SYNTHESIS AND CHARACTERIZATION OF THE $FeIn_{0.8}Cr_{1.2}S_4$ SEMICONDUCTOR VIA CHEMICAL VAPOUR TRANSPORT: INFLUENCE OF TRANSPORTING AGENT ON CRYSTAL MORPHOLOGY AND MAGNETIC PROPERTIES

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ABSTRACT

This study investigates the synthesis of the semiconductor $FeIn_{0.8}Cr_{1.2}S_4$ using Chemical Vapor Transport (CVT) with various transporting agents, including chromium trichloride ($CrCl_3$), ammonium chloride (NH_4Cl), and iodine (I_2). The resulting crystal structures were analyzed using Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (XEDS). Using $CrCl_3$ as the transport agent resulted in the formation of large, pyramid-shaped crystals up to *3.0 mm* in length, Iodine produced crystals with well-defined edges, whereas ammonium chloride yielded crystals of diverse shapes and sizes. Elemental composition analysis indicated good overall homogeneity within the samples, though some deviations from the intended stoichiometry were noted, particularly in samples grown with $CrCl_3$. Electron spin resonance (ESR) was employed to assess the magnetic behavior of the samples. At room temperature, ESR spectra exhibited a single signal around $g \approx 2$ overlapped by a wider signal for samples grown with I_2 and NH_4Cl, while samples grown with $CrCl_3$ showed a symmetric unique signal. The choice of transport agent significantly influences both the morphological and magnetic properties of the synthesized crystals.

Keywords: Semiconductor, transporting agents, Chemical Vapor transport, structural properties.

SÍNTESIS Y CARACTERIZACIÓN DEL SEMICONDUCTOR $FeIn_{0.8}Cr_{1.2}S_4$ MEDIANTE TRANSPORTE DE VAPOR QUÍMICO: INFLUENCIA DEL AGENTE DE TRANSPORTE EN LA MORFOLOGÍA DEL CRISTAL Y PROPIEDADES MAGNÉTICAS

RESUMEN

Este estudio investiga la síntesis del semiconductor $FeIn_{0.8}Cr_{1.2}S_4$ utilizando el transporte químico en fase vapor (CVT, por sus siglas en inglés) con varios agentes de transporte, incluyendo tricloruro de cromo ($CrCl_3$), cloruro de amonio (NH_4Cl) y yodo (I_2). Las estructuras cristalinas resultantes fueron analizadas utilizando Microscopía Electrónica de Barrido (SEM, por sus siglas en inglés) y Espectroscopía de Rayos X por dispersión de energía (XEDS, por sus siglas en inglés). El uso de $CrCl_3$ como agente de transporte resultó en la formación de cristales grandes, con forma de pirámide, de hasta *3.0 mm* de longitud; el yodo produjo cristales con bordes bien definidos, mientras que el cloruro de amonio generó cristales de formas y tamaños diversos. El análisis de la composición elemental indicó una buena homogeneidad general dentro de las muestras, aunque se observaron algunas desviaciones de la estequiometría prevista, particularmente en las muestras crecidas con $CrCl_3$. Se empleó la resonancia de espín electrónico (ESR, por sus siglas en inglés) para evaluar el comportamiento magnético de las muestras. A temperatura ambiente, los espectros de ESR exhibieron una señal única alrededor de $g \approx 2$ superpuesta por una señal más amplia para las muestras cultivadas con I_2 y NH_4Cl, mientras que las muestras crecidas con $CrCl_3$ mostraron una señal única simétrica. La elección del agente de transporte influye significativamente tanto en las propiedades morfológicas como en las magnéticas de los cristales sintetizados.

