	48h Air
	SG3.1						
Sol-gel	SG4	Urea+Citric Acid	(NH ₂) ₂ CO+C ₆ H ₈ O ₇	4.2	12h Air	24h O ₂	24h O ₂
	SG5	Urea+Ethylene Glycol	(NH ₂) ₂ CO+C ₂ H ₆ O ₂				
	SG6	Citric Acid	C ₆ H ₈ O ₇				
	SG7	Ethylene Glycol	(NH ₂) ₂ CO				
	SG8	Glycine	C ₂ H ₅ NO ₂				

Table 3.1.1: Table of AgCrO_2 summarizing synthesis conditions by Sol-Gel Combustion and Sol-gel Microwave Synthesis.

In the following, the sol-gel method used for sample preparation is shortly described. To prepare the delafossite samples a similar methodology to the one described by C. Vázquez-Vázquez and co-authors^[49] with the appropriated changes for the delafossite system was used. We can also find reference to the sol-gel synthesis process, in the preparation of noble metal oxides in *Moore et al*^[83] and for delafossite systems in *Marquardt et al*^[76].

Stoichiometric amounts of silver nitrate and chromium (III) nitrate nonahydrate¹ were used as starting materials. Each of the reactants was first dissolved in millipore water² and then mixed together with constant swirling.

An aqueous solution of nitric acid HNO_3 was then added to ensure the desired nitrates were obtained. These nitrates were mixed and the pH solution was adjusted to a maximum value without allowing precipitation to occur. The pH of the solution was controlled by adding diluted ammonia $(\text{NH}_3)/\text{acid nitric } (\text{HNO}_3)$ to the solution. If the solution precipitates, it is possible to reverse that condition. Urea, nitric acid, ethylene glycol or glycine were used as gelling agents (see table 3.1.1). In the urea case an optimal molar relationship $[\text{urea}]/[\text{Cations}]=3$ ^[73] was used. The same molar

¹ $(\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$, Sigma-Aldrich, purity of 99%, CAS-NUMBER 7789-02-8

²Water with high purity is required, that is, without ions dissolved. Otherwise silver ions will react with the chloride ions (Cl^-) forming silver chloride, that is extremely difficult to dissolve again

relationship was adopted for the other gelling agents. Since the syntheses has similar procedures for the different combustion/gelling agents, in the following we will refer only to the urea case, see table 3.2.1. Next the solution was left in constant agitation during the night for aging.

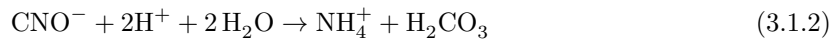
In the following day the same solution was vigorously stirred and the solvent evaporated in a hot plate at temperature around 80 °C. When almost all solvent was evaporated, the plate temperature was increased and at $T \approx 137$ °C urea started to decompose yielding NH_3 . The decomposition of urea is clearly indicated by the smell of ammonia and bubbles observed in the mixture. After, a dried gel was formed and was heated at 250 °C until combustion occurred. The combustion resulting powders were then submitted to different high temperature annealings, see table 3.1.1.

Combustion synthesis tend to generate large volumes of gases in the short interval of time of the combustion reaction, which makes the product foamy and facilitates the formation of soft agglomerate of fine particles. Therefore, the product obtained in combustion synthesis can be easily brought down to fine particles by minimum mechanical milling.

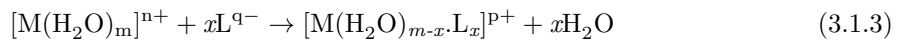
The role of the urea in the synthesis is very important. In aqueous solution, metallic ions are coordinated by water molecules, but when an aqueous solution of urea is heated at temperatures above 75 °C the decomposition of urea to CO_3^{2-} and NH_3 (with release of hydroxide ions) becomes significant. In the absence of acids the following reaction takes place:



In acid media a rapid and complete conversion of the cyanate ion to ammonium ion occurs:



The rate of decomposition depends on the temperature and urea concentration^[49]. Some new ligands which can substitute water molecules in their coordination positions around the metal ions (NH_4^+ , OH^- , CO_3^{2-}) appear in solution. The degree substitution of the water molecule by other ligands depends on the nature and concentration of metallic ions and ligands. The removal of water by evaporation promotes the substitution of ligands, according to the following equation:



where $\text{M}=\text{Ag}$ or Cr and $\text{L}=\text{NH}_3$, OH^- , CO_3^{2-} or urea. Urea ligands can coordinate metallic ions through the carbonyl or the amino group.

The initial aqueous solution has slightly acidic pH. The pH remains acidic during most of the evaporation process, increasing a little as water removal proceeds owing to the decomposition of urea, and the solution reaches neutral pH value. The small increase in pH is an indication that urea decomposes to only a small extent. This decomposition releases hydroxide ions which favors the hydrolysis of cations which leads to the formation of small amounts of a precipitate, usually cations with higher valence^[49].

In the specific case of the delafossite-type oxides, Shannon, Rogers, and Prewitt^[27–29] have presented that the noble A-site metal oxidizing state (where A-cation can be Ag, Pd or Pt for example) is stabilized by the base character of the B-site cation metal oxide. The B-site metal oxide and oxide hydroxides acidity permits them to be dissolved in the form of a metal hydroxo species, $[\text{B}(\text{OH})_y]^{3-y}$ (aq), when the appropriated conditions are gathered, *i.e.* elevated temperature and alkaline aqueous solutions. The acidic character of the B-site metal oxide is only revealed in strongly

alkaline solutions and is an important factor in the preparation of the delafossite type oxides^[81]. In this way, the silver delafossite oxide final product outcomes due to the reaction that occurs between the A and B-site cations present in the solution. The B-site metal cation can react in solution and different products are obtained, going from the desired delafossite structure to undesired Cr_2O_3 , oxide hydroxides, (CrOOH) or trihydroxides $(\text{Cr}(\text{OH})_3)$, that result from no reactivity to side products.

Both proton and hydroxide concentration (but to a lesser degree), increases the solubility of $\text{Cr}(\text{OH})_3$. The alkaline conditions favors the valence 3+ of the chromium cation because it is stabilized due to the formation of the aqueous soluble $\text{Cr}(\text{OH})_4^-$ species. The $\text{Cr}(\text{OH})_3$ behaves like a weak amphoteric hydroxide despite the fact that its basic character is more declared than its acidic character.

The chromium-water Pourbaix diagram^[84] analysis indicates that for elevated temperatures the alkaline degree of $\text{Cr}(\text{OH})_3$ is unknown, while the region for $\text{Cr}(\text{OH})_4^-$ increases, indicating an temperature dependence with the concentration. At 200 °C the solubility of Cr_2O_3 in a alkaline media is almost nonexistent^[81]. Also in the study of *Abu-zied et al.*^[81] where the preparation of silver and copper delafossite oxides was accomplished, is reported that both $\text{Cr}(\text{OH})_3$ and CrOOH react with Cu_2O to form a pure phase of the 3R-polymorph CuCrO_2 at a temperature of 210 °C in a hydroxide concentration. However, the author observed that Cr_2O_3 didn't react to form CuCrO_2 when similar conditions were in place. Their observations and conclusions report that the hydrated metal oxides have an amphoteric behavior, and that the formation of the desired phase is limited by its slow transition to a more soluble reactant. Differently of other amphoteric transition metal oxide/hydroxides, CrOOH and $\text{Cr}(\text{OH})_3$ instead of reacting with Ag_2O , allow the formation of great quantities of metallic silver.

It has been proposed that, when in an air atmosphere and at elevated temperatures (but below the decomposition temperature of 300 °C), Ag_2O undergoes slow dissociative evaporation to molecular oxygen and free silver atoms, which immediately condense as metallic silver. On the other hand, $\text{Ag}(\text{OH})_2$ is stable under solution and therefore can react and yield silver delafossite type oxides with other trivalent transition metals (e.g., iron), in the presence of Cr^{3+} ions^[81]. One important thing that has to be taken into account is the fact that Cr^{3+} can be oxidized to Cr^{6+} , and in this way limit the decomposition of Ag_2O to metallic silver and therefore limit the formation of AgCrO_2 . In order to produce the silver chromium oxide, the B-site cation can present an amphoteric behavior, but it cannot be allowed to oxidize.

Having in mind the properties of urea described above a set of samples with different complexant/combustion agents was tested. For example the glycine nitrate process (GNP) SG8 (see table 3.1.1) is a self-combustion method using glycine as fuel and the nitrates of the metal components of the material to be synthesized as oxidant. However, chromium in the materials is easily oxidized in air at high temperatures to form vaporizing compounds such as CrO_x , $\text{CrO}_x(\text{OH})_y$ and $\text{Cr}(\text{OH})_y$, what causes some difficulties in the process synthesis. Glycine ($\text{C}_2\text{H}_5\text{NO}_2$) is used not only as the fuel but also as the complexing agent, where the amine group ($-\text{NH}_2$) in glycine can complex with the transition metal ions, and the carboxyl group ($-\text{COO}$) can complex with alkaline earth metal ions.

• SOL-GEL MICROWAVE METHOD

In the case of samples SG1 and SG2 a different approach to the method was tested and is described in the following.

A new way to synthesize the delafossite structure AgCrO_2 was tested. This method differs from the previous in the following way: after the addition of the gelling agent, the solution was placed

in the microwave during 5 to 10 minutes. When a gel like phase was formed a small aluminium metal piece was placed together with the gel, and then the microwave was operated at its maximum power. This provokes the combustion of the materials inside.



Figure 3.1.1: Picture of sample after the combustion.

The result was a dark green tree polymer powder that was grounded in an agate mortar with a pestle yielding the precursor to prepare the final samples (see figure 3.1.1). The grains are united in branched chains. The colonies of particles linked in chains retain the structure of the gel. As discussed before in order to favor further polycondensation and enhance mechanical properties and structural stability, densification and grain growth, this precursor was pelletized and annealing treatments at 700 °C and 900 °C in alumina crucibles inside a furnace were performed. Subsequent annealing treatments were performed to obtain the desired final samples. Between each heat treatment the samples were grounded in an agate mortar with a pestle and pressed into pellets.

- Sol-Gel Template Method

A nanoporous alumina membrane was used in an attempt to produce silver chromium oxide nanotubes via the sol-gel template method. It should be noticed that this was only a glim into the future in the production of nanostructures and that wasn't part of the objectives of this work. However in the future we expect to dedicate more time into this subject, and to go forward into this amazing area of physics and chemistry. The alumina templates can be easily fabricated using adequate anodization conditions and the pore size and interpore distance easily varied [85]. Furthermore, their use for growth of nanotubes has enormous advantages: the possibility to build a net of aligned and ordered nanostructures, the chance to fill or functionalize their inner side without affecting their outer surface and the ability to control the dimensions required. Using this method, not only the length of the nanotubes is controlled, but we can also control their diameter and thickness, allowing us to vary these characteristics along their surface. The nanoporous alumina template was produced by other members of the group who are developing this work for a different type of compounds. The sol-gel template method takes advantage of an alumina template emersed in the solution when the gel like phase is forming and remains there until it combusts. The preliminary results can be observed in Appendix B.

Solid State Reaction

To prepare de delafossite sample by high temperature solid state reaction the method description reported by *Shannon et al* [28] and mainly by *Abu-Zied et al* [81], using chromium (III) oxide³ and silver

³Cr₂O₃ - Merck, metal basis with a purity of 99 %, CAS-NUMBER 1308-38-9.

nitrate⁴ as starting materials was followed. However, different reactants can be used as described in a series of works by *Rogers, Shannon and Prewitt*^[27,29] or *Oohara et al.*^[34].

Stoichiometric amounts of these powders (for a final sample mass of $\text{AgCrO}_2 \approx 1$ g) were mixed and grinded several times in an agate mortar⁵ until a very fine mixture was obtained.

The mixture was then pressed into a round pellet, of about 13 mm in diameter, with approximated $6.89 \times 10^7 \text{ N.m}^{-2}$ of applied pressure, using a press (12 Ton E-Z Press from ICL). The pellets were placed inside a high purity Al_2O_3 crucibles and surrounded by a small amount of sacrificial powder of the same nominal composition in order to prevent reaction between the pellet and the crucible. A calcination step at 500 °C during 12 hours (initial temperature rise with 5 °C/min ramp), using a tubular furnace (TZF1200C from Carbolite Furnaces) was performed. The idea behind this first step was the removal of any organic impurities and the release of NO_x from the reactants. This could be observed as a yellowish vapor left out the furnace as the temperature increased. After the calcination the sample was slowly cooled down to room temperature (RT) with a 10 °C/min cooling ramp. Once the sample was cooled to RT, a small amount of sample was investigated by x-ray diffraction and the rest of the sample was grinded again several times until a good homogeneity and fine powders were obtained. A new pellet was made and a new firing at 700 °C was performed. The process was repeated again but this time at a final temperature of 900 °C. Typically from literature^[81] two firing cycles are enough to obtain a pure phase sample.

Several attempts were made to synthesize the delafossite structure, meaning that, different final annealing conditions were tested, namely by changing the duration and the atmosphere of the annealings (see table 3.1.2). To achieve this, an annealing system with oxygen flow, was developed and mounted in a tubular furnace⁶.

A 50% gas mixture of O_2/N_2 was used in order to create the O_2 rich gas flow.

Table 3.1.2 summarizes the conditions of the different experiments, as also the different tags, used for cataloguing the samples.

Calcination	TAG	Annealing #1 700 °C	Annealing #2 900 °C	
500°C 12h Air	SS1	24h Air	24h Air	SS1A
			24h O_2	SS1B
			48h O_2	SS1C
	SS2	12h O_2	12h O_2	SS2A
	SS3	24h O_2	24h O_2	SS3A
			48h O_2	SS3B

Table 3.1.2: Table summarizing AgCrO_2 synthesis conditions by Solid State Reaction.

⁴ AgNO_3 - Alfa Aesar, ultra dry, metal basis with a purity of 99.9+%, CAS-NUMBER 7761-88-8

⁵The number one purpose of any mortar and pestle set is to grind solids into fine powders but under conditions that are highly controlled as to not produce any heating effects and to minimize and control any effects due to stretching of sometimes deformable materials. This is probably the most ancient device one is likely to find in a modern scientific laboratory or kitchen. Give its ability to control the grinding, with virtually no contamination.

⁶The system wasn't ideal because the O_2 flow was unstable when the temperature changed and for that reason a constant monitoring and therefore a regular adjustment in the flow was required. For future sintering a new flowmeter will certainly solve this problem.

3.2 Structural and Morphological Characterization

3.2.1 X-Ray Diffraction

Structural characterization is always the first, and sometimes one of the most difficult and time consuming step after synthesis. The most common tool for the identification of polycrystalline solids, and in this case the AgCrO_2 samples, is powder x-ray diffraction, as presented before in section 2.2.1.

The x-ray diffraction patterns presented in this work, were used to characterize the polycrystalline AgCrO_2 samples, after the different annealing conditions in which they were prepared. The patterns are grouped aiming a good visualization of the different results. In some cases an alternative organization of the data is showed in the end of the work (see appendix A). When this is the case, a reference will be given.

An effort was made to characterize the samples using powder specimens. A large difference in relative intensities of some peaks when comparing with the theoretical pattern generated was observed when pellet specimens were used. When peak intensities are altered due to preferential growth of the polycrystalline sample it is very difficult to distinguish in the pattern background the presence of other peaks. This is the case of AgCrO_2 samples where a preferential crystal growth is observed.

Le Baile and Rietveld refinements with FULLPROF software were used to determine the structural parameters and the existence of secondary or impurity phases.

Sol-Gel Combustion Synthesis Samples

- SOL-GEL COMBUSTION METHOD SAMPLES

In table 3.2.1 we present once more the different annealings and complexing agent used in the synthesis of the AgCrO_2 samples by sol-gel combustion method.

Process	TAG	Complexing Agent		pH	Calc.	Anneal. #1 700 °C	Anneal. #2 900 °C
Sol-gel	SG3.0	Urea	(NH ₂) ₂ CO	3.5	12h Air	24h O ₂	24h O ₂
	SG3.1						
	SG4	Urea+Citric Acid	(NH ₂) ₂ CO+C ₆ H ₈ O ₇	4.2			
	SG5	Urea+Ethylene Glycol	(NH ₂) ₂ CO+C ₂ H ₆ O ₂				
	SG6	Citric Acid	C ₆ H ₈ O ₇				
	SG7	Ethylene Glycol	(NH ₂) ₂ CO				
	SG8	Glycine	C ₂ H ₅ NO ₂				

Table 3.2.1: Table summarizing AgCrO_2 synthesis conditions by Sol-Gel Combustion Synthesis.

In the preparation, by the sol-gel combustion method, of the silver chromium oxide delafossite we have tested both the influence of complexing/combustion agent, as well the influence of pH, see table 3.2.1.

In this synthesis process an effort was also made in order to characterize the samples in every step. In the following we will present several XRD patterns organized by stages of the sintering process. However, in Appendix A the XRD patterns are presented by sample with all the performed heat treatments. In this way its possible to examine each sample individually.

In total, with all the complexing agents and the different combinations used, six different samples were synthesized. Urea was used for samples SG3.0 and SG3.1, a combination of Urea and citric acid for sample SG4, urea and ethylene glycol for sample SG5, citric acid for sample SG6, ethylene glycol for sample SG7 and glycine for sample SG8, as it can be seen in table 3.2.1.

In figure 3.2.1 are presented the XRD patterns performed in the set of samples SG3-SG8 after the combustion in the hot plate (a) and the XRD patterns performed in the set of samples SG3-SG8 after the calcination step to a temperature of 500 °C during 12 hours in air (b). All of the XRD patterns presented in the figure are of powder samples.

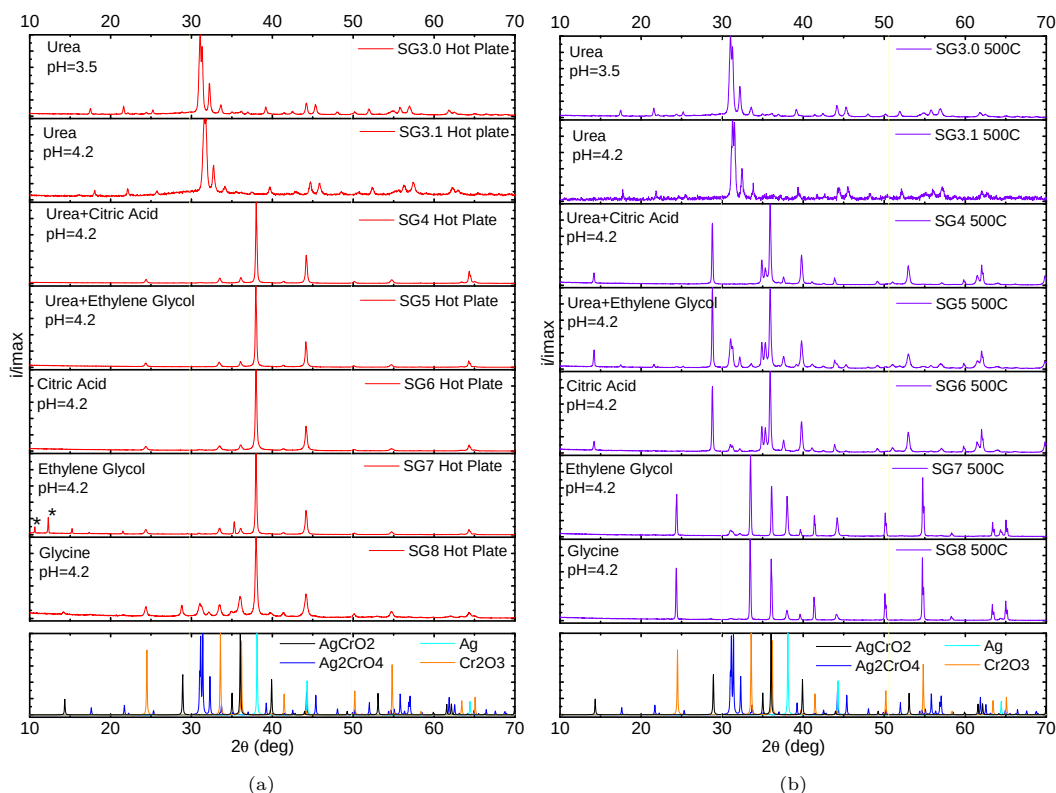


Figure 3.2.1: X-ray diffraction patterns performed in the set of samples SG3-SG8 synthesized by sol-gel. After the combustion in the hot plate (top)(a). After the calcination at 500 °C in air during 12 hours (top)(b). Expected diffraction pattern of AgCrO_2 , Ag_2CrO_4 , Ag , Cr_2O_3 for comparison (bottom). All patterns were normalized to the intensity of the most intense peak.

Hot Plate - From PXRD patterns present in figure 3.2.1 (a), collected after the gel combustion in the hot plate, one can see significant differences between samples prepared using urea, from those prepared with the other complexing agents (urea+citric acid, urea+ethylene glycol, citric acid, ethylene glycol and glycine).

Samples with urea, SG3.0-Urea-pH=3.5 and SG3.1-Urea-pH=4.2, present a pattern that can be associated, with the one of silver chromate (Ag_2CrO_4) with an orthorhombic structure and space group $Pnma$ with also traces of chromium (III) oxide. The difference of the pH values in the synthesis process between these two samples is not significative, for no distinctive peak is present. While samples SG4-Urea+Citric Acid, SG5-Urea+ethylene Glycol, SG6-Citric Acid to SG7-Ethylene Glycol exhibit the presence of a major phase associated to metallic silver and trace amounts of Cr_2O_3 , as can be seen by comparing it to the calculated PXRD patterns of this phases shown in figure 3.2.1 (a) at the bottom. The pattern collected from sample SG7-Ethylene Glycol in figure 3.2.1 (a), has two peaks marked with "*" corresponding to an unknown phase. A series of patterns, from various silver

oxides to chromium oxides passing through trivalent compounds of silver, chromium and oxygen, were tested in order to find same peak reflections but with no results. This also can be related to some impurity phase that came into contact with the sample.

The last PXRD patterns presented in figure 3.2.1 (a), where glycine was used as a complexing agent, SG8-Glycine, is the most promising one since the delafossite structure can be already identified, although still at small amounts. Ag_2CrO_4 and Cr_2O_3 are the other phases that are also present in a trace basis, leaving the metallic silver as a major component in this pattern.

After this first sintering step the sample prepared with glycine is the only one that has evidence of the presence of silver chromium oxide with the delafossite structure. From the notes collected from combustion reaction that occurred during the first part of the synthesis, one can say that the solutions that had urea were the ones that presented a more vigorous combustion.

Calcination - 500 °C 12 hours Air - After combustion in the hot plate, grinding and pelletizing, the samples were then fired in air during 12 hours at 500 °C. In figure 3.2.1 (b) are presented the PXRD patterns collected after this procedure. The PXRD patterns of the samples SG3.0-Urea-pH=3.5 and SG3.1-Urea-pH=4.2 presented in figure 3.2.1 (a) (after combustion) and (b) (after calcination step) are quite similar. No evidence for modification could be detected in the PXRD patterns. As described in section 2.1.1 one of the purposes of the complexing agent is that its decomposition is a very energetic reaction which provides the combustion with enough energy for self propagating until all reactant are ended.

As noted before, the reactions where only urea was present were more energetic than the others. Therefore the temperature that the samples were submitted during the process was almost enough to do the same purpose as the calcination step. This being one explanation for the fact that after an heat treatment at 500 °C the samples kept their properties.

For the rest of the samples, a less energetic combustion was observed and the same supposition can't be made because the patterns collected after the firing at 500 °C exhibit more evident differences. The PXRD pattern collected for SG4, urea+citric acid, after the calcination step exhibit already the presence of a major phase of AgCrO_2 . The calcination step favored the formation of the delafossite structure that wasn't present in the previous step. Nevertheless a trace of metallic silver still persisted in the sample.

The sample SG5-Urea+Ethylene Glycol, also presents the AgCrO_2 as major phase but with a minor contribution of Ag_2CrO_4 , Cr_2O_3 and Ag. With this heat treatment the delafossite phase was formed but with secondary phases. The same is observed for sample SG6-Citric Acid, where secondary phases are Ag_2CrO_4 and Ag.

However for the samples SG7-Ethylene Glycol, and SG8-Glycine, it is only possible to match the PXRD pattern to the calculated pattern of Ag and Cr_2O_3 with a trace of Ag_2CrO_4 . Intriguingly, these two samples were, from the point of view of the pattern obtained after the combustion, the most promising ones. In fact after the combustion they already presented the peaks corresponding to the delafossite phase but they disappear after the treatment at 500 °C.

Annealing - 700 °C 24 hours O_2 - In figure 3.2.2 are presented the XRD patterns performed in the set of samples SG3-SG8 synthesized by sol-gel after the annealing at 700 °C in O_2 flow during 24 hours (a) and the XRD patterns of the same samples after the annealing at 900 °C in O_2 flow during 24 hours (b).

