

Crystal growth of the $\text{CdGa}_{2(1-x)}\text{Cr}_{2x}\text{Se}_4$ compounds by chemical transport method

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Single crystals of $\text{CdGa}_{2(1-x)}\text{Cr}_{2x}\text{Se}_4$ compounds for $0 \leq x \leq 1$ have been grown by using the chemical vapor transport technique in a closed system. The transporting agent was CdCl_2 in a proportion of 0.75 mg/cc of capsule. The starting material was previously synthesized. The structural characterization on the crystals were done by powder x-ray diffraction studies. The results show three different phases for various Cr concentration ranges: spinel structure for $x \geq 0.7$, rhombohedral for $0.6 \geq x \geq 0.5$ and tetragonal for $0.4 \geq x \geq 0$. That is, the chromium dilution in the CdCr_2Se_4 compound by Ga atoms produces very significant changes in the structural atomic arrangement

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1 Introduction

Since the discovery of the colossal magnetoresistance (CMR) effect in the spinel FeCr_2S_4 special attention has been paid to the chromium chalcogenide compounds. [1,2,3] The chromium spinel semiconductors like CdCr_2S_4 and CdCr_2Se_4 are also interesting in the electric-magnetic inter-related research. [4]

CdCr_2Se_4 is a spinel ferromagnetic semiconductor ($T_c = 130$ K). Single crystals of this compound has been previously grown by many authors, following the chemical transport method. [5,6] The mentioned compound belongs to the II-III₃-VI₄ ternary semiconductor family. One of the characteristic features of this system is that it contains vacancies-defect if crystallizes into the so called defect chalcopyrite structure. In most cases the defect is due to a vacancy originated from the lack of II elements in a chalcopyrite cell. This fact favored the appearance of structural disorder. Another possibility to create some kind or order-disorder states, is because normally the III atoms tends to occupy tetrahedral site [7].

We present in this work an study on the single crystal growth and structural characterization of the $\text{CdGa}_{2-2x}\text{Cr}_{2x}\text{Se}_4$ compounds with $0 \leq x \leq 1$. Although there are numerous data available for CdCr_2Se_4 compound, the studies on effect of dilution of chromium atoms by non magnetic gallium atoms are very scarce. This becomes a very interesting problem from the structural and magnetic point of view.

2 Experiment

Single crystals of the $\text{CdGa}_{2-2x}\text{Cr}_{2x}\text{Se}_4$ system were grown by the chemical transport technique in closed quartz capsules. The starting materials, polycrystalline compounds, were previously synthesized from pure elements with 4N or 5N as purity. The stoichiometric mixtures of the elements were sealed in evacuated quartz capsules (11 cm long and 9 mm as internal diameter). The capsules were slowly heated by means of an automatic

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temperature controller, from RT to 925°C over a period of 10-15 days, depending upon de chromium concentration. The obtained product looked as a very homogeneous material.

The previously synthesized material, about 1.4 gr, was sealed in a large quartz ampoules: 20 cm long and 20 mm in inner diameter under vacuum of 10^{-5} Torr. I_2 , CrCl_3 or CdCl_2 compound were used as transport agent, in a concentration of about 0.75 mg/cc of ampoule in the case of CdCl_2 and 5 mg/cc for the iodine. The selected amount of agent depend on the chromium concentration, thus I_2 was used for the low concentration Cr sample and CrCl_3 was used in samples with $x = 0.5$; 0.8. The ampoules were place in an closed horizontal two zone furnace. The furnace temperature was raised over a 9 hour period to 700°C in the charge zone and 800°C in the deposition zone. After one day the temperature gradient was inverted, in a period of 4 hrs, to get the working gradient.

Concerning to the gradient temperature and the deposition temperature, they are shown in Table 1 for the different compounds. It is possible to see that sample with $x = 0.1$ was grown in two ways, by using I_2 or CdCl_2 , the result suggest that CdCl_2 favored the crystal growing process.

In order to guess what is the chemical process during the crystal growth we started considering the behavior of CdCr_2Se_4 polycrystalline compound (starting material) at high temperature. Previous reports shows that CdSe is deposited on the cooler part of the ampoule, however Wehmeier [8] suggested that an excess of selenium prevented the deposition of CdSe . [8,9] Therefore we decided to charge the ampoule with our polycrystalline starting material plus an excess of Se and the transporting agent as is shown in Table 1.

The transport yielded, in general, crystals of different colors suggesting the deposition of different phases. We selected the dark-red color crystals after different try in the diffraction procedure including the previously synthesized material. The stoichiometry of those crystal were checked by EDX technique obtaining values in a good agreement with the nominal ones.

