

Optical Properties of $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ Single Crystals

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Abstract $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals were grown by the Bridgman-Stockbarger method. The single crystals crystallized into a defect chalcopyrite structure. The optical energy band gap of the single crystals was investigated in the temperature range 11-300 K. The optical energy band gap of the $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystal was smaller than that of the $\text{ZnHgGa}_4\text{Se}_8$ single crystal. The temperature dependence of the optical energy band gap of the single crystals was well fitted by the Varshni equation. The impurity optical absorption spectrum of the $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystal was measured in the wavelength region 300-2300 nm at 80 K. Impurity absorption peaks in the spectrum were analyzed within the framework of the crystal field theory and were attributed to the electron transitions between the energy levels of Co^{2+} sited in the Td symmetry point.

Key words $\text{ZnHgGa}_4\text{Se}_8$, cobalt, optical absorption.

1. Introduction

Ternary compound semiconductors of the II-III₂-IV₄ type have been regarded as promising materials applicable to optoelectronic devices¹⁾ because of their high photosensitivity²⁾ and strong luminescence properties^{3,4)} in the visible wavelength region. In the II-III₂-IV₄ type semiconductors, ZnGa_2Se_4 and HgGa_2Se_4 single crystals with the direct energy band gap of about 2.49 and 1.99 eV, respectively, have been studied by many researchers.^{1,4-13)} When 3d transition elements as impurities are doped into the single crystals, significant changes in their optical and electrical properties appear. The optical and electrical properties of $\text{ZnGa}_2\text{Se}_4:\text{Co}^{2+}$,^{9,10)} $\text{ZnGa}_2\text{Se}_4:\text{Cr}^{2+}$,¹¹⁾ $\text{ZnGa}_2\text{Se}_4:\text{Ni}^{2+}$,¹²⁾ and $\text{HgGa}_2\text{Se}_4:\text{Co}^{2+}$ ¹³⁾ single crystals have been studied.

However, no study on $\text{ZnHgGa}_4\text{Se}_8$ as a solid solution of ZnGa_2Se_4 and HgGa_2Se_4 has been reported as yet. In this work, we first grew $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals. Their crystal structure and optical energy band gap were examined. The temperature dependence of the optical energy band gap of the single crystals was identified. The impurity optical absorption spectrum of the $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystal was measured and the electron transition mechanism due to Co^{2+} in the single crystal was analyzed within the framework of the crystal-field theory.¹⁴⁾

2. Experimental Procedure

$\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals were grown by the Bridgman-Stockbarger method. Firstly, $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ ingots were synthesized by direct melting of constituent elements Zn (purity 99.9999%), Ga (purity 99.9999%), Se (purity 99.9999%), HgSe (purity 99.999%), and Co (purity 99.999%). Stoichiometric quantities (total amount of about 20 g) of the elements and excessive Se of 5 mol% were used as source materials of $\text{ZnHgGa}_4\text{Se}_8$. Cobalt metal powder of 2 mol% was introduced to the source materials in order to synthesize the $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ ingot. Secondly, $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals were grown by using the ingots by the Bridgman-Stockbarger method. Then, the ampule was pulled down at a speed of 0.3 mm/h. Lastly, the obtained single crystals were annealed at 600°C for 20 days and cooled down slowly to room temperature.

The grown single crystals were light red color. The composition of the single crystals was confirmed by electron probe microanalysis. From the analysis of their x-ray diffraction patterns measured by using an x-ray diffractometer (Rigaku, DMAX-2000), the crystal structure of the single crystals was determined. Optical absorption spectra near the fundamental absorption edge were measured by using a uv-vis-nir spectrophotometer (Hitachi, U3501) equipped with a cryogenic system (Janis, SVT-400) over the temperature region 11-300 K. Impurity optical absorption spectra of the $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystal were measured by the

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spectrophotometer at 80 K.

3. Results and Discussion

3.1 A. Crystal structures and optical energy band gaps of the $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals

The powdered x-ray diffraction patterns of the $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals were measured. The crystal structure of the single crystals was identified by analyzing the x-ray diffraction patterns. The single crystals crystallized into a defect chalcopyrite structure. The lattice constants a and c of the single crystals were found to be $a=5.584\text{\AA}$ and $c=10.943\text{\AA}$ for $\text{ZnHgGa}_4\text{Se}_8$ and $a=5.623\text{\AA}$ and $c=10.985\text{\AA}$ for $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$. The values of the lattice constants a and c are listed in Table I. Considering the previously reported values for ZnGa_2Se_4 and HgGa_2Se_4 single crystals,^{10,13} these values of the lattice constants are reasonable. When Co was doped into the $\text{ZnHgGa}_4\text{Se}_8$ single crystal, the lattice constants a and c slightly increased, as seen in Table I.

