

Crystal growth and characterization of the $\text{CdGaCrSe}_{(4-x)}\text{S}_{(x)}$ system

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Single-crystal of the $\text{CdGaCrSe}_{(4-x)}\text{S}_{(x)}$ system ($x = 0; 1; 2; 3; 4$) were grown by the chemical vapour-phase transport technique. The crystals were obtained by using CdCl_2 as transporting agent for the composition with $x = 1$, and CrCl_3 for those with $x = 0; 2; 3$ and 4 . X-ray powder diffraction analysis indicated that some of the samples crystallize in the tetragonal system with space group I-4 ($\text{CdGaCrSe}_3\text{S}$, $x = 1$; $\text{CdGaCrSe}_2\text{S}_2$, $x = 2$), or in a cubic system with space group Fd-3m (CdGaCrSeS_3 , $x = 3$; CdGaCrS_4 , $x = 4$), however the sample of CdGaCrSe_4 ($x = 0$) crystallizes in rhombohedral system. Magnetic measurements show significant changes in the magnetic interactions behaviour probably due to the anionic substitutions.

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1 Introduction

During the past years diluted magnetic semiconductors (DMS) have been frequently investigated because of their magnetic, magneto-optical and magneto-transport properties arising from the presence of magnetic ions, mainly manganese ions in the cations sites [1,2]. Another family of semiconductors which shows very attractive structural characteristic and optical properties is the AB_2X_4 . These ternary semiconductor compounds can be described, from the structural point of view, by one of the following three major structure types: the cubic spinel, the tetragonal defective zinc-blend and the rhombohedral ZnIn_2S_4 -type structure. Recently, we have studied the crystallographic and magnetic aspects of the $\text{CdGa}_{(2-2x)}\text{Cr}_{(2x)}\text{S}_4$ [3-5] and $\text{CdGa}_{(2-2x)}\text{Cr}_{(2x)}\text{Se}_4$ [6] systems, respectively. In this work we report the crystal growth and X-ray powder diffraction characterization of the semiconducting system $\text{CdGaCrSe}_{(4-x)}\text{S}_{(x)}$ with $x = 0; 1; 2; 3; 4$. Magnetic measurement of the compositions with $x = 0; 1$ and 4 , are also reported.

2 Experiment

Single crystals of the $\text{CdGaCrSe}_{(4-x)}\text{S}_{(x)}$ system were grown by using the chemical vapour-phase transport technique. Previously, synthesis of the compounds was prepared by direct fusion of pure elements (purity 4N, 5N). Stoichiometric amounts of the powders were mixed into a sealed quartz ampoule (10 cm long and 8 mm internal diameter) under vacuum at 10^{-5} Torr. One zone furnace was used. The compounds were then slowly heated from room temperature to 925 °C, ($x = 0; 1$) and to 1100 °C for all the other compositions. The heating

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and cooling lasted two weeks, while an annealing process of one week was necessary for the compositions $x = 2$; 3 and 4. All the samples were looked at microscope, showing homogeneity in all the ingots. The resultant product was ground and introduced into a new quartz ampoule (20 cm length; 17 mm inner diameter) with suitable amount of the transport agent. For $x = 1$, CdCl₂ was used as transporting agent (0.75 mg/cm³), while CrCl₃ (2-3 mg/cm³) was used for the others compositions. The single crystals were grown by placing the ampoule in a two temperature zone furnace keeping the source temperature and deposition temperature at 850 °C and 790 °C for $x = 0$, and 1, respectively. For $x = 2$; 3; 4, the corresponding temperatures were (1000-900)°C and (950-900)°C for source and deposition zone, respectively. The grown time for all samples was three weeks.

X-ray powder diffraction data of all compositions were collected at room temperature with a Siemens D5005 diffractometer, using a diffracted beam graphite monochromator (CuK_α radiation: $\lambda = 1.5418 \text{ \AA}$). The diffraction patterns were collected by steps of 0.02° (2 θ) over the angular range 10-100°, with a counting time of 50 s per step. Quartz was used as an external standard. Magnetic measurements were carried out with a commercial SQUID magnetometer ($x = 0$; 1) and with a Faraday system for $x = 4$.

