Research Paper

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

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Abstract

The structural and optical properties of Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ mixed crystals were investigated in the range 0.0 ≤ x ≤ 1.0 by measuring the X-ray diffraction and optical absorption. The X-ray diffraction analysis demonstrated that Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ crystallized into a tetragonal structure for 0.0 ≤ x ≤ 1.0. The tetragonal lattice constants were $a = 5.744$ Å and $c = 10.784$ Å for CdGa$_2$Se$_4$ (x = 0.0), and $a = 5.611$ Å and $c = 10.913$ Å for CoGa$_2$Se$_4$ (x = 1.0), which are the end members of the Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ system, exhibiting a composition dependence that varied linearly with composition x. The tetragonal structural properties of Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ were investigated by taking into account the compositional dependence of the tetragonal distortion, 2-c(a), and bonding distances $R_{CdGaSe}$ and $R_{GaSe}$. The optical absorption spectra exhibited triplet absorption bands in the range 650 - 900 nm corresponding to the $^4A_2(^4F) → ^4T_1(^4P)$ transition of the Co$^{2+}$ ions with $T_d$ symmetry sites, and a broad band in the range 1100 - 2200 nm corresponding to the $^4A_2(^4F) → ^4T_1(^4F)$ 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: Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$, Tetragonal structure, Optical absorption, Co$^{2+}$ ions, Crystal-field approximation

I. Introduction

CdGa$_2$Se$_4$, is one of the A$^{III}$B$_2$[VI]C$_4$ (A = Cd, Zn, Hg, B = Ga, In, Al, C = 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$_2$Se$_4$, namely optical absorption [2], photoconductivity [3,4], photoluminescence [5], and Raman scattering [6,7]. The doping effects of cobalt metals as impurities in CdGa$_2$Se$_4$ have also been studied [4,8]. To increase the applicability of CdGa$_2$Se$_4$, 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 ≤ x ≤ 0.5 in Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ mixed crystals, which were replaced by Co instead of Cd in the CdGa$_2$Se$_4$. These lead to an increase in the applicability of CdGa$_2$Se$_4$ through tuning the energy gap and lattice constants by varying the Co content. However, the Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ system has not been studied over the full range of 0.0 ≤ x ≤ 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 ≤ x ≤ 1.0, in Cd$_{1-x}$Co$_x$Ga$_2$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 ≤ x ≤ 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 Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ system are also discussed.

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II. Experimental details

The Cd$_{1-x}$Co$_x$Ga$_2$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 Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ crystals. The compound CdGa$_2$Se$_4$, which corresponds to the end member ($x = 0.0$) of the Cd$_{1-x}$Co$_x$Ga$_2$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.

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 ($2c/a$), which originates from the characteristics of the tetragonal structure, obtained by ordering two cations on one

| Composition ($x$) | Structure | Lattice constants | $2\eta$ ($=c/a$) | 2$-c/a$ | $u$ | $R_{Cd(Co):Se}$ | $R_{Ga-Se}$ |
|------------------|-----------|------------------|-----------------|---------|-----|----------------|-------------|
| 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      |
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 electronegativity of the constituent atoms in the tetragonal ABC2-type compounds, as follows:

\[
2 - (c/a) \propto (X_A - X_B)^2
\]  

(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]

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

(2)

where the Se atom coordinate, \( u \), was obtained by

\[
u = 1/2 - 1/4(c^2/2a^2 - 1)^{1/2}.
\]  

(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...
(x = 1.0) with increasing x, approaching the value of a cubic zinc-blende structure (0.25) [13]. On the other hand, decreasing $R_{\text{Cd(Co)-Se}}$ 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 Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ system.

Figure 5 shows the optical absorption spectra for the composition 0.0 ≤ x ≤ 1.0 of the Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ 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 $^4A_2^\Gamma\rightarrow^4T_1^\Gamma$ transition of the Co$^{2+}$ ions with $T_d$ symmetry sites, and a broad band in the range 1100 - 2200 nm corresponding to the $^4A_2^\Gamma\rightarrow^4T_1^\Gamma$ transition. Similar absorption bands for all of the investigated compositions are presented. However, in Figs. 6 and 7, the triplet absorption bands of the $^4A_2^\Gamma\rightarrow^4T_1^\Gamma$ tran-

![Figure 5](Image)

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

![Figure 6](Image)

**Figure 6.** (Color online) Composition dependence of the optical absorption bands corresponding to the $^4A_2^\Gamma\rightarrow^4T_1^\Gamma$ of the tetrahedral Co$^{2+}$ ions in the Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ (0.0 ≤ x ≤ 1.0) crystals.