The optical absorption spectra of the $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals were measured in the wavelength region 380-440 nm over the temperature range 11-300 K. The optical absorption spectra at 11 K are shown in Fig. 1. Optical absorption in the single crystals increased abruptly near the fundamental absorption edge of the single crystals. This means that the single crystals have the direct energy band structure.

The optical energy band gap E_g of a semiconductor with the direct band structure can be obtained from the following relation¹⁵:

$$(\alpha h\nu)^2 \sim (h\nu - E_g) \quad (1)$$

where $h\nu$ is the incident photon energy and α is optical absorption coefficient near the fundamental absorption edge. Fig. 2 shows the values of $(\alpha h\nu)^2$ plotted as a function of the incident photon energy $h\nu$ for the

Table 1. Lattice constants and value of $E_g(0)$, α and β from the Varshni equation.

materials		$\text{ZnHgGa}_4\text{Se}_8$	$\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$
Lattice constants	$a(\text{\AA})$	5.584	5.623
	$c(\text{\AA})$	10.943	10.985
Varshni constants	E_g (eV)	2.452	2.372
	α (eV/K)	9.23×10^{-4}	2.34×10^{-3}
	β (K)	385	437

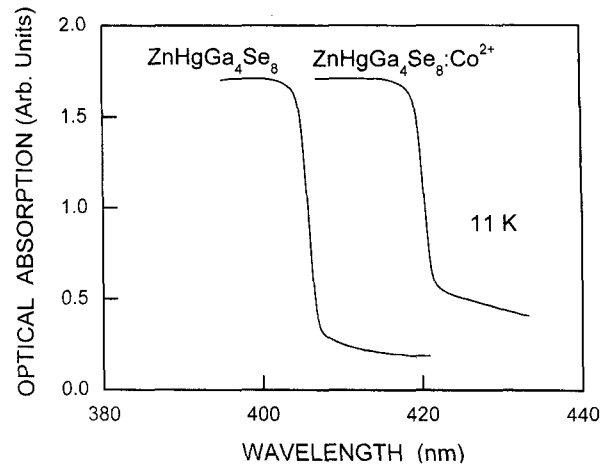


Fig. 1. Optical absorption spectra of the $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals at 11 K.

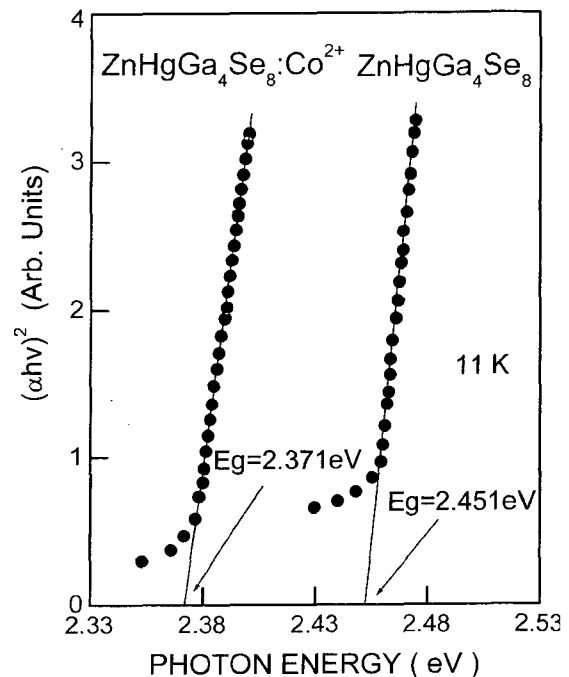


Fig. 2. Plots of $(\alpha h\nu)^2$ as a function of the incident photon energy $h\nu$ for the $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals at 11 K.

$\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals at 11 K. By extrapolating the straight line portion of the plots to $(\alpha h\nu)^2=0$, the optical energy band gap E_g was found to be 2.451 and 2.371 eV for the $\text{ZnHgGa}_4\text{Se}_8$ and $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystals, respectively, at 11 K.

When Co was doped into the $\text{ZnHgGa}_4\text{Se}_8$ single crystal, the optical energy band gap decreased. Namely, the optical energy band gap of the $\text{ZnHgGa}_4\text{Se}_8:\text{Co}^{2+}$ single crystal was smaller than that of the $\text{ZnHgGa}_4\text{Se}_8$ single crystal.

