

CaGa₂(S,Se)₄ : Co²⁺ 및 CaIn₂(S,Se)₄ : Co²⁺

단결정의 광학적 특성

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Optical Properties of Undoped and Co²⁺ Doped CaGa₂(S,Se)₄ and CaIn₂(S,Se)₄ Single Crystals

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Abstract

Undoped and Co²⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ single crystals were grown by using the chemical transport reaction method. The temperature dependence of the optical energy gap was well fitted by the Varshni equation. In the Co²⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ single crystals, two groups of impurity optical absorption peaks due to Co²⁺ sited in a T_d symmetry were observed in the wavelength regions of 600-900 nm and 1350-1950 nm at 11 K.

1. INTRODUCTION

Ternary compound semiconductors of the type A^{II}-B^{III}-(S, Se)₄ (A = Ca, Sr, and Ba; B = Ga, In, and Tl) have been studied by many authors because of their applicability to thin film electroluminescent devices and laser materials[1-20]. Rare-earth elements can substitute for the alkaline earth elements(Ca, Sr, and Ba) in the A^{II}-B^{III}-(S, Se)₄ compounds because of the closeness of ionic radii. The optical properties (especially, the luminescence properties) of Ce³⁺-, Eu²⁺-, Yb²⁺-, Er²⁺-, Nd³⁺-, Sm³⁺-, Dy³⁺-, Ho³⁺-, Tm³⁺-, and Pr³⁺-doped CaGa₂S₄ [3,4,6,8,10,14,15,18], Eu²⁺-doped CaGa₂Se₄[4], Yb²⁺-doped CaIn₂S₄[14], and

Yb³⁺-doped CaIn₂S₄[20] have been reported until the present. When cobalt is doped into compound semiconductors, strong optical absorption bands appear in the visible to near infrared wavelength region [21-24], so it should be possible to develop functional materials by using the absorption bands. It has also been reported that the position of the absorption bands depends on the valence and site symmetry of the cobalt dopant.

The optical properties of Co²⁺-, Ho³⁺-, Er³⁺-, and Tm³⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ single crystals have not been systematically studied as yet. The purpose of this study was to investigate systematically the fundamental optical properties of undoped and

Co²⁺-, Ho³⁺-, Er³⁺-, and Tm³⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ single crystals. These single crystals were grown by using the chemical transport reaction (CTR) method. The optical energy gap of the single crystals was investigated, and the temperature dependence of the optical energy gap was identified for the first time. The impurity optical absorption properties of the Co²⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ single crystals were also examined for the first time. Finally, the photoluminescence(PL) spectra of the Ho³⁺-, Er³⁺-, and Tm³⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ single crystals were measured, and the emission peaks due to Ho³⁺-, Er³⁺-, and Tm³⁺ were investigated.

II. EXPERIMENTAL PROCEDURE

II-1. Crystal Growth of Undoped and Co²⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ single crystals

Undoped and Co²⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ single crystals were grown by using the CTR method with iodine (purity 99.999%, 6 mg/cm³) as a transport agent. In order to obtain the starting materials, we first synthesized undoped and Co²⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ ingots by direct melting in a horizontal electric furnace. High-purity CaS(4N), CaSe(4N), Ga(6N), In(6N), S(6N), and Se(6N), according to stoichiometry of the compounds (total about 5g), were sealed in quartz ampules (10 mm in diameter, 2 mm in thickness, 190 mm in length) under a vacuum of 5×10^{-6} Torr. Then, 8 mol% of excess S and 4 mol% of excess Se were added to the quartz ampules for the sulfides and selenides, respectively, in order to avoid deficiencies of S and Se caused by their vaporization during crystal growth due to their boiling temperatures being lower than those of the other elements. CoS (powder, 3N) and CoSe (powder, 3N) were weighed for Co to be 0.2 mol% of the

Co²⁺-doped sulfide and selenide compounds, respectively, and added to the quartz ampules.

