Photoluminescence spectra of $Zn_{1-x}Cd_xAl_2Se_4$ single crystals

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We investigated the photoluminescence spectra as well as the crystal structure and optical energy gaps of the $Zn_{1-x}Cd_xAl_2Se_4$ single crystals grown by the chemical transport reaction method. It was shown from the analysis of the observed x-ray diffraction patterns that these crystals have a defect chalcopyrite structure for a whole composition. The lattice constant a increases from 5.5561 A for x = 0.0 (ZnAl₂Se₄) to 5.6361 A for x = 1.0 (CdAl₂Se₄) with increasing x, whereas the lattice constant c decreases from 10.8890 A for x = 0.0 to 10.7194 A for x = 1.0. The optical energy gaps at 13 K were found to range from 3.082 eV (x = 1.0) to 3.525 eV (x = 0.0). The temperature dependence of the optical energy gaps was well fitted with the Varshni equation. We observed two emission bands consisting of a strong blue emission band and a weak broad emission band due to donor-acceptor pair recombination in the $Zn_{1-x}Cd_xAl_2Se_4$ for $0.0 \le x \le 1.0$. These emission bands showed a red shift with increasing x. The energy band scheme for the radiative mechanism of the $Zn_{1-x}Cd_xAl_2Se_4$ was proposed on the basis of the photoluminescence thermal quenching analysis along with the measurements of photo-induced current transient spectroscopy. The proposed energy band model permits us to assign the observed emission bands.

I. INTRODUCTION

ZnAl₂Se₄ and CdAl₂Se₄ are promising materials with potential applications in optoelectronic devices. These compounds belong to a wide band gap material and crystallize into a defect chalcopyrite. However, very little is known about the physical properties of these compounds because of difficulties with their crystal growth resulting from a reducing reaction between aluminium of the constituent elements and the quartz tube used.¹⁻⁴ Furthermore, no study of the solid solution based on ZnAl₂Se₄ and CdAl₂Se₄ has been reported so far. In a previous paper,⁵ we reported on the optical properties of CdAl₂Se₄ single crystals and on the effects of doping of cobalt and erbium in the crystals from the measurements of optical absorption and photoluminescence. In the present paper, we report on the photoluminescence spectra of $Zn_{1-x}Cd_xAl_2Se_4$ mixed single crystals grown by the chemical transport reaction method. The energy band scheme for the radiative mechanism of the mixed single crystals is also proposed on the basis of our experimental results.

II. EXPERIMENTAL

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Single crystals of the $Zn_{1-x}Cd_xAl_2Se_4$ solid solutions were grown for a whole composition of $0.0 \le x \le 1.0$ by the chemical transport reaction (CTR) method.⁵ ZnCl₂, Cd, Al, and Se of high purity (99.9999%) were used as starting materials and chlorine of 6 mg cm⁻³ as a transporting material. In order to obtain the crystals with a stoichiometric composition, excess selenium of 10 mol%

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was then added. The inner walls of the source zone of the quartz tubes used were coated with carbon to prevent aluminium of the constituent elements from reacting with the quartz tubes at high temperatures. After clearing the quartz walls of the growth zone,⁶ the source- and growth-zone temperatures were kept at 950 and 850 °C for 7 days for the crystal growth. The resulting single crystals showed a colorless and transparent crystal with a dimension of about $5 \times 6 \times 1.5$ mm³ for a whole composition. The chemical composition of the grown single crystals was determined by an energy-dispersive x-ray microanalyzer (EDAX).

The photoluminescence spectra were recorded using a conventional measurement system consisting of a double-grating monochromator (Spex 1403, U.S.A., f = 0.85 m), a photomultiplier (RCA, C31034, Japan), and a cryogenerator (Air Products, CSA-202B, U.S.A.). The 325-nm line of an He–Cd laser (LiConix, 3650N, U.S.A.) was used as an excitation source. The crystal structure and lattice constants were determined from x-ray powder diffraction measurements (Rigaku, DMAX2000, Japan). The optical absorption spectra were obtained by using an ultraviolet–visible–near-infrared spectrophotometer (Hitachi, U3501, Japan) equipped with a cryogenic system (Air Products, CSA-202B, Japan).