After the annealing to 700 °C in an O_2 flow during 24 hours all PXRD patterns presented the

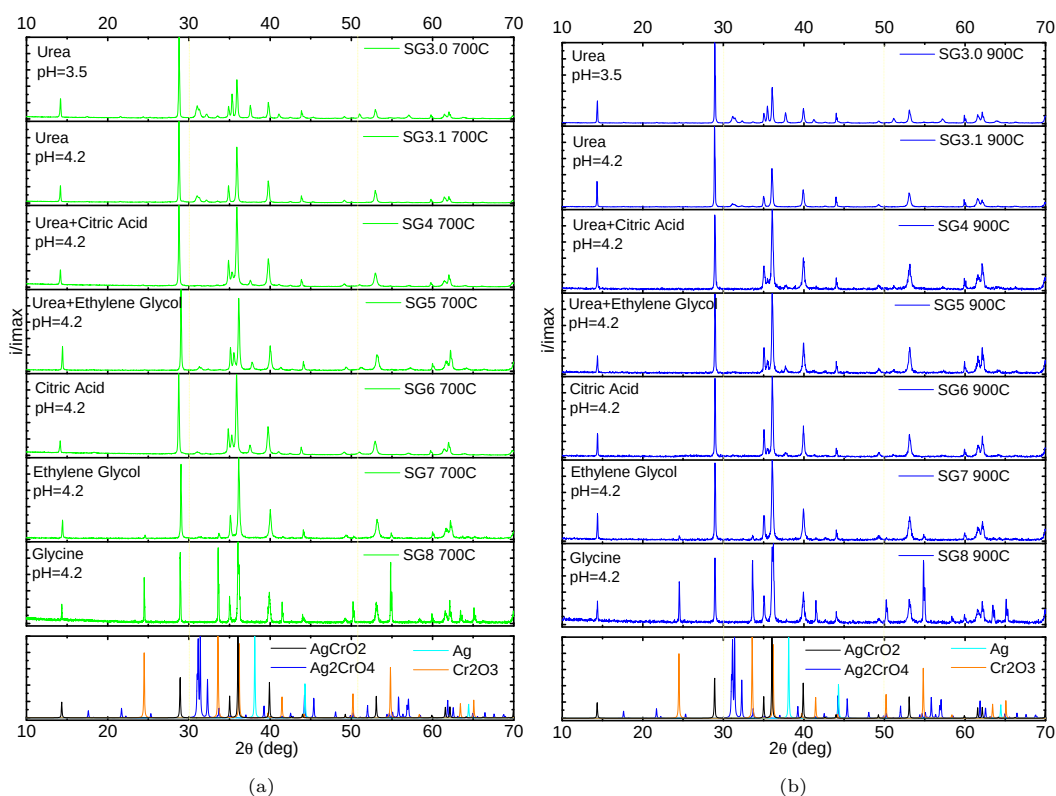


Figure 3.2.2: X-ray diffraction patterns performed in the set of samples SG3-SG8 synthesized by sol-gel. After the annealing at 700 °C in O_2 during 24 hours (top)(a). After the annealing at 900 °C in O_2 during 24 hours (top)(b). Expected diffraction pattern of AgCrO_2 , Ag_2CrO_4 , Ag, Cr_2O_3 for comparison (bottom). All patterns were normalized to the intensity of the most intense peak.

delafossite structure. The samples SG3.0-Urea to SG6-Citric Acid, along with the peaks corresponding to the rhombohedral structure of the delafossite also present a minor phase of Ag_2CrO_4 and traces of Ag. The same doesn't happen with samples SG7-Ethylene Glycol and SG8-Glycine that present instead a second phase corresponding to Cr_2O_3 . In the case of sample SG7-Ethylene Glycol only a small contribution of this second phase is present. In sample SG8-Glycine this second phase is present in almost the same quantity as the delafossite phase, as can be seen in figure 3.2.2 (a).

Annealing - 900 °C 24 hours O_2 - A third heat treatment at high temperature was performed in order to achieve pure samples of silver chromium oxide. The heat treatment was performed during 24 hours in an O_2 flow at a temperature of 900 °C. The PXRD patterns collected after this last firing step are presented in figure 3.2.2 (b).

Analyzing the PXRD patterns obtained from the samples after the third annealing, presented in figure 3.2.2 (b), one can observe that the patterns are very similar to the ones obtained after the annealing at 700 °C. However, some differences can be observed, namely in samples SG5-Urea+ethylene Glycol and SG6-Citric Acid now only one secondary phase is present, the Ag phase. The same secondary phase can also now be found in sample SG8-Glycine although is only a very small trace along with the Cr_2O_3 major phase that didn't decompose to form the delafossite structure.

For a better visual understanding of the phase's evolution, Table 3.2.2 summarizes the composition of the samples in the different steps of the annealing.

TAG	Complexing Agent	pH	Phases ^a	Hot Plate	Calcination 500 °C	Annealing 700 °C	Annealing 900 °C	Lattice Parameters <i>a, b, c</i> (Å)	Space Group
SG3.0	Urea	3.5	AgCrO ₂	-	-	M	74.8%(5)	2.985;2.985;18.499	<i>R3m</i>
			Ag ₂ CrO ₄	M	M	m	25.2%(5)	10.052;7.017;5.530	<i>Pnma</i>
			Cr ₂ O ₃	M	M	-	-		
			Ag	-	-	t	-		
SG3.1	Urea	3.5	AgCrO ₂	-	-	M	82.1%(9)	2.985;2.985;18.499	<i>R3m</i>
			Ag ₂ CrO ₄	M	M	m	17.9%(9)	10.052;7.018;5.521	<i>Pnma</i>
			Cr ₂ O ₃	M	M	-	-		
			Ag	-	-	t	-		
SG4	Urea+Citric Acid	3.5	AgCrO ₂	-	M	M	98.0%(10)	2.987;2.987;18.511	<i>R3m</i>
			Ag ₂ CrO ₄	-	-	m	-		
			Cr ₂ O ₃	t	-	-	-		
			Ag	M	t	t	2.0%(10)	4.085;4.085;4.085	<i>Fm3m</i>
SG5	Urea+Ethylene Glycol	4.2	AgCrO ₂	-	M	M	98.0%(10)	2.986;2.986;18.511	<i>R3m</i>
			Ag ₂ CrO ₄	-	m	m	-		
			Cr ₂ O ₃	t	m	-	-		
			Ag	M	m	t	2.0%(10)	4.086;4.086;4.086	<i>Fm3m</i>
SG6	Citric Acid	4.2	AgCrO ₂	-	M	M	97.2%(8)	2.986;2.986;18.511	<i>R3m</i>
			Ag ₂ CrO ₄	-	m	m	-		
			Cr ₂ O ₃	t	-	-	-		
			Ag	M	m	t	2.8%(8)	4.068;4.068;4.068	<i>Fm3m</i>
SG7	Ethylene Glycol	4.2	AgCrO ₂	-	-	M	94.8%(6)	2.987;2.987;18.509	<i>R3m</i>
			Ag ₂ CrO ₄	-	t	-	-		
			Cr ₂ O ₃	t	M	t	5.2%(6)	4.953;4.953;13.604	<i>R3c</i>
			Ag	M	M	-	-		
SG8	Glycine	4.2	AgCrO ₂	t	-	M	49.3%(7)	2.987;2.987;18.515	<i>R3m</i>
			Ag ₂ CrO ₄	t	t	-	-		
			Cr ₂ O ₃	t	M	M	50.7%(7)	4.960;4.960;13.598	<i>R3c</i>
			Ag	M	M	-	t		

^aM: major; m: minor; t: trace

Table 3.2.2: Structural information of the samples synthesized by Sol-Gel Combustion method in the different steps of sintering.

The sol-gel combustion method allowed the preparation of samples with good quality, yielding after the annealing at 900 °C almost single phases of AgCrO₂ in the cases of samples SG4 to SG7. In these samples only small traces of secondary phases can be encountered. Samples prepared with urea as the only complexing agent, ended having Ag₂CrO₄ phase as minor contaminant phases and the samples prepared with glycine that is composed by a mixture of AgCrO₂ and Cr₂O₃ present in the same proportion. Maybe with another annealing at a higher temperature or with a longer duration a pure phase with no spurious secondary phases could be obtained.

• SOL-GEL MICROWAVE METHOD SAMPLES

Part of table 3.1.1 is presented below as table 3.2.3 to facilitate the access to the different annealings and atmospheres used in the synthesis of the AgCrO₂ samples by sol-gel microwave method, with urea as a complexing/combustion agent.

Process	TAG	Complexant Agent	pH	Calc.	Anneal. #1 700 °C	Anneal. #2 900 °C
Sol-gel + Microwave	SG1	Urea (NH ₂) ₂ CO	4.2	X	24h Air	24h Air - SG1A
	SG2		4.7		24h Air	48h O ₂ - SG1B 48h Air - SG2A

Table 3.2.3: Table summarizing of AgCrO₂ synthesis conditions by Sol-Gel Microwave Synthesis.

The x-ray diffraction patterns performed along the several synthesis steps are presented in figure 3.2.3, for the samples SG1 (pH=4.2) in (a) and for samples SG2 (pH=4.7) in (b), permitting to follow the evolution of the sample along the several heat treatments.

In the synthesis process of the samples SG1-4.2 and SG2-4.7 two different values of pH (4.2 and 4.7, respectively) were tested to acquire information about the optimum pH value required for the synthesis of the AgCrO_2 samples by sol-gel microwave combustion method.

Microwave - Through x-ray diffraction it is possible to detect that after the combustion process a

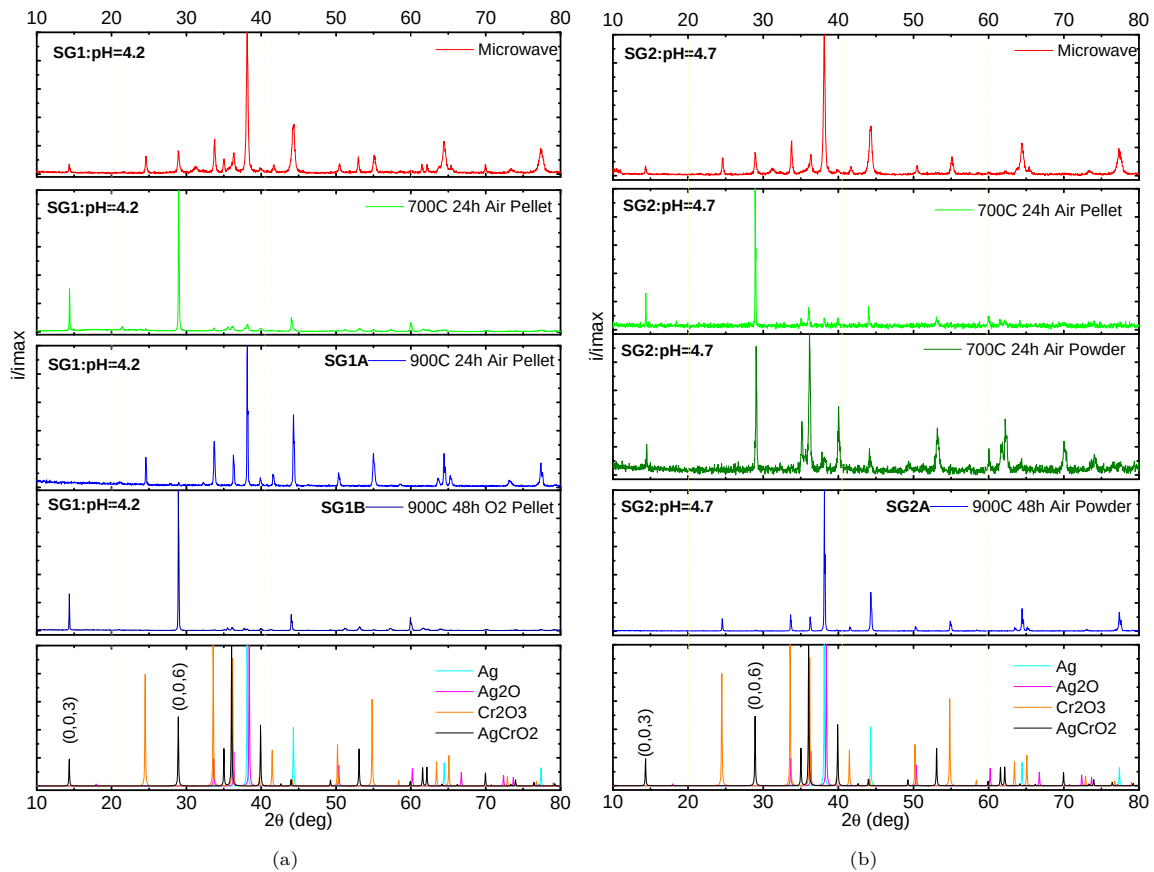


Figure 3.2.3: X-ray diffraction patterns performed for the set of samples synthesized by mixed sol-gel microwave method using urea as a complex agent. In (a) the samples synthesized with a pH of 4.2 and in (b) with a pH of 4.7 in the different firing stages. All patterns were normalized to the intensity of the most intense peak. X-ray diffraction patterns performed in the set of samples SG1 (top)(a). X-ray diffraction patterns performed in the set of samples SG2 in the different firing stages (top)(b). Expected diffraction pattern of Ag, Ag_2O , Cr_2O_3 and AgCrO_2 for comparison (bottom).

mixture of different phases is present in the sample, as shown in Fig.3.2.3 a) and b), in the microwave corresponding patterns. From matching this XRD profile with the calculated profiles presented in the bottom of the figure, three different phases were identified, two major phases corresponding to metallic silver (Ag), chromium sesquioxide (Cr_2O_3 one of the reactants) and one minor phase corresponding to the silver chromium oxide AgCrO_2 desired structure. This can be observed in both patterns (a) and (b), but in XRD pattern from sample SG1-pH4.2 a set of more pronounced peaks

corresponding to the delafossite system are evident.

Annealing 700 °C - A first heat treatment at 700 °C during 24 hours in an air atmosphere was performed in both samples. The patterns — 700C 24h Air Pellet for SG1-pH4.2 and SG2-pH4.7, presented in figure 3.2.3 (a) and (b) respectively, show as the major phase the delafossite structure. After the treatment at 700 °C, the XRD patterns for both samples, SG1-pH4.2 and SG2-pH4.7, are very similar, and therefore a study of the atmosphere and annealing time influence in the synthesis of this system is possible.

As referred before, the polycrystalline AgCrO₂ samples exhibit a preferential orientation growth. Pattern — 700C 24h Air Pellet collected using a sample in the form of a pellet, substantiate this feature. As we can see in the referred pattern, the peaks corresponding to $2\theta \approx 14$ and $2\theta \approx 28$ have much higher intensities than the rest of the peaks in the pattern. When comparing this pattern to the pattern — 700C 24h Air Powder in figure 3.2.3 (b), one can observe that these relative intensities become much smaller when it is collected in a powder form sample.

Due to the fact that c is much greater than a or b , the polycrystalline samples grow preferentially along the c -axis of the structure, showing that they are texturized. The most intense peaks correspond to reflections due to the planes (0,0,3) and (0,0,6), evidently planes perpendicular to the c -axis. This evident texture of the sample, also can be observed by the data collected by scanning electron microscopy SEM technique, discussed in section 3.2.2.

Also in the XRD pattern shown in figure 3.2.3 (b), — 700C 24h Air Powder, among with the delafossite phase peak reflections metallic silver (Ag) peaks are present. In addition peaks that had low relative intensities when the pattern was collected in the pellet form are visible in the powder spectrum.

Annealing 900 °C - Both samples after the firing at 700 °C suffered new heat treatments but at higher temperature of 900 °C. Three different annealings were performed to the samples SG1-pH4.2 and SG2-pH4.7. The SG1-pH4.2 sample suffer one annealing at 900 °C during 24 hours in air SG1A and one at 900 °C during 48 hours in a O₂ atmosphere SG1B. XRD patterns — 900C 24h Air Pellet and — 900C 48h O₂ Pellet, respectively, can be observed in figure 3.2.3 (a). Sample SG2-pH4.7 suffer an annealing at 900 °C during 48 hours in air SG2A, see — 900C 48 Air Pellet in figure 3.2.3 (b).

Looking at the XRD patterns obtained by sample — 900C 24h Air Pellet SG1A, two phases are identified. One minor belonging to metallic silver (Ag) and one major to chromium sesquioxide (Cr₂O₃), with space group $Fm\bar{3}m$ and $R\bar{3}c$ respectively. The sample — 900C 48h Air Powder SG2A, in figure 3.2.3 (b), show the presence of metallic silver (Ag major phase) and chromium sesquioxide (Cr₂O₃ minor phase). While in the sample that was fired at 900 °C during 48 hours in rich O₂ atmosphere SG1B, — 900C 48 Air Pellet, there are three phases present, the same that in the sample — 700C 24h Air Pellet (a), a major phase of silver chromium oxide and traces of metallic silver and chromium (III) oxide. In this sample is also evident the preferential orientation growth along c -axis.

However, attention is needed when comparing the final patterns at 900 °C because of the sample texturing present in the patterns of the pellet samples. By comparing the patterns that were fired at 900 °C its possible to verify that annealings at this temperature in an air atmosphere decompose the already formed phase of silver chromium oxide that was present after the treatment at 700 °C. It is also possible to verify from the pattern presented, — 900C 24h Air Pellet SG1A, that after 24 hours at 900 °C in air atmosphere the delafossite was already decomposed.

A Le Baile refinement was performed to the samples after the final heat treatment at 900°C for retrieving the sample's structure information, using a pseudo-voigt function to generate the line shape of the diffraction peaks. The results can be seen in table 3.2.4. By the width of the peaks one can assume that these are samples with very large grain size.

TAG	Complexing Agent	pH	Phases ^a	Hot Plate	700 °C	Annealing 900 °C	Lattice Parameters <i>a, b, c</i> (Å)	<i>α, β, γ</i> (°)	Space Group	
SG1A	Urea	4.2	AgCrO ₂	m	M	-	-	-	-	
			Cr ₂ O ₃	M	-	57.5%(5)	24H Air	4.951,4.951,13.565	90, 90, 120	<i>R</i> $\bar{3}$ <i>c</i>
			Ag	M	t	42.5%(5)		4.089,4.089,4.089	90,90,90	<i>Fm</i> 3 <i>m</i>
AgCrO ₂			m	M	88.2%(5)	2.981,2.981,18.500		90,90,120	<i>R</i> 3 <i>m</i>	
Cr ₂ O ₃			M	-	4.5%(5)	48H O ₂	4.060,4.060,13.564	90, 90, 120	<i>R</i> 3 <i>c</i>	
Ag			M	t	6.7%(5)		4.059,4.059,4.059	90,90,90	<i>Fm</i> 3 <i>m</i>	
SG2A		4.7	AgCrO ₂	m	M		-	-	-	-
Cr ₂ O ₃			M	-	23.4%(6)	48H Air	4.954,4.954,13.505	90,90,120	<i>R</i> 3 <i>c</i>	
Ag			M	t	76.6%(6)		4.085,4.085,4.085	90,90,90	<i>Fm</i> 3 <i>m</i>	

^aM:major; m:minor; t:trace

Table 3.2.4: Structural information of the samples synthesized by Sol-Gel Microwave Method in the different steps of sintering. Lattice parameters retrieved by Le Baile refinement of the XRD patterns from samples after the final annealing at 900°C .

Solid State Reaction

The preparation of the silver chromium oxide delafossite was tested by the high temperature solid state reaction synthesis. This three step synthesis process is composed by one calcination step at 500°C during 12 hours in air, one step at 700°C and one final step at 900°C . For the last annealing steps, different atmospheres and annealing times where tested.

XRD patterns were collected after each heat treatment. They will be presented next as a sequence of heat treatments that each sample has endured.

Table 3.2.5 is presented below to facilitate the access of the different annealings times, temperatures and atmospheres used in the synthesis of the AgCrO_2 samples by solid state reaction, as also the different tags used for cataloging the samples.

Calcination	Annealing #1 700 °C	Annealing #2 900 °C	TAG
500°C 12h Air	24h Air	24h Air	SS1A
		24h O ₂	SS1B
		48h O ₂	SS1C
	12h O ₂	12h O ₂	SS2A
	24h O ₂	24h O ₂	SS3A
		48h O ₂	SS3B

Table 3.2.5: Table of AgCrO_2 synthesis conditions by Solid State Reaction.

• SOLID STATE SS1

In this way in figure 3.2.4 are presented the XRD patterns of the set of samples SS1 and the calculated diffraction pattern of AgCrO_2 , Ag_2CrO_4 , Ag, Cr_2O_3 for phase identification.

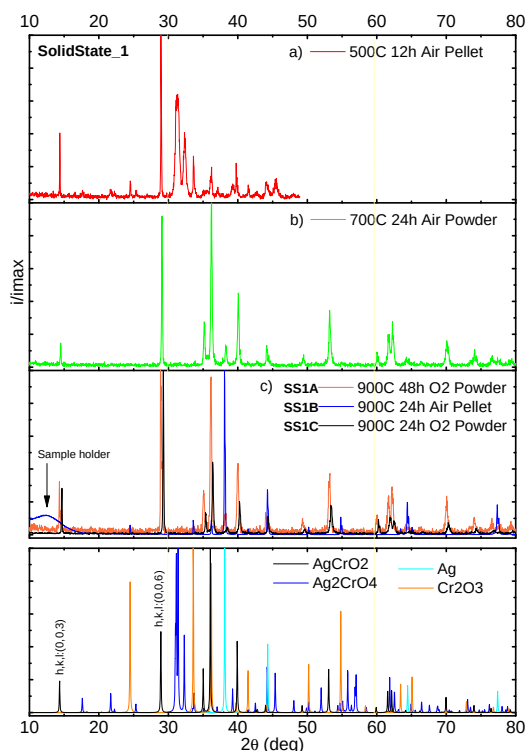


Figure 3.2.4: X-ray diffraction patterns performed for the set of samples SS1. (Top) After the calcination at 500 °C in air during 12 hours (a), after the annealing at 700 °C in air during 24 hours (b) after the annealing at 900 °C (c). (Bottom) Calculated diffraction pattern of AgCrO_2 , Ag_2CrO_4 , Ag, Cr_2O_3 for comparison.

Calcination 500 °C - After the reactants powders were mixed, grinded and pelletized, a calcination treatment was performed in air during 12 hours at a temperature of 500 °C. After this treatment was performed a XRD pattern was collected, and is shown in see figure 3.2.4 a). At this sintering stage, a XRD scan $[2\theta] = [10 - 50^\circ]$ was performed. This was enough to verify that the silver chromium oxide AgCrO_2 was present. In detail the sample was a mixture of three crystallographic phases: AgCrO_2 , Ag_2CrO_4 and Cr_2O_3 .

Like in the samples prepared by sol-gel method, the delafossite phase here exhibits a preferential growth orientation along the c-axis of the crystal. This can be observed as the relative intensities of the peaks $2\theta = 14.4$ and 28.9 are much higher in compararison with the rest. Texturization of the samples, is a characteristic of the system and does not depend on the sintering method, has it is present in samples prepared by sol-gel combustion method and by solid state reaction. Notice that although in most of the times we have tried hard to reduce the samples to fine grain powders the grinding performed doesn't seem to be enough to entirely destroy the texture.

Annealing 700 °C - The annealing performed at a temperature of 700 °C during 24 hours in air, seemed enough to decompose the Ag_2CrO_4 and Cr_2O_3 . The sample presents as a majority phase the delafossite AgCrO_2 , but traces of Ag have appeared with this annealing, see figure 3.2.4 b).

Annealing 900 °C - After this treatment the sample was divided into three pieces and each

one was fired in different conditions in a temperature of 900 °C. In figure 3.2.4 c) are represented the XRD patterns collected after this final annealing. The sample that was soaking during 48 hours in an O_2 flow is represented by ss1C— 900C 48h O_2 Powder, for the sample that was soaked during 24 hours in air by ss1A— 900C 24h Air Pellet and by ss1B— 900C 24h O_2 Powder the sample that was 24 hours in O_2 flow.

The pattern ss1A— 900C 24h Air Pellet was fitted with two fractions, one of Ag and Cr_2O_3 . Also in this pattern is observable for the lower angle a bump due to defects in the sample holder that cause the x-rays to disperse. The pattern — 900C 24h O_2 Powder was fitted with also two fractions, one of Ag and AgCrO_2 . The pattern ss1C— 900C 48h O_2 Powder was fitted with also two fractions, one of Ag and AgCrO_2 . These last two patterns exhibit nearly free single phases of silver chromium oxide. However the secondary phase is undesirable and an optimization of the synthesis method is still required.

The resulting XRD patterns were analyzed by Le Baile refinement applying pseudo-Voigt functions to fit the peak shape (The results are summarized in table 3.2.7).

- SOLID STATE SS2

A different set of annealings was performed to study the optimum synthesis conditions in the preparation of the silver chromium oxide by solid state reaction. In figure 3.2.5 are presented the XRD patterns of the set of samples ss2 (top) and the calculated diffraction pattern of AgCrO_2 , Ag_2CrO_4 , Ag, Cr_2O_3 (bottom) for phase identification.

Annealing 700 °C - The XRD pattern measured after the annealing at 700 °C, — 700C 12h O_2 Powder, shown in figure 3.2.5, presents a mixture of three crystallographic phases, a major of AgCrO_2 , a minor phase of Ag_2CrO_4 and traces of Ag.

Annealing 900 °C - The sample — 900C 12h O_2 Pellet, in figure 3.2.5, annealed during 12 hours in an O_2 flow, presents a silver chromium oxide single phase with no spurious secondary phases. The XRD pattern of the sample fired at 900 °C, was fitted for phase identification. The parameters obtained are presented in table 3.2.6.

Space group	$R\bar{3}m$
Unit Cell	$a, b = 2.986 \text{ \AA}, c = 18.509 \text{ \AA}$
Cell Volume	$142.930 \text{ \AA}^3$
Z	3
Points	2662
Effective 2θ	10-90
Refined Parameters	11

Table 3.2.6: Table summarizing Lattice Parameters refinement on AgCrO_2 ss2 sample.

Figure 3.2.6 presents the observed pattern (◦ red dots), calculated (— black solid line), reflections of the correspondent phases (| green tick marks) and fit deviation (— blue solid line in the bottom) are shown.

- SOLID STATE SS3

A third set of samples was synthesized with different annealing conditions, see Table 3.2.5. XRD patterns collected from this set of samples is presented in figure 3.2.7 (top) and calculated patterns

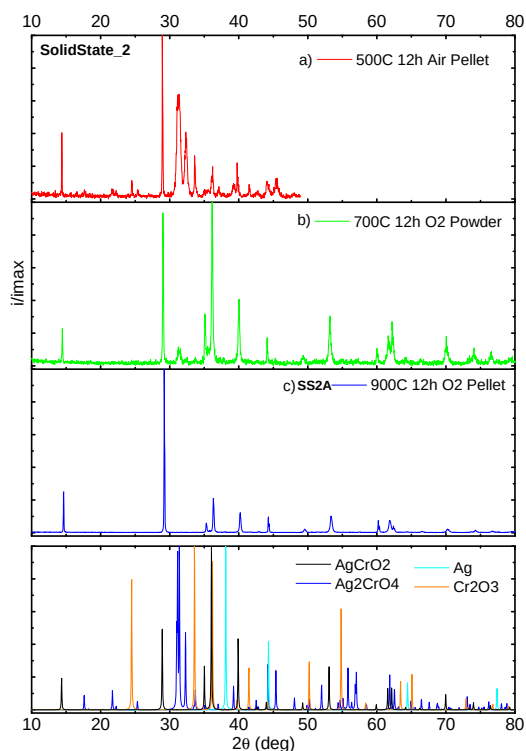


Figure 3.2.5: X-ray diffraction patterns performed for the set of samples ss2. (Top) After the calcination at 500 °C in air during 12 hours (a), after the annealing at 700 °C in O₂ during 12 hours (b) after the annealing at 900 °C during 12 hours in O₂ flow (c). (Bottom) Calculated diffraction pattern of AgCrO₂, Ag₂CrO₄, Ag, Cr₂O₃ for comparison.