This phenomenon can be described as follows. Cobalt atoms in the ZnHgGa₄Se₈:Co²⁺ single crystal may partially form cobalt-compounds. The cobalt-compounds with smaller energy band gaps will make solid solutions with the host compound ZnHgGa₄Se₈. Therefore, such a decrease in the optical energy band gap appears in the ZnHgGa₄Se₈:Co²⁺ single crystal.

Fig. 3 shows the temperature dependence of the optical energy band gap of the ZnHgGa₄Se₈ and ZnHgGa₄Se₈:Co²⁺ single crystals. The optical energy band gap decreased with increasing temperature. The temperature dependence of the optical energy band gap was well described by the Varshni equation¹⁶⁾:

$$E_g(T) = E_g(0) - (\alpha T^2)/(T + \beta) \quad (2)$$

where $E_g(T)$ and $E_g(0)$ are the optical energy band gap at T K and 0 K, and α and β are constants. The values of $E_g(0)$, α , and β for the ZnHgGa₄Se₈ and ZnHgGa₄Se₈:Co²⁺ single crystals are listed in Table I.

3.2 Impurity optical absorption in the ZnHgGa₄Se₈:Co²⁺ single crystal

The optical absorption spectra of the ZnHgGa₄Se₈ and ZnHgGa₄Se₈:Co²⁺ single crystals were measured in the wavelength region 300-2300 nm at 80 K. Fig. 4 shows the optical absorption spectra. The ZnHgGa₄Se₈ single crystal

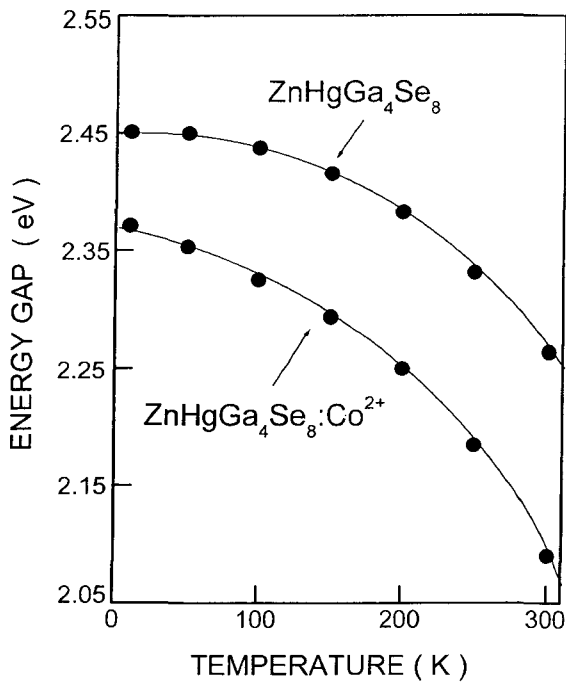


Fig. 3. Temperature dependence of the optical energy band gap for the ZnHgGa₄Se₈ and ZnHgGa₄Se₈:Co²⁺ single crystals.

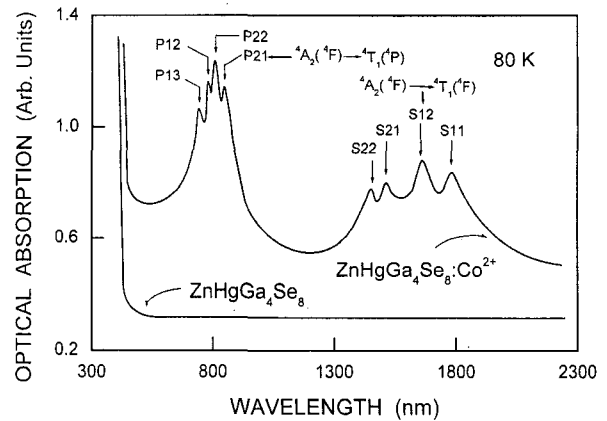


Fig. 4. Optical absorption spectra of the ZnHgGa₄Se₈ and ZnHgGa₄Se₈:Co²⁺ single crystals in the wavelength region 300-2300 nm at 80 K.

has no absorption peak as seen in Fig. 4. However the ZnHgGa₄Se₈:Co²⁺ single crystal has well-resolved absorption peaks in the wavelength regions 700-900 nm and 1400-1800 nm. By comparing two absorption spectra in Fig. 4, the absorption peaks in the ZnHgGa₄Se₈:Co²⁺ single crystal, can be thought to appear due to Co doped as an impurity into the single crystal.

