Optical properties of β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} Thin Films

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β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} thin films were grown using the spray pyrolysis method. The thin films crystallized into tetragonal structures. The indirect energy band gap of the thin films was found to be 2.32 eV for β-In$_2$S$_3$ and 1.81 eV for β-In$_2$S$_3$:Co^{2+} (Co:1.0 mol%) at 298 K. The direct energy band gap was found to be 2.67 eV for β-In$_2$S$_3$ and 2.17 eV for β-In$_2$S$_3$:Co^{2+} (Co:1.0 mol%). Impurity optical absorption peaks were observed for the β-In$_2$S$_3$:Co^{2+} thin films. These impurity absorption peaks are assigned, based on the crystal field theory, to the electron transitions between the energy levels of the Co^{2+} ion sited in T$_d$ symmetry.

Keywords : In$_2$S$_3$, In$_2$S$_3$:Co^{2+}, thin film, energy band gap, impurity optical absorption

1. INTRODUCTION

Because of the In$_2$S$_3$ compound semiconductor's high photoelectric sensitivity and intensive fluorescence properties in the visible wavelength region, it is a favorable material for optoelectric devices. However, there are possible problems, including internal structure defects and a deep level originated from sulfur vacancy due to sulfur vaporization during growth. Therefore, there have not been enough studies until now. Recently, there has been a renewed interest in β-In$_2$S$_3$ since it has been used in studying defect engineering [1]. Among the various In$_2$S$_3$ compounds(i.e., α-, β-, and γ-types), β-In$_2$S$_3$ is stable at room temperature. In our laboratory, we have grown β-In$_2$S$_3$ thin films satisfying stoichiometry using the spray pyrolysis method without sulfur loss due to vaporization [2]. We have reported that the optical energy gap of the thin films increased to 2.43 eV with an increase in the quantity of excessive S [3]. In the case of

the β-In$_2$S$_3$ thin film in which the half of the In was replaced by Ga, its optical energy band gap was identified as 2.30 eV [4]. We observed an impurity optical absorption in the β-In$_2$S$_3$:Co^{2+} thin film and have decided it was caused by electron transitions between the energy levels of the Co^{2+} ion sited in T$_d$ symmetry [5, 6]. However, impurity optical absorption peaks split by the first- and second-order spin-orbit coupling effects have not been studied, in detail, and impurity optical absorption by the transition of ^{4}A$_2$(^{4}F) → ^{4}T$_2$(^{4}F) has not yet been studied.

In this paper, β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} thin films were produced using the spray pyrolysis method. The optical energy gaps of the β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} thin films were investigated. Impurity optical absorption peaks were carefully investigated from the impurity optical absorption spectra of the β-In$_2$S$_3$:Co^{2+} thin film, and the origin of the impurity optical absorption peaks was identified within the framework of the crystal field

theory [7].

2. EXPERIMENTAL PROCEDURE

β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} thin films were grown on throughly cleaned slide glass (Corning-2948) by spraying solutions prepared with the following: InCl$_2$, thiourea, and ZnCl$_2$ were dissolved in methanol to create a 0.25 molar solution. In order to grow the β-In$_2$S$_3$:Co^{2+} thin films, InCl$_2$, thiourea, ZnCl$_2$, and CoCl$_2$ (Co:0.2, 0.4, 0.6, 0.8, and 1.0 mol%) were dissolved in methanol. The additional 30% of thiourea was added to the solution in order to compensate for the loss of sulfur caused by vaporization during preparation. The solution was then diluted with pure distilled water at a 1:1 ratio. When the solution was sprayed at the rate of 6~15 mℓ/min for 20 min with the substrate temperature of 350℃, the thin films (thickness of about 1μm) were obtained. The resulting β-In$_2$S$_3$ film was yellow and the β-In$_2$S$_3$:Co^{2+} thin films was soft, reddish brown.

The crystal structures and the lattice constant of the thin films were determined using X-ray diffraction measurements (Rigaku, DMAX2000). The thin films were crystallized into tetragonal structures with lattice constants: a = 7.587Å and c = 32.298Å for β-In$_2$S$_3$ and a = 7.647Å and c = 32.923Å for β-In$_2$S$_3$:Co^{2+} (Co:1.0mol%). Optical absorption spectra were measured using a UV-VIS-NIR spectrophotometer (Hitachi, U3501) equipped with a cryogenic system (Janis, SVT-400) at wavelengths 200~3200 nm. Optical absorption spectra in the range of 400~4000 cm^{-1} were measured using a FT-IR spectrophotometer (Bomen, DA-8), and these spectra were used to reform and correct the optical absorption spectra measured by the UV-VIS-NIR spectrophotometer. The second derivative spectra of the impurity optical absorption spectra of the β-In$_2$S$_3$:Co^{2+} thin film were derived and were used to obtain the exact positions of impurity optical absorption peaks.