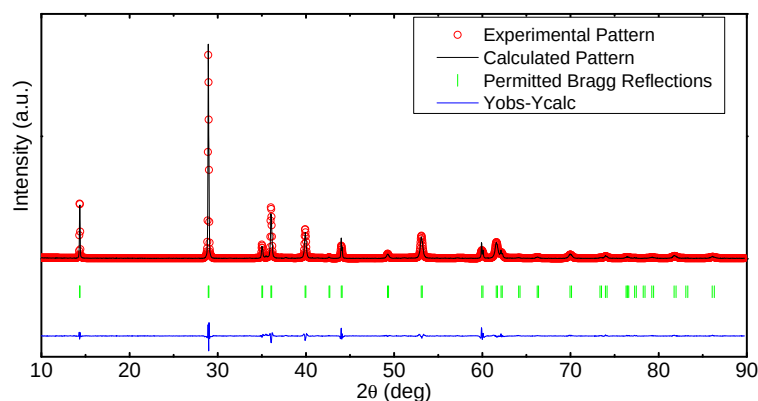


Figure 3.2.6: AgCrO₂ room temperature representative x-ray diffraction pattern of sample ss2 after the final annealing at 900 °C. The observed pattern $\circ$, calculated —, reflections of the correspondent phase $|$ and fit deviation —.

for reference (bottom).

Annealing 700 °C - In this set of samples the same calcination step was performed, but the annealing at 700 °C also performed in an O₂ flow had a longer duration that in sample ss2A. Since the annealings in O₂ flow seem to favor the formation of the delafossite phase while Air atmosphere

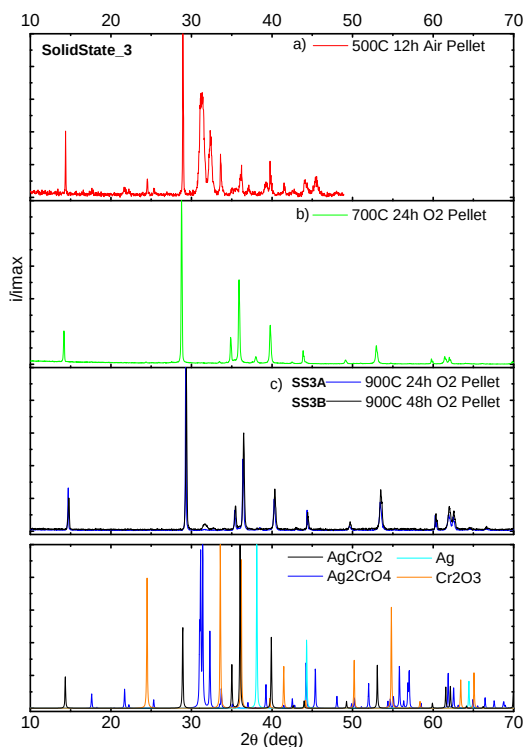


Figure 3.2.7: X-ray diffraction patterns performed for the set of samples ss3. (Top) After the calcination at 500 °C in air during 12 hours (a), after the annealing at 700 °C in O_2 during 24 hours (b) and after the annealing at 900 °C during 24 and 48 hours in O_2 flow (c). (Bottom) Calculated diffraction pattern of AgCrO_2 , Ag_2CrO_4 , Ag, Cr_2O_3 for comparison.

favor its decomposition, we wanted to test a longer annealing at 700 °C (O_2 atmosphere) to see if it was possible to obtain a AgCrO_2 single phase without recurring to a third annealing at higher temperatures.

The annealing with a longer duration (24 hours) in a rich O_2 atmosphere resulted in an almost single phase AgCrO_2 with traces of Ag, instead of the two secondary phases (Ag_2CrO_4 and Ag) present in sample ss2 after the annealing at same temperature, in air.

Annealing 900°C - For annealing at 900 °C we tested two soaking times with the same O_2 atmosphere flow, one during 24 hours and the other during 48 hours. Both final samples present the silver chromium oxide with delafossite structure. The sample ss3A— 900C 24h O_2 pellet (calcination 500 °C 12 hours air + annealing 24 hours O_2 700 °C + annealing 24 hours O_2 900 °C) presents small traces of Ag and the sample ss3B— 900C 48h O_2 Pellet (calcination 500 °C 12 hours air + annealing 24 hours O_2 700 °C + annealing 48 hours O_2 900 °C) traces of Ag_2CrO_4 . As discussed before all samples in figure 3.2.7 are textured with the preferential crystal growth along the c-axis. In section 3.2.2 we will further show this texture by SEM analysis.

From the different conditions tested, the sample ss2A — 900C 12h O_2 Pellet (calcination 500 °C 12 hours air + annealing 12 hours O_2 700 °C + annealing 12 hours O_2 900 °C) presented in figure 3.2.5 and the sample ss3A — 900C 24h O_2 Pellet (calcination 500 °C 12 hours air + annealing 24 hours O_2 700 °C + annealing 24 hours O_2 900 °C) presented in figure 3.2.7 show the best results,

that is, the best samples.

However for future synthesis the method described by the conditions in ss2A table 3.1.2 was chosen by two reasons. First its a method with shorter time annealings than the ones referred in ss3 and second because sample ss3 — 900C 24h O₂ Pellet presents a small amount of impurity phase, around < 6%.

• STABILITY ANNEALING TEST

We further tested if the system is stable at high temperature under two different atmospheres. For this sample ss2A was divided and one part of the sample was annealed in Air and the other in O₂ during 3 days at a temperature of 800 °C . The XRD patterns collected are presented next in figure 3.2.8.

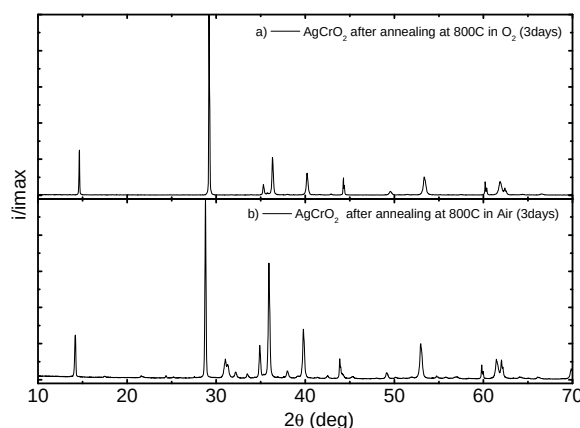


Figure 3.2.8: X-ray diffraction patterns performed for the sample AgCrO₂ ss2 a) and after the annealing at a temperature of 800°C in in Air during 3 days b).

XRD analysis of the patterns layed out in figure 3.2.8 show that the high temperature 3 days annealing in Air has changed the sample composition while the annealing in O₂ maintained the initial characteristics. The XRD pattern of the sample annealed in Air exhibits a small contribution of a silver chromate Ag₂CrO₄ along with the AgCrO₂ phase that still constitutes the bulk of the sample.

Table 3.2.7 summarizes the different phases present in the samples synthesized by solid state reaction. In this way one can see the structural evolution along the different annealings that each sample has undergone. The lattice parameters of the samples after the final annealing at 900 °C are also present in this table.

TAG	Phases ^a	500 °C		700 °C		Annealing 900 °C		Lattice Parameters a, b, c (Å)		α, β, γ (°)		Space Group
SS1A	AgCrO_2	M		M		-		-		-		-
	Ag_2CrO_4	M		-		-		-		-		-
	Cr_2O_3	m		-		23%(3)	24H Air	4.959,4.959,13.598		90, 90, 120		$R\bar{3}c$
	Ag	-		t		77%(3)		4.088,4.088,4.088		90,90,90		$Fm\bar{3}m$
SS1B	AgCrO_2					93.8%(9)		2.984,2.984,18.499		90,90,120		$R\bar{3}m$
	Ag_2CrO_4				24H Air	-		-		-		-
	Cr_2O_3					-	24H O_2	-		-		-
	Ag					6.2%(9)		4.089,4.089,4.089		90,90,90		$Fm\bar{3}m$
SS1C	AgCrO_2					98%(1)		2.984,2.984,18.507		90,90,120		$R\bar{3}m$
	Ag_2CrO_4					-	48H O_2	-		-		-
	Cr_2O_3					-		-		-		-
	Ag					2%(1)		4.081,4.081,4.081		90,90,90		$Fm\bar{3}m$
SS2A	AgCrO_2		12H Air	M		100%		2.986,2.986,18.510		90,90,120		$R\bar{3}m$
	Ag_2CrO_4			m	12H O_2	-		-		-		-
	Cr_2O_3			-		-	12H O_2	-		-		-
	Ag			t		-		-		-		-
SS3A	AgCrO_2			M		98%(9)		2.981,2.981,18.484		90,90,120		$R\bar{3}m$
	Ag_2CrO_4			-		-		-		-		-
	Cr_2O_3			-		-	24H O_2	-		-		-
	Ag			t		2%(9)		4.079,4.079,4.079		90,90,90		$Fm\bar{3}m$
SS3B	AgCrO_2				24H O_2	98%(1)		2.986,2.986,18.509		90,90,120		$R\bar{3}m$
	Ag_2CrO_4					2%(1)		10.059,7.034,5.540		90, 90, 90		$Pnma$
	Cr_2O_3					-	48H O_2	-		-		-
	Ag					-		-		-		-

^aS:single phase; M:major; m:minor; t:trace

Table 3.2.7: Structural information of the samples synthesized by SSR Method in the different steps of sintering. Lattice parameters retrieved by Le Baile refinement of the XRD patterns from samples after the final annealing at 900°C.

3.2.2 Scanning Electron Microscopy

The silver chromium oxide sample AgCrO_2 synthesized by high temperature solid state reaction that presented single phase content by XRD measurements SS2 (Calcination at 500 °C 12 hours in Air + Annealing at 700 °C 12 hours in O_2 flow + Annealing at 900 °C 12 hours in O_2 flow) was morphologically characterized by scanning electron microscopy. In figure 3.2.9 a set of photographs with different magnifications performed in this sample at room temperature.

According to figure 3.2.9 a) taken with secondary electrons (SE) the sample surface topography seems homogeneous and with backscattered electrons (BSE) b) the sample compositions seems homogeneous. When the magnification increases c) the polycrystals boundaries appear very delineated, exhibiting a mixing of different crystal sizes. From the photograph obtained with the same magnification but with BS electrons, figure 3.2.9 d), a contrast between lighter and darker areas emerges (shown as red squares with z1 and z2), implying that different compositions may be present in the sample or simply that the pre-treatment performed in the sample with the sandpaper to obtain a polished surface was insufficient and we are facing a depth resolution problem. Results presented in section 3.2.3, show that the sample is structurally homogeneous all over the entire surface.

SEM photograph taken with a magnification factor of 10000 with BSE in e) and with a magnification factor of 20000 with SE in f) are also a testimony of the sample homogeneity and large polycrystals constitution. It is possible to observe that we are in the presence of polycrystals having sizes, at least, up to $10\mu\text{m}$. If we recall that the AgCrO_2 unit cell as c-axis $\approx 18\text{ Å}$ giving about 800 unit cells along this direction.

A 30000 magnification allows the sample texture to be evidenced in g) where the yellow arrows show, the hexagonal shape of the crystallites in the ab-plane (observe also the yellow hexagon) and the

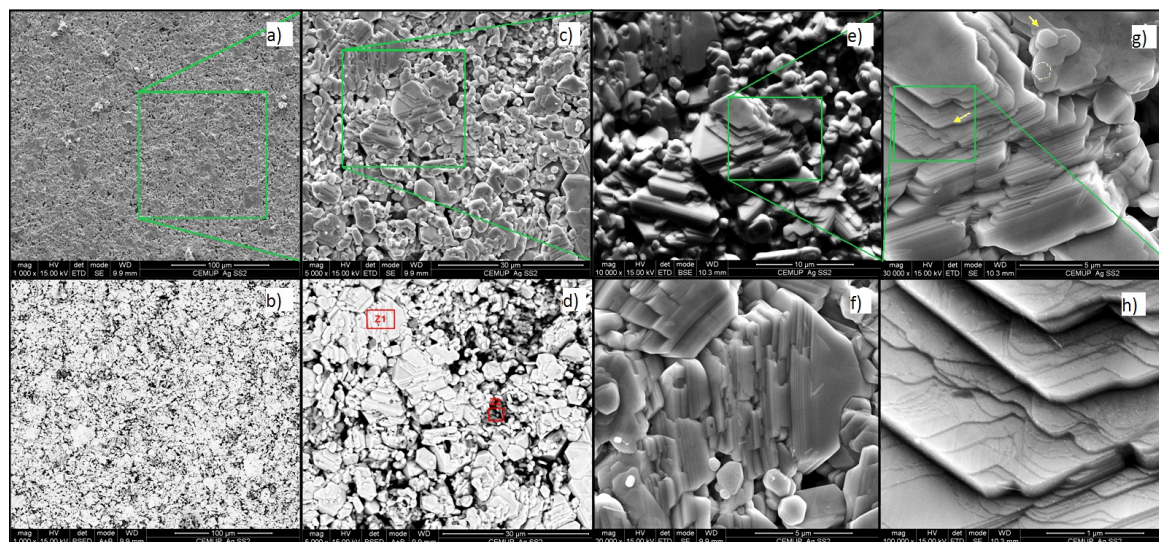


Figure 3.2.9: Scanning electron microscope photographs performed in sample ss2 (after the final annealing step) using secondary electrons (SE) and backscattered electrons (BSE). With a magnification $1000\times$ (SE) a), magnification $1000\times$ (BSED) b), magnification $5000\times$ (SE) c), magnification $5000\times$ (BSED) d), magnification $10000\times$ (BSE) e), magnification $20000\times$ (SE) f), magnification $30000\times$ (SE) g), magnification $100000\times$ (SE) h). The green squares point out the magnified area.

plateaus formed by the successive layers. This plateaus are shown in detail in h) with a magnification of 100000 times.

3.2.3 Energy Dispersive X-ray Spectroscopy

EDS pictograph retrieved from polycrystalline sample of AgCrO_2 synthesized by solid state reaction (ss2 - Calcination at 500°C 12 hours in Air + Annealing at 700°C 12 hours in O_2 flow + Annealing at 900°C 12 hours in O_2 flow) is presented in figure 3.2.10.

Different random areas of the sample surface were analyzed to verify sample stoichiometric homogeneity. An EDS pictograph that is representative of the different areas tested is represented in figure 3.2.9 a).

Pictograph show the presence of the expected elements Ag, Cr, O with the atomic percentages in agreement with what was expected ($\text{Ag } 24\%$, $\text{Cr } 23\%$ and $\text{O } 53\%$) for the delafossite structure ($\text{Ag}_2\text{Cr}_2\text{O}_7 \Rightarrow 1:1:2$). Similar results were obtained when a global sample analysis was performed. This is observed in b) where the entire sample is analyzed and the atoms are also in the right stoichiometric proportion ($\text{Ag } 21\%$, $\text{Cr } 23\%$ and $\text{O } 56\%$) and again ($\text{Ag}_2\text{Cr}_2\text{O}_7 \Rightarrow 1:1:2$). Again, this results attest the good quality of the produced sample.

3.2.4 X-ray Photoelectron Spectroscopy

The study of materials like AgCrO_2 can be enriched by the understanding of the way in which elements in the structure are bonded. Moreover, for this type of compounds, oxygen and transition metal elements present in the structure play a very important role in material catalytic performance^[86]. The X-ray Photoelectron Spectroscopy (XPS) analysis method, is an effective tool for this purposes.

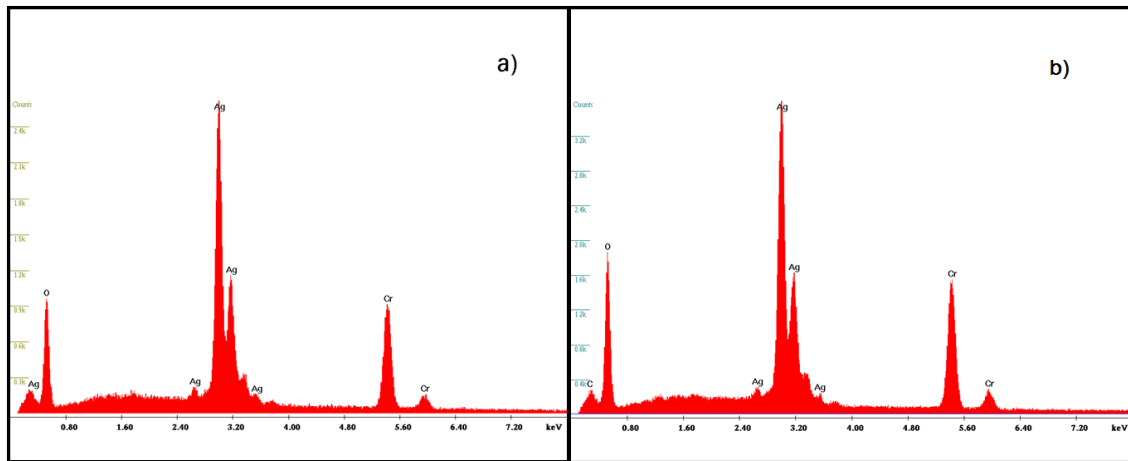


Figure 3.2.10: EDS pictograph retrieved from polycrystalline sample of AgCrO_2 . Random zone analysis a) and global sample analysis b).

A surface element composition analysis was performed in a sample of AgCrO_2 prepared by solid state reaction in the same way of sample AgCrO_2 -ss2A (Calcination at 500 °C 12 hours in Air + Annealing at 700 °C 12 hours in O_2 flow + Annealing at 900 °C 12 hours in O_2 flow). The XRD pattern performed in this sample has identified the presence of two phases one of AgCrO_2 ($\approx 87\%$) and one of Ag_2CrO_4 ($\approx 13\%$).

In order to interpret the XPS results it is important to know how atoms are arranged in the crystal structure. The Cr atoms in AgCrO_2 (Cr^{III}) and in Ag_2CrO_4 (Cr^{VI}) form CrO_6 tetrahedrons and CrO_4 octahedrons, respectively. While the AgCrO_2 structure crystalizes in a hexagonal crystal structure with the space group $R\bar{3}m$, Ag_2CrO_4 crystalizes in an orthorhombic structure with the space group $Pnma$. In the crystal of AgCrO_2 , the CrO_6 octahedra connect each other in ab-plane to form a layer by sharing edges. Between the two CrO_6 octahedron layers are silver atoms. The Ag_2CrO_4 crystal consists of two kinds of tetrahedra, the AgO_4 tetrahedron and CrO_4 tetrahedron, and a kind of octahedron, AgO_6 . In ab-plane, the AgO_4 and CrO_4 tetrahedra connect each other to form layers by sharing vertices, while the AgO_6 octahedra connect each other to form chains by sharing edges. Then the chains of AgO_6 octahedra link the layers that are constructed by AgO_4 and CrO_4 tetrahedra to construct the three dimensional network.

To index the different peaks the binding energies of the high resolution XPS spectra of a certain element were searched and associated using XPS binding energies table^[68].

The XPS survey spectrum of the sample was collected in the range of energy [0;1300] eV and is shown in figure 3.2.11. From that we can determine/identify qualitatively the surface chemical composition of the material, being detected the following elements: sodium, carbon, oxygen, chromium and silver.

As introduced before in section 2.2.4, XPS analysis retrieves information based on the fact that each element present in the material surface has an unique spectra. Moreover, since a certain element can be bounded in different ways in different materials, one can, from the observed binding energies, acquire information about the type of binding. From the intensities or counts, quantitative information can also be resolved.

An online database *LaSurface*^[87] was consulted for comparing and associate the different

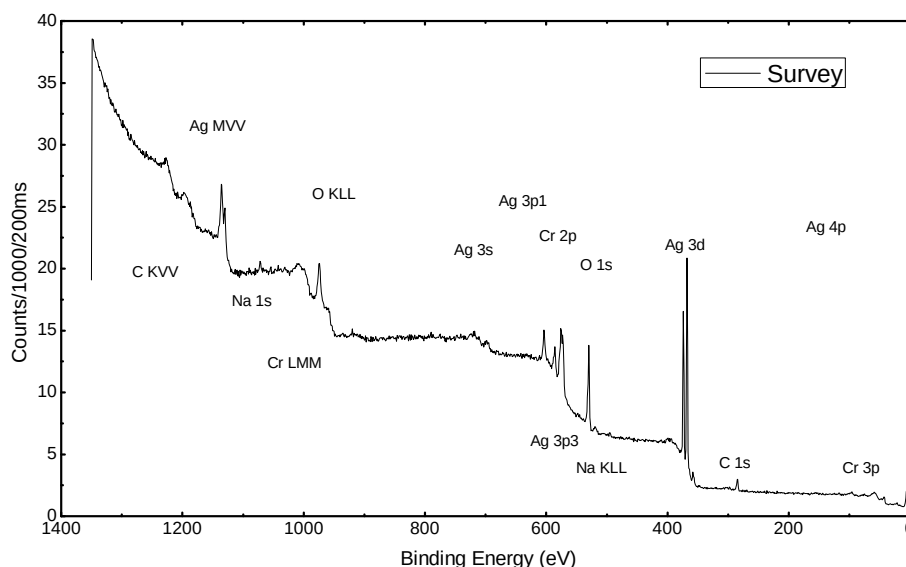


Figure 3.2.11: XPS Survey Scan of polycrystalline sample of AgCrO_2 .

binding energies observed. The references presented in this section refer to the ones presented in this online database.

The Na 1s high resolution spectrum wasn't collected because it is a contaminant of the sample due to the material preparation (gloves, tweezers and press) and material manipulation.

Figure 3.2.12 presents the high-resolution, O 1s a) spectra and corresponding curve fits.

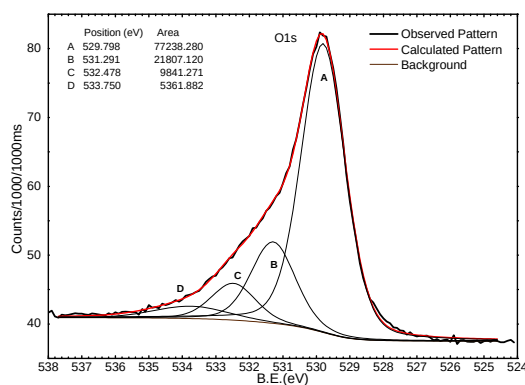


Figure 3.2.12: High-Resolution O 1s spectrum and curve fitting.

Oxygen - The O 1s high-resolution spectrum, presented in figure 3.2.12 a), was fitted with resource to four different peaks. The peaks [C,D] (532.48, 533.75) are easily associated with the presence of water on the surface of the sample^[88,89]. However the first two peaks (A- 529.80 and B-531.29) are not easily asserted to their origin. When comparing the binding energies for the two peaks with values found in the literature^[68] (530.1 for Li_2CrO_4 , 530 for CuCrO_2 and 531.4 for Cr-O bonding) and those with the work of *Ma et al.*^[90] (531.6 and 529.0 corresponding to the chemical adsorptive oxygen and the lattice oxygen in Ag_2CrO_4) we find that the different binding energies for

these two kinds of compounds silver chromite and silver chromate are very near one to the other, what makes very difficult to assert any conclusion about their origin.

Figure 3.2.13 presents the XPS high resolution Cr 2p a) and Ag 3d b) spectra and the corresponding bands/peak fitting deconvolution.

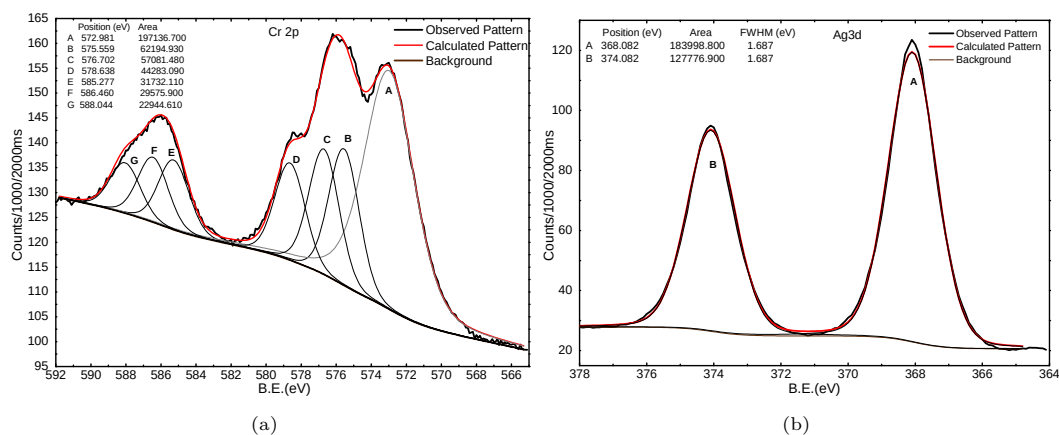


Figure 3.2.13: XPS High Resolution Spectrum of AgCrO_2 in the Cr 2p a) and Ag 3d core-level regions and curve fitting.