Comparing the impurity optical absorption peaks with the previously reported peaks in ZnGa₂Se₄:Co²⁺⁹⁾ and HgGa₂Se₄:Co²⁺¹³⁾ single crystals, we can assign the impurity absorption peaks in the wavelength regions 700-900 nm and 1400-1800 nm to the electron transitions from the ground state ⁴A₂(⁴F) to the excited states ⁴T₁(⁴P) and ⁴T₁(⁴F), respectively, of Co²⁺ sited in Td symmetry.

Taking into account the crystal field theory¹⁴⁾ in order to identify the impurity absorption peaks in detail, the energy terms of Co²⁺(3d⁷) in the free ion are given by ⁴F and ⁴P in the visible to infrared wavelength region. When Co²⁺ is located in a single crystal, the energy levels of the free ion are split by the Coulomb repulsion. Namely, when Co²⁺ is located at the cubic Td symmetry point, the degenerate ground level ⁴F is split into three energy levels ⁴T₁(⁴F), ⁴T₂(⁴F), and ⁴A₂(⁴F). And also, the excited level ⁴P becomes ⁴T₁(⁴P). In the case of 3d transition metal ions, the energy level splitting due to the first- and the second-order spin-orbit interactions is smaller than that due to crystal fields, and so the spin-orbit interactions are treated as perturbations. Therefore, under the first-order spin-orbit interaction, the ground state ⁴A₂(⁴F) becomes Γ_8 , the excited state ⁴T₁(⁴F) is split into the three levels $\Gamma_8 + \Gamma_7$, Γ_8 , and Γ_6 , the excited state ⁴T₂(⁴F) into the three levels Γ_7 , Γ_8 , and $\Gamma_6 + \Gamma_8$, and the excited state ⁴T₁(⁴P) into the three

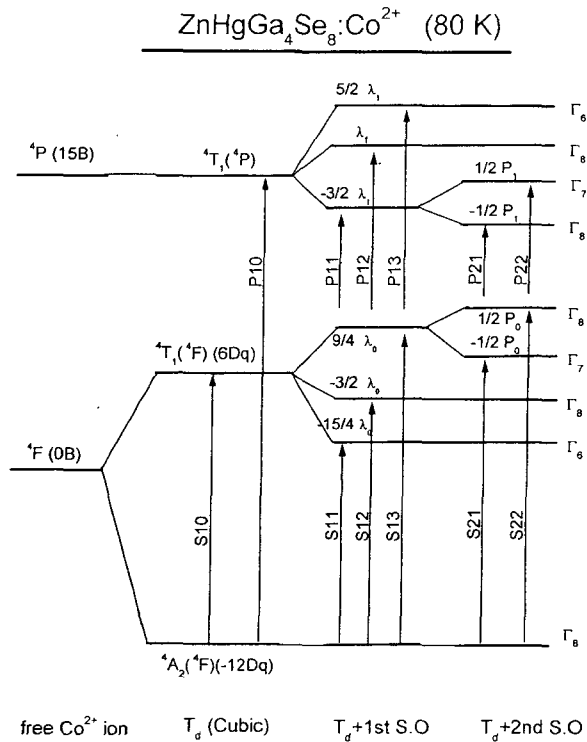


Fig. 5. Energy level splittings and electron transitions of Co²⁺ in the ZnHgGa₄Se₈:Co²⁺ single crystals at 80 K.

levels Γ_6 , Γ_8 , and $\Gamma_7+\Gamma_8$. Then, under the second-order spin-orbit interaction, the $\Gamma_8+\Gamma_7$ of ${}^4T_1(4F)$, $\Gamma_6+\Gamma_8$ of ${}^4T_2(4F)$, and $\Gamma_7+\Gamma_8$ of ${}^4T_1(4P)$ are again split into Γ_8 and Γ_7 , Γ_6 and Γ_8 , and Γ_7 and Γ_8 , respectively. This energy level splitting of Co²⁺ in Td symmetry is depicted for ${}^4T_1(4P)$ and ${}^4T_1(4F)$ in Fig. 5.

Thus the impurity optical absorption peaks P13, P12,

P22, and P21 in the wavelength region 700-900 nm shown in Fig. 4 can be attributed to the electron transitions from the ground level $\Gamma_8[{}^4A_2(4F)]$ to the split levels Γ_6 , Γ_8 , Γ_7 , and Γ_8 of the excited state ${}^4T_1(4P)$, respectively. The impurity optical absorption peaks S22, S21, S12, and S11 in the wavelength region 1400-1800 nm can be attributed to the electron transitions from the ground level $\Gamma_8[{}^4A_2(4F)]$ to the split levels Γ_8 , Γ_7 , Γ_8 , and Γ_6 of the excited state ${}^4T_1(4F)$, respectively. These electron transitions are depicted in Fig. 5.