Palabras claves: Semiconductor, agente transportante, transporte químico en fase de vapor

INTRODUCTION

Spinel compounds with the general formula AB_2X_4, are a group of materials that arouse great interest in the scientific community, due to their wide range of physical properties [1]. Some spinels are characterized by their potential for various technological applications. The intriguing semiconducting behavior and versatile crystal structures of multinary chalcogenides position them as promising materials for a multitude of industrial applications, such as catalysts, lubricants, high-temperature refractories, pigments, battery technologies, and devices utilizing light and magnetism [2]. This is why ternary compounds of $FeCr_2S_4$, with substitutions of elements such as In, Cu, and Co, are chalcogenide magnetic semiconductors with strongly correlated magnetic and transport properties. Recent observations of colossal magnetoresistance, similar to manganese perovskite and semi-metallic behavior, have renewed interest in this type of material [3]. Unfortunately, $FeCr_2S_4$ is very sensitive to even minor variations in its elemental composition (stoichiometry). This sensitivity makes it challenging to pinpoint the exact microscopic mechanisms behind the observed phenomena. In other words, slight deviations from the ideal atomic ratios can significantly alter the material's magnetic and structural properties [4]. For instance, the reported phase transition at 9 K in $FeCr_2S_4$ single crystals, observed through magnetization and specific heat measurements [5], is strictly dependent on the material's stoichiometry being close to ideal. $FeIn_2S_4$ and $FeCr_2S_4$ are well-studied examples of ternary chromium chalcogenide; they crystallize in a cubic spinel structure, a specific arrangement of atoms categorized by the space group Fd3m (number 227). This structure is based on a close-packed lattice of sulfide (S^{2-}) ions in a face-centered cubic (fcc) formation. This arrangement creates two types of empty spaces within the structure: tetrahedral (A) and octahedral (B) voids. Fe^{2+} cations fill one-eighth of the tetrahedral voids, while Cr^{3+} cations occupy half of the octahedral positions [6].

The central idea of this work is to conduct a comparative study of the morphological and magnetic properties of the compound $FeIn_{0.8}Cr_{1.2}S_4$ as a function of the synthesis and growth methods, using different transport agents.

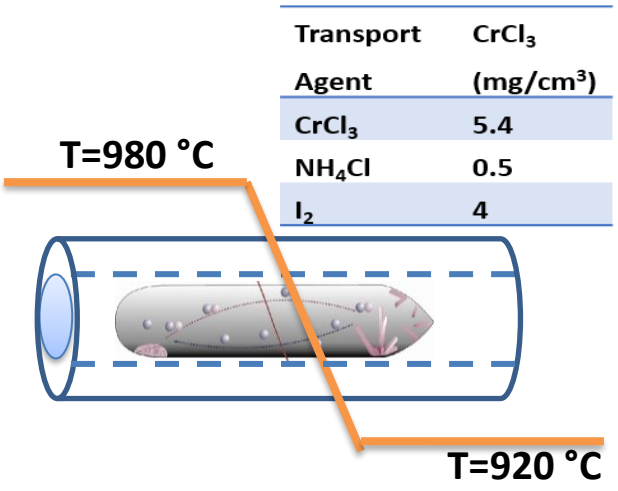
MATERIALS AND METHODS

Synthesis of $FeIn_{0.8}Cr_{1.2}S_4$

High-purity Fe, Cr, In, and S elements (5N purity) were meticulously weighed in their exact atomic ratios (stoichiometric proportions) to create $FeIn_{0.8}Cr_{1.2}S_4$. These elements were then loaded into a pre-cleaned quartz ampoule. After evacuation, the ampoule was sealed under a high vacuum (10^{-7} Torr). This initial stage ensures the purity of the starting material. The sealed ampoule was then placed in a furnace and heated to 950 °C for a week (7 days) using a gradual temperature increase to promote uniformity within the sample. The resulting material was subsequently ground into a fine powder using an agate mortar. For the second stage, the appropriate amount of the chosen transporting agent ($CrCl_3$, I_2, or NH_4Cl - see Table 1 for details in the insert of the Figure 1) was added to the ground material. This mixture was then loaded into another quartz capsule and evacuated to the same high vacuum (10^{-7} Torr) before being sealed.