Chromium - The high-resolution Cr 2p Spectrum shows three peaks at 575.56, 576.70 and 578.64 eV associated with Cr $2p_{3/2}$ (B,C,D) and other three at 585.28, 586.46 and 588.04 eV associated with Cr $2p_{1/2}$ (E,F,G), and one peak for Ag $3p_{3/2}$ with a binding energy of 572.98 eV, peak [A]. The Cr $2p_{3/2}$ and $2p_{1/2}$ peaks found are representative of the element with a valence of (+3) and (+6), peaks [B,E and C,F] for the AgCrO_2 and peaks [D,G] for Ag_2CrO_4 , respectively. Peaks [B,C] with lower binding energies, are associated with chromium with lower oxidation number corresponding to chromium in $\text{A}^+\text{Cr}^{3+}\text{O}_2$ compound and peak [D] with higher binding energy because a higher valence state of chromium characteristically of $\text{A}_2\text{Cr}^{6+}\text{O}_4$ compounds.

Silver - The high-resolution Spectrum of Ag 3d, in figure 3.2.13 b) shows a peak [A] at 368 eV for Ag $3d_{5/2}$ and peak [B] at 374 eV for Ag $3d_{3/2}$, corresponding to Ag_2O in the tables, that is, with valence of +1 as it would be expected in any of the cases of silver chromite or silver chromate. Silver spectrum can't give much more information, besides the element quantity.

Considering the sample as a mixture of two phases, silver chromite (87%) and silver chromate (13%), as obtained with XRD, the atomic proportion of the elements present is 1.07 Ag: 1.00 Cr.

Oxygen	58(10)%
Silver	26(10)%
Chromium	16(10)%

Table 3.2.8: XPS superficial elemental composition in AgCrO_2 sample.

XPS superficial elemental composition in AgCrO_2 sample, presented in table 3.2.8, exhibits, inside a reasonable error ($\approx 10\%$ as shown before), the expected elements proportion.

The high-resolution spectrum of Cr gives information about the relative quantities of AgCrO_2 and Ag_2CrO_4 . Analysing the Cr^{3+} and Cr^{6+} peak areas, we can determine that from the 16% Cr in the sample, 12% are of Cr^{3+} and 4% are of Cr^{6+} . From these values we can calculate the total percentage of AgCrO_2 and Ag_2CrO_4 in the sample, 70% and 30%, respectively.

As indicated before different materials within the top 10 nm of the surface can be identified with XPS while a much larger depth can be obtained with XRD. Ag_2CrO_4 phase distribution mainly at the surface while the AgCrO_2 phase constitutes the bulk part of the sample can be a justification for this difference in the results.

3.3 Magnetic and Electric Characterization

Correlation of magnetic and dielectric properties has been attracting the attention in condensed matter physics^[20]. Attempts to maximize the magneto-electric coupling in materials that undergo magnetic and dielectric phase transitions at the same temperature have been made^[16] but sometimes not fully successful^[33].

Recently, AgCrO_2 delafossite has been reported as another multiferroic material and a correlation between the electric and the magnetic structures of this system has been claimed^[33].

3.3.1 Magnetic characterization

In the literature this system is quoted as being an antiferromagnetic material with a para/antiferromagnetic transition at 21 K^[33], although initial works reported 24 K^[34]. In this material Cr^{3+} ions with $S = 3/2$ spin, are arranged in a triangular lattice and thus geometrical frustration due to antiferromagnetic interactions emerges^[33].

To ensure that the synthesized AgCrO_2 samples had the expected magnetic properties we have performed magnetization measurements with a constant applied magnetic field, while heating in the range of temperatures from 5 to 380 K. In order to obtain the sample magnetic parameters such as Néel Temperature (T_N) or the paramagnetic moment μ_p low field magnetization measurements were performed. For this purpose the thermal dependence of magnetization (in low fields) was acquired after the sample has been cooled without applied magnetic Field (ZFC) and/or Field cooled (FC), such that:

ZFC - Zero field cooling - sample cooled with $H=0$ to the lowest temperature then, the magnetic field was applied and the subsequent magnetization measurement was performed while sweeping the temperature in a range from 5 K up to 380 K.

FC - Field cooling - sample cooled down to the desired temperature under an applied magnetic field and then the measurement was performed while heating in the same range of temperatures. Most of the samples were measured using only the field cooling sequence.

Several AgCrO_2 samples with different annealing treatments were characterized with this technique.

SG1B - 900 °C - In figure 3.3.1 are presented the magnetic susceptibility χ a) and reciprocal magnetic susceptibility $1/\chi$ b) as a function of temperature. The field cooling (FC) curve obtained from sample SG1 (Urea - Microwave + annealing 700 °C 24 hours in Air + annealing 900 °C 48 hours in O_2), was collected using a 105 Oe applied magnetic field in a 5 K < T < 300 K temperature range.

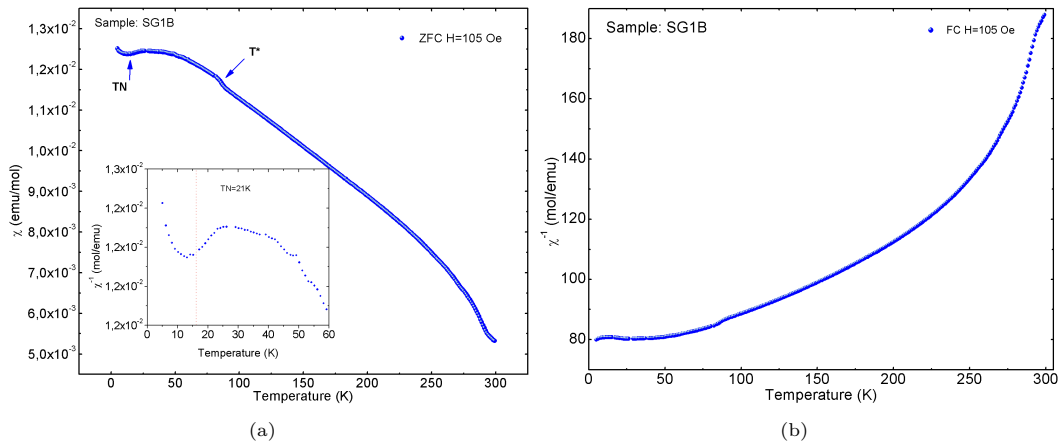


Figure 3.3.1: Temperature dependence of the magnetic susceptibility a) and reciprocal magnetic susceptibility b) of the sample sintered by sol-gel after the final annealing at 900 °C during 48 hours in O_2 (SG1B), measured in the field-cooling mode with $H=105$ Oe. The inset in a) shows in detail the $5 \text{ K} < T < 60 \text{ K}$ range.

The low field FC curve exhibit an atypical shape of an antiferromagnet (see figure 3.3.1). As presented before, the XRD data showed the presence of a major phase from AgCrO_2 (88%) and two minors of Ag (7%) and Cr_2O_3 (5%).

Nevertheless the low field FC curve allowed to extract the critical temperature $T_N = 21 \text{ K}$ obtained through the maximum of the derivative of χ . This transition temperature is characteristic of the silver chromium oxide delafossite^[33]. On the inset in figure 3.3.1 a) this critical temperature is marked. In the same $\chi = f(T)$ plot two other anomalies can be observed; one around room temperature and the other at $T = 88 \text{ K}$. The anomaly around room temperature can be associated with the Cr_2O_3 secondary phase. In fact, from the literature it is known that this oxide presents an antiferromagnetic phase transition at approximately 307 K^[70,91].

The anomaly at 88 K was not possible to associate with any of the secondary phases observed by x-ray. Nevertheless the susceptibility behavior around that temperature might be connected with the measurement system contamination *e.g.* oxygen contamination (see appendix D). In addition, we also can observe that the reciprocal susceptibility in the paramagnetic phase has a high deviation from the Curie-Weiss linear regime. This abnormal trend might be connected with the presence of the Cr_2O_3 antiferromagnetic phase ($\chi \sim 254 \times 10^{-6} \text{ emu mol}^{-1}$ at 300 K)^[38] and also with diamagnetic contributions from silver impurities, though this last contribution should be very small ($\chi \sim -25 \times 10^{-6} \text{ emu mol}^{-1}$)^[70].

SS1A - 700 °C - The magnetic susceptibility and reciprocal magnetic susceptibility dependence with temperature, of the sample SS1 (calcination 500 °C 12 hours in Air + annealing 700 °C 24 hours in Air), after the annealing at 700 °C are presented in figure 3.3.2 a) and b), respectively. The XRD data showed that the sample was constituted by a major phase of AgCrO_2 and traces of Ag.

This sample also presents the transition between the para/antiferromagnetic phase, at the Néel temperature of 21 K. In the inset of figure 3.3.2 a) a zoom near the transition is shown. The red line shows $d\chi/dT$ and evidences the inflection point of the magnetic susceptibility curve of the Néel temperature.

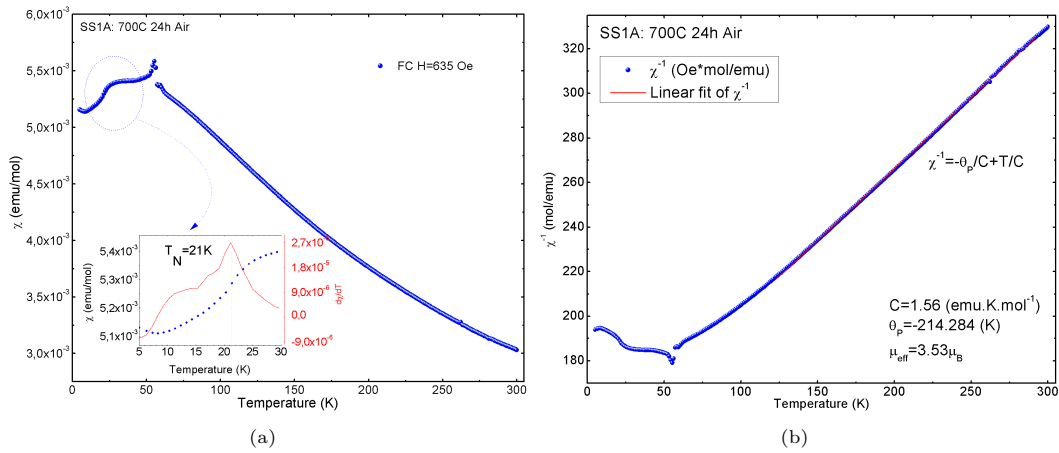


Figure 3.3.2: Temperature dependence of the magnetic susceptibility a) and reciprocal magnetic susceptibility b) of the sample ss1 sintered by solid state reaction after the annealing at 700 °C during 24 hours in air, measured in the field-cooling mode with $H=635$ Oe. The inset in a) shows in detail χ and $d\chi/dT$ in the $5\text{ K} < T < 40\text{ K}$ temperature range.

In figure 3.3.2 b) the temperature dependence of reciprocal susceptibility is shown. Despite of the presence of small traces of silver, here and contrarily to previous analyzed sample (SG1A), the linear behavior characteristic of the *Curie-Weiss* law for high temperatures is clearly observed. Nevertheless, below 150 K the linearity starts to disappear. This low temperature behavior, also present in other samples, seems to be an intrinsic effect of the AgCrO_2 system and will be discussed in more detail later.

Applying the Curie-Weiss law, equation 2.3.2 for high temperatures, the *Curie-Weiss* temperature, θ_p , can be found as the temperature where the linear fit to χ^{-1} versus T curve intersects the T -axis. From this curve other characteristic magnetic parameters can be determined, namely the *Curie-Weiss* constant, C and the corresponding Cr paramagnetic moment.

The value of the effective paramagnetic moment obtained, $\mu_{eff} = 3.53\mu_B$, can be compared to the theoretical one calculated taking into account spin only, $\mu_{eff} = 3.87\mu_B$, characteristic of the magnetic ion Cr^{3+} . This and the other magnetic parameters obtained for this sample are presented in table 3.3.1.

Finally, remark that, besides the AgCrO_2 phase transition at 21 K, another anomaly can be observed in these plots around $T=56$ K. As before, it was not possible to associate this behavior to any secondary phases observed by x-ray. Again, the susceptibility behavior around that temperature might be connected with a measurement system contamination, *e.g.*, oxygen contamination (see appendix D).

SS1C - 900 °C - Magnetic susceptibility and reciprocal magnetic susceptibility dependence with temperature, of the sample ss1 (calcination 500 °C 12 hours in Air + annealing 700 °C 24 hours in Air + 900 °C 48 hours in O_2), after the final annealing at 900 °C are presented in figure 3.3.3 a) and b), respectively.

This sample also presents the transition from the antiferromagnetic to paramagnetic phase, at Néel temperature of 21 K^[33]. In the inset of figure 3.3.3 a) a zoom of the temperature region near the phase transition is shown. The red line represents $d\chi/dT$, evidencing the inflection point of the

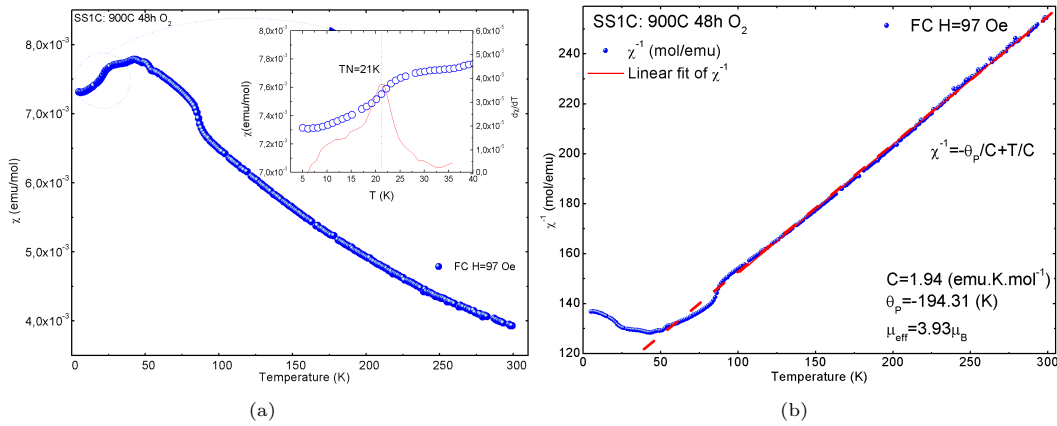


Figure 3.3.3: Temperature dependence of the magnetic susceptibility a) and reciprocal magnetic susceptibility b) of the sample SS1 sintered by solid state reaction after the final annealing at 900 °C during 48 hours in O_2 flow, measured in the field-cooling mode with $H=97$ Oe. The inset in a) shows in detail χ and $d\chi/dT$ in the 5 K < T < 40 K temperature range.

curve. In figure 3.3.3 b) the temperature dependence of the reciprocal magnetization is shown, where the high temperature linear behavior characteristic of the *Curie-Weiss* (CW) law is visible.

The values obtained from the CW behavior fit, shown in the graphic and presented in table 3.3.1, are near those in literature [33,34,92].

The next set of samples, SS2, were the ones presenting the best AgCrO_2 synthesis results. In fact, a single AgCrO_2 crystallographic phase is observed by XRD after the final annealing treatment (SS2A-900 °C). Note however that upon the intermediate annealing stage (SS2A-700 °C) XRD data showed the presence of a minor Ag_2CrO_4 phase and traces of Ag. The magnetization results are presented below.

SS2A - 700 °C - The magnetic susceptibility and reciprocal magnetic susceptibility dependence with temperature, of the sample SS2A (calcination 500 °C 12 hours in Air + annealing 700 °C 12 hours in O_2), after the annealing at 700 °C are presented in figure 3.3.4 a) and b), respectively.

This sample also presents the transition between the antiferromagnetic and paramagnetic phase at the Néel temperature of 21 K [33]. In the inset of figure 3.3.4 a) a zoom of the temperature region near the transition is shown. The red line shows $d\chi/dT$, evidencing the kink in the magnetic susceptibility observed at $T_N = 21$ K. The temperature dependence of reciprocal magnetization is shown in figure 3.3.4 b), here the high temperature linear behavior characteristic of the CW law is also clearly visible. The values obtained from the CW behavior fit are shown in the graph (and table 3.3.1) and are near those of the literature.

Despite of the presence of small traces of silver and Ag_2CrO_4 , the linear behavior at high temperatures is clearly observed, as mentioned. Nevertheless, below ≈ 150 K, the linearity starts to disappear. Again, this low temperature behavior, intrinsic from AgCrO_2 system, will be discussed in more detailed later.

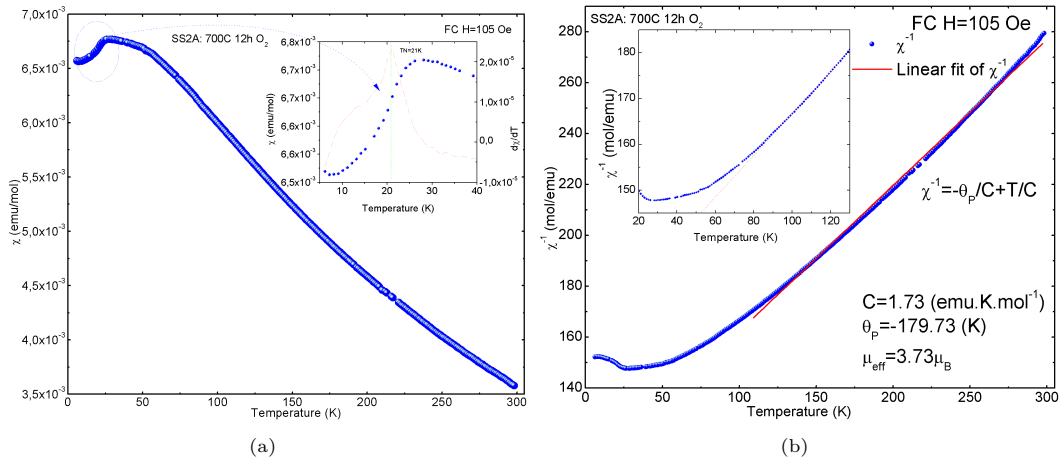


Figure 3.3.4: Temperature dependence of the magnetic susceptibility a) and reciprocal magnetic susceptibility b) of the sample SS2 sintered by solid state reaction after the annealing at 700 °C during 12 hours in O₂ flow, measured in the field-cooling mode with H=105 Oe. The inset in a) presents in detail χ and $d\chi/dT$ in the 5 K < T < 40 K temperature range.

SS2A - 900 °C - The magnetic susceptibility and reciprocal magnetic susceptibility dependence with temperature, of the sample SS2 (calcination 500 °C 12 hours in Air + annealing 700 °C 12 hours in O₂ + 900 °C 12 hours in O₂), after the final annealing at 900 °C are presented in figure 3.3.5 a) and b), respectively. From the XRD data, the sample SS2 was the one that presented a silver chromium oxide single phase.

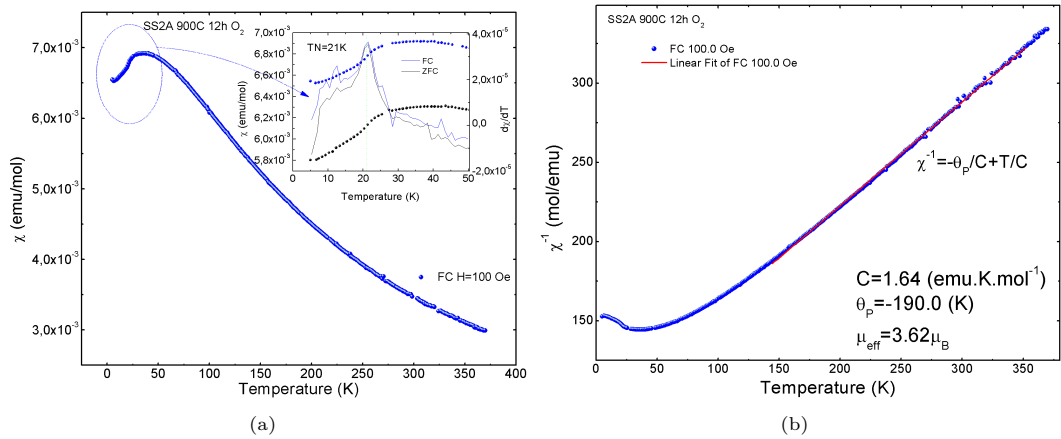


Figure 3.3.5: Temperature dependence of the magnetic susceptibility a) and reciprocal magnetic susceptibility b) of the sample SS2 sintered by solid state reaction after the annealing at 900 °C during 12 hours in O₂ flow, measured in the FC mode with H=100 Oe. The inset in a) presents in detail χ and $d\chi/dT$ (ZFC and FC) in the 5 K < T < 40 K temperature range.

As expected this sample also presents the Néel temperature at 21 K. In the upper inset of figure 3.3.5 a) a zoom of the set of temperatures near the transition is shown. The lines show $d\chi/dT$, evidencing the kink in magnetic susceptibility observed at $T_N = 21$ K, both in the ZFC and

FC curves. In figure 3.3.5 b) the temperature dependence of reciprocal magnetization is shown. Also here the high temperatures linear behavior characteristic of the CW law is clearly observed. The values obtained from the CW behavior fit are shown in the graphic (and table 3.3.1) and are near those in literature.

In figure 3.3.5 b) the temperature dependence of reciprocal magnetization shows, like in the samples presented before, that the data starts to deviate a little from linearity below 150 K.

Table 3.3.1 summarizes the determined magnetic parameters associated to each sample.

Sample	θ_P (K)	C ($\frac{\text{emu}\cdot\text{K}}{\text{mol}}$)	T_N (K)	μ_{eff} (μ_B)
ss1A 700	-214.3	1.56	21	3.53
ss1c 900	-194.3	1.94	21	3.93
ss2A 700	-179.7	1.73	21	3.73
ss2B 900	-190.0	1.64	21	3.62
Literature	-132 ^[34] ; -140 ^[92]	1.87 ^a	21 ^[33] ; 24 ^[34]	3.87 ^a ; 3.91 ^[34]

^aCalculated for Cr^{3+}

Table 3.3.1: Table of the measured AgCrO_2 samples magnetic properties

Summarizing, the magnetization results for all the analyzed samples have shown the onset, at 21 K, of a paramagnetic to antiferromagnetic phase transition.

This is an indication that despite of the magnetic frustration, commonly observed in this systems, a long-range 3D order is present below T_N ^[93]. A negative CW temperature around -200 K is observed and the strong spin frustration, expected in triangular spin lattices, is confirmed ($|\theta_P|/T_N \sim 9$). These results are in good agreement with the literature^[33,34,92] ones for the AgCrO_2 system. The effective paramagnetic moment obtained in the several AgCrO_2 samples ranges from 3.53 to 3.93 μ_B confirming that the magnetic properties are due to the presence of the Cr^{3+} ions in the system, what can be verified when compared with the value calculated for a Cr^{3+} ion (3.87 μ_B).

Also, in all the samples, especially in the last presented one (ss2A-900°C), the magnetization curves exhibit the typical behavior of an antiferromagnetic material as shown in figure 2.3.2. In common, all the samples also present susceptibility curves with systematic deviations from the *Curie-Weiss* law below approximately 150 K and above T_N . Deviations to the CW law have been also observed, below 200 K in magnetic susceptibility, when the in-plane magnetic correlations develop in some 2D antiferromagnetic systems^[92]. In fact, in different ABO_2 triangular lattices several authors reported a similar susceptibility behavior. This behavior is being attributed to the development of short-range magnetic order in the two-dimensional triangular-lattice planes^[34].

3.3.2 Dielectric characterization

The knowledge of the dielectric properties and their variation with temperature is important for the settling of the magnetoelectric properties in the AgCrO_2 material.

Thus, to study the dielectric properties of the produced system, dielectric constant measurements were performed, as described in section 2.3.2 in the AgCrO_2 single phase sample. This measurements can be observed in figure 3.3.6, under an applied frequency of 1 MHz.

We can observe that both ϵ' and ϵ'' , in the 30 K - 300 K, temperature range, increase substantially with increasing temperatures, and faster at higher temperatures. Such increase is probably related with the increase of the electrical conductivity of the sample. In fact, in figure 3.3.7

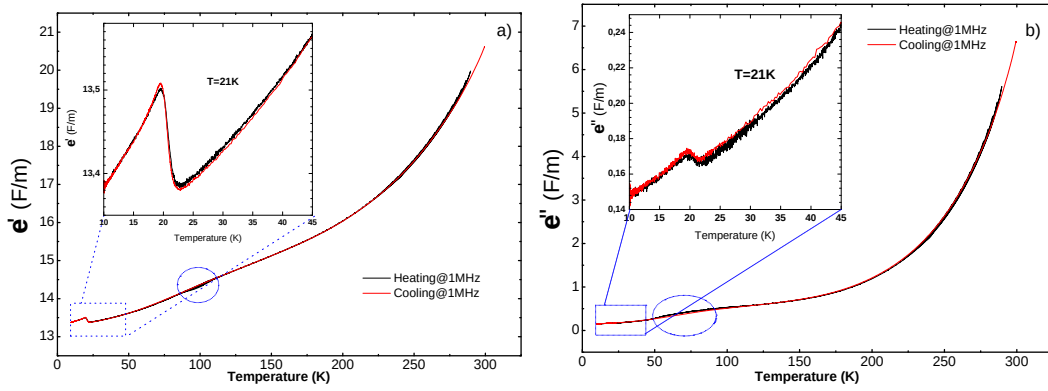


Figure 3.3.6: Temperature dependence of real part of complex dielectric constant a) and imaginary part b). The sample AgCrO_2 ss2A sintered by solid state reaction after the annealing at 900C during 12 hours in O_2 flow, measured to a frequency of 1 MHz. In the inset the temperature range 10-45 K.

we plot the dielectric loss angle as a function of temperature which also demonstrates a substantial increase with increasing temperature easily attributed to the increase of conductivity (see section 2.3.2).

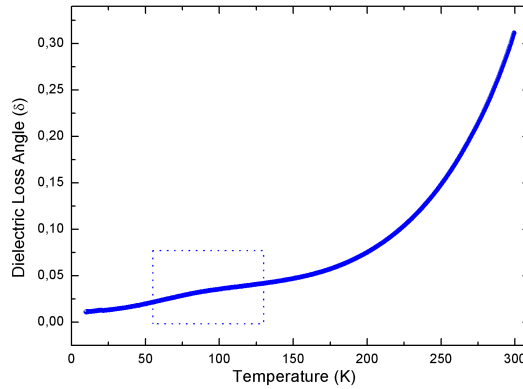


Figure 3.3.7: Temperature dependence of the dielectric loss angle.