The observed values of the impurity optical absorption peaks shown in Fig. 4 are listed in the third column of Table II. The fine structures corresponding to the impurity absorption peaks were obtained within the framework of the crystal field theory¹⁴⁾ and are listed in the fourth column of Table II which are represented by using the Racah parameter B, the crystal field parameter Dq, and the first- and the second-order spin-orbit coupling parameters λ and P.

By applying the observed values of the impurity absorption peaks to the fine structures, the values of the parameters B, Dq, λ , and P were calculated and are listed in the second column of Table III. In addition, there are values of the parameters B, Dq, λ , and P obtained in CuAlS₂:Co²⁺¹⁷⁾ and ZnS:Co²⁺¹⁸⁾ single crystals in which Co²⁺ sites at the Td symmetry point. By comparing the values of the parameters Dq, B, λ , and P in this work with those of CuAlS₂:Co²⁺ and ZnS:Co²⁺ single crystals, we can see that the analysis for Co²⁺ in this work is reasonable.

Table 2. Peak position of the absorption bands observed in ZnGa₄Se₈:Co²⁺ single crystals at 80 K

(Units: cm⁻¹)

Band	ZnHgGa ₄ Se ₈ :Co ²⁺		Fine structure	Assignment
	THE ^a	EXPT ^b		
S10	6372	6372	18Dq	${}^4A_2(4F) \rightarrow {}^4T_1(4F)$
S11	5678	5675	$18Dq - 15/4\lambda_0$	$\rightarrow \Gamma_7$
S12	6094	6096	$18Dq - 3/2\lambda_0$	$\rightarrow \Gamma_8$
S13	6788	6790	$18Dq + 9/4\lambda_0$	$\rightarrow \Gamma_7 + \Gamma_8$
S21	6667	6668	$18Dq + 9/4\lambda_0 - 1/2P_0$	$\rightarrow \Gamma_7$
S22	6988	6987	$18Dq + 9/4\lambda_0 + 1/2P_0$	$\rightarrow \Gamma_8$
P10	12933	12933	$15B + 12Dq$	${}^4A_2(4F) \rightarrow {}^4T_1(4P)$
P11	12447	12450	$15B + 12Dq - 3/2\lambda_1$	$\rightarrow \Gamma_8 + \Gamma_7$
P12	13257	12926	$15B + 12Dq + \lambda_1$	$\rightarrow \Gamma_8$
P13	13743	13740	$15B + 12Dq + 5/2\lambda_1$	$\rightarrow \Gamma_6$
P21	12165	12167	$15B + 12Dq - 3/2\lambda_1 - 1/2P_1$	$\rightarrow \Gamma_8$
P22	12728	12726	$15B + 12Dq - 3/2\lambda_1 + 1/2P_1$	$\rightarrow \Gamma_7$

^aTheoretically calculated values.

^bExperimental values.

Table 3. Values of Dq, B, λ , P and optical transition energies of Co²⁺ ion in the ZnHgGa₄Se₈:Co²⁺ single crystals at 80 K (Units: cm⁻¹).

Item	ZnHgGa ₄ Se ₈ :Co ²⁺	Other Works	
		CuAlS ₂ : Co ²⁺ ¹⁷⁾	ZnS : Co ²⁺ ¹⁸⁾
⁴ A ₂ (⁴ F) → ⁴ T ₁ (⁴ P)	6372	6940	
Dq	354	390	6750
λ_0	-185	-185	375
P ₀	241	240	-198
⁴ A ₂ (⁴ F) → ⁴ T ₁ (⁴ P)	12933	12845	
B	579	575	13650
λ_1	-324	-396	610
P ₁	563	547	

4. Conclusions

ZnHgGa₄Se₈ and ZnHgGa₄Se₈:Co²⁺ single crystals with a defect chalcopyrite structure were grown by the Bridgman-Stockbarger method. The optical energy band gap of the ZnHgGa₄Se₈ single crystal was smaller than that of the ZnHgGa₄Se₈:Co²⁺ single crystal. The optical energy band gap of the single crystals was investigated in the temperature range 11-300 K. The temperature dependence of the optical energy band gap was well fitted with the Varshni equation. Impurity optical absorption peaks were observed in the ZnHgGa₄Se₈:Co²⁺ single crystal. Within the framework of the crystal field theory, the impurity absorption peaks were attributed to the electron transitions between the energy levels of the Co²⁺ ion sited in Td symmetry.

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