Research Paper

Structural and Optical Properties of $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) Mixed Crystals

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Abstract

The structural and optical properties of $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ mixed crystals were investigated in the range $0.0 \leq x \leq 1.0$ by measuring the X-ray diffraction and optical absorption. The X-ray diffraction analysis demonstrated that $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ crystalized into a tetragonal structure for $0.0 \leq x \leq 1.0$. The tetragonal lattice constants were $a = 5.744 \text{ \AA}$ and $c = 10.784 \text{ \AA}$ for CdGa_2Se_4 ($x = 0.0$), and $a = 5.611 \text{ \AA}$ and $c = 10.913 \text{ \AA}$ for CoGa_2Se_4 ($x = 1.0$), which are the end members of the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ system, exhibiting a composition dependence that varied linearly with composition x . The tetragonal structural properties of $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ were investigated by taking into account the compositional dependence of the tetragonal distortion, $2-(c/a)$, and bonding distances $R_{\text{Cd}(\text{Co})-\text{Se}}$ and $R_{\text{Ga}-\text{Se}}$. The optical absorption spectra exhibited triplet absorption bands in the range 650 - 900 nm corresponding to the $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{P})$ transition of the Co^{2+} ions with T_d symmetry sites, and a broad band in the range 1100 - 2200 nm corresponding to the $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{F})$ transition, for all investigated compositions. The composition dependencies of the crystal-field parameter, Dq , and Racah parameter, B , are discussed on the basis of a tetrahedral crystal-field approximation and composition dependent tetragonal structure.

Keywords: $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$, Tetragonal structure, Optical absorption, Co^{2+} ions, Crystal-field approximation

1. Introduction

CdGa_2Se_4 , is one of the $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{C}_4^{\text{VI}}$ ($\text{A} = \text{Cd, Zn, Hg, B} = \text{Ga, In, Al, C} = \text{S, Se, and Te}$)-type ternary semiconductors, and has become a subject of interest as a material with potential applications in optoelectronics owing to its high photosensitivity and strong luminescence in the visible region [1]. Many studies have been performed on the optical characterizations of CdGa_2Se_4 , namely optical absorption [2], photoconductivity [3,4], photoluminescence [5], and Raman scattering [6,7]. The doping effects of cobalt metals as impurities in CdGa_2Se_4 have also been studied [4,8]. To increase the applicability of CdGa_2Se_4 , a method of controlling its fundamental properties by doping impurities is required. In previous works [9,10], we studied the structural and optical properties for $0.0 \leq$

$x \leq 0.5$ in $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ mixed crystals, which were replaced by Co instead of Cd in the CdGa_2Se_4 . These lead to an increase in the applicability of CdGa_2Se_4 through tuning the energy gap and lattice constants by varying the Co content. However, the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ system has not been studied over the full range of $0.0 \leq x \leq 1.0$ owing to the difficulty of crystal growth near $x = 1.0$.

In this paper, we investigate the composition-dependent behavior of the structural and optical properties for the full range, $0.0 \leq x \leq 1.0$, in $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ mixed crystals grown by the directional melt technique. The structural properties, such as the lattice constants, tetragonal distortion, and atomic coordinates, are investigated as a function of x in the range $0.0 \leq x \leq 1.0$. The optical absorption spectra for 300 - 2400 nm are analyzed in the framework of the crystal-field theory. The variations of the crystal-field and Racah parameters, Dq and B , respectively, with x in the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ system are also discussed.

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II. Experimental details

The $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ mixed crystals were prepared in the range $0.0 \leq x \leq 1.0$ using the directional melt technique described in Ref. [9]. However, for the crystals with $x \geq 0.5$, the temperature of the horizontal furnace was maintained at 1200 °C for approximately 12 days. To achieve homogeneous crystals, the furnace was also rotated at a speed of 4 rpm during the growth procedure.

The composition of the grown crystals was determined by means of inductively coupled plasma mass spectroscopy (JY 38 PLUS, France). The crystals within the error limits of 3 % from their start compositions were used in the measurements. The analysis of the crystal structure was performed using an X-ray diffractometer (Rigaku DMAX 2000, Japan). The optical absorption spectra were measured in the range 300-2400 nm at 300 K using a UV-VIS-NIR spectrophotometer (Hitachi U-3501, Japan) equipped with a 60-mm integrating sphere.

III. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) pattern spectra for the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ crystals. The compound CdGa_2Se_4 , which corresponds to the end member ($x = 0.0$) of the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ system, is known to have a tetragonal structure [1]. The XRD spectrum, for the case $x = 0.0$ in Fig. 1, shows a typical tetragonal structure. For the other compositions, the XRD patterns are similar to that of the $x = 0.0$ case, without extra peaks related to the individual elements or binary alloy. The dominant (112) diffraction peak of the tetragonal structure exhibits a composition dependence that shifts toward higher 2θ angles with increasing x , as shown in Fig. 2.

Figure 1. (Color online) X-ray diffraction patterns of the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystal powders.

dence that shifts toward higher 2θ angles with increasing x , as shown in Fig. 2.