III. RESULTS AND DISCUSSION

The analysis of the x-ray diffraction (XRD) patterns measured for the $Zn_{1-x}Cd_xAl_2Se_4$ in powder form showed that these crystals have a defect chalcopyrite structure for a whole composition, and revealed that the lattice constant *a* increases from 5.5561 A for x = $0.0(ZnAl_2Se_4)$ to 5.6361 A for $x = 1.0(CdAl_2Se_4)$ with increasing *x*, whereas the lattice constant *c* decreases from 10.8890 A for x = 0.0 to 10.7194 A for x = 1.0(see Table I). The optical energy gaps of the $Zn_{1-x}Cd_xAl_2Se_4$ single crystals were obtained from the measurements of the optical absorption spectra near the fundamental absorption edge in the temperature region of 13 to 289 K. Figure 1 depicts the plots of the relation between $(\alpha h \nu)^2$ and $h\nu$ for a direct allowed transition at 13 K. The optical energy gap at 13 K, deduced by extrapolation of the plot to $(\alpha h \nu)^2 = 0$, is found to be 3.082 (x = 1.0), 3.169 (x = 0.8), 3.258 (x = 0.6), 3.347 (x = 0.4), 3.436 (x = 0.2), and 3.525 eV (x = 0.0), respectively. The temperature dependence of the optical energy gaps was also investigated in the temperature range of 13 to 285 K, and was well fitted with the Varshni equation⁷

$$E_{\rm g}(T) = E_{\rm g}(0) - (\alpha T^2)/(T + \beta)$$
, (1)

where $E_g(T)$ is the energy gap at T K, $E_g(0)$ at 0 K, and α and β are constants. The obtained parameters are given in Table I.

The photoluminescence spectra of the $Zn_{1-x}Cd_xAl_2Se_4$ single crystals were investigated in the temperature region of 13 to 289 K and in the wavelength region of 400 to 600 nm. Figure 2 represents the photoluminescence spectra at 13 K for the $Zn_{1-x}Cd_xAl_2Se_4$ in the composition region of $0.0 \le x \le 1.0$. The photoluminescence spectrum of the $ZnAl_2Se_4$ (x = 0.0) shows a strong broad emission band at 2.870 eV and a weak broad emission band at 2.638 eV. The same feature of these bands is also observed for the crystals with x = 0.2, excepting a red shift of the bands. The red shift of the bands appears up to x = 0.6. However, the emission bands for the crystals with x = 0.8 and 1.0 are observed in higher energy regions than the emission bands observed for the Zn-rich crystals. Also these emission bands show a red shift without a change of their shape with increasing x, as in the case of the Zn-rich crystals. For the crystals with x = 1.0(CdAl₂Se₄), the emission bands are observed at 2.707 and 2.292 eV, which are considered to be due to donor-acceptor pair recombination⁵.

Figure 3 shows the temperature dependence of the photoluminescence spectra for the $Zn_{0.8}Cd_{0.2}Al_2Se_4$ single crystals with x = 0.2. The emission bands are observed to be quenched at high temperatures. The pho-

	x and crystal structure									
	x = 0.0 Defect chalcopyrite	x = 0.2 Defect chalcopyrite	x = 0.4 Defect chalcopyrite	x = 0.6 Defect chalcopyrite	x = 0.8 Defect chalcopyrite	x = 1.0 Defect chalcopyrite				
Lattice constant										
a (Å)	5.5561	5.5723	5.5884	5.6045	5.6207	5.6361				
c (Å)	10.8890	10.8551	10.8212	10.7873	10.7534	10.7194				
Energy gap (eV)										
13 K	3.525	3.436	3.347	3.258	3.169	3.082				
289 K	3.312	3.241	3.172	3.103	3.034	2.965				
Constant of Varshni equation										
Eg(0) (eV)	3.527	3.439	3.349	3.260	3.171	3.084				
α (eV/K)	2.03×10^{-3}	1.88×10^{-3}	1.69×10^{-3}	1.51×10^{-3}	1.33×10^{-3}	1.16×10^{-3}				
β (K)	501.89	507.01	512.12	517.23	522.34	527.45				

TABLE I. Values of lattice constants, optical energy gaps, and Eg(0), α , and β from the Varshni equation of $Zn_{1-x}Cd_xAl_2Se_4$ single crystals.