Table 1 Summary of the experimental conditions for the crystal growing of $\text{CdGa}_{2-2x}\text{Cr}_{2x}\text{Se}_4$ compounds.

x	M_m (g)	T.Agent	M_T (g)	M_{Se} (g)	T_s °C	T_d °C	Comments
0.05	1.4230	I_2	0.1972	---	820	750	Very tiny crystals: 20%
0.1	1.4163	I_2	0.1910	---	820	750	Very tiny crystals
	1.4372	CdCl_2	0.0384	0.0697	850	790	1-2 mm, red and black . 30%
0.2	1.4001	CdCl_2	0.0384	0.0697	850	790	Dark red crytals 1-2mm. 50%
0.3	1.10	CdCl_2	0.0384	0.0691	820	750	Dark red crystals 2-3 mm 72%,
0.4	1.179	CdCl_2	0.02335	0.0449	800	750	Dark red crystal . 60 %
0.5	1.450	CrCl_3	0.0680	0.0507	800	750	Very tiny crystals
0.6	1.4832	CdCl_2	0.0384	0.0691	820	750	Dark red crystals 2mm .60 %
0.8	1.378	CrCl_3	0.0679	0.0507	795	710	Very tiny crystals 80%
1.0	1.3870	CdCl_2	0.0226	0.0435	800	750	Very tiny crystals

X-ray powder diffraction studies were carried out with a Siemens D5005 diffractometer equipped with $\text{CuK}\alpha$ radiation tube ($\lambda = 1.54059 \text{ \AA}$, 40 Kv y 30 mA), in a $2\theta/\theta$ configuration. The 2θ range was 10-100 ° with a step with of 0.02° and integration time 35 s.

The refinement of the lattice parameters by least squares method was obtained by using NBS*AIDS93 [10] X-ray powder diffraction studies of the samples showed that the obtained single crystals present different crystal structures for different chromium concentrations ranges, thus for $0 \leq x \leq 0.4$ the samples crystallices in tetragonal structure, for samples with $0.5 \leq x \leq 0.6$ the structure is rhombohedral and a spinel structure appears for samples with $0.7 \leq x \leq 1$. The lattices parameter for all the studied samples are shown in Table 2.The structural refinement was executed according to the Rietveld method by using the program Win-M-pro [11,12].

The structure calculations were started by using the structural model of the CdGa_2Se_4 for the tetragonal phase, the Cr_2Se_3 model for the hexagonal one and the CdCr_2Se_4 model for the spinel phase and the lattice parameters obtained with the program NBS*AIDS93. The calculations were based on the assumption of an

statistical distribution of Cr atoms in the two Ga sites, while the occupation of the anion sites were refined along the calculations.

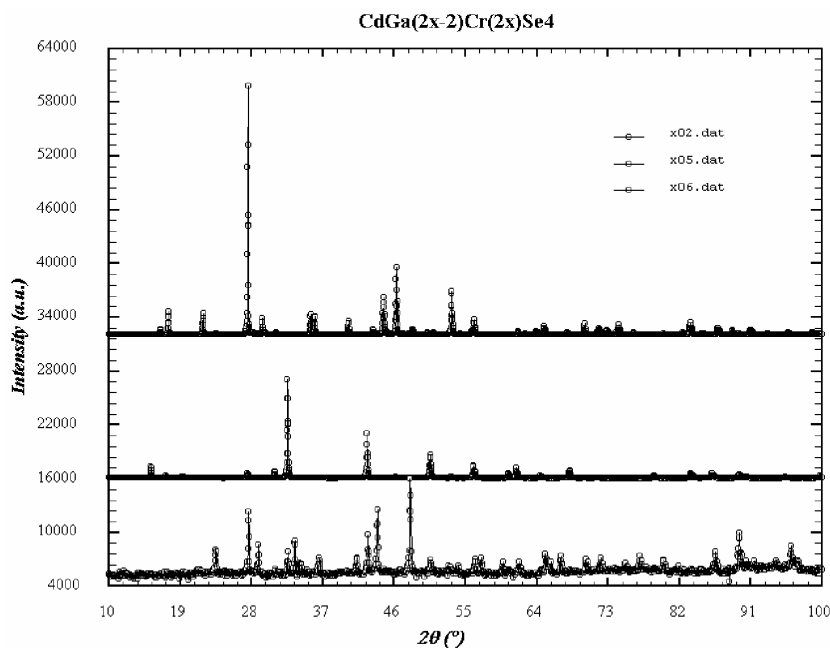


Fig. 1 Observed x-ray diffraction pattern for samples with $x = 0.3$; 0.5 ; 0.6 .