| Composition (x) | $^4T_1^\Gamma$ | $^4T_1^\Gamma$ | Dq | B |
|----------------|---------------|---------------|----|---|
|                | $^4T_1^\Gamma$ | $^4T_1^\Gamma$ | cm$^{-1}$ | cm$^{-1}$ |
| 0.1            | 719           | 13908         | 678 | 13020 |
| 0.3            | 723           | 13831         | 768 | 13020 |
| 0.5            | 725           | 13793         | 771 | 12970 |
| 0.7            | 728           | 13736         | 775 | 12903 |
| 0.9            | 738           | 13550         | 783 | 12771 |
| 1.0            | 740           | 13514         | 785 | 12739 |

**Table II.** Values of the observed absorption band energies, crystal-field parameter Dq, and Racah parameter B for the Cd$_{1-x}$Co$_x$Ga$_2$Se$_4$ (0.0 ≤ x ≤ 1.0) crystals.
sition shift toward longer wavelength regions with increasing x, whereas the broad band of the \( ^4 \text{A}_2(4F) \rightarrow {}^4 \text{T}_1(4F) \) transition shifts to shorter wavelength regions. The observed bands are summarized in Table II, and the corresponding transitions between the split energy levels of \( \text{Co}^{2+} \) are shown in the inset of Fig. 7. From the observed absorption bands, we can deduce the crystal-field and Racah parameters, \( D_q \) and \( B \), respectively, using the following relations [14]

\[
\begin{align*}
E_1 &= E[{}^4 \text{T}_1 (4F) - {}^4 \text{A}_2 (4F)] = 18D_q \\
E_2 &= E[{}^4 \text{T}_1 (4F) - {}^4 \text{A}_2 (4F)] \\
&= 15D_q + (15/2)B + (1/2)b \\
E_3 &= E[{}^4 \text{T}_1 (4F) - {}^4 \text{A}_2 (4F)] \\
&= 15D_q + (15/2)B - (1/2)b \\
\end{align*}
\]

where \( b = [(10D_q - 9B)^2 + 144B^2]^{1/2} \). The obtained parameters are also given in Table II. The \( D_q \)-values range from 333 to 357 cm\(^{-1} \), which are in agreement with \( D_q \approx 400 \) cm\(^{-1} \) for tetrahedral \( \text{Co}^{2+} \) ions, compared with \( D_q \approx 900 \) cm\(^{-1} \) for octahedral \( \text{Co}^{2+} \) ions, \( D_q \approx 700 \) cm\(^{-1} \) for tetrahedral \( \text{Co}^{3+} \) ions, and \( D_q \approx 1600 \) cm\(^{-1} \) for octahedral \( \text{Co}^{3+} \) ions [15]. This implies that the Co atoms in \( \text{Cd}_x\text{Co}_y\text{Ga}_z\text{Se}_4 \) occupy the tetrahedral sites of the host lattice as \( \text{Co}^{2+} \) ions.

The \( D_q \) and \( B \) values are plotted in Fig. 8 as a function of the composition \( x \). The composition dependence of \( D_q \) 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 \( D_q \) and \( B \), i.e., \( D_q \) increases and \( B \) decreases, with increasing pressure. It was shown that the pressure-induced shifts of \( D_q \) 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., \( R_{\text{Co}(\text{Co}-\text{Se})} \), decreases with the increasing \( \text{Co} \) composition \( x \) (see Fig. 4).

IV. Conclusions

In this work, the structural and optical properties of \( \text{Cd}_x\text{Co}_y\text{Ga}_z\text{Se}_4 \) 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 \( \text{Cd}_x\text{Co}_y\text{Ga}_z\text{Se}_4 \) crystallized into a tetragonal structure for \( 0.0 \leq x \leq 1.0 \) and formed a solid solution between \( \text{CdGaSe}_2 \) \((x = 0.0)\) and \( \text{CoGaSe}_2 \) \((x = 1.0)\). The tetragonal lattice constants exhibited a composition dependence that varied linearly with the composition \( x \). The composition-dependent properties of the tetragonal distortion, \( 2\text{–}(\text{ca}) \), were investigated by introducing the electronegativity of the constituent atoms, and then, by considering the composition dependence of \( R_{\text{Cd}(\text{Co}-\text{Se})} \) and \( R_{\text{Ga} \text{Se}_4} \), and the nearest-neighbor bonding distances between the cations atoms and the Se atom. The composition-dependent optical transitions of \( ^4 \text{A}_2(4F) \rightarrow {}^4 \text{T}_1(4P) \) and \( ^4 \text{A}_2(4F) \rightarrow {}^4 \text{T}_1(4F) \) of the tetrahedral \( \text{Co}^{2+} \) ions were analyzed on the basis of a tetrahedral crystal-field approximation, providing the crystal-field and Racah parameters, \( D_q \) and \( B \), respectively. The composition dependences of the parameters \( D_q \) 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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