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toluminenscence thermal quenching analysis of the 2.756-eV band, shown in the inset of Fig. 3, yields the activation energy of 0.061 eV. For the crystals with different compositions, the photoluminescnece thermal quenching is also observed (not shown in the figure).



FIG. 1. Optical energy gaps of $Zn_{1-x}Cd_xAl_2Se_4$ single crystals at 13 K.



FIG. 2. Photoluminescence sprectra at 13 K of Zn₁ , Cd₂Al₂Se₄ single crystals for (a) x = 0.0, 0.2; (b) x = 0.4, 0.6; and (c) x = 0.8, 1.0.

From the thermal quenching analysis the activation energies for the other crystals are obtained and given in Table II.

In order to clarify the mechanism of the observed photoluminescence spectra, we carried out the measurements of the photo-induced current transient spectroscopy (PICTS),⁸ exchanging the polarity of electric field applied to samples illuminated in proximity to a contact. As a result of experiment, the depth of electron traps as donors and hole traps as acceptors was obtained. The results are summarized in Table II. On the basis of our experimental results, the radiative processes in the $Zn_{1-x}Cd_xAl_2Se_4$ are proposed as shown in Fig. 4. In the proposed scheme, two donor levels and two acceptor levels are introduced in the forbidden band gap; two donor levels (D1, D2) and one acceptor level (A2) for the crystals with $0.0 \le x \le 0.6$, and one donor level (D1) and two acceptor levels (A1, A2) for the crystals with $0.8 \leq$ $x \leq 1.0$. The proposed energy band scheme allows that the observed emission bands are assigned as due to donor-acceptor pair recombination between the defect energy levels in the forbidden band gap. However, the origin of the discrepancy in the defect energy levels according to a composition variation of different cations in the defect chalcopyrite $Zn_{1-x}Cd_xAl_2Se_4$ with the same anion is not clear in present.

IV. CONCLUSION

In summary, we investigated the composition dependence of the photoluminescence spectra for the $Zn_{1-r}Cd_rAl_2Se_4$ single crystals grown by the CTR method. For a whole composition, a strong emission band and a weak broad emission band were observed in blue to green spectral regions. These emission bands were assigned due to donor-acceptor pair recombination, and showed a red shift with increasing x. We suggested the energy band model of the $Zn_{1-x}Cd_xAl_2Se_4$ from the



FIG. 3. Temperature dependence of the photoluminescence spectrum of Zn_{0.8}Cd_{0.2}Al₂Se₄ single crystals.

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	Composition (<i>x</i>)												
	x = 0.0		x = 0.2		x = 0.4		x = 0.6		x = 0.8		x = 1.0		
	EE(eV) ^a	EM ^b	EE(eV)	EM									
Emission peaks (at 13 K)	2.870	DA12	2.756	DA12	2.638	DA12	2.520	DA12	2.812	DA11	2.707	DA11	
	2.638	DA22	2.510	DA22	2.380	DA22	2.250	DA22	2.403	DA12	2.292	DA12	
Defect energy levels (eV)													
D1	0.058		0.061		0.066		0.070		0.074		0.077		
D2	0.290		0.307		0.324		0.341						
A1									0.283		0.298		
A2	0.59	0.597		0.619		0.643		0.668		0.692		0.713	

TABLE II. Emission energy, emission mechanism, and defect energy levels of $Zn_{1-x}Cd_xAl_2Se_4$ single crystals.

^aEE, Emission energy.

^bEM, Emission mechanism.



FIG. 4. Proposed energy band scheme for the radiative mechanism of $Zn_{1-x}Cd_xAl_2Se_4$ single crystals at 13 K.

measurements of optical absorption and PICTS. The proposed energy band model permitted us to assign the observed emission bands.

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