The final capsule was placed in a furnace with two distinct temperature zones. The source zone, containing the reaction mixture, was maintained at 980 °C. The deposition zone, where the crystals would form, was held at a cooler temperature of 920 °C. This temperature difference drives the transport process. The entire process lasted for 342 hours. Another detail that must be taken into account is that the oven must be tilted a few degrees to help the convection process. The transport agent favors the transport process within the capsule.

The concentrations of the transport agent are carefully chosen, because the internal pressures, temperature and its gradient must be taken into account for favorable growth to occur.



Transport Agent	$CrCl_3$ (mg/cm³)
$CrCl_3$	5.4
NH_4Cl	0.5
I_2	4

Figure 1. Scheme of growth conditions for CVT.
Table 1. The appropriate amount of the chosen transport agent

By balancing these factors, we can achieve efficient transportation while maintaining safe operating pressures within the ampoule. For all samples, the initial amount prepared was 2 g, and the yield was 0.8 g or less for all transport agents due to the high melting points of the starting elements, Fe and Cr.

Structural and magnetic characterization

An X-ray diffraction analysis of the samples revealed the formation of a crystalline structure with a spinel configuration as the majority phase, belonging to the Fd3m space group [7]. Structural characterization was performed using an FEI Quanta 200F XEDS/SEM microscope. The Electron Spin Resonance (ESR) technique has been used on the samples of $FeIn_{0.8}Cr_{1.2}S_4$ to obtain the EPR spectra. The ESR measurements were carried out in a Bruker EMX spectrometer, with a rectangular cavity and 100 kHz modulation, working in the X-band (~ 9.4 GHz). Experimental conditions (microwave power and modulation amplitude) were adjusted to avoid saturation effects.

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM)

Figure 2 shows micrographs of $FeIn_{0.8}Cr_{1.2}S_4$ with different transport agents: $CrCl_3$ (Figure 2a), NH_4Cl (Figure 2b), and I_2 (Figure 2c). These images reveal changes in morphology as the transport agent is varied.

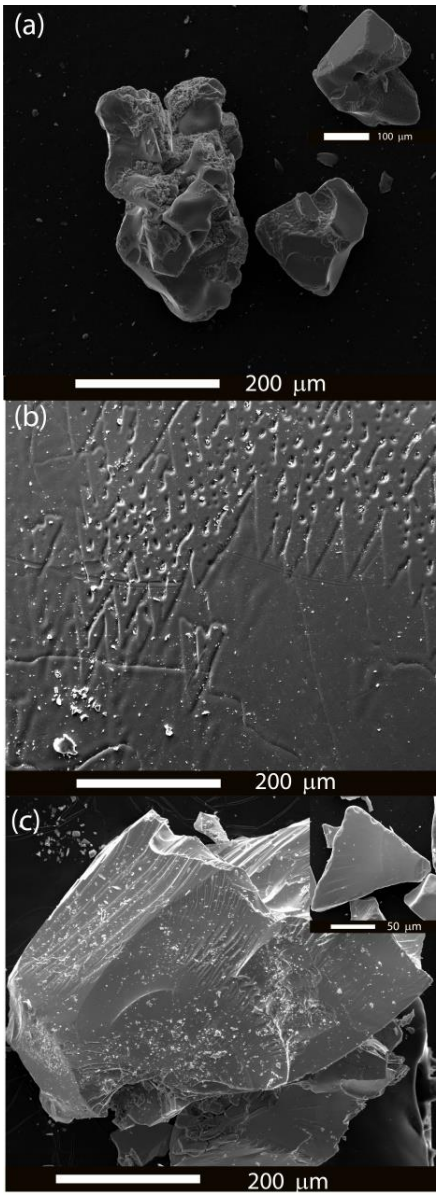


Figure 2. Micrographs of the $FeIn_{0.8}Cr_{1.2}S_4$ with different transport agents: (a) $CrCl_3$, (b) NH_4Cl and (c) I_2.