We can see in the figures 3.3.6 a) and b) two anomalies. In fact just below 100 K there is a small irreversibility between the cooling and heating runs, in ϵ' and ϵ'' marked by a small circle. In addition there is a small shoulder in $\tan \delta$ near 100 K. Moreover, a sharp peak in ϵ' around 21 K is clearly seen and associated with the ferroelectric transition. This is also corroborated by a smaller peak in ϵ'' . Comparing these results with the magnetization ones one can observe that this transition occurs simultaneously with the magnetic one. These results point⁷ to the multiferroic nature (antiferromagnetic and ferroelectric) of this system where the ferroelectric order is claimed to be induced by the magnetic one [24,31,33,94].

The nature of these anomalies will become more clear after the analysis of the perturbed angular correlation data in next section (Section 3.4).

⁷The dielectric constant sharp anomaly in T_N , is a necessary conditions but not a proof for the the existence of polarization in the sample.

3.4 Electric Field Gradient Characterization - PAC

One of the main objectives of this work was to obtain high quality samples to perform a local scale characterization by Perturbed Angular Correlation (PAC).

Accordingly, in the previous sections of this chapter a description of the optimization synthesis process and a thorough characterization of the produced systems was given. In this section the PAC study on the single phase ss2A sample is presented in order to characterize locally the electronic structure of the AgCrO_2 compound.

The perturbed angular correlation measurements were performed using the radioactive ^{111}In probe. The radioactive probes were implanted at ISOLDE-CERN by ion implantation at 30 KeV with an average of $10^{12}/\text{area}$ ^{111}In probes. After the implantation an annealing⁸ was performed to the samples in oxygen flow during 20 minutes at a temperature of 700 °C (993 K). The PAC measurements were performed using a six detector spectrometer in temperatures ranging from 450 K to 11 K. By performing these measurements in different temperatures the evolution of the EFG can be studied.

The representative $R(t)$ experimental functions, corresponding fits and the respective Fourier transforms, collected at different temperatures for the AgCrO_2 system, are presented in the figure 3.4.1 for $T_M=294$ K, 148 K, 100 K, 87 K, 72 K, 49 K, 25 K and 21 K.

The fit to the experimental PAC spectrum, continuous lines in the $R(t)$, was performed using the *Nfit* program^[95]. In all temperature range those fits were made considering static EFG distributions which were assumed to be Lorentzian-like. For temperatures above 100 K, as one can observe from the Fourier transforms of the $R(t)$ functions, one frequency triplet, corresponding to one EFG, can be clearly identified (see figure 3.4.1). Thus the analysis of the results show that only one local environment, EFG₁ with axial symmetry ($\eta \approx 0$ *i.e.* $\omega_2 \sim 2\omega_1$ and $\omega_3 \sim 3\omega_1$) is sufficient to characterize the probe's surrounding. It shows also nearly no temperature dependence until around 100 K. Below that temperature the need for a second EFG₂ was imperative.

In fact, below that temperature, visible changes can be observed by simple inspections to the $R(t)$ function and Fourier transforms. In detail, in the Fourier transforms one can see that the ω_1 relative amplitude starts to decrease when lowering the temperature below 100 K. This is due to an extra frequency triplet that emerges (see figure 3.4.1) below 100 K and its abundance increases with decreasing temperature. Hence the number of probes interacting with each local environment (EFG₁ and EFG₂) is temperature dependent. Accordingly, to perform proper fits, the percentage of probes interacting with each local environment was allowed to vary with temperature⁹.

The spectrum obtained at room temperature (RT) revealed a local environment, EFG₁, characterized by a quadrupole frequency of $\omega_0 = 123.0(5) \text{ Mrad.s}^{-1}$ ($\nu_{Q1} = 131(2) \text{ MHz}$ or $V_{zz} = 6.57(4) \times 10^{21} \text{ V/m}^2$) and an asymmetry parameter $\eta = 0.0$ (1), characteristic of an EFG with axial symmetry. EFG with axial symmetric EFG was expected for probe substitution in either A or B sites, by symmetry arguments, however it will be discussed below that the probe replaces the trivalent B-site, *i.e.*, the Cr^{3+} position. The EFG parameters are in agreement with the ones reported in the literature for RT measurement^[22].

The emerging EFG₂ below 100 K is characterized by a quadrupole frequency $\nu_{Q2} = 137(4) \text{ MHz}$ ($V_{zz} = 6.84(4) \times 10^{21} \text{ V/m}^2$) and an asymmetry parameter $\eta_2 = 0.5(1)$.

⁸Remember that the annealing performed has the objective to remove the radiation-induced damage created by the implantation, as presented before in section 2.4.

⁹This fact made us reconsider the unique EFG above the 100 K, so an attempt to fit the representative $R(t)$ functions with the two EFG's was made. It was verified that the inclusion of this second EFG above 100 K, did not improve the fit. So it was concluded that in principle it wasn't present at higher temperature.

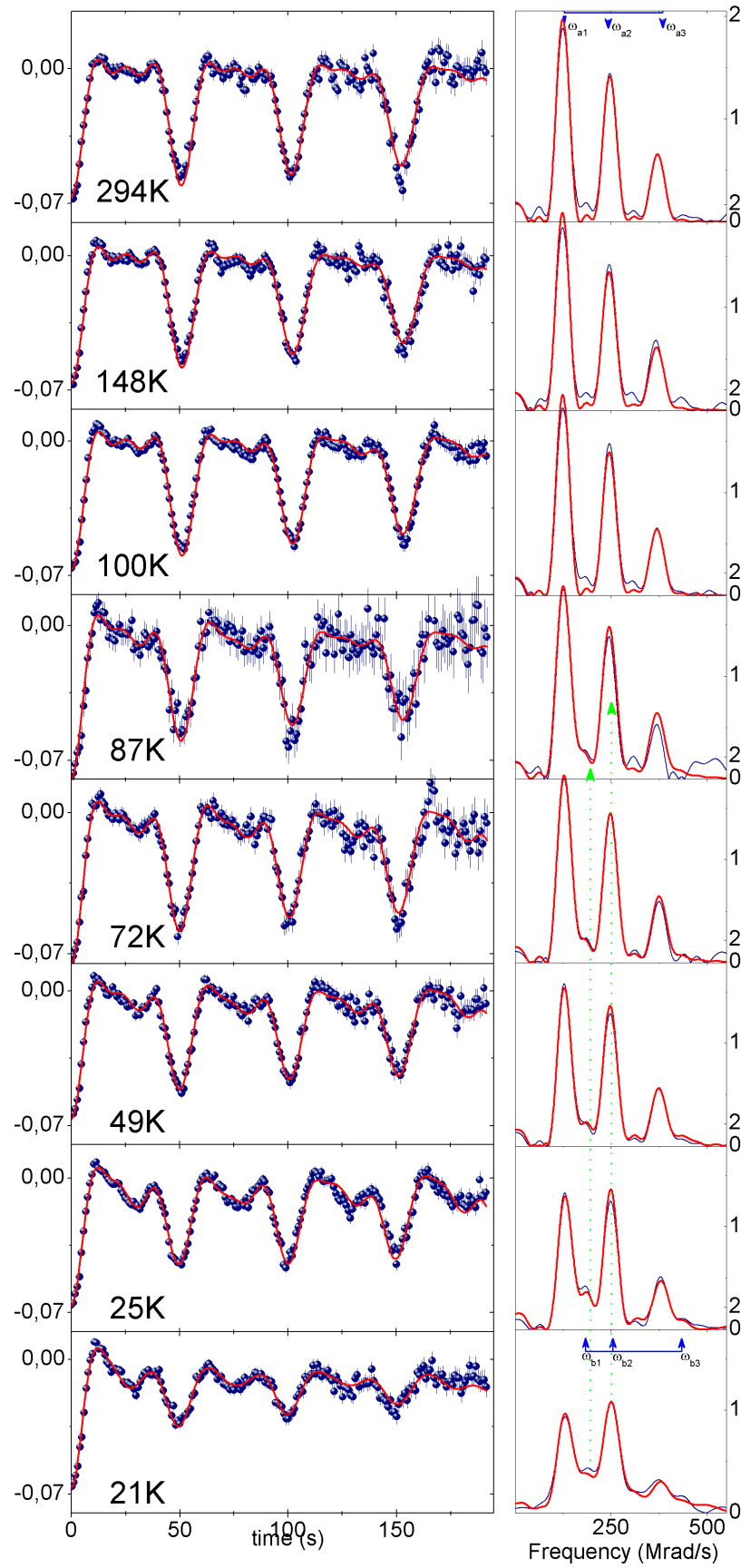


Figure 3.4.1: Representative $R(t)$ experimental functions (blue solid points and $\bar{Y}$ -error) and correspondent fits (red line) for AgCrO_2 samples at $T_M = 295\text{ K}$ to 21 K . Corresponding Fourier transforms are displayed on the right side.

The thermal dependence of the EFG parameter w_0 , η and fraction of probes distributed in each EFG, is shown in figure 3.4.2.

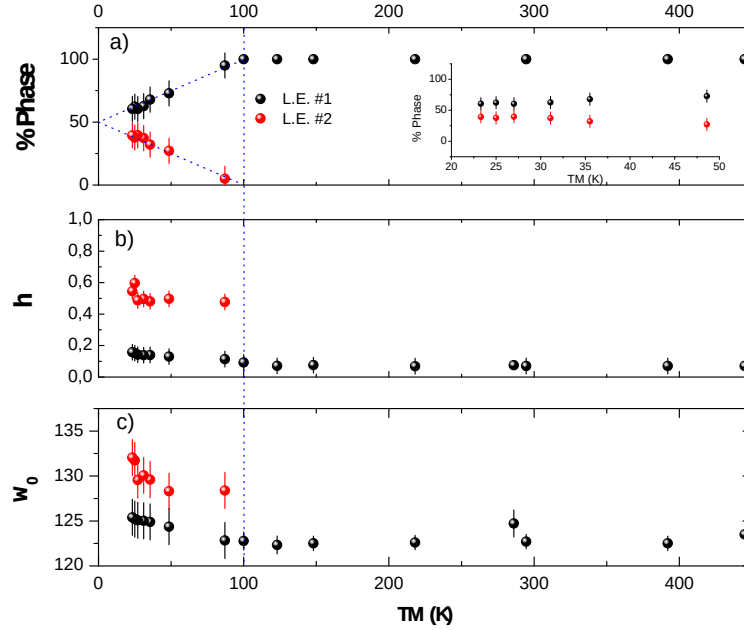


Figure 3.4.2: Temperature dependence of the EFG parameters in the AgCrO_2 system. In a) the fraction of probes interacting with each EFG, b) the asymmetry parameter and c) fundamental frequency

As one can observe in figure 3.4.2 the EFG parameters (w_0 and η) of both EFG_1 and EFG_2 are almost temperature independent. In fact, only a slight increase of those parameters when approaching T_N is observed. One can also realize that in all temperature range the major distinction between EFG_1 and EFG_2 is their asymmetry parameter's. While EFG_1 is axial symmetric, $\eta = 0$ as mentioned above, EFG_2 is a non axial symmetric local environment. One should also stress that the relative widths of the EFG distributions are nearly temperature independent (not shown).

In the same figure (Fig. 3.4.2 a)) it is also presented the temperature evolution of the number of probes interacting with each EFG, *i.e.*, each local environment. As it can be seen, at high temperatures all the probes interact with the EFG_1 . On decreasing temperature and below 100 K the number of probes experiencing the EFG_2 increases in detriment of the number of probes experiencing EFG_1 . This change seems to stop when the fraction of both local environments reaches nearly equal amounts (see inset in figure 3.4.2 a)). This occurs close to the Néel temperature, T_N . Moreover, those changes follow a linear trend with temperature and seem to extrapolate to 50% at $T=0$ K.

Now, and before discussing the nature of this second local environment one should discuss the probe location in the crystallographic structure. It is thus important to remember that the delafossite oxides ABO_2 have two nonequivalent cation sites in their structure. The A element with valency +1 which is linearly coordinated to two O ions, and the B element with valency +3 occupying the center of an O octahedron. Unfortunately, symmetry arguments only do not allow to differentiate between the two sites, since both will produce an asymmetry parameter $\eta = 0$, as seen experimentally^[22]. However, with previous experimental PAC works in delafossite systems and with EFG calculations (*ab initio* and point charge model (PCM) calculations)^[22,30,96,97] the location of the ^{111}In probes can be

asserted.

The replacement of the implanted trivalent ^{111}In ions for the B site position was claimed for oxide compounds of the delafossite family, namely in CuFeO_2 , CuCrO_2 , and AgCrO_2 . In addition from conversion electron Mössbauer spectroscopy measurements in CuFeO_2 , the EFG measured with ^{57}Fe was found to be very close to the one measured with ^{111}In probe by PAC.

The EFG measured by PAC in AgInO_2 using ^{111}Ag ($V_{zz} = 31.34 \times 10^{21} \text{V/m}^2$) and ^{111}In ($V_{zz} = 4.53 \times 10^{21} \text{V/m}^2$) both with axial symmetry are not the same, or otherwise they would have given identical quadrupole frequencies since they decay through the same intermediate state. These results are very important because in this case the probe atoms are not impurities and therefore are most likely to replace in the substitutional sites.

The experimental ($V_{zz} = 26.62 \times 10^{21} \text{V/m}^2$ for ^{111}Ag probe and $V_{zz} = 6.53 \times 10^{21} \text{V/m}^2$ for ^{111}In probe, $\eta_{\text{Ag,In}} = 0$) and point charge model PCM and *ab initio* calculations results for this systems, present in the literature^[30], give calculated ($(V_{zz} = 32.99 \times 10^{21} \text{V/m}^2$ for the A site and $V_{zz} = 2.42 \times 10^{21} \text{V/m}^2$ for ^{111}In in the B site, $\eta_{\text{A,B}} = 0$) values of the EFG in these works show that the EFG in the A site is many times larger than that in the B site.

To confirm these values we also performed EFG calculations using a Point charge model (PCM). This method, described in section 2.4, is useful for determine the theoretical value of V_{zz} and η . For our calculations lattice parameters and atomic positions were retrieved from literature^[29,65] and charges +1, +3 and -2 were associated to Ag, Cr and O, respectively. The values that resulted from these calculations V_{zz}^{latt} were multiplied by the Sternheimer antishielding factor^[73] for the probe, in order to obtain the EFG at the probes nuclear site, V_{zz}^{PCM} . In our simulations we have tried several calculations where different contributions to the EFG were taken into account. We performed the EFG calculations for both cations positions, the A and B-sites, with the contribution of all elements in a radius of $20\text{\AA}$. The EFG calculated by the PCM is shown in table 3.4.1.

Table lists the resulting values of V_{zz}^{PCM} and η in comparison with the measured parameters obtained with the ^{111}In probes.

Compound	^{111}In		A SITE		B SITE		Reference
	V_{zz}^{exp} (10^{21}V/m^2)	η	V_{zz}^{PCM} (10^{21}V/m^2)	η	V_{zz}^{PCM} (10^{21}V/m^2)	η	
AgCrO_2	6.53	0	-32.99	0	2.42	0	[30]
	6.84	0	-26.85	0	6.91	0	Our Work

Table 3.4.1: Experimental and calculated values of V_{zz} using PCM for A and B sites in delafossites.

As one can observe in table 3.4.1 the predicted V_{zz} and η for the B site and measured in this work are in perfect agreement with each other while the calculated for the A site is 5 times higher than the measured one. This is an additional evidence that the In probes are located at the B-site.

From the arguments presented above and comparing the obtained EFG_1 parameters with the ones reported in the literature for the B site one can claim that the EFG_1 measured in the entire range of temperatures is attributed to probes on the substitutional B site, *i.e.*, the Cr site.

Many possibilities were analyzed to describe the emerging of a second EFG below 100 K. The hypothesis of ^{111}In probe diffusion as being in the origin of EFG_2 can be ruled out since atomic diffusion is not expect at such low temperatures. Other explanation for the EFG_2 , could be the presence of radiation damage, ruled out also by the fact that the EFG_2 is not observed at RT and in a large range of temperatures.

The presence of a secondary crystallographic phase was ruled out because it wasn't detected

at RT and also because in such case one would expect that its percentage in the sample would be constant in the whole temperature range, thus the number of probes interacting with that local environment should be constant, what is not the case. Also the possibility of diffusion/trapping of defects or charge carriers as being in the origin of the EFG_2 was discussed, but such frequencies should be quite distinct from the one of the local environment without the defect. More important, the diffusion/trapping mechanisms are usually thermal activated and thus the thermal dependency of the fraction of probes interacting with the EFG_2 should follow an Arrhenius law. As mentioned above the thermal dependency of the fraction of probes sensing the EFG_2 follows a linear regime. At last one should mention that diffusion/trapping are dynamic mechanisms and thus at some temperature dynamic effects should be observed in the PAC spectra (additional attenuation of PAC spectra). As also mentioned above the relative width of the EFG distributions are nearly temperature independent. For these reasons diffusion/trapping of defects/carriers cannot justify the existence of the EFG_2 and its origin has to be found in other grounds.

The representative $R(t)$ experimental functions, corresponding fits and the respective Fourier transforms, collected below the magnetic temperature transition show a clear influence of the magnetic hyperfine field (B_{hf}) demonstrated by the spectrum attenuation. See figure 3.4.3 where different temperatures ($T=294$ K, 21 K, 20 K and 12 K) are represented for a better visualization of the effect of the magnetic hyperfine field.

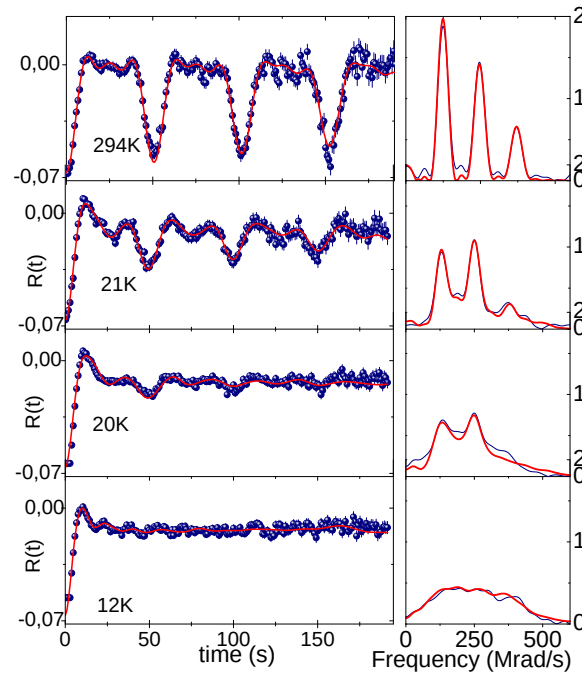


Figure 3.4.3: Representative $R(t)$ experimental functions (blue solid points and $\bar{Y}$ -bar error) and correspondent fits (red line) for AgCrO_2 samples at $T_M=294$ K, 21 K, 20 K and 12 K. Corresponding Fourier transform is displayed on the right side.

From these PAC measurements below the magnetic transition one can verify the presence of a magnetic hyperfine field (B_{hf}) for both local environments (LE) considered. In the figure 3.4.4 the magnetic hyperfine field at the two local environments is plotted as a function of the temperature.

Both environments show an increase of B_{hf} , although that effect is clearer for LE_2 where

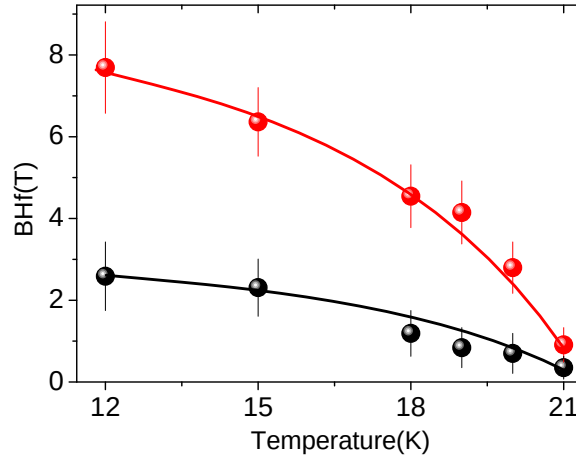


Figure 3.4.4: Hyperfine field dependence with temperature at local environment 1 (blue spheres) and at local environment 2 (red spheres).

$B_{hf} = 2.0(5)$ T at T_N rises to $B_{hf} = 8(2)$ T when reaching 12 K. In fact this second local environment can be related with the small anomaly found in ϵ' and ϵ'' (and loss angle δ) just below 100 K, pointing to some structural effect that affects the dielectric constant. However to clarify this issue further studies are needed.

3.5 Discussion and Conclusions

In this work, we proposed to prepare the silver chromium oxide (AgCrO_2) with the delafossite structure and study its properties, with special emphasis on the use of the local probe technique, perturbed angular correlation (PAC).

From the sintering techniques used, the solid state reaction technique in oxygen flow has proven to be an adequate method to produce the desired silver chromium oxide with the delafossite structure, as the results presented before confirm. In fact, we were able to perform a thorough structural analysis by x-ray diffraction in all sintering stages, which allowed us to follow the evolution of the process of delafossite formation along the several heat treatments performed. The method also allowed the determination of the lattice parameters of the produced samples allowing their comparison with the ones available in the literature. From all the different tests performed in this study the best samples were obtained using the conditions described for sample SS2A, namely, calcination temperature of 500 °C during 12 hours in Air, followed by a sintering stage at 700 °C during 12 hours and under O_2 flow and a final heat treatment at 900 °C for 12 hours, also in O_2 flow.

The sol-gel combustion technique has also proven to be an adequate method to produce the desired structure at lower sintering temperatures. This technique offered, in principle, advantages over the solid state reaction method, however, in the particular case of AgCrO_2 with delafossite structure it was not possible to develop a process that yielded single phase samples, as trace amounts of metallic Ag and $\text{Ag}_2\text{Cr}_2\text{O}_4$ were always found. The results obtained and presented before suggest that some of the conditions used to prepare this compound by sol-gel method still need to be optimized. In particular, as sometimes we use hydrated nitrates as reactants a precise control of the amount of water molecules present in the reactant would be valuable in order to be fully sure that stoichiometry

amounts are being used. This can be performed using TGA, a technique that we had the opportunity to become familiar with during the development of this work (see appendix C) and thus this procedure will be shortly implemented.

Our x-ray diffraction study has also shown that, despite the sintering method used to prepare the AgCrO_2 samples, a tendency for texturization is always present due to the high asymmetry of the unit cell ($c \gg a \sim b$), and AgCrO_2 samples tend to grow preferentially along the c -axis of the unit cell. This tendency can be used in the future in order to produce single crystals of the compound.

In order to check that the produced samples had the magnetic and electric properties reported in the literature we have also performed a detailed physical characterization, with particular emphasis on their magnetic and electrical properties. As is described in the literature AgCrO_2 revealed to be multiferroic material^[33], in which ferroelectricity is driven by the magnetic phase transition. A peak in the real and imaginary parts of the dielectric constant at the paramagnetic to antiferromagnetic phase transition signalizes this effect.

Interestingly, above T_N and up to around 100 K the magnetism in the sample seems dominated by short range magnetic interactions. This is seen as a deviation from the normal Curie-Weiss behavior and can be attributed to the strong frustration effects that occur in antiferromagnetically coupled triangular lattices. Similar effects were already reported in the work of *Oohara et al*^[34] and others^[98–100] and in fact attributed to 2D short-range magnetic correlations.

We have studied in detail the temperature dependence of the electric field gradients at the Cr site via measurements of perturbed angular correlations with the ^{111}In probe. Our data is consistent with previous work performed around room temperature that did not explore in detail the region around 100 K where deviations of the CW law start to appear. Our study, in this temperature range showed that, below 100 K, a second EFG appears and maintains down to the lowest measured temperatures. In addition the relative abundance of these two local environments varies linearly extrapolating to 50% at $T=0$ K.

Given the strong interplay between magnetic and electric degrees of freedom present in AgCrO_2 these short range magnetic correlations can facilitate the onset of a second EFG (EFG_2) that has a relatively close frequency to the one characteristic for first one (EFG_1), but with a different asymmetry parameter (η_2). Recent studies, however, performed by Muon Spin Rotation (μSR) did not show evidence for short-range magnetic correlations in this compound. Although still very speculative a possibility that could explain our data is connected with Ag polar displacements that would start below 100 K. A-site displacements were also suggested in LiCrO_2 . In this scenario the second local environment would be connect with a distortion due to the displacement of Ag atoms that being next-near neighbors would only give rise to small deviation from the normal frequency and give rise to an increase of η . What we can be witnessing with our local probe method is the development of a double-well potential as it occurs in some dielectrics that show order-disorder ferroelectric phase transitions. This explains why the abundances of the local environments cease to vary when the antiferromagnetic-ferroelectric phase transition takes place. The linear extrapolation to 50% abundance at $T=0$ K could be related with the symmetry of the double potential which is developing.

Below T_N both local environments experience strong magnetic hyperfine fields that increase with decreasing temperature. Notice, however, that although we are in antiferromagnetic compound, the fact that the probe substitutes the Cr ion implies that an uncompensated moment will arise and, accordingly, our probe will experience a non vanishing local magnetic field. The studies will proceed in the near future, aiming to develop a physical model that explains our observations and in this way contribute to unveil the nature of the magnetoelectric coupling in these compounds. At

this point we can only suggest that the second local environment emerging below 100 K together with the anomalies in the magnetization and dielectric constant data may be associated to Ag lattice displacements being a precursor effects of the ferroelectric/antiferromagnetic phase transition.

Chapter 4

Synthesis and Characterization of the CdCr_2S_4 Spinel

The discovery, characterization and investigation of solid inorganic materials is at the heart of solid state and materials chemistry. The ternary ACr_2X_4 (where $\text{A}=\text{Cd}, \text{Hg}, \text{Cu}, \text{Mg}, \dots$ and $\text{X}=\text{S}, \text{Se}, \text{O}$) with Cr as transition metal form a special group of magnetic semiconductors and therefore creating a lot of possibilities for technical applications^[1]. In particular, the CdCr_2S_4 thio chalcogenide spinel has been getting considerable attention^[9] also due to the recent indication that coexistence of ferromagnetism and relaxor ferroelectricity together with colossal magnetocapacitive effects exists. However, these results also raised some discussion ^[7,41].