The prepared ampules were placed in the center of a horizontal electric furnace. The ampules were heated to 300 °C at a rate of 20 °C/hr, kept at 300 °C for 14 hours, heated to 600 °C at a rate of 10 °C/hr, kept at 600 °C for 30 hours, heated to 950 °C at a rate of with 10 °C/hr, kept at 950 °C for 5 hours, heated to 1150 °C at a rate of 10 °C/hr, kept at 1150 °C for 20 hours, and slowly cooled to room temperature. In the process, the ampules were rotated clockwise and counterclockwise at 2 rpm. After that, we obtained the undoped and Co²⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ ingots.

The sealed quartz ampules were placed in the center of a horizontal two-zone electric furnace in order to grow single crystals. The temperature of the growth and the source zones were kept at 800 °C 900 °C and 700 °C, respectively, for 12 hours in order to clean the growth zone and to reduce the number of growth nuclei. After that, the temperatures of the growth and the source zones were kept at 800 °C 900 °C and 950 °C 1050 °C, respectively, for 20 days to grow the undoped and Co²⁺-doped CaGa₂S₄, CaGa₂Se₄, CaIn₂S₄, and CaIn₂Se₄ single crystals. Colorless transparent to dark red single crystals with typical dimensions of about 1.8 mm × 2.3 mm × 0.2 mm were obtained.

II-2. Measurement Method

The X-ray diffraction patterns of the single crystals were measured by using an X-ray diffractometer (Rigaku, DMAX-2000). The crystal structure of the single crystals was identified by analyzing the X-ray diffraction patterns. Optical absorption spectra were measured by using a uv-vis-nir spectrophotometer (Hitachi, U-3501) equipped with a cryogenic system (Janis, SVT-400) over the temperature range of 11 298 K. Photoluminescence spectra were measured at 11

K by using a conventional PL measurement system consisting of a double monochromator (Spex 1403, $f = 0.85$ m), a photomultiplier tube (RCA, C31034), a liquid-nitrogen cooled Ge-detector (North Coast Scientific Corp., E0-817L), and a cryogenic system (Janis, SVT-400). The 325 nm line of a He-Cd laser (LiConix, 3650N) was used as an excitation source.

III. RESULTS AND DISCUSSION

III-1. Optical Energy Gaps of Undoped and Co^{2+} -doped CaGa_2S_4 , CaGa_2Se_4 , CaIn_2S_4 , and CaIn_2Se_4 single crystals

The X-ray diffraction patterns of the single crystals were measured at room temperature. When the X-ray diffraction patterns were compared with the diffraction data of JCPDS card number 25-134, the undoped and Co^{2+} -doped CaGa_2S_4 , CaGa_2Se_4 , CaIn_2S_4 , and CaIn_2Se_4 single crystals were identified as being crystalline with an orthorhombic structure.

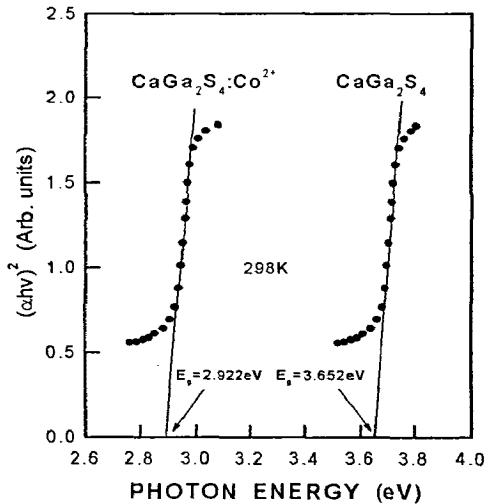


Fig. 1. Plots of $(\alpha h\nu)^2$ as functions of the incident photon energy $h\nu$ for the undoped and Co^{2+} -doped CaGa_2S_4 single crystals at 298 K.

The optical energy gap E_g , of a semiconductor with a direct band structure can be deduced from the following relation [25]

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

where α is the optical absorption coefficient near the fundamental absorption edge and $h\nu$ is the incident photon energy. In order to obtain the optical energy gap of the single crystals, we measured the optical absorption spectra near the fundamental absorption edge of the single crystals in the temperature region 11 298 K. The value of $(\alpha h\nu)^2$ was plotted as a function of the incident photon energy $h\nu$.