Table 2 Structural data and experimental details of Rietveld refinement of $\text{CdGa}_{2-2x}\text{Cr}_{2x}\text{Se}_4$ system.

	$x = 0.2$	$x = 0.3$	$x = 0.5$	$x = 0.6$	$x = 1.0$
Wavelength (Å)	1.5406	1.5406	1.5406	1.5406	1.5406
Monochromator	Grafite	Grafite	Grafite	Grafite	Grafite
Voltage (KV)	40	40	40	40	40
Current (mA)	30	30	25	25	25
2θ range (°)	10-100	10-100	10 - 100	2 - 110	2 - 110
Configuración	$2\theta/\theta$	$2\theta/\theta$	$2\theta/\theta$	$2\theta/\theta$	$2\theta/\theta$
Scan velocity	0.02	0.02	0.02	0.05	0.05
Integration time	35 s	35 s	35 s	10 s	10 s
Crystal system	Tetragonal	Tetragonal	Hexagonal	Cubic	Cubic
Space Group	I-4	I-4	R3m	Fd-3m	Fd-3m
a (Å)	5.7401(1)	5.7449(0)	3.6088(6)	10.718(5)	10.734(2)
c (Å)	10.7513(1)	10.7514(1)	40.489(1)		
V (Å) ³	354.723(7)	354.839(7)	456.68(2)	1231.23(5)	1236.75(8)
Z	2	2	0.67	8	8
Background	Polynomial function	Polynomial function	Polynomial function	Polynomial function	Polynomial function
Peak function	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt
Number of parameters	34	27	20	22	22
R_I	9.31	11.31	9.73	9.06	8.72
R_p	23.6	24.43	25.2	34.7	25.7
R_{wp}	27.61	28.15	38.3	47.2	31.5
R_{exp}	9.88	9.76	10.2	13.02	8.41
Chisq	7.80	8.31	14.09	13.14	14.02

The results of the structural analysis for a representative sample of each structure are given in Table 2. Moreover, in Fig.1 are shown the diffraction pattern for samples with $x = 0.3$; 0.5 , 0.6 , with tetragonal, hexagonal and spinel structure respectively.

Table 2 shows the refined parameters: zero shift, scale factor, asymmetry parameter, and mixing parameter of the pseudo-Voigt peak shape function, two or one unit cell parameter, six positional parameters and three isotropic temperature factors. The refinement of 20-34 parameters converged to the final profile agreements factor of R_t , R_p , R_{wp} . As can be seen our factor values are fairly large that means our preliminary results needs more refinement process on the data

Recent studies of the x-ray structure analysis showed that the Ga^{3+} and the Cr^{3+} ions shares the octahedral sites in the compounds with spinel structure, while in the tetrahedral structure compounds both ions share the tetrahedral sites [3]

To obtain more information about the crystal growth process, micrographs were taken using an Scanning Electron Microscope. The morphological behaviour of sample $\text{CdGa}_{1.4}\text{Cr}_{0.6}\text{Se}_4$ ($x = 0.3$) is shown in Fig. 2.

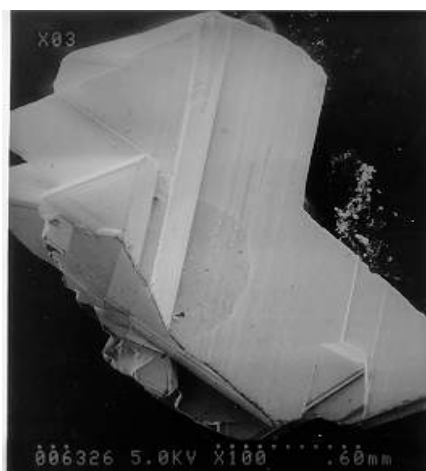


Fig. 2 Microphotograph of $\text{CdGa}_{1.4}\text{Cr}_{0.6}\text{Se}_4$ ($x = 0.3$) sample.

As a conclusion we could say that the transportant agent CdCl_2 produces a very good yielding during the transport process for the single crystal growth of the $\text{CdGa}_{2-2x}\text{Cr}_{2x}\text{Se}_4$ system for concentrations below $x = 0.6$. However the size of the crystals are not large enough for other types of measurements than the magnetics like for optical or electrical studies. Further studies are necessary to obtain larger crystals to be used in electrical measurements as magnetoresistance.

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