Aiming to contribute to enlight some aspects on the unsolved issues of this system in particular on the above mentioned controversial existence of polar domains we have produced, characterized and performed a detailed magnetic and local probe study on CdCr_2S_4 spinel compound. The results obtained on this study are presented in the following, along with some general conclusions.

4.1 Sample Preparation

The polycrystalline samples of Cadmium Chromium sulphide (CdCr_2S_4) of the spinel family were first synthesized by *Passerini et al.*^[101] and later by *Haul and Schöning*^[39]. In this work, in order to obtain the CdCr_2S_4 system, the samples had to be prepared by a variant of solid state reaction method, where the annealing procedure had to be performed in double evacuated quartz ampoule. There are two major reasons for the necessity of the double evacuated quartz ampoule in the synthesis process. First, to avoid oxide formation and thus obtain the desired phase. The second reason is related with safety reasons due to the high partial pressure that sulphur reaches when submitted to the sintering temperatures, which can break the first ampoule. In this way, the use of a second one, conserves the vacuum required if the first breaks.

Stoichiometric amounts of cadmium sulphide¹, chromium² and sulphur³ were mixed and grinded together until very fine powders were obtained. The powders were then pressed into a pellet of ≈ 1 g. Then the pellets were weighted and introduced into a quartz tube and closed in

¹CdS, metal basis, 99.999% purity, CAS-NUMBER:1306-23-6

²Cr, -60 mesh metal basis, purity 99.99%,CAS-NUMBER:7440-47-3

³S, purity 99.98%,CAS-NUMBER:7704-34-9

vacuum (10^{-5} Torr) with the help of a burner. This ampoule was then introduced into a larger one that was also filled in vacuum, see figure 4.1.1.

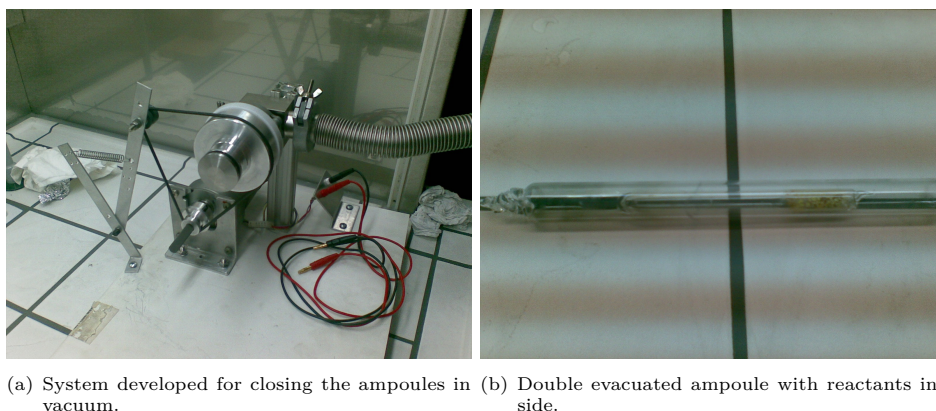


Figure 4.1.1: Pictures of the system used for spinel synthesis.

The double ampoule was placed into an alumina tube for greater protection because of the high temperature that the ampoule was going to suffer (sulphur vapor pressure at the temperatures of annealing could break the ampoules and therefore cause the contamination of the furnace).

This firing procedures were performed in several steps. The furnace was heated up to $400\text{ }^{\circ}\text{C}$ ($6.25\text{ }^{\circ}\text{C}/\text{min}$), where it rested for 5 hours and then up to $650\text{ }^{\circ}\text{C}$ ($0.1\text{ }^{\circ}\text{C}/\text{min}$). After 5 days at $650\text{ }^{\circ}\text{C}$ the vapor in the ampoule became more transparent indicating that the majority of sulphur had already reacted and thus the oven temperature was increased up to $750\text{ }^{\circ}\text{C}$ ($0.1\text{ }^{\circ}\text{C}/\text{min}$). After being at this temperature for 4 days the furnace was slowly cooled to room temperature ($\approx 1\text{ }^{\circ}\text{C}/\text{min}$).

After this first heat treatment we could observed that, as expected, a small part of the sulphur did not react remaining in the ampoule wall. After weighting the pellets the mass loss was compensated by adding sulphur. A new grinding, pelletizing and weighing of the pellets was then performed.

The heat treatment process was repeated again. This time a ramp of $10.8\text{ }^{\circ}\text{C}/\text{min}$ was used to reach the $650\text{ }^{\circ}\text{C}$ and from there to the $750\text{ }^{\circ}\text{C}$ at $0.1\text{ }^{\circ}\text{C}/\text{min}$ rate. Finally the temperature was raised to $800\text{ }^{\circ}\text{C}$ ($1.0\text{ }^{\circ}\text{C}/\text{min}$) where it stayed for a week. Again $\approx 1\text{ }^{\circ}\text{C}/\text{min}$ rate was used to slowly cool the furnace to room temperature. After this annealing procedure the sample weight was again measured, compensated with sulphur for the mass loss, grinded, pressed into a pellet and was annealed to a maximum temperature of $850\text{ }^{\circ}\text{C}$. The last process was repeated one more time, in order to obtain homogeneous polycrystalline material with no spurious phases.

This preparation of the chalcogenide (CdCr_2S_4) was performed following a method kindly provided by Dr. Tsurkan of the Institute of Applied Physics of Moldova University^[102].

4.2 Structural and Morphological Characterization

4.2.1 X-Ray Diffraction

The most common tool for the identification of polycrystalline solids is powder x-ray diffraction, as presented before in section 2.2.1.

After every step of the synthesis process a XRD pattern was collected allowing to follow the evolution of the diffusion reaction. Its possible to observe in figure 4.2.1, the referred evolution in the XRD pattern after each step and compare the resulting powder with the XRD patterns available in the literature^[103].

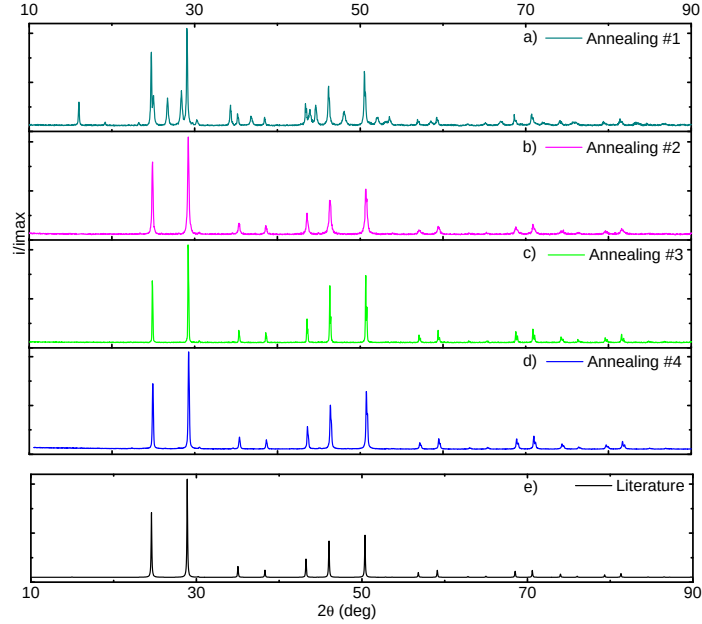


Figure 4.2.1: XRD patterns of the different synthesis steps (top) and the reference literature (bottom).

After the first synthesis step the XRD pattern already shows the presence of the desired spinel structure but also the presence of reflections corresponding to the reactants, and to Cr_2S_3 . The second heat treatment proved to be very fruitful, because it managed to convert almost all reactants into the final product. The third heat treatment, was enough in order to yield a single phase sample. Nevertheless a fourth treatment was performed in order to ensure that we would obtain a single phase with no spurious secondary phases. Is also possible to observe that, as desired, the last two treatments improved the sharpness of the peaks, thus increasing grain size.

The high quality XRD pattern of the CdCr_2S_4 final sample was analyzed by Le Baile refinement (applying a pseudo-voigt function to fit the peak shape), allowing the determination of the space group and cell parameters. Next the full Rietveld refinement was performed and parameters like the atomic positions, isothermic vibration factor and atomic site occupancy were determined. Figure 4.2.2 presents the observed pattern (red dots), calculated (black solid line), reflections of the correspondent phases (green tick marks) and fit deviation (blue solid line in the bottom) of the resulting Rietveld refinement. The fit deviation line shows the good quality of the performed refinement.

The XRD pattern was fitted with only one phase corresponding to the group $\text{Fd}\bar{3}\text{m}$ ^[39] expected for the chalcogenide spinel CdCr_2S_4 . The refinement parameters obtained are summarized in table 4.2.1, allowing to verify the high quality sample, and that the lattice parameters are also in a good agreement in those found in the literature^[38].

A good way of following and guide a Rietveld profile is by observing the graphical representation given in figure 4.2.2, minimizing the difference between the experimental and calculated profile. A more quantitative way of doing so is following the reliability factors (R_P ; R_{wp} ; R_{exp}) follow the

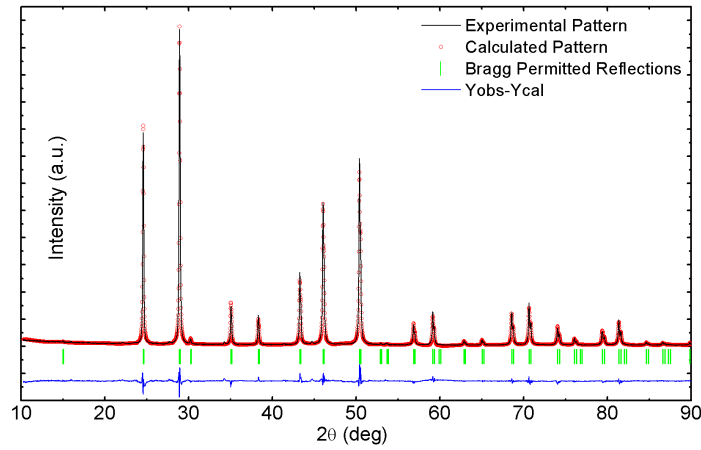


Figure 4.2.2: Rietveld Fit of XRD pattern of CdCr_2S_4 .

Space group	$Fd\bar{3}m$				
Unit Cell	$a = 10.23234(17)\text{\AA}$ $b = 10.23234(17)\text{\AA}$ $c = 10.23234(17)\text{\AA}$				
Cell Volume	$1071.334(31)\text{\AA}^3$				
Z	8				
Points	4993				
Effective 2θ	10-90				
Refined Parameters	15				
$R_P; R_{wp}; R_{exp}$	4.54; 4.77; 2.80				
χ^2	3.51				
Atom	x	y	z	B_{iso}	F_{occ}
Cd	0.12500(0)	0.12500(0)	0.12500(0)	1.699(44)	0.233(313)
Cr	0.50000(0)	0.50000(0)	0.50000(0)	1.492(94)	0.465(62)
S	0.26478(16)	0.26478(16)	0.26478(16)	2.081(110)	0.993(99)

Table 4.2.1: Rietveld refinement parameters CdCr_2S_4 .

evolution of the fit. As can be seen in table 4.2.1 the profile, the weighted-profile and experimental reliability factors are present. It can be observed by the low value of the $\chi^2 = 3.51$ the goodness of the fit, where $\chi^2 = R_{WP}/R_{exp}$.

After PAC measurements it was necessary to ensure that the crystallographic properties remained unchanged, i.e. after performing the annealing for recovering of implantation damage, a XRD pattern of the CdCr_2S_4 was collected. In figure 4.2.3 the XRD pattern of the sample after sintering a) and after PAC measurements b) is presented.

The XRD patterns permit to observe that the sample didn't suffer any alterations and keeps the same crystallographic properties after the annealing performed to recover from the implantation process. This also allowed to verify that the annealing performed after the implantation was appropriated.

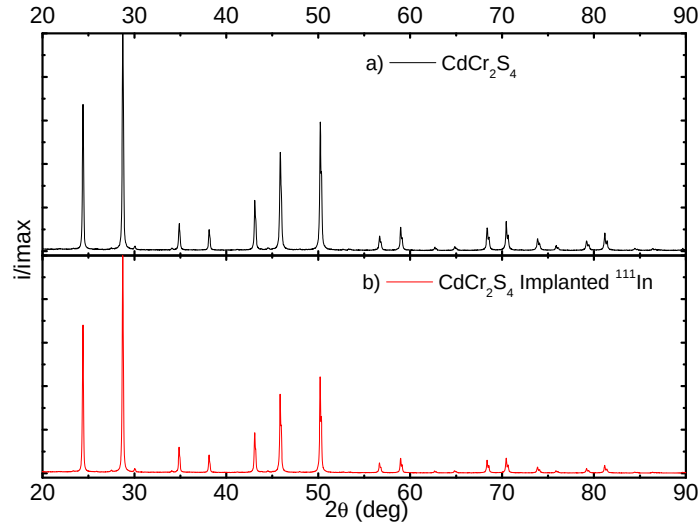


Figure 4.2.3: XRD patterns of the spinel sample before and after the annealing performed to recover from ^{111}In implantation damage.

4.3 Magnetic and Electric Characterization

The spinel type compound CdCr_2S_4 has drawn the attention of the scientific communities when it was recently discovered the coexistence of ferromagnetism and relaxor ferroelectricity together with colossal magnetocapacitive effect [9]. This led to controversial opinions [7,40] and in the last years much effort is being made to unveil the nature of the magnetoelectric effects and to establish multiferroism in this system [41,43].

One thus realizes that the detailed knowledge of the magnetic and electric properties of this system is of crucial importance. In order to analyze if our system presents the same properties as reported in literature a thorough magnetic study and a dielectric characterization was performed and is presented in the next subsection.

4.3.1 Magnetic characterization

In the literature this system is quoted as being a typical ferromagnetic material with a para/ferromagnetic transition at 84.5 K [1,38].

To ensure that the system has the expected magnetic properties we have performed magnetization measurements with constant applied field (103 Oe) while heating in the range of temperatures of 5 to 380 K.

Figure 4.3.1 shows the reciprocal magnetic susceptibility $1/\chi$ and the low-temperature (low-T) susceptibility χ (inset). The straight line indicates the fit to the paramagnetic susceptibility. Figure 4.3.1 shows that $\chi(T)$ has strong increase at T_C , indicating a well defined phase transition from paramagnetic to ferromagnetic.

As expected, CdCr_2S_4 seems to have a typical soft ferromagnet magnetization curve. The obtained magnetic parameters from the fit of CW law were a Curie-Weiss temperature of 128 K and an effective paramagnetic moment of $4.15 \mu_B$ (see table 4.3.1) are near those reported in the literature [9,34,40].

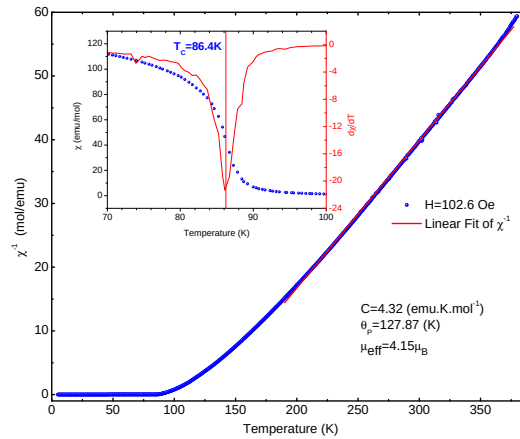


Figure 4.3.1: Inverse dc magnetic susceptibility of CdCr_2S_4 as a function of temperature. In the inset a detailed T_C zone temperature in a $\chi = f(T)$ and $d\chi/dT$.

Sample	θ_P (K)	C ($\frac{\text{emu.K}}{\text{mol}}$)	T_C (K)	μ_{eff} (μ_B)
CdCr_2S_4	128	4.32	86	4.15
Literature	152 ^[1,38]	3.74 ^a	84 ^[1,38]	3.87 ^a

^aCalculated for Cr^{3+}

Table 4.3.1: Table of the measured CdCr_2S_4 samples magnetic properties

As one can observe in figure 4.3.1 where the reciprocal susceptibility is presented, for T below 250 K a deviation from linearity is observed.

To study in more detailed the deviation from the Curie-Weiss law at low temperatures, we performed a study of the magnetic susceptibility dependence with the temperature in a set of low magnetic fields [1 to 100 Oe]⁴. The magnetic susceptibility curves for the different fields applied are shown in the figure 4.3.2 a). From this graphic one can easily realize that as the field decreases the deviation from the CW law becomes more pronounced. Moreover, the temperature where the deviation starts seems to be field independent therefore, additionally to T_C , another common temperature, T_G , can be defined as the onset of the CW linear regime deviation.

This picture suggests the appearance of short-range magnetic correlations (SRMC) (or spin-cluster) in the PM phase and we can define a new temperature scale T_G (85 K < T < 116 K) where these clusters start to form. It seems that the size of these SRMC depends largely on the applied magnetic field, being almost destroyed for field higher than $H > 100$ Oe. In agreement with our findings recent Electron Spin Resonance ESR studies reported a split of a single and slightly asymmetrical ESR line into two in the same temperature range for a similar spinel compound^[104]. These authors associated the observed ESR line broadening/splitting to clustering phase as observed in manganites^[105].

To our knowledge these magnetization results haven't been reported in the literature and a model is being developed to interpret these results.

⁴Note that in the literature most of the presented magnetization data in this system was obtained with high applied magnetic fields ($H > 100$ Oe) and thus this behavior has been masked.

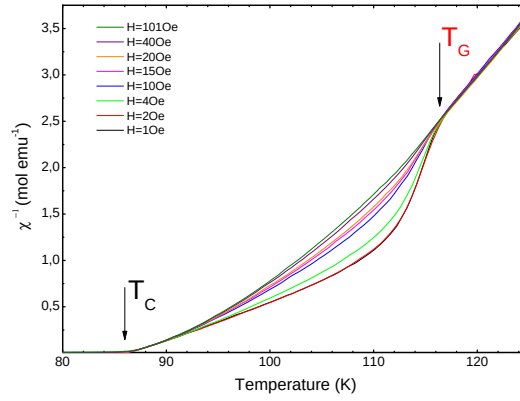


Figure 4.3.2: Inverse DC magnetic susceptibility of CdCr_2S_4 as a function of temperature and magnetic field.

4.3.2 Electric Characterization

The knowledge of the dielectric properties and their variation with temperature is important for the settling of the magnetoelectric properties in CdCr_2S_4 material.

Thus, to study the dielectric properties of the produced system, dielectric constant measurements were performed, as described in subsection 2.3.2 in the CdCr_2S_4 single phase sample. These measurements of the real part of the dielectric constant can be observed in figure 4.3.3, at frequency of 500 KHz, 1 and 5 MHz (applied field 1 V/m). The inset on the graphic present the individual measurement with a frequency of 1 MHz. It is possible to observe a small increase on the real part of the complex dielectric constant ϵ' at T_C .

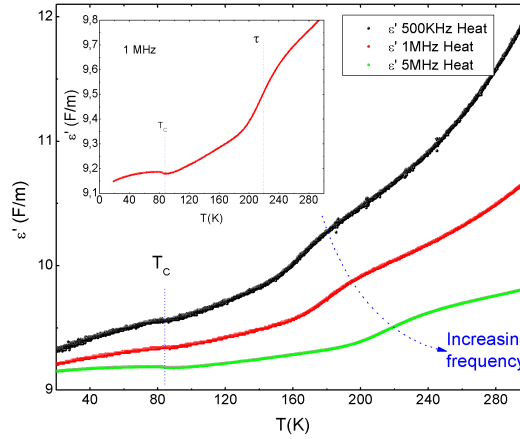


Figure 4.3.3: Temperature dependence of real part of complex dielectric constant. The CdCr_2S_4 sample was measured to a frequency of 500 KHz, 1 and 5 MHz. In the inset the 1MHz measurement.

No clear features connected with ferroelectric order were found. However, the measurement performed by *Sun et al*^[41] were done with much-higher electric fields. Further studies with higher electric fields are currently under way to clarify this issue as claimed in the literature^[40].

4.4 Electric Field Gradient Characterization - PAC

In order to characterize locally the electronic and magnetic structure of the CdCr_2S_4 compound, the perturbed angular correlation technique was used with radioactive ^{111}In isotope probe. The radioactive probes were implanted at ISOLDE-CERN by ion implantation at 30 KeV of the sample with an average 10^{12} /area of ^{111}In probes. After the implantation an annealing⁵ was performed to the samples in an evacuated quartz ampoule with a sulphur excess. The annealing was performed during 20 minutes at a temperature of 500 °C (793 K). This annealing conditions had proven to be ideal to allow the system to recover from the implantation damage and keep unchanged the sample properties (see XRD patterns in figure 4.2.3).

The PAC measurements, electrical field gradient and magnetic hyperfine field measurements, were performed using a six detector spectrometer in temperature ranging from 300 K to 10 K. By performing these measurements in different temperatures the evolution of the EFG can be studied.

Representative $R(t)$ experimental function, correspondent fits and respective Fourier transform obtained at different temperatures are presented in the figure 4.4.1.

In all temperature range the fits to the experimental PAC spectra, continuous lines in the $R(t)$, were made considering Lorentzian-like EFG distributions. Since in the study presented here the ^{111}In isotope was used and in the literature is reported that ^{111}In isotope can replace either the Cd or Cr atoms^[1] two EFG distributions were used to performe the fits. In all temperature range the fraction of probes that was considered to be interacting with each EFG was nearly 30 % and 70 %. In fact, for a similar after implantation annealing as the one performed here it is expected that ~ 30 % of the atoms goes to the Cd site being the other ~ 70 % substituting Cr atom ^[1]. The existence of the two local probe surroundings, two EFG, can be clearly identified in the Fourier transforms of the $R(t)$ functions, as shown in figure 4.4.1. An apparent frequency triplet, corresponding to one EFG, EFG_1 , with frequencies at $\omega_1 \sim 70$ Mrad/s, $\omega_2 \sim 2\omega_1$ and $\omega_3 \sim 3\omega_1$, is observed. The second EFG, EFG_2 , can be identified by the observable frequency close to zero. The contribution of this EFG_2 can also be clearly recognized by an extra modulation with very long period ($T \gg 200$ ns) in the $R(t)$ function (see $R(T)$ functions in figure 4.4.1).

At high temperatures, $T \geq 200$ K, the fit performed with static EFG distributions held an EFG_1 characterized by a observable frequency, $\omega_{01} = 68(2)$ Mrad/s ($\nu_{Q1} = 72(2)$ MHz and $V_{zz} = 3.6(2) \times 10^{21}$ V/m²), and an asymmetry parameter, $\eta = 0.10(5)$, characteristic of an EFG with axial asymmetry, as expected for probes at Cr site. The EFG_2 is characterized by an extremely broad frequency distribution with $\omega_{02} \approx 0$ Mrad/s. This second EFG is associated with probes in the Cd cubic site. Note that due to symmetry considerations the EFG at this site should vanish.

At lower temperature, visible changes can be observed by a simple inspections to the $R(t)$ function and Fourier transforms. In fact, between 119 K and 98 K although no apparent changes are observed in the frequencies values the spectra continually becomes more attenuated as the temperature decreases. In this way, different systematic fitting approaches were performed in this range of temperatures, *i.e.*, fits with hyperfine magnetic field and/or high values of the static attenuation but neither of then was able to account correctly for the effect observed in the experimental data. On the other hand, considering a dynamic attenuation term on the fit function (using a dynamic attenuation parameter λ) one was able to perform high-quality fits. In fact, the best fits were obtained admitting a fluctuating EFG_1 ($\lambda_1 \neq 0$ and $\delta_1 = 2$ %) and a static $\text{EFG}_2 \sim 0$ in the $T = 119$ K to $T = 92$

⁵Remember that the annealing performed has the objective to remove the radiation-induced damage created by the implantation, as presented before in section 2.4.

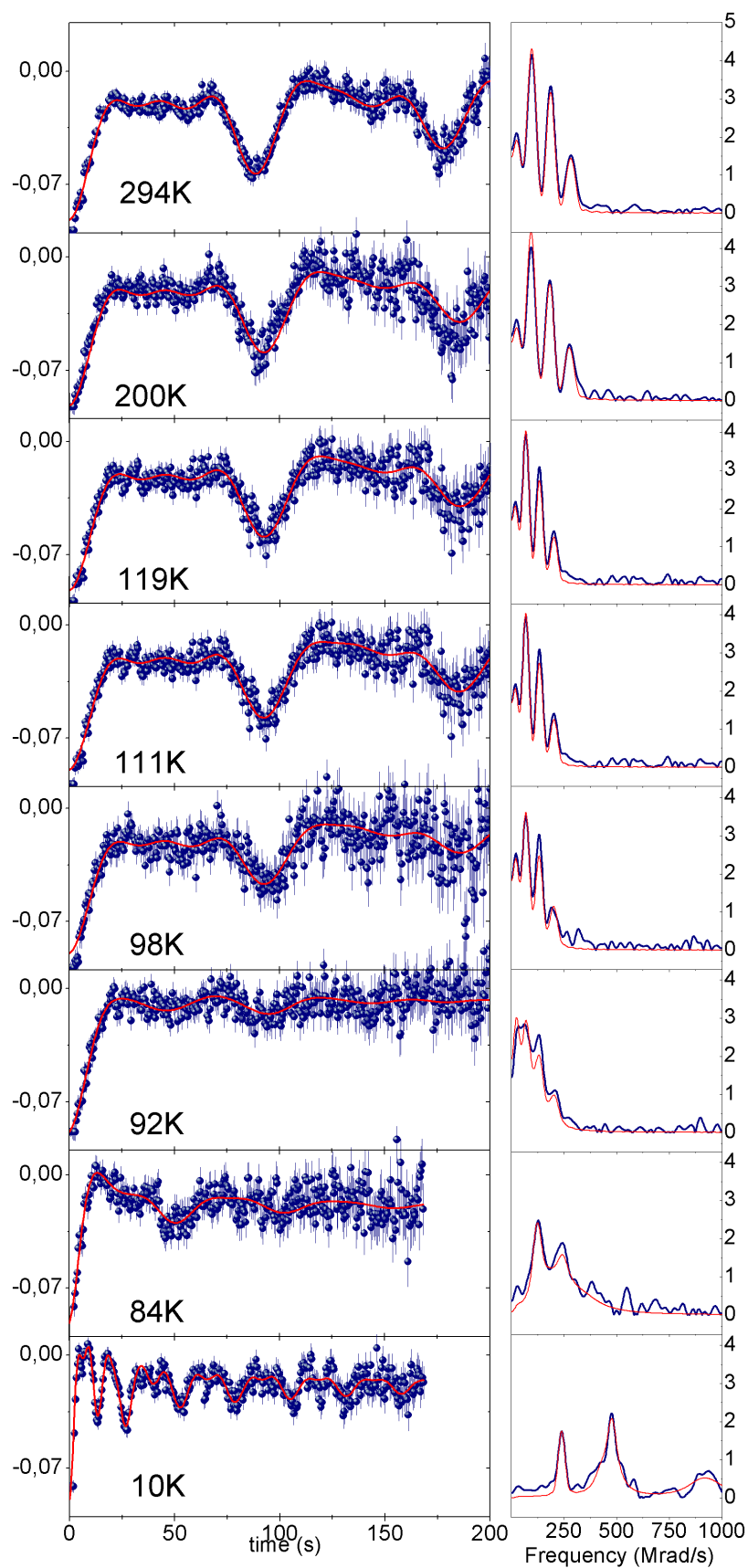


Figure 4.4.1: Representative $R(t)$ functions, correspondent fits and respective Fourier transform taken at different temperatures.