Considering the optical energy gap of the single crystals over the temperature region 11 298 K, we can see that it decreased with increasing temperature of the single crystals. The temperature dependence of the optical energy gap was well fitted with the Varshni equation [26]

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \quad (2)$$

where $E_g(T)$ is the optical energy gap at T K, $E_g(0)$ is the optical energy gap at 0 K, and α and β for the single crystals are listed in Table 1.

Material	Eg at 298 K (eV)	Varshni Coefficients		
		Eg(0) (eV)	α (eV/K)	β (K)
CaGa_2S_4	3.652	3.855	1.72×10^{-3}	452
$\text{CaGa}_2\text{S}_4 : \text{Co}^{2+}$	2.922	3.213	2.32×10^{-3}	410
CaGa_2Se_4	2.583	2.857	2.35×10^{-3}	463
$\text{CaGa}_2\text{Se}_4 : \text{Co}^{2+}$	1.898	2.331	3.51×10^{-3}	421
CaIn_2S_4	2.825	2.203	3.45×10^{-3}	512
$\text{CaIn}_2\text{S}_4 : \text{Co}^{2+}$	2.158	2.585	3.72×10^{-3}	475
CaIn_2Se_4	2.235	2.650	3.91×10^{-3}	537
$\text{CaIn}_2\text{Se}_4 : \text{Co}^{2+}$	1.674	2.132	4.01×10^{-3}	479

Table 1. Optical energy gap, E_g , of undoped and Co^{2+} -doped CaGa_2S_4 , CaGa_2Se_4 , CaIn_2S_4 , and CaIn_2Se_4 single crystals at 298 K, and the values of $E_g(0)$, α , and β in the Varshni equation.

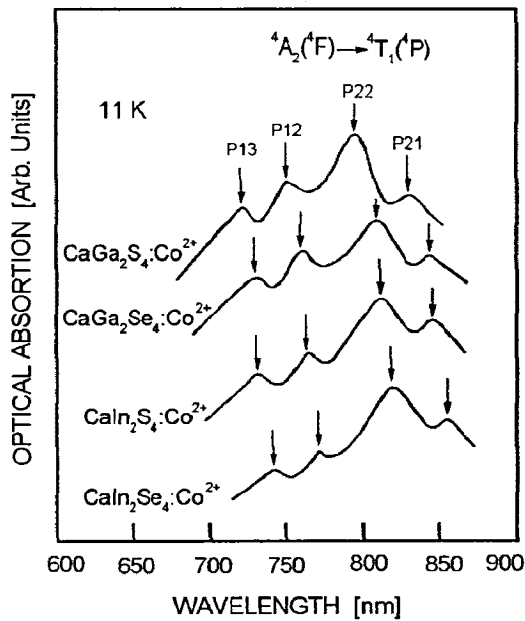


Fig. 2. Optical absorption spectra of the Co^{2+} -doped CaGa_2S_4 , CaGa_2Se_4 , CaIn_2S_4 , and CaIn_2Se_4 single crystals in the wavelength region of 600–900 nm at 11 K.

III-2. Impurity Optical Absorption of Co^{2+} -doped CaGa_2S_4 , CaGa_2Se_4 , CaIn_2S_4 , and CaIn_2Se_4 single crystals

Figures 2 and 3 show the impurity optical absorption spectra of the Co^{2+} -doped CaGa_2S_4 , CaGa_2Se_4 , CaIn_2S_4 , and CaIn_2Se_4 single crystals in the wavelength region of 600–900 nm and 1350–1950 nm, respectively, at 11 K. As shown in Figs. 2 and 3, four impurity optical absorption peaks were observed in the wavelength region of 600–900 nm and another four impurity absorption peaks in the wavelength region of 1350–1950 nm. If the optical absorption spectra are compared with the optical absorption spectra of $\text{MgAl}_2\text{S}_4:\text{Co}^{2+}$, $\text{CaAl}_2\text{S}_4:\text{Co}^{2+}$, $\text{MgAl}_2\text{Se}_4:\text{Co}^{2+}$, and $\text{CaAl}_2\text{Se}_4:\text{Co}^{2+}$ single crystals [27, 28], the impurity absorption peaks can be thought to be due to electron transitions between the energy levels of Co^{2+} sited at the Td symmetry point. The impurity absorption peaks in the wavelength region of 600–900 nm and 1350–1950

nm correspond to the transitions ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ and ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{F})$, respectively.