3 Results and discussion

A summary of the grown conditions are given in Table 1. For high Se concentrations samples single crystal were obtained for both transport agents, but using CdCl₂ the obtained crystals were of larger dimensions. For high S concentrations samples, grown suitable conditions were obtained for the CrCl₃. The Fig. 1 shows a microphotograph in the case the CdGaCrSe₃S ($x = 1$), it is possible to see a good appearance of the grown crystals.



Fig. 1 Microphotograph for the composition $x = 1$; CdGaCrSe₃S.

Table 1 Summary of growth conditions of the CdGaCrSe_(4-x)S_x system for $x = 0$; 1; 2; 3; and 4.

Compound	M _{sample} (g)	T. agent	M _T (g)	M _{Se} (g)	T _s (°C)	T _d (°C)	Observation
CdGaCrSe ₄	1.45	CrCl ₃	0.0680	0.0507	850	790	Tiny crystal (layer crystal)
CdGaCrSe ₃ S	1.25	CdCl ₂	0.0697	0.0384	850	790	Dark brown (1.5-2.5 mm)
CdCrSe ₂ S ₂	0.9	CrCl ₃	0.093	---	975	925	Dark brown crystals
CdCrSeS ₃	0.85	CrCl ₃	0.148	---	950	900	Dark black crystals
CdGaCrS ₄	0.95	CrCl ₃	0.095	---	1000	950	Dark black crystals

As was found by Wehmeier [7], some chemical process during the single crystal grown of the CdCr₂Se₄ produces CdSe deposition on the cooler part of the ampoule. Following this idea we decided to use excess of selenium in concentration of the 1.44 g/cc as is show in Table 1.

For pattern indexing and unit cell parameters refinement, the precise determination of peaks positions was carried out by means of the diffractometer analytical software. A search in the ICDD-PDF database [7] using the Bruker AXS software available with the instrument was performed, and three known phases present in small quantities (secondary phases) were readily identified: CdGa₂S₄ (PDF N° 33-234), Cr₂S₃ (PDF N° 10-340) and CdSe (PDF N° 8-459). Indexing of the remaining peaks in each X-ray powder diffraction pattern was performed by means of the program Dicvol91 [8], and the complete dataset were reviewed and the unit cell refined using the NBS*AIDS program [9]. The results of the crystal system and the unit cell parameters found for each composition are summarized in Table 1. The powder diffraction patterns are shown in Fig.2. In this figure is possible to observe the three different structures present in the system.

Table 2 Crystallographic data for the system CdGaCrSe_(4-x)S_(x).

Compound	Crystal system	Space group	<i>a</i> (Å)	<i>c</i> (Å)	V (Å ³)
CdGaCrSe ₄	Rhombohedral	R-3m (N° 166)	3.608(7)	40.48(1)	456.4(1)
CdGaCrSe ₃ S	Tetragonal	I-4 (N° 82)	5.7020(4)	10.6305(8)	345.63(4)
CdGaCrSe ₂ S ₂	Tetragonal	I-4 (N° 82)	5.6760(2)	10.5303(4)	339.25(2)
CdGaCrSe ₃ S	Cubic	Fd-3m (N° 227)	10.2129(6)	-	1065.2(1)
CdGaCrS ₄	Cubic	Fd-3m (N° 227)	10.1800(3)	-	1054.98(5)