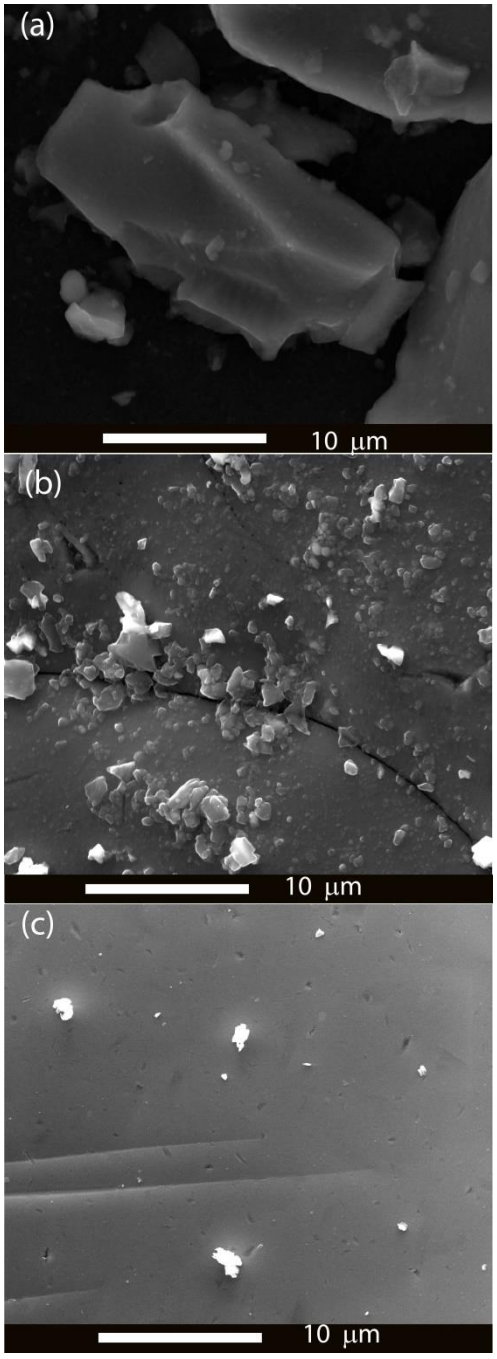


Figure 3. Magnification of the Micrographs of the $FeIn_{0.8}Cr_{1.2}S_4$ with different transport agents: (a) $CrCl_3$, (b) NH_4Cl, and (c) I_2.

In Figure 2(a) we show the micrographs for the $CrCl_3$ transporting agent. The figure shows large, rock-like crystals composed of smaller crystals with varying shapes that collectively form the $FeIn_{0.8}Cr_{1.2}S_4$ crystal. In addition, pyramid-shaped crystals are observed, with a dimension that reaches up to three millimeters. In Figure 2(b), with NH_4Cl as the transport agent, it can be observed that the small crystals combine to form a large, smooth surface, albeit with some macroscopic defects. Additionally, there is evidence of crystalline powder present. In Figure 2(c), with I_2 as the transport agent, crystals with irregular shapes are apparent, growing in overlapping planes. However, some crystals exhibit at least one edge but do not form a pyramidal shape; instead, they appear flatter. Overall, macroscopic defects are observed in all samples regardless of the transport agent used. Despite the high melting points of chromium and iron in this compound, the use of a transport agent facilitates crystal growth. In this case, the $CrCl_3$, achieved the highest yield among the samples.

On the other hand, when examining micrographs with higher magnification in Fig. 3, we can observe distinct characteristics. The $CrCl_3$ sample displays a porous structure with numerous defects. In contrast, the NH_4Cl sample reveals the presence of a large grain comprising many smaller grains on its surface. Meanwhile, the I_2 sample exhibits a smooth surface structure due to the larger size of the crystals. Furthermore, there are no very notable variations in the contrast of the samples obtained, so the formation of the phase is the majority.