K temperature region.

On further decreasing temperature, around and below T_C , additional changes are observed (see spectra in figure 4.4.1 T=84 K and 10 K) the frequencies shift to much higher values and slightly split. This effect should be connected with the presence of a high hyperfine magnetic field as expected (below T_C the system becomes ferromagnetic). In accordance, around and below the magnetic phase transition, the fit was performed using combined interactions (EFG plus MHF) and both sites were considered to experience a magnetic hyperfine field.

Performing the fits in the different temperatures ranges the evolution of the EFG's and MHF's parameters was obtained. The thermal dependence of those parameters is presented in the figures below. In particular the thermal dependence of the EFG₁ parameter ω_{01} , η_1 and the percentage of probes interacting with each local environment, is shown in figure 4.4.2. As one can observe the EFG parameters (ω_0 and η) are almost temperature independent and no anomaly can be observed. In fact, the outstanding result on these PAC measurements is the existence of a dynamic attenuation on the PAC spectra as can be clearly observed in the R(t) functions for T<120 K.

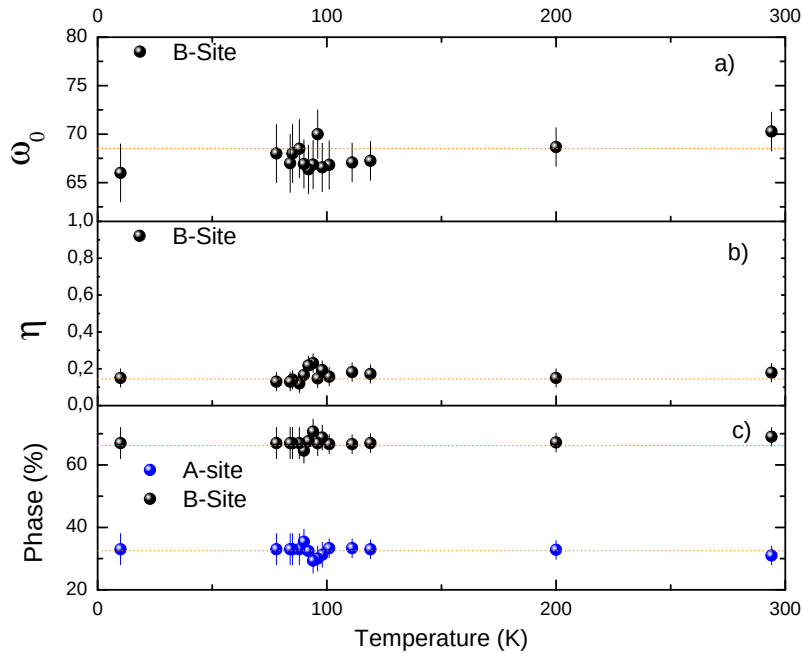


Figure 4.4.2: EFG parameters in the CdCr_2S_4 system. In a) fundamental frequency, b) the asymmetry parameter and c) the fraction of each EFG.

The temperature dependence of the dynamic attenuation parameter, λ , used to perform the presented fits, can be used to estimate the activation energy, E_a , that is behind the physical process that induced the spectra damping. This energy can be obtained from $\lambda_1 = \lambda_\infty e^{\frac{E_a}{kT}}$. In figure 4.4.3 is depicted in an Arrhenius plot ($\ln\lambda$ is plotted against the reciprocal temperature). By performing a linear fit the slope of the curve can be obtained and consequently the activation: $E_a=0.1$ eV. This result gives evidences for the existence of a slow thermally activated dynamic process occurring in a time range between ns and μs (PAC time window) between 119 K to 92 K.

As mentioned before, at low temperatures, below the magnetic phase transition, both sites experience a magnetic hyperfine field (B_{hf}) compatible with Cr ferromagnetic spin alignment (see

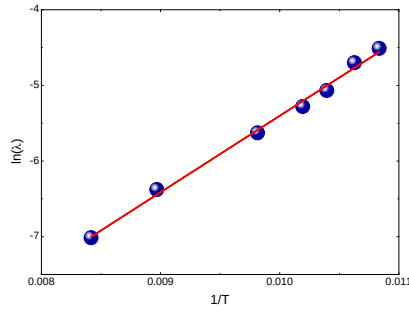


Figure 4.4.3: Dynamic attenuation parameter as a function of temperature.

table 4.4.1). When comparing our work to the work of *Samohvalov*^[1] measurement at the same temperature (77 K), see table 4.4.1, we can see that the the values are in fair agreement.

¹¹¹ In					
Compound		Technique	A-Site	B-Site	
CdCr ₂ S ₄	V_{zz} (10^{21}V/m^2)	PAC	-	3.6(1)	Our Work [1]
		PAC	-	3.5	
	ω_L (Mrads/s)	PAC	146(3)	213(3)	Our Work [1]
		PAC	149(1)	228(4)	
	B_{hf} (T)	PAC	10.0(1)	14.5(1)	Our Work [1]
		PAC	10.2(1)	19.5(4)	
		NMR	16.7 (¹¹¹ Cd)	19.1 (¹¹¹ Cd)	[38]

Table 4.4.1: Comparison of the measured B_{hf} , ω_L and V_{zz} in the ferromagnetic spinel with ¹¹¹In probe at $T_M = 77$ K and NMR carried out at 4.2 K. A-site for Cd and B-site for Cr.

In the figure 4.4.4 the magnetic hyperfine field at Cr and Cd sites is plotted together with macroscopic magnetization curve. A good correlation between all these curves can be observed. Nevertheless, upon a closer inspection it is possible to note that before the magnetic phase transition occurs a local magnetic component is already present (B_{hf} 's $\neq 0$ for $T > T_C$).

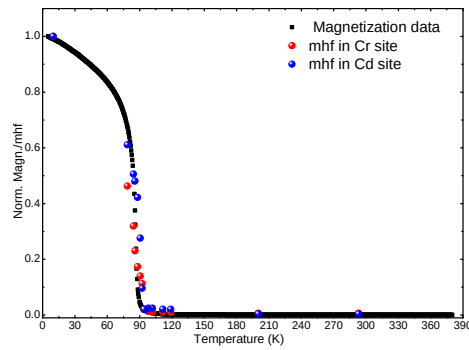


Figure 4.4.4: Normalized magnetization data obtained with an applied field of 100 Oe (black squares), normalized hyperfine field dependence with temperature in Cr site (red spheres) and in Cd site (blue spheres).

4.5 Discussion and Conclusions

In this work we proposed to prepare the CdCr_2S_4 with spinel structure and study its properties. High quality polycrystalline samples were prepared using a double evacuated quartz ampoule, a branch of the solid state reaction method. The x-ray analysis of the CdCr_2S_4 spinel allowed to verify that the experimental set-up developed during this work is able to produce high quality single phase samples based on sulfur. In this way, the set-up can, and will be now used to produce other sulfur based compounds.

We have performed a detailed structural analysis by x-ray diffraction in all sintering stages. This analysis allowed us to follow the evolution of the sintering process during the system formation. We have also performed Rietveld refinement of the produced sulfide spinel and the obtained lattice parameters are in an excellent agreement in those found in the literature.

A magnetic characterization of the CdCr_2S_4 sample was performed showing that besides the good agreement of the T_C and μ_{eff} , short-range magnetic correlations (SRMC) (or spin-clusters) in the PM phase were observed and it was possible to define a new temperature scale $T_G \sim 116$ K where these clusters start to form. Moreover, we have seen that these SRMC depended largely on the applied magnetic field, being almost destroyed for fields higher than $H > 100$ Oe. To our knowledge, this is the first time that such SRMC were directly observed in very low field magnetization data. However several techniques have reported strong anomalies in the same range of temperatures. In fact it was reported for CdCr_2S_4 a negative thermal expansion below 150 K^[106], and an anomalous broadening of the Bragg reflections in x-ray diffraction experiments at temperatures above the ferromagnetic phase transition^[106], thus providing experimental evidence for short-range structural distortions close to 150 K. In addition, synchrotron radiation experiments provide evidence for the existence of a (200) reflection below 200 K and with increasing intensity towards 0 K, forbidden for spinel structure. The onset of local polar distortions also has been claimed in recent Raman scattering experiments,^[43,107] where pronounced anomalies in the Raman modes appear below a characteristic temperature $T^* = 130$ K.

This also correlates very well with our local probe studies performed by PAC using the ^{111}In probe that revealed in the same range of temperature *i.e.* for temperatures below 120 K a dynamic interaction appears meaning that EFG fluctuations occur within the PAC measuring time-scale (*i.e.* ns time scale). These results, correlated with those of the literature point to the onset of local distortions associated with magnetic short-range correlations also observed in our magnetization data. Further studies are needed in order to develop a complete physical model to fully explain the obtained data.

These results give additional support to the suggestion that the magnetic ordering in CdCr_2S_4 chalcogenide spinels is strongly coupled with electric properties and that locally this coupling can be witness at temperatures much above then T_C . In fact the observed time dependent EFG interactions can be attributed to the onset of local polar distortions triggered by the magnetic short-range correlations observed in the magnetization data.

Conclusions

The synthesis of silver chromium oxide delafossite AgCrO_2 was tested using two different methods, solid-state reaction and sol-gel combustion synthesis. To prepare de delafossite sample by sol-gel combustion synthesis several experiments were conducted. Different complexant agents/combustion initiators were tested. After each annealing stage x-ray powder analysis was performed to characterize the resulting phases.

In the solid-state reaction synthesis different annealing conditions were tested, i.e., different annealings times and atmospheres were used.

To study the results of each synthesis stage x-ray diffraction measurements were performed for each sample after each annealing step. The good quality of the sample was confirmed by the results of the different characterization techniques. Different fit analysis were performed considering a single phase with Rhombohedral structure ($R\bar{3}m$ space group) or a mixture of phases, depending the case. The obtained XRD fit parameters, most of the times $a, b = 2.986$ and $c = 18.506$, are in very good agreement with the expected ones.

To evaluate at the micrometer scale the sample quality and its stoichiometry, scanning electron microscope measurements, SEM/EDS, were performed. The EDS analysis showed that the atomic percentages of the elements present in the AgCrO_2 sample (Ag 24 %, Cr 23 % and O 53 %) are in good agreement with what is expected for the delafossite structure. The SEM images allowed to verify the sample morphology. The sample composition showed to be homogeneous with a mixing of different sized crystals and well delineated grain boundaries. The observed plateaus/layers were related with the high asymmetric crystallographic structure of this system ($c \gg a = b$).

A surface element composition analysis was also performed in the AgCrO_2 system by x-ray photoelectron spectroscopy (XPS). Fitting of the respective Cr, Ag and O spectra allowed to verify the presence of a Ag_2CrO_4 minor phase in the sample analysed.

The magnetic characterization of the AgCrO_2 system allowed to extract the temperature of the paramagnetic to antiferromagnetic phase transition, $T_N = 21$ K, the Curie-Weiss temperature $\theta_P = -180$ K, and the paramagnetic moment $\mu_{eff} = 3.7 \mu_B$. The magnetic properties are in agreement with those found in the literature attesting the high quality of the samples.

The AgCrO_2 measurements with perturbed angular correlation using ^{111}In isotope were performed. The ^{111}In probes occupied the B (Cr) site of the delafossite system. The results analysis showed that only one local environment, EFG_1 , with axial symmetry ($\eta=0$) was observed in a wide range of temperatures, from 450 K to 100 K. Also the EFG parameters, ω_0 , η and attenuation, σ , showed nearly no temperature dependence until around 100 K. Below that temperature, was necessary to consider a second EFG_2 .

The EFG_1 was characterized by a quadrupole frequency of $\nu_Q = 131(2)$ MHz and an asymmetry parameter $\eta=0$ characteristic of an EFG_1 with axial asymmetry, as expected for probes at Cr

site. The EFG_2 was characterized by a quadrupole frequency very similar to ν_{Q1} , $\nu_{Q2} = 137(4)$ MHz, and an asymmetry parameter $\eta = 0.5$. It was possible to verify that the second local environment, associated with EFG_2 , appeared only below 100 K. Decreasing temperature, below 100 K, the fraction of probes experiencing the EFG_2 continuously increases in detriment of the fraction of probes experiencing EFG_1 . Those changes seemed to halt when the fraction of both local environments reached approximately $f_1 \approx 60\%$ and $f_2 \approx 40\%$. This occurs very close to the antiferroelectric/antiferromagnetic transition. Its correlation with ferroelectric distortions and with the anomaly observed in the reciprocal susceptibility was considered.

The compound CdCr_2S_4 was prepared by a variant of solid state reaction method, where the annealing procedure had to be performed in double evacuated quartz ampoule. After each annealing stage x-ray powder analysis was performed to characterize the resulting phases.

Rietveld refinement of the room temperature x-ray powder diffraction pattern has been performed confirming the presence of a single $Fd-3m$ phase. The lattice parameters ($a, b, c = 10.232$) and atomic position were obtained. Those parameters were in good agreement with those in literature.

A detailed magnetic characterization was performed in this system. Magnetization measurements revealed a Curie temperature, $T_C = 85$ K, an effective paramagnetic moment of $4.1 \mu_B$, close to the theoretically expected value of $3.9 \mu_B$ per Cr^{3+} . Moreover the results showed that for temperatures below 250 K a deviation from linearity in the reciprocal susceptibility is observed. This picture clearly illustrates the appearance of short-range magnetic correlations (SRMC) (or spin-cluster) in the PM phase ($85 \text{ K} < T < 116 \text{ K}$) and defined a new temperature scale $T_G \approx 116 \text{ K}$ where this clusters start to form. We show that the size of these SRMC depends largely on the applied magnetic field, being destroyed only for fields higher than 100 Oe. Note that even for high magnetic fields the reciprocal susceptibility didn't follow the typical Curie-Weiss law.

We also performed electrical field gradient and magnetic hyperfine field measurements using PAC technique. For the study presented here the ^{111}In isotope was used. In the literature is stated that ^{111}In isotope replaces $\sim 30\%$ of the atoms in the Cd site and $\sim 70\%$ substitutes the Cr site, as obtained in this work. In fact, while performing the fits to the $R(t)$ experimental functions two different local environments, two EFGs, were considered. The fraction of probes interacting with each EFG was found to be constant in all temperature range, as expected.

The EFG_1 was characterized by an observable frequency, $\omega_{01} = 68$ Mrad/s, and an asymmetry parameter, $\eta = 0.1$, characteristic of an EFG with axial asymmetry, as expected for probes at Cr site. The EFG_2 was characterized by an extremely broad frequency distribution with $\omega_{02} \sim 0$ Mrad/s. This second EFG was associated with probes in the Cd cubic site. At low temperatures, below the magnetic phase transition, both sites experience a B_{hf} compatible with Cr ferromagnetic spin alignment.

A good correlation between the magnetization and the B_{hf} curves for Cadmium and Chromium site was obtained. It was possible to observe that before the magnetic phase transition occurred, a local magnetic component was already present ($B_{hfs} \neq 0$ for $T > T_N$).

A dynamic attenuation in the $R(t)$ functions was observed below approximately 120 K. This result gave evidences for the existence of a slow thermally activated dynamic process occurring in the 120 K to 90 K temperature range. A Arrhenius plot of the dynamic attenuation was presented and from the linear fit an activation energy was determined, $\Delta E = 0.1$ eV.

A explanation for the observed dynamics was suggested, by being related with off-center displacements of the Cr^{3+} atom, i.e., with the onset of local polar distortions triggered by the magnetic short-range correlations that were observed in the magnetization measurements. The observed magnetization anomalies occurred in the same temperature range. Recent works showed pronounced

anomalies in the Raman modes below a characteristic temperature $T^*=130$ K, that can be related to the results presented in this work.

Appendix A

XRD Sol-gel Series

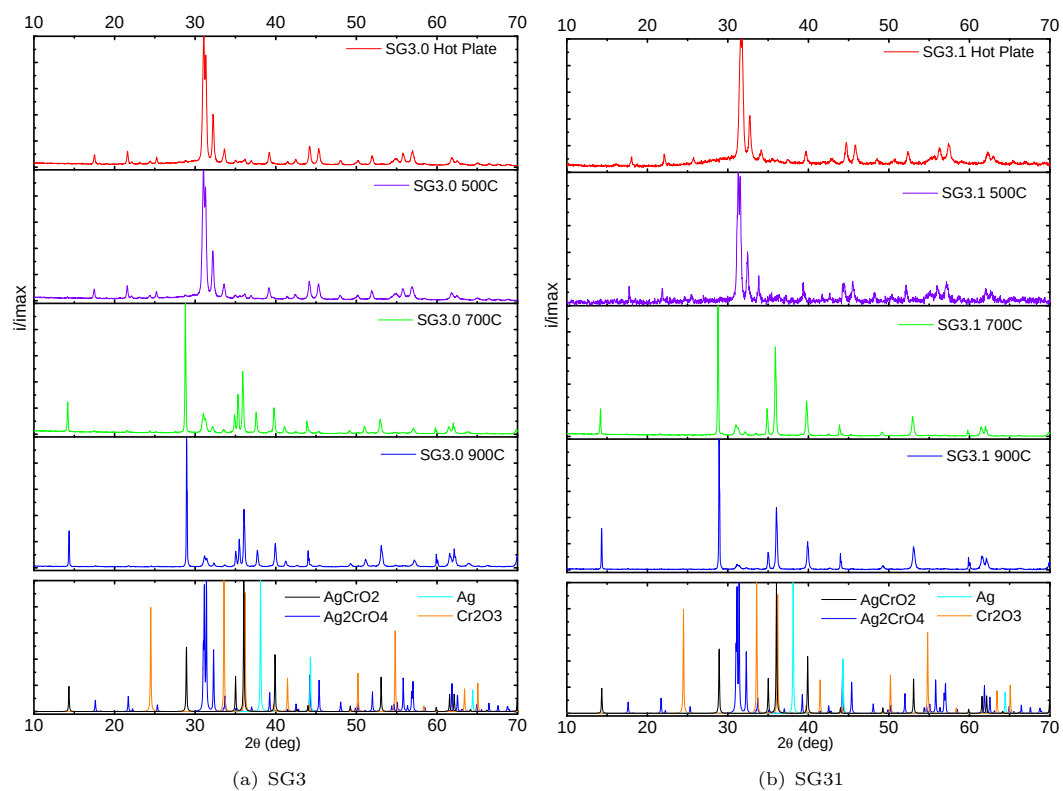


Figure A.0.1: AgCrO₂ synthesized by sol-gel combustion synthesis using Urea and a pH of 3.5 a) and 4.2 b).

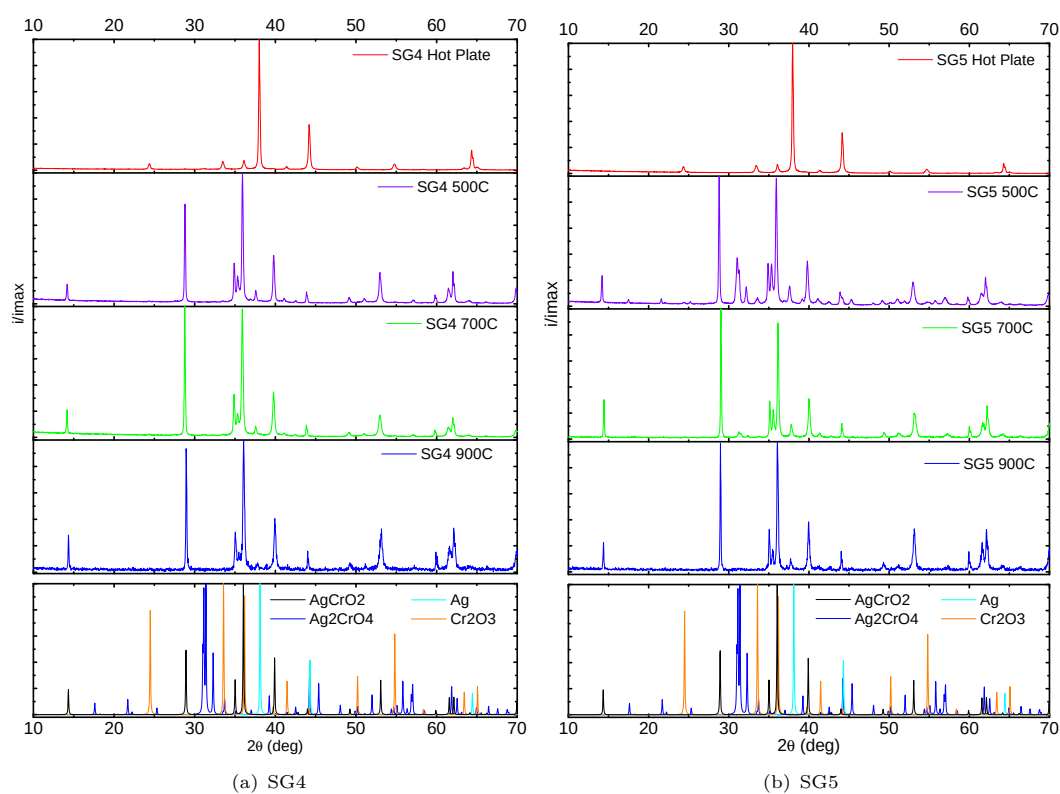


Figure A.0.2: AgCrO_2 synthesized by sol-gel combustion synthesis using Urea+citric acid a) and Urea+Ethylene Glycol b).

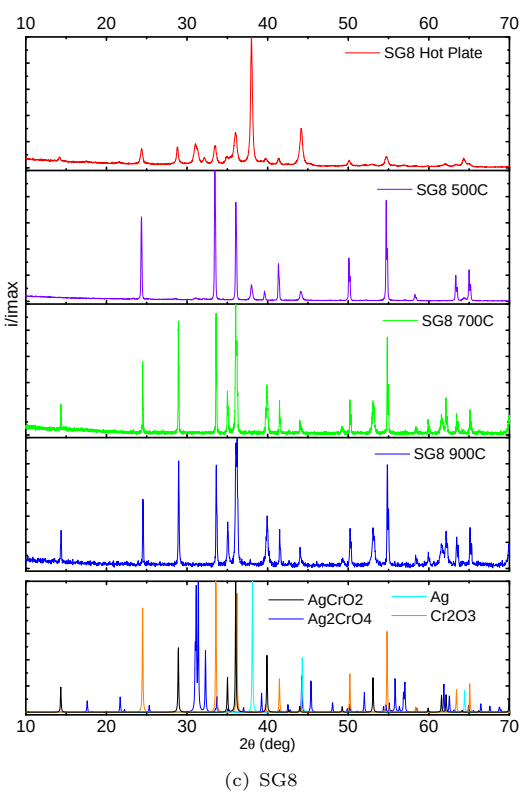
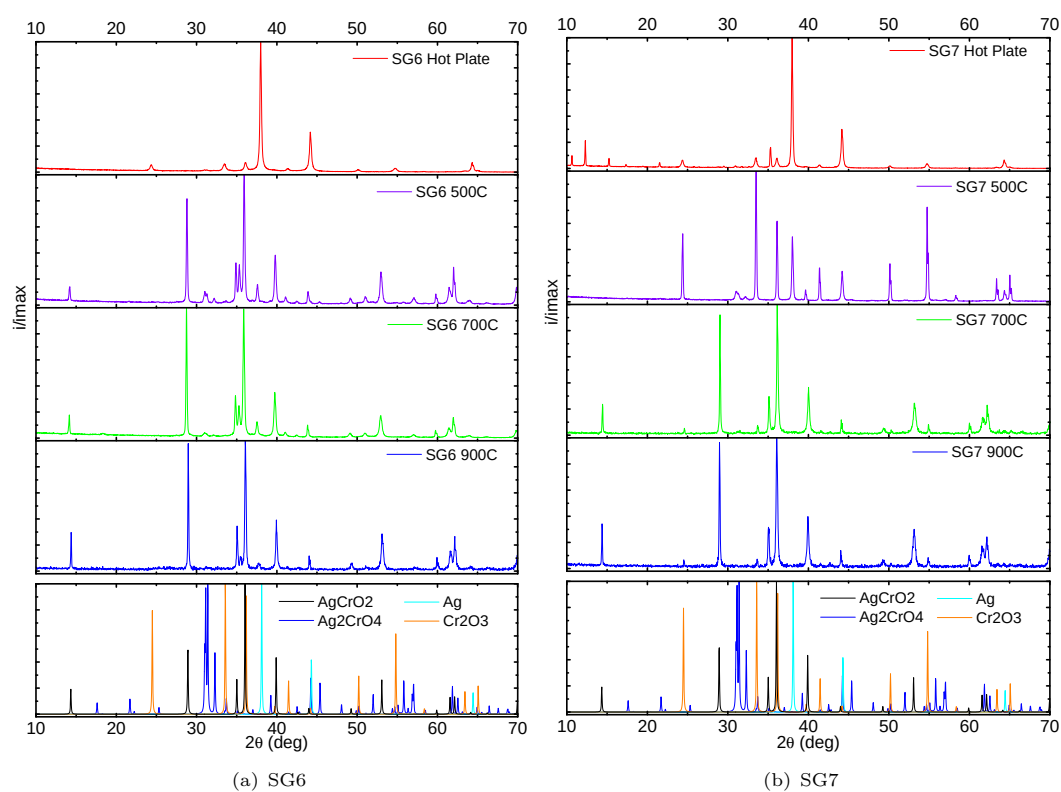


Figure A.0.3: AgCrO_2 synthesized by sol-gel combustion synthesis using Citric Acid a), Ethylene Glycol b) and Glycine c).