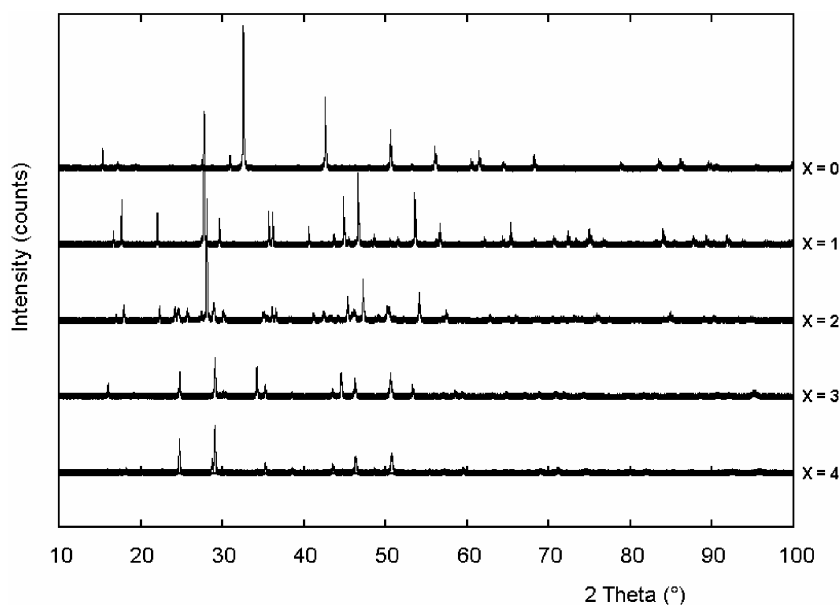


Fig. 2 Powder patterns for the CdGaCrSe_(4-x)S_(x) system.

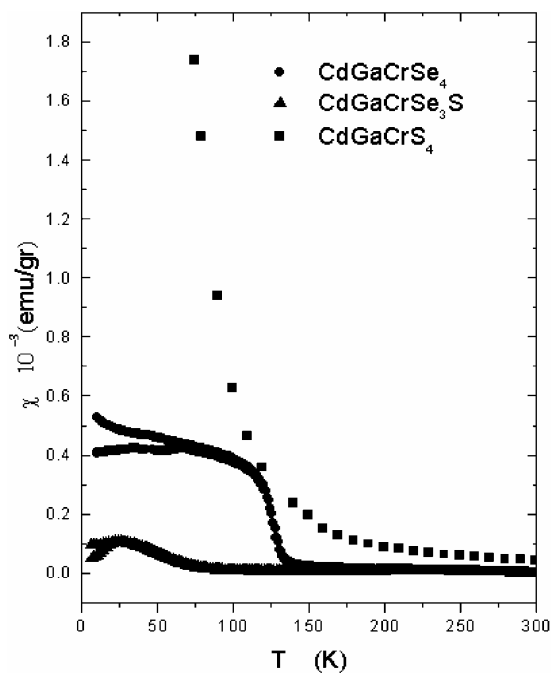
The temperature dependence of the magnetic susceptibility for the samples with $x = 0; 1; 4$ is shown in Fig. 3. These curves show different magnetic behaviour according to the x value. In fact the transition temperature and low temperature irreversibility appears at different temperatures. The magnetic parameters: Curie constant, Curie-Weiss temperature and the effective magnetic moment, obtained from the high temperature data are given in Table 3.

4 Conclusions

Single crystals of the CdGaCrSe_(4-x)S_(x) system were grown under the established experimental conditions. From X-ray diffraction results is possible to observe three different crystallographic arrangements depending on the S/Se ratio. Also significant changes in the magnetic behaviour are present. There is clearly a need for more detailed structural and magnetic data in order to test the ideas proposed above.

Table 3 Magnetic parameters for the system CdGaCrSe_(4-x)S_(x) (x = 0; 1; 4).

Compound	C x 10 ⁻⁴ (cm ³ /gK)	θ _{C-W} (K)	T _c (K)	μ _{eff} (μ _B)
CdGaCrSe ₄	2.3	-1.07	125.25	3.21
CdGaCrSe ₃ S	3.19	-95.50	51.70	3.58
CdGaCrS ₄	84.0	104.6	---	4.94

**Fig. 3** Temperature dependence of the magnetic susceptibility of the CdGaCrSe_(4-x)S_(x) system for x = 0; 1; and 4.

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