The tetragonal lattice constants, a and c , obtained from the data of Fig. 1, are listed in Table I, and plotted in Fig. 3 as a function of x . As shown in the top panel of Fig. 3, the lattice constants have a composition dependence which the lattice constant a decreases linearly with increasing x , while the lattice constant c increases linearly, satisfying Vegard's law [11]. Moreover, the tetragonal distortion ($2-c/a$), which originates from the characteristics of the tetragonal structure, obtained by ordering two cations on one

Table I. Various values of the lattice constants, tetragonal distortion, and atomic coordinate for the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystals.

Composition (x)	Structure	Lattice constants		2η ($=c/a$)	$2-c/a$	u	$R_{\text{Cd(Co-Se)}}$	$R_{\text{Ga-Se}}$
		a (Å)	c (Å)					
0.0	tetragonal	5.744	10.784	1.877	0.123	0.282	2.5503	2.3342
0.1	tetragonal	5.726	10.790	1.884	0.116	0.280	2.5373	2.3355
0.3	tetragonal	5.691	10.820	1.901	0.098	0.275	2.5108	2.3440
0.5	tetragonal	5.680	10.840	1.908	0.092	0.273	2.5012	2.3482
0.7	tetragonal	5.648	10.874	1.925	0.075	0.269	2.4801	2.3548
0.9	tetragonal	5.629	10.900	1.936	0.064	0.266	2.4653	2.3603
1.0	tetragonal	5.611	10.913	1.945	0.055	0.264	2.4546	2.3631

Figure 2. (Color online) Composition dependence of the (112) plane in the X-ray diffraction patterns of the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystal powders.

Figure 3. (Color online) Composition dependence of the lattice constants and tetragonal distortion for the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystals.

cation in a zinc-blende structure, exhibits a composition dependence that decreases with increasing composition x , as can be seen in the bottom panel of Fig. 3. Wearie and Noolandi [12] suggested an empirical relationship between the tetragonal distortion and

Figure 4. (Color online) Composition dependence of the Se atom coordinate and bonding distance $R_{\text{Cd(Co)-Se}}$, $R_{\text{Ga-Se}}$, for the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystals.

electronegativity of the constituent atoms in the tetragonal ABC_2 -type compounds, as follows:

$$2 - (c/a) \propto (X_A - X_B)^2 \quad (1)$$

where X_A and X_B denote the electronegativity of the two cations. Assuming the Pauling electronegativity values of 1.69 for Cd, 1.88 for Co, and 1.81 for Ga, the tetragonal distortion in the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ system is expected to decrease with increasing Co content, and is in good accordance with the results of Fig. 3. We calculated the bonding distance between the two nearest-neighbor cations and Se atom, i.e., $R_{\text{Cd(Co)-Se}}$ and $R_{\text{Ga-Se}}$, respectively, using the following relation [13]

$$\begin{aligned} R_{\text{Cd(Co)-Se}} &= [u^2 + (1 + \eta^2)/16]^{1/2}a, \\ R_{\text{Ga-Se}} &= [(u - 1/2)^2 + (1 + \eta^2)/16]^{1/2}a \end{aligned} \quad (2)$$

where the Se atom coordinate, u , was obtained by

$$u = 1/2 - 1/4(c^2/2a^2 - 1)^{1/2}. \quad (3)$$

The results are summarized in Table I, and are plotted in Fig. 4 as a function of x . In Fig. 4, the Se atom coordinate u varies from 0.282 ($x = 0.0$) to 0.264

Figure 5. (Color online) Optical absorption spectra of the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystals at 300 K.

($x = 1.0$) with increasing x , approaching the value of a cubic zinc-blende structure (0.25) [13]. On the other hand, decreasing $R_{\text{Cd}(\text{Co})\text{-Se}}$ and increasing $R_{\text{Ga-Se}}$ leads to a smaller difference in the bonding distance between each the cations with the Se atom for increasing x . This is in accordance with our results for the composition dependent-tetragonal distortion of the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ system.

Figure 5 shows the optical absorption spectra for the composition $0.0 \leq x \leq 1.0$ of the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$

Figure 6. (Color online) Composition dependence of the optical absorption bands corresponding to the ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ of the tetrahedral Co^{2+} ions in the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystals.

mixed crystals in the range 300 - 2400 nm at 300 K. These are three sharp absorption bands in the range 650 - 900 nm corresponding to the ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ transition of the Co^{2+} ions with T_d symmetry sites, and a broad band in the range 1100 - 2200 nm corresponding to the ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{F})$ transition. Similar absorption bands for all of the investigated compositions are presented. However, in Figs. 6 and 7, the triplet absorption bands of the ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ tran-

Table II. Values of the observed absorption band energies, crystal-field parameter Dq , and Racah parameter B for the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystals.