Within the framework of crystal field theory [29, 30], an energy state ${}^4\text{F}$ of a free Co^{2+} is split into ${}^4\text{A}_2({}^4\text{F})$, ${}^4\text{T}_2({}^4\text{F})$, and ${}^4\text{T}_1({}^4\text{F})$ levels, and an energy state ${}^4\text{P}$ is changed to a ${}^4\text{T}_1({}^4\text{P})$ level under a Td crystal field.

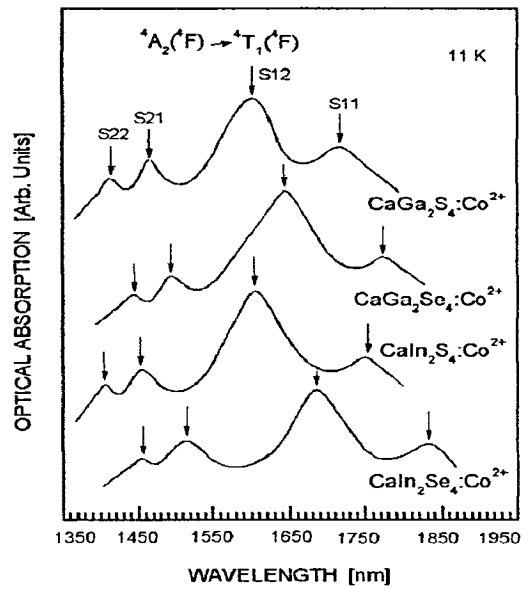


Fig. 3. Optical absorption spectra of the Co^{2+} -doped CaGa_2S_4 , CaGa_2Se_4 , CaIn_2S_4 , and CaIn_2Se_4 single crystals in the wavelength region of 1350–1950 nm at 11 K.

The energy splitting by the spin-orbit coupling interaction effect is much smaller than that of the crystal field and can be treated as a perturbation. By the first order spin-orbit coupling interaction, the energy level ${}^4\text{A}_2({}^4\text{F})$ is changed to a ground energy level $\Gamma_8[{}^4\text{A}_2({}^4\text{F})]$, the energy level ${}^4\text{T}_2({}^4\text{F})$ is split into three energy levels $\Gamma_6 + \Gamma_8[{}^4\text{T}_2({}^4\text{F})]$, $\Gamma_8[{}^4\text{T}_2({}^4\text{F})]$, and $\Gamma_7[{}^4\text{T}_2({}^4\text{F})]$, the energy level ${}^4\text{T}_1({}^4\text{F})$ is split into three energy levels $\Gamma_6[{}^4\text{T}_1({}^4\text{F})]$, $\Gamma_8[{}^4\text{T}_1({}^4\text{F})]$, and $\Gamma_8 + \Gamma_7[{}^4\text{T}_1({}^4\text{F})]$, and the energy level ${}^4\text{T}_1({}^4\text{P})$ is split into three energy levels $\Gamma_7 + \Gamma_8[{}^4\text{T}_1({}^4\text{P})]$, $\Gamma_8[{}^4\text{T}_1({}^4\text{P})]$, and $\Gamma_6[{}^4\text{T}_1({}^4\text{P})]$. By the second-order spin-orbit coupling effect, the energy level $\Gamma_6 + \Gamma_8[{}^4\text{T}_2({}^4\text{F})]$ is split into $\Gamma_8[{}^4\text{T}_2({}^4\text{F})]$ and $\Gamma_6[$

${}^4T_2(4F)$, the energy level $\Gamma_8 + \Gamma_7[{}^4T_1(4F)]$ is split into $\Gamma_8[{}^4T_1(4F)]$, and $\Gamma_7[{}^4T_1(4F)]$, and the energy level $\Gamma_7 + \Gamma_8[{}^4T_1(4P)]$ is split into $\Gamma_7[{}^4T_1(4P)]$, and $\Gamma_8[{}^4T_1(4P)]$. Figure 4 depicts the above energy level splitting processes corresponding to the observed impurity absorption peaks shown in Figs. 2 and 3. As a result, the impurity optical absorption peaks shown in Figs. 2 and 3 can be identified as shown in Figs. 4.