Table 2. Stoichiometric of the semiconductor $FeIn_{0.8}Cr_{1.2}S_4$

Transporting Agent	Semiconductor	Nominal Concentration
$CrCl_3$	$Fe_{0.97}In_{0.55}Cr_{1.68}S_{3.80}$	$FeIn_{0.8}Cr_{1.2}S_4$
NH_4Cl	$Fe_{1.05}In_{0.7}Cr_{1.15}S_{3.45}$	$FeIn_{0.8}Cr_{1.2}S_4$
I_2	$Fe_{0.97}In_{0.7}Cr_{1.16}S_{4.02}$	$FeIn_{0.8}Cr_{1.2}S_4$

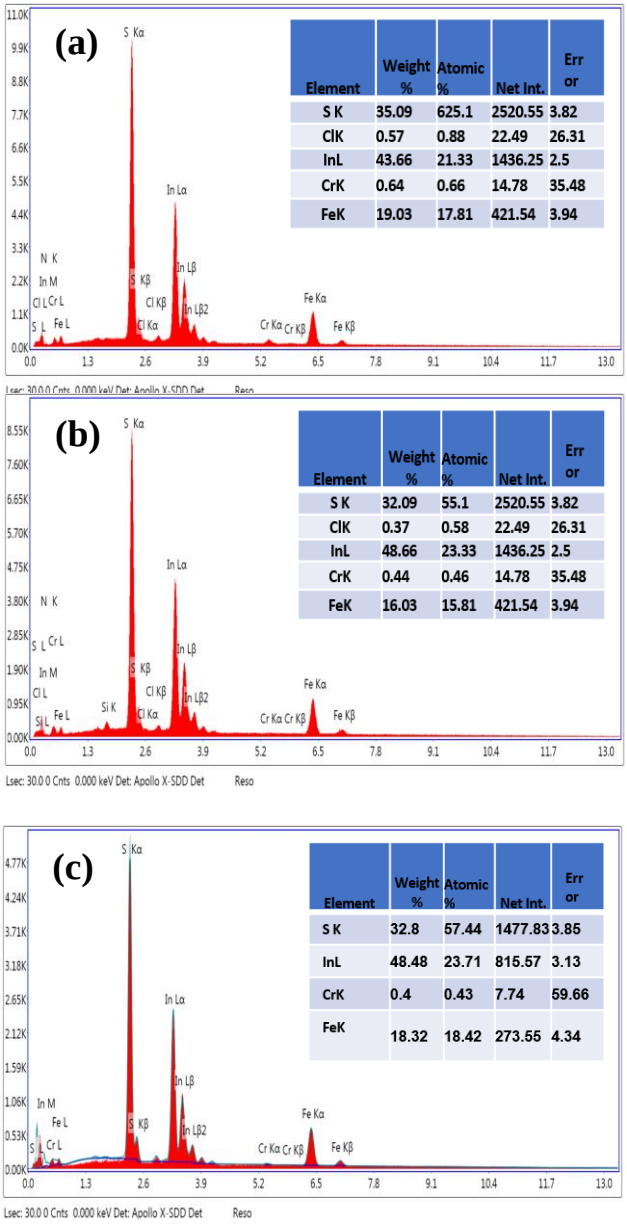


Figure 4. XEDS spectra of the $FeIn_{0.8}Cr_{1.2}S_4$ with different transport agent: (a) $CrCl_3$, (b) NH_4Cl and (c) I_2

Table 3 presents the nominal and experimental concentrations of the semiconductor $FeIn_{0.8}Cr_{1.2}S_4$. In the stoichiometry determination, it is note d that the chromium concentration increases for $CrCl_3$, likely due to the incorporation of the transport agent into the crystalline structure. Conversely, for the other transport agents, the chromium concentration falls below the nominal elemental concentration.

Electron Paramagnetic Resonance (EPR)

Figure 5 showcases the Electron Spin Resonance (ESR) spectra collected at room temperature for $FeIn_{0.8}Cr_{1.2}S_4$ samples prepared using different transport agents. The ESR spectra displayed a single signal around $g \approx 2$ overlapped by a broader signal for samples grown with I_2 and NH_4Cl, potentially indicating the presence of two distinct phases in these samples. Conversely, samples grown with $CrCl_3$ exhibited a symmetric, unique signal. Based on these observations, we infer that the sample synthesized with $CrCl_3$ yields the most favorable result due to the symmetry and intensity of its signal.