3. RESULTS AND DISCUSSION

3.1. Optical energy band gaps of β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} thin films

The optical absorption spectra of the β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} thin films were measured near fundamental absorption edge in order to obtain their energy band gaps. The optical energy band gap (E$_g$) of semiconductors can be found using equation (1) which relates the incident photon energy (hv) with the optical absorption coefficient (α) deduced from optical absorption spectra
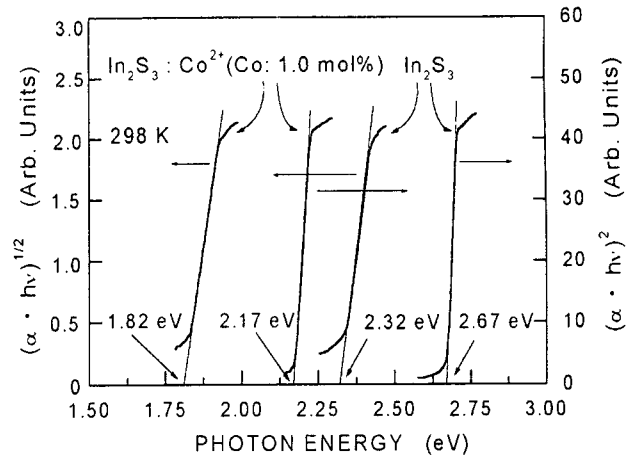

Fig. 1. Plots of $(\alpha hv)^n$ vs. incident photon energy (hv) for the β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} thin films.Good quality figure with clear lettering.
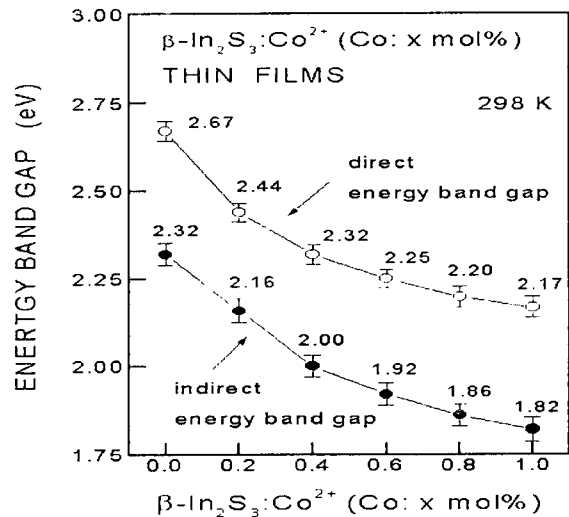
Fig. 2. Variation of energy gaps for the β-In$_2$S$_3$:Co^{2+} and β-In$_2$S$_3$:Co^{2+} thin films with the x (x:the quantity of the cobalt added into the β-In$_2$S$_3$:Co^{2+} thin films in the growth)

measured near the fundamental absorption edge[8].

$$(\alpha hv)^n \sim (hv - E_g) \tag{1}$$

The value of the exponent n is 1/2 for the indirect energy band gap and 2 for the direct energy band gap. The value of $(\alpha hv)^n$ are plotted as a function of the incident photon energy (hv) in Fig. 1. Then, the value of (hv) at $(\alpha hv)^n$ = 0, obtained by extrapolation, is the optical energy band gap. As seen in Fig. 1, the optical energy band gaps at 298K were given by the following:

the indirect energy band gap was 2.32 eV for β-In$_2$S$_3$ and 1.81 eV for β-In$_2$S$_3$:Co^{2+} (1.0mol%); the direct energy band gap was 2.67 eV for β-In$_2$S$_3$ and 2.17 eV for β-In$_2$S$_3$:Co^{2+} (1.0mol%).