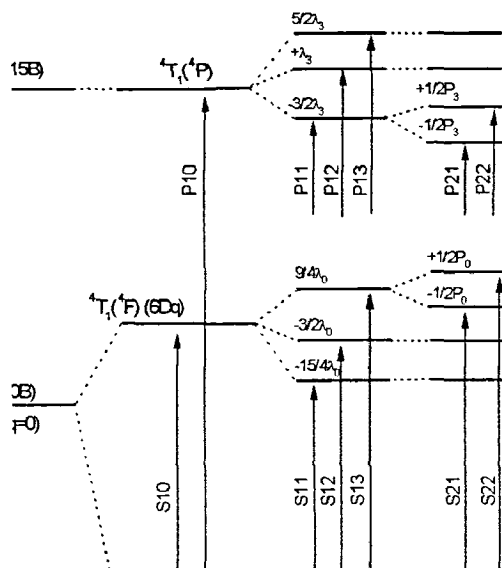


Fig. 4. Energy level splitting and electron transitions of Co^{2+} in the $Co^{2+} - CaGa_2S_4$, $CaGa_2Se_4$, $CaIn_2S_4$, and $CaIn_2Se_4$ single crystals at 11 K.

Item	$CaGa_2S_4 : Co^{2+}$	$CaGa_2Se_4 : Co^{2+}$	$CaIn_2S_4 : Co^{2+}$	$CaIn_2Se_4 : Co^{2+}$
${}^4A_2(4F) \rightarrow {}^4T_1(4F)$	6516	6390	6534	6282
Dq	362	355	363	349
λ_o	-192	-195	-209	-212
P_o	226	237	242	249
${}^4A_2(4F) \rightarrow {}^4T_1(4F)$	12819	12675	12651	12558
B	565	561	553	558
λ	-372	-383	-364	-381
P	430	445	447	453

Table 2. Optical transition energies and values of Dq, B, λ , and P of Co^{2+} -doped $CaGa_2S_4$,

$CaGa_2Se_4$, $CaIn_2S_4$, and $CaIn_2Se_4$ single crystals at 11 K (Units: cm^{-1}).

By application of the crystal field theory to the impurity optical absorption peaks of the Co^{2+} -doped $CaGa_2S_4$, $CaGa_2Se_4$, $CaIn_2S_4$, and $CaIn_2Se_4$ single crystals, the values of the Racah parameter B, the crystal field parameter Dq, the first and the second order spin-orbit coupling parameters λ and P were calculated and are listed in Table 2. If the values are compared with those of $MgAl_2S_4:Co^{2+}$, $CaAl_2S_4:Co^{2+}$, $MgAl_2Se_4:Co^{2+}$, and $CaAl_2Se_4:Co^{2+}$ single crystals [27, 28], the obtained values of B, Dq, λ , and P for the Co^{2+} -doped $CaGa_2S_4$, $CaGa_2Se_4$, $CaIn_2S_4$, and $CaIn_2Se_4$ single crystals are reasonable.

IV. CONCLUSION

Undoped and Co^{2+} -doped $CaGa_2S_4$, $CaGa_2Se_4$, $CaIn_2S_4$, and $CaIn_2Se_4$ single crystals were grown by using the chemical transport reaction (CTR) method. The optical energy gap of the single crystals was investigated in the temperature region 11–298 K. The temperature dependence of the optical energy gap was well fitted by the Varshni equation

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$

Typically, the values of $E_g(0)$, α , and β for the $CaGa_2S_4$ single crystals were given by 3.855 eV, 1.72×10^{-3} eV/K, and 452 K, respectively. In the Co^{2+} -doped $CaGa_2S_4$, $CaGa_2Se_4$, $CaIn_2S_4$, and $CaIn_2Se_4$ single crystals, two groups of impurity optical absorption peaks were observed, one each in the wavelength regions of 600–900 nm and 1350–1950 nm. Analyzing the impurity optical absorption peaks within the framework of the crystal field theory, we identified these peaks as being due to Co^{2+} sited at the Td symmetry point and as corresponding to the transitions ${}^4A_2(4F) \rightarrow {}^4T_1(4P)$ and ${}^4A_2(4F) \rightarrow {}^4T_1(4F)$, respectively.

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