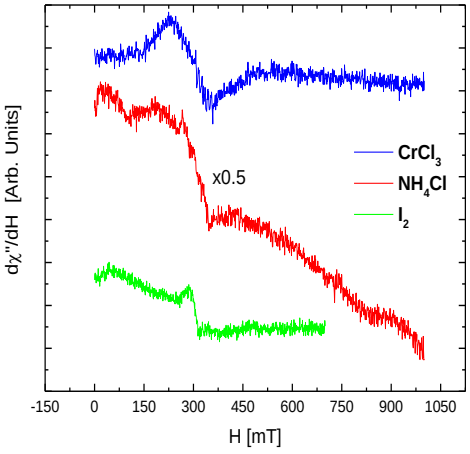


Figure 5. Room temperature ESR spectra for all $FeIn_{0.8}Cr_{1.2}S_4$ samples.

Table 3 presents the values of H_R, ΔH_{pp}, and 1/An for the various transport agents.

Table 3. H_R, ΔH_{PP}, $1/A_N$ of the semiconductor $FeIn_{0.8}Cr_{1.2}S_4$

Transporting Agents	H_R [Oe]	ΔH_{PP} [Oe]	$1/A_N$
$CrCl_3$	3076	1280	$2.27*10^{-7}$
NH_4Cl	3087	1977	$1.72*10^{-7}$
I_2	3250	476	$8.48*10^{-8}$

The resonance field position (H_R) in EPR is determined by the combined effects of the sample's orientation, anisotropy parameters, g-factor, total magnetization, and internal field, including its contribution from anisotropic and demagnetized fields. The H_R remains invariant for the samples of $CrCl_3$ and NH_4Cl. However, for I_2, it decreases to approximately 3250 Oe in accordance with a different neighborhood for the magnetic moment. The linewidth (ΔH_{pp}) provides a direct measure of the relaxation processes within the material and their interactions dipolar or exchange. The ΔH_{pp} increases its value for $CrCl_3$ and NH_4Cl with the change of transport agent, while for the I_2 sample, the linewidth value is 476 Oe. The inverse of the normalized area $1/A_N$, which is proportional to the magnetic susceptibility, is also affected.

CONCLUSIONS

1. *Effect of Transporting Agents on Crystal Morphology*: The choice of transport agent significantly influences the morphology of the synthesized crystals. Crystals grown with $CrCl_3$ exhibited large, pyramid-shaped structures, while those grown with NH_4Cl showed a large smooth surface with some macroscopic defects. Crystals grown with I_2 displayed irregular shapes with overlapping planes.

2. *Chemical Composition and Stoichiometry*: Analysis of the elemental composition revealed deviations from the intended stoichiometry, particularly with Cr_3Cl, where an increase in chromium concentration was observed, likely due to the incorporation of the transport agent into the crystalline structure.

3. *Magnetic Properties*: Electron Spin Resonance (ESR) spectra analysis showed distinct magnetic behaviors among samples grown with different transport agents. Samples grown with $CrCl_3$ exhibited a symmetric, unique signal, while those grown with I_2 and NH_4Cl displayed a broader signal potentially indicating the presence of two phases. The resonance field (H_R) remained invariant for samples of $CrCl_3$ and NH_4Cl but decreased for samples grown with I_2.

4. *Overall Synthesis Performance*: Considering the symmetry and intensity of the ESR signal, the sample synthesized with $CrCl_3$ appears to yield the most favorable synthesis result.

5. *Transport Efficiency and Yield*: Despite variations in crystal morphology and magnetic properties, the yield of synthesized samples was consistent across all transport agents, with a prepared amount of 2 g yielding 0.8 g or less, likely due to the high melting points of the starting elements Fe and Cr.

In conclusion, the study highlights the importance of transport agents in controlling the morphology and magnetic properties of synthesized semiconductor crystals. Additionally, it underscores the significance of careful stoichiometric control and analysis to understand the impact of transport agents on the final product.

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Conflicts of interest

The authors declare that they have no conflict of interest.

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