Appendix B

AgCrO₂ Nanostructures

An attempt was made to synthesize silver chromium oxide nanotubes. The method is described in section 3.1. A solution of stoichiometric amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, AgNO_3 and $(\text{NH}_2)_2\text{CO}$ with a pH of 4.2. The result product, after the combustion of the gel/alumina template was morphological characterized by SEM and EDS.

Results of this preliminary work are presented in the follow.

B.1 Scanning Electron Microscopy

In Fig.B.1.1 a scanning electron microscope photograph performed in the sample (SG-TEMPLATE) after combustion inside a nanoporous alumina template, using the secondary electrons (a) and the backscattered electrons (b) is presented.

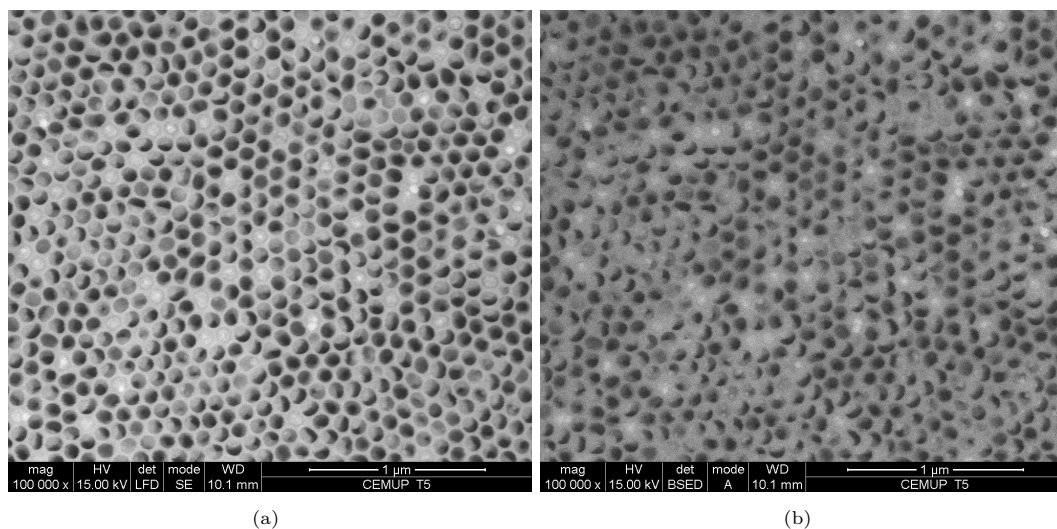


Figure B.1.1: Scanning electron microscope photograph performed in the sample SG1 after combustion inside a nanoporous alumina template. Using the secondary electrons (a). With the backscattered electrons (b).

The inhomogeneity of the template contents is clearly exhibited in figure B.1.1 (a) and (b).

From this images is possible to verify that the incorporation of the oxide inside the nanoporous alumina template was unsuccessful. Only some of the pores exhibit the presence of the oxide and in most of the cases only a partial filling.

This experiment was performed in an early stage of this work. Now from the results obtained from the work of other fellow researchers we know that its necessary to have a very strict control in the solution viscosity when the nanoporous alumina template is inserted in the sol-gel. Otherwise the sol-gel will only go randomly into the porous and to those where it actually goes, only fill superficially the nanoporous alumina template.

B.2 Energy Dispersive X-ray Spectroscopy

In figure B.2.1 an EDS spectrum of the sample SG-TEMPLATE is presented.

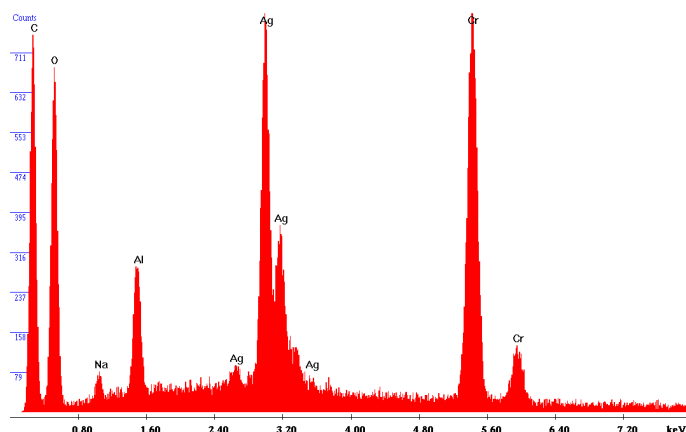


Figure B.2.1: EDS pictograph retrieved from the nanoporous alumina template with sample SD-TEMPLATE inside the tubes.

Several elements were detected in the sample, namely carbon, oxygen, sodium, aluminium, silver and chromium. The presence of carbon, probably is due to the carbon tape used to fix the sample. Oxygen from oxides present in the sample compounds and from the alumina template. Sodium presence can be explained by the preparation and placing of the sample into the sample holder, where at some point contact with hands must occurred. Aluminium peak is due to the alumina template.

The EDS peak integration register an atomic percentage of silver and chromium of 30 and 70 percent, respectively. Taking into account the accuracy of the spectrometer and the reasons above mentioned, these values could not be totally correct. However its possible to verify the larger quantity of chromium atoms in comparison with the ones of silver, showing that besides the incorporation of the gel phase into the nanoporous alumina template wasn't successful, the silver chromium oxide phase formation wasn't also achieved .

Appendix C

Thermogravimetry (TGA)

C.1 Technique Principles

Thermogravimetry (also known by the acronym "TG") is the branch of thermal analysis, physical chemistry and materials research which examines the mass change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. A schematic conformation of a thermogravimeter is shown in Fig. C.1.1 (From ^[108]). At the present, almost all apparatus used in the measurements are those which enable simultaneous measurement of TG and differential thermal analysis(DTA) to be carried out. It is based on continuous recording of mass changes of a sample of material, as a function of a combination of temperature with time, and additionally of pressure and gas composition.

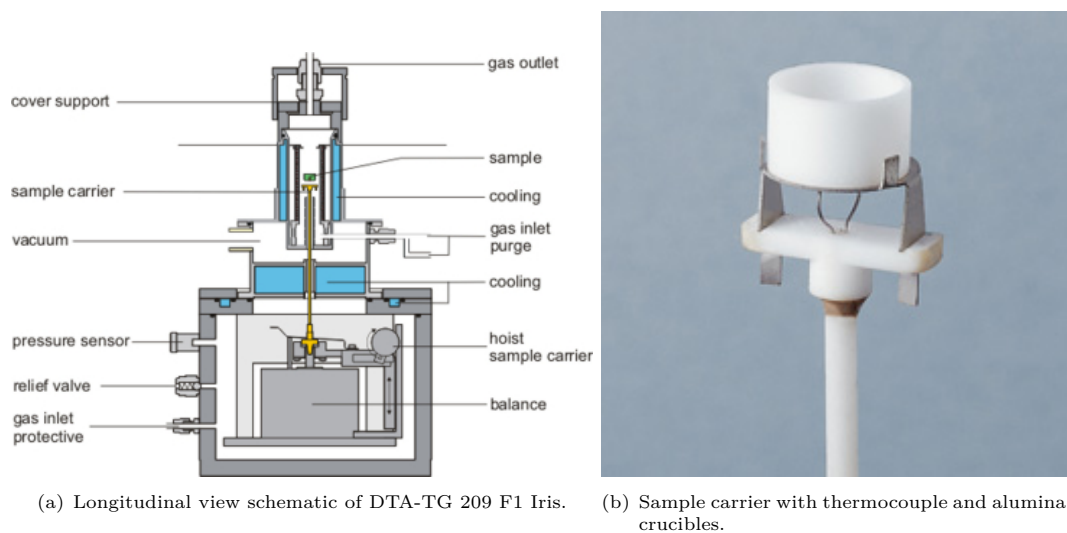


Figure C.1.1: DTA-TG 209 F1 Iris.

A sample of material (ranging from 1 mg to 100 mg, but sometimes as large as 100 g) is placed on an arm of a recording microbalance, also called thermobalance where that arm and the sample are placed in a furnace. The furnace temperature is controlled in a pre-programmed temperature/time profile (most commonly), or in the rate-controlled mode, where the pre-programmed value of the

weight changes imposes the temperature change in the way necessary to achieve and maintain the desired weight-change rate. The most common temperature profiles are: jumping to isotherm and holding there for a specified time ("soak"), temperature ramping at constant rate (linear heating or cooling, and combination of ramp and soak segments.

The gaseous environment of the sample can be: air, vacuum, inert gas, oxidizing/reducing gases, corrosive gases, carburizing gases, vapors of liquids or "self-generating atmosphere".

The commonly investigated processes are: thermal stability and decomposition, dehydration, oxidation, determination of volatile content and other compositional analysis, binder-burnout, high-temperature gas corrosion, etc. The kinetic data obtained by TG are reliable only for irreversible processes, whereas reversible ones are grossly affected by diffusion, and only special procedures can handle them.

The conventional TG focuses on various aspects of analysis of materials, but another facet of thermogravimetry is synthesis studying, e.g. using a thermobalance for monitoring the synthesis of materials.

Thermogravimetric analysis is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues.

The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample. The pan is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions.

A computer is used to control the instrument. After the data is obtained, curve smoothing and other operations may be done such as to find the exact points of inflection.

For a larger knowledge about this technique and for more information about special components and attachments, more information can be found in reference ^[109].

C.2 Experimental Results

The thermogravimetric analysis and differential thermal analysis are of great importance for the studying of phase stability, decomposition temperatures and water content among other possibilities. Having this in mind, an optimization of AgCrO_2 and CdCr_2S_4 polycrystalline samples synthesis process was pursued along with a better understanding of the reactants purity and system stability in different atmosphere and temperatures. A preliminary series of measurements was initiated but unfortunately some set backs forced these measurements to be interrupted. Nevertheless, this is still a work in progress that we desire to explore in more depth in a near future.

The TG measurements were performed in the Chemistry Department of the Faculty of Sciences of University of Porto, in a DTA-TG 209 F1 Iris Thermo-Microbalance using an inert atmosphere of

N_2 and a Al ($m=23.031$ mg) or Pt/Rh ($m=180.426$ mg) crucible. Different heating and cooling rates as a N_2 flow of 20 or 40 ml/min were used that will be presented in the follow. The results presented next are representative of some of the difficulties that we have encountered.

Pt/Rh Crucible - In figure C.2.1 thermographs obtained from measurements performed using an empty Pt/Rh crucible in a N_2 flow ($20\text{ ml}\cdot\text{min}^{-1}$), with a heating step of $20\text{ }^\circ\text{C}/\text{min}$, a cooling rate of $10\text{ }^\circ\text{C}/\text{min}$ and a isothermal rate at $500\text{ }^\circ\text{C}$ during 3 hours are exhibited.

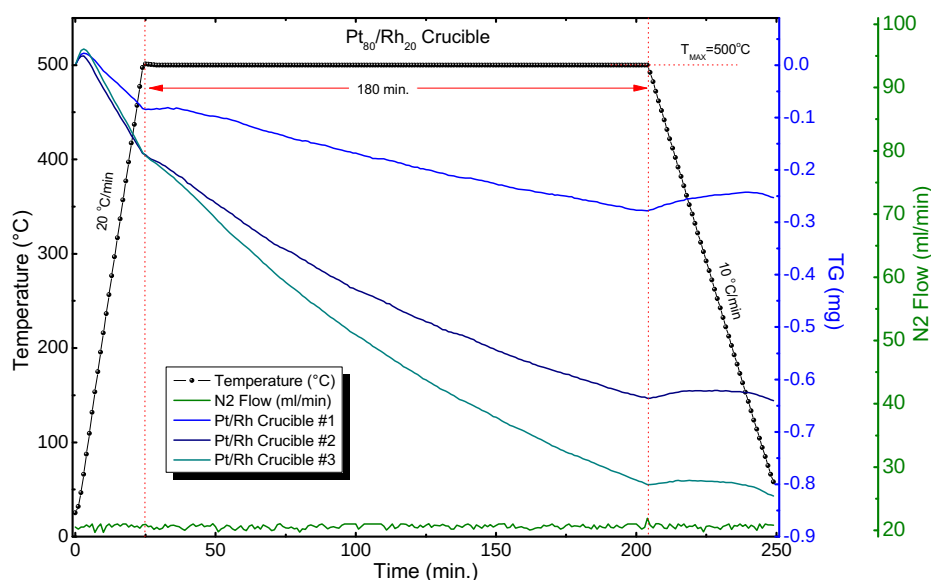


Figure C.2.1: Thermograph of Pt/Rh crucible.

We can see that with only the crucible inside the Thermo-Microbalance a reproducibility of the data is not accomplished. Measurements "Pt/Rh Crucible #3" were performed in the morning after the crucible pass the night inside the instrument. Right after the end of the measurement a new test "Pt/Rh Crucible #2" was performed showing that the crucible lost less mass. "Pt/Rh Crucible #1" was performed after crucible has been cleaned with a bunsen burner, and is the curve that exhibits less mass lost. Because in most of the cases we want to be working with sample masses smaller than the crucible mass, an optimal characterization of the crucible behavior has to be accomplished before more measurements are performed.

AgCrO₂ Sample - In figure C.2.2 a thermograph of AgCrO₂ sample is presented. In this measurement a Al crucible in a N_2 flow ($40\text{ ml}\cdot\text{min}^{-1}$), with a heating and cooling step of $10\text{ }^\circ\text{C}/\text{min}$ and a isothermal step at $550\text{ }^\circ\text{C}$ during 30 minutes is exhibited.

The TG thermograph of the AgCrO₂ sample ($m=13.423$ mg) exhibits a similar behavior as the Pt/Rh crucibles. We weren't expecting to observe any changes in the thermograph, however with the result obtained measuring the empty crucible the observed curve wasn't so surprising. In this way we don't want to force any conclusions about the results obtained without performing more detailed tests. At this moment we can't attribute the observable mass loss to the sample, to the crucible or even to the sample carrier or sample holder.

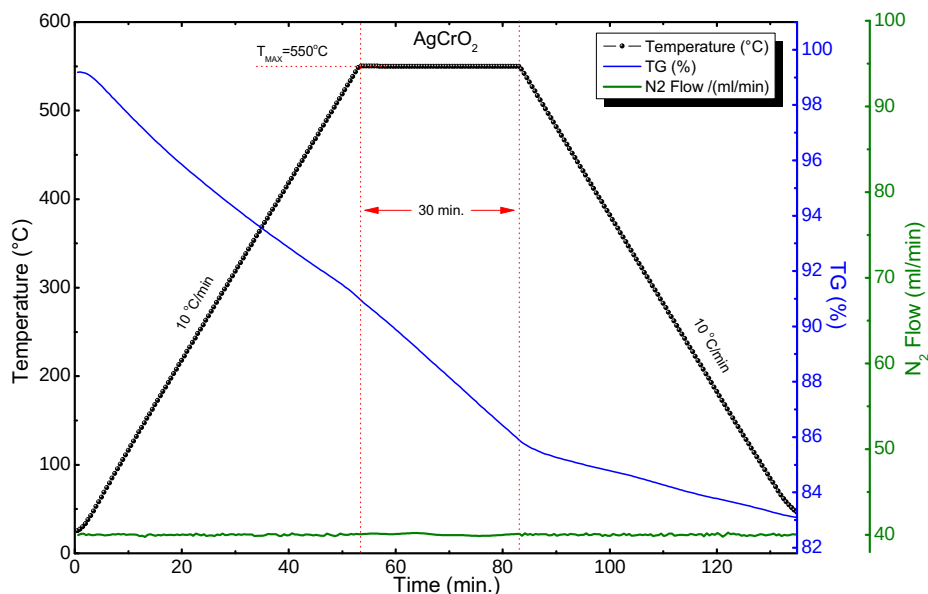


Figure C.2.2: Thermograph of AgCrO_2 sample.

CdCr_2S_4 Sample - A test to verify the CdCr_2S_4 stability was performed. In Fig.C.2.2 a thermograph of CdCr_2S_4 sample ($m=6.253$ mg) is presented using a Pt/Rh crucible in a N_2 flow ($20 \text{ ml} \cdot \text{min}^{-1}$), with a heating step of 20°C/min , a cooling rate of 10°C/min and a isothermal step at 500°C during 3 hours are exhibited.

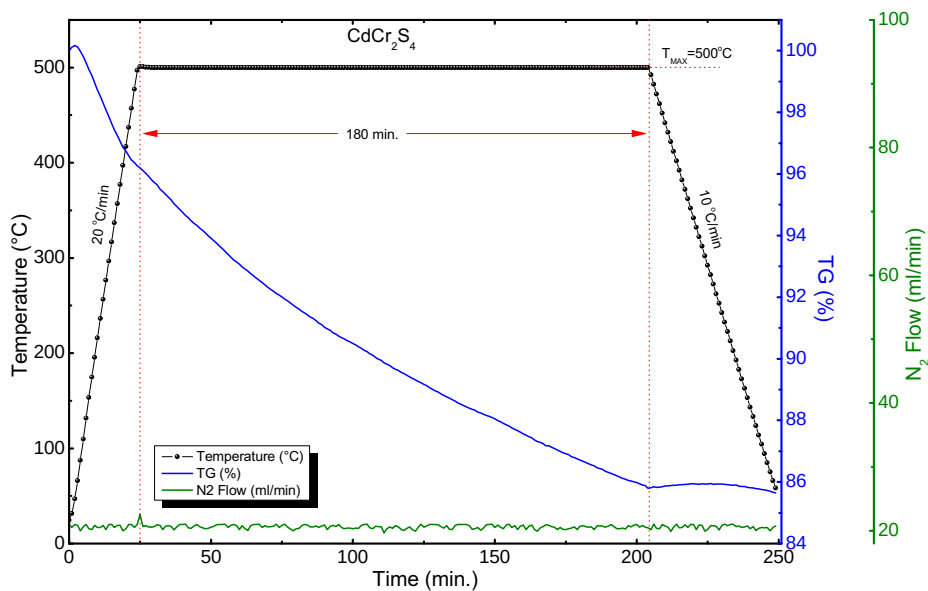


Figure C.2.3: Thermograph of CdCr_2S_4 sample.

Once more the curve is similar to the one obtained using the empty crucible and once more the need for a good characterization of the crucible behavior is essential.

In the future we hope to continue with this work but with a different approach. Several modifications to the work methodology will be implemented.

- The Pt/Rh crucibles that were chosen by their good thermic response and possibility to perform measurements to a higher set of temperatures will be changed by Al_2O_3 crucibles. It was verified that the Pt/Rh crucibles are very sensitive to the work conditions and are very difficult to recycle after a measurement with the type of compounds that we intend to study¹ AgCrO_2 and CdCr_2S_4 . Also the elevated cost of the same increases the difficulty to replace them if needed. Another reason why the Al_2O_3 crucibles will be adopted is because the heat treatment that the samples are submitted during the sintering process are performed also in alumina boat crucibles.
- We intend to perform a set of calibration measurements to characterize in detail the behavior of the instrument and crucibles. It is necessary to understand what kind of treatment the crucible has to endure in order to have reproducible measurements.
- Reactants used to synthesize the samples will be studied in different work conditions. A knowledge of phase stability, decomposition temperatures and water content are required for good synthesis control.
- Different atmospheres and gases fluxes will be tested. Oxidizing, reducing conditions or inert gases flows are important in the sintering conditions of the AgCrO_2 and CdCr_2S_4 structures.
- The sample in the different sintering stages will be characterized. Performing different heating and cooling ramps as different annealing times have great influence in the final product.
- An attempt to simulate the sintering conditions inside the Thermo-Microbalance are in our order of work.

¹A TG measurement of AgNO_3 using the Pt/Rh crucible was performed and it was verified that the sample reacted with the crucible. A crucible cleaning procedure suggested by the manufacturer didn't prove to be adequate because it result in its destruction.

Appendix D

SQUID Contamination

In order to evaluate the nature of the anomalies at $T \approx 87$ K and 56 K observed on the different samples the following data analysis has been performed.

The magnetic susceptibility of the samples was plotted against the magnetic susceptibility of the sample SS2A900, that is, the sample showing a single magnetic phase transition and also a single phase by x-ray diffraction analysis. Here the values were obtained by interpolating the values of the magnetic susceptibility to an equivalent temperature scale.

The correlation between susceptibilities of the samples with that of SS2A900 sample data is shown in figure D.0.1 a).

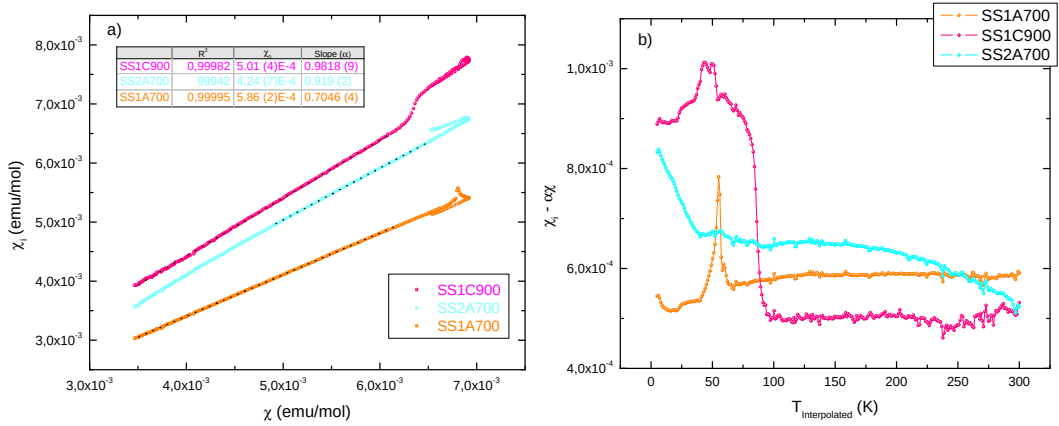


Figure D.0.1: Magnetic susceptibility of the AgCrO_2 samples plotted against the magnetic susceptibility of the sample SS2A900 a). $\chi = \chi_{\text{sample}} - \alpha\chi_{\text{AgCrO}_2}$ as a function of the temperature b).

We can see from figure D.0.1 regions where the correlation is linear. Thus, performing a linear fit to the different data typically in the high temperature and paramagnetic regime, we can extract the contribution from the secondary magnetic phases in the different samples. Subtracting the AgCrO_2 phase contribution we should obtain the contributions of the secondary phases. Those contributions are depicted in the figure D.0.1 b) as $\chi = \chi_{\text{sample}} - \alpha\chi_{\text{AgCrO}_2}$ as a function of the temperature, where α is the curve slope obtained from the linear fit, and is a good approximation of the AgCrO_2 phase contribution to the overall signal.

From the above figure, figure D.0.1 b), one realizes that χ is positive in all temperature range.

This result is somehow in contrast with what one could expect if the major secondary magnetic phase contribution would arise from the diamagnetism associates with Ag and/or Ag_2CrO_4 phases (present in this samples as verified by x-ray). Thus, these positive contributions as well as the anomalies below 100 K, emphasized in the figure D.0.1 b), have to be found in other grounds. In fact these anomalies can be ascribed to oxygen phase transitions ($T=43$ K, 51 K and 59 K, see figure D.0.2^[110,111]) as observed in a Palladium sample measured with an oxygen contamination due to oxygen contamination on the SQUID chamber.

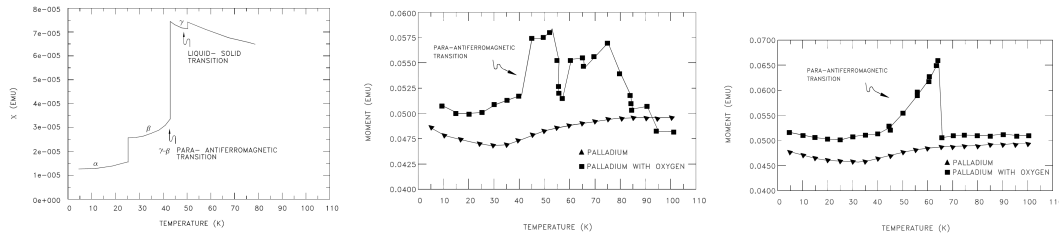


Figure D.0.2: Temperature dependence of the magnetic susceptibility of solid oxygen taken from Quantum Design technical notes. The curve represents the susceptibility of 250.1 mg of bulk oxygen. α , β and γ are three different phases of solid oxygen. α and β are anti-ferromagnetic, whereas γ is paramagnetic a). The effect of oxygen contamination on measurements of a Palladium reference sample introduced at RT b) and at 5 K c).

In sample ss1c900 an increase in the magnetic susceptibility is observed at ~ 92 K and it was not possible to associate to any chromium/silver oxide magnetic phase transition. However, from research in the SQUID measurement logbook, it was possible to verify that a series of manganite with the general formula ABO_3 was measured prior to this sample. In this way, a possible explanation for the increase in the magnetic susceptibility verified, could be a contamination due to pre-measurement sample preparation¹. In lack of additional information, another possible explanation to this increase could be given in terms of the oxygen gas to liquid phase transition, condensation, which is reported to be around 91K, although we consider the latter explanation less probable.

¹For example, LuMnO_3 which has a transition temperature around 90K.

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