Composition (x)	Observed absorption bands									
	${}^4\text{T}_1({}^4\text{P})$						${}^4\text{T}_1({}^4\text{F})$	Dq	B	
	Γ_6		Γ_8		$\Gamma_7 + \Gamma_8$					
	nm	cm^{-1}	nm	cm^{-1}	nm	cm^{-1}				nm
0.1	719	13908	768	13020	799	12516	1670	5988	333	614
0.3	723	13831	768	13020	799	12516	1630	6135	341	605
0.5	725	13793	771	12970	800	12500	1620	6173	343	602
0.7	728	13736	775	12903	825	12121	1580	6329	352	580
0.9	738	13550	783	12771	820	12195	1585	6309	351	577
1.0	740	13514	785	12739	830	12048	1555	6431	357	567

Figure 7. (Color online) Composition dependence of the optical absorption band corresponding to the $^4A_2(^4F) \rightarrow ^4T_1(^4F)$ of the tetrahedral Co^{2+} ions in the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystals.

Figure 8. (Color online) Composition dependence of the parameters Dq (■) and B (●) in the $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ ($0.0 \leq x \leq 1.0$) crystals.

sition shift toward longer wavelength regions with increasing x , whereas the broad band of the $^4A_2(^4F) \rightarrow ^4T_1(^4F)$ transition shifts to shorter wavelength regions. The observed bands are summarized in Table II, and the corresponding transitions between the split energy levels of Co^{2+} are shown in the inset of Fig. 7. From the observed absorption bands, we can deduce the crystal-field and Racah parameters, Dq and B , respectively, using the following relations [14]

$$\begin{aligned} E_1 &= E[{}^4T_1(^4F) - {}^4A_2(^4F)] = 18Dq \\ E_2 &= E[{}^4T_1(^4P) - {}^4A_2(^4F)] \\ &= 15Dq + (15/2)B + (1/2)b \\ E_3 &= E[{}^4T_1(^4F) - {}^4A_2(^4F)] \\ &= 15Dq + (15/2)B - (1/2)b \end{aligned} \quad (4)$$

where $b = [(10Dq - 9B)^2 + 144B^2]^{1/2}$. The obtained parameters are also given in Table II. The Dq -values

range from 333 to 357 cm^{-1} , which are in agreement with $Dq \approx 400 \text{ cm}^{-1}$ for tetrahedral Co^{2+} ions, compared with $Dq \approx 900 \text{ cm}^{-1}$ for octahedral Co^{2+} ions, $Dq \approx 700 \text{ cm}^{-1}$ for tetrahedral Co^{3+} ions, and $Dq \approx 1600 \text{ cm}^{-1}$ for octahedral Co^{3+} ions [15]. This implies that the Co atoms in $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ occupy the tetrahedral sites of the host lattice as Co^{2+} ions.

The Dq and B values are plotted in Fig. 8 as a function of the composition x . The composition dependence of Dq increases from 333 to 357 cm^{-1} , whereas that of B decreases from 614 to 567 cm^{-1} , with increasing x . A similar behavior for the variation of Dq and B was also observed in a pressure study of $\text{CdTe}:\text{Co}$ [16]. The study provided the pressure dependence of Dq and B , i.e., Dq increases and B decreases, with increasing pressure. It was shown that the pressure-induced shifts of Dq and B are connected with changes of the interatomic distance and ionicity of the CdTe . These are in a good agreement with our results of the composition dependent properties of the interatomic distance between a cobalt-metal atom and its ligands, i.e., $R_{\text{Cd}(\text{Co})-\text{Se}}$, decreases with the increasing Co composition x (see Fig. 4).

IV. Conclusions

In this work, the structural and optical properties of $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ mixed crystals grown by the directional melt technique were investigated in the range $0.0 \leq x \leq 1.0$. The XRD analysis demonstrated that $\text{Cd}_{1-x}\text{Co}_x\text{Ga}_2\text{Se}_4$ crystalized into a tetragonal structure for $0.0 \leq x \leq 1.0$ and formed a solid solution between CdGa_2Se_4 ($x = 0.0$) and CoGa_2Se_4 ($x = 1.0$). The tetragonal lattice constants exhibited a composition dependence that varied linearly with the composition x . The composition-dependent properties of the tetragonal distortion, $2-(c/a)$, were investigated by introducing the electronegativity of the constituent atoms, and by considering the composition dependence of $R_{\text{Cd}(\text{Co})-\text{Se}}$ and $R_{\text{Ga}-\text{Se}}$, and the nearest-neighbor bonding distances between the cations atoms and the Se atom. The composition-dependent optical transitions of $^4A_2(^4F) \rightarrow ^4T_1(^4P)$ and $^4A_2(^4F) \rightarrow ^4T_1(^4F)$ of the tetrahedral Co^{2+} ions were analyzed on the basis of a tetrahedral crystal-field approximation, providing the crystal-field and Racah parameters, Dq and B , respectively. The composition dependences of the parameters Dq and B were explained based on the composition

dependent-tetragonal structure. It was shown that the Dq and B depend strongly on the variations of the tetragonal structure with composition x .

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