As shown in Fig. 2, with an increase in x of the doped cobalt in the growth from 0.0 (the pure β-In$_2$S$_3$ thin film) to 0.2, 0.4, 0.6, 0.8, and 1.0 mol%, the indirect optical energy band gap of the β-In$_2$S$_3$:Co^{2+} thin films decreased from 2.32 to 2.16, 2.00, 1.92, 1.86, and 1.81 eV, respectively. With an increase in x from 0.0 to 0.2, 0.4, 0.6, 0.8, and 1.0 mol%, the direct optical energy band gap was decreased from 2.67 to 2.44, 2.32, 2.25, 2.20, and 2.17 eV, respectively.

3.2. Impurity optical absorption of β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} thin films

Figure 3 shows the optical absorption spectra of the β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} (1.0 mol%) thin films at 298 K. A broad defect peak (D) in the wavelength range 2700~3300 nm appeared for the β-In$_2$S$_3$ thin film. A similar defect peak has been reported for a Ga$_2$S$_3$ single crystal [9]. The defect peak in a Ga$_2$S$_3$ single crystal has been described as caused by Ga vacancy. Similarly, the defect peak (D) is thought to be due to In vacancy in β-In$_2$S$_3$.

Three groups of impurity optical absorption peaks for the β-In$_2$S$_3$:Co^{2+} (1.0 mol%) thin film appeared in the wavelengths between 650~850 nm, 1300~2000 nm, and 2750~3200 nm. By comparing these peaks with those of a CdIn$_2$S$_4$:Co^{2+} single crystal [9] and a CuAlS$_2$:Co^{2+} single crystal [10], we find that these peaks correspond to the electron transitions between the energy levels of Co^{2+} ion sited in T$_d$ symmetry. The impurity optical absorption peaks in the wavelength range 650~850 nm, 1300~2000 nm, and 2750~3200 nm are assigned to the transitions $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$, $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$, and $^4A_2(^4F) \rightarrow {}^4T_2(^4F)$, respectively.

In order to investigate the transitions in detail, the impurity optical absorption spectra of the β-In$_2$S$_3$:Co^{2+} (1.0 mol%) thin film were carefully measured at 298 K and 5 K. As shown in Fig. 4, the transition $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ splits into three and four peaks at 298 K and 5 K, respectively. Taking into account crystal field theory, the $^4T_1(^4P)$ state of the Co^{2+} ion sited in T$_d$ symmetry splits into three sub-levels Γ_6, Γ_8, and Γ_7+ Γ_8 due to the first-order spin-orbit coupling effect and four sub-levels Γ_6, Γ_8, Γ_7, and Γ_8 due to the second-order spin-orbit coupling effect. Therefore, the three and four impurity optical absorption peaks shown in Fig. 4 are assigned to the electron transitions from the ground state $^4A_2(^4F)$ to the three and four sub-levels.
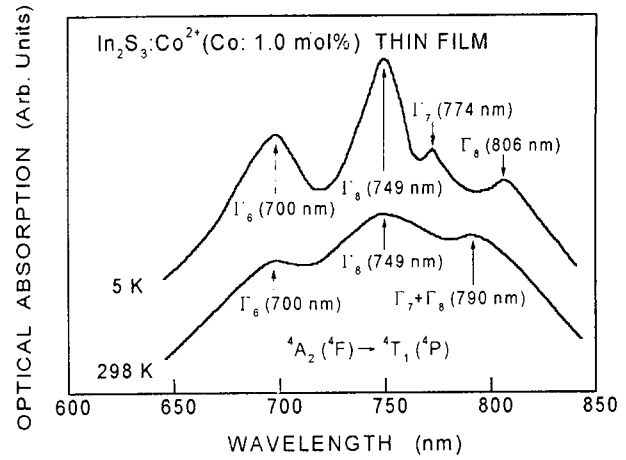

Fig. 3. Optical absorption spectra of the β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} (Co:1.0 mol%) thin films at 298 K.

Fig. 4. Impurity optical absorption spectra of the β-In$_2$S$_3$:Co^{2+} (Co:1.0 mol%) thin films in the wavelength range 600~850nm at 5 K and 298 K.

As shown in Fig. 5, the transition $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ splits into three peaks at 1410 nm, 1604 nm, and 1772 nm at 298 K, and splits into four peaks at 1384 nm, 1436 nm, 1604 nm, and 1772 nm, respectively, at 5 K. The $^4T_1(^4F)$ state of the Co^{2+} ion splits into three sub-levels $\Gamma_8 + \Gamma_7$, Γ_8, and Γ_6 due to the first-order spin-orbit coupling effect and four sub-levels Γ_8, Γ_7, Γ_8, and Γ_8 due to the second-order spin-orbit coupling effect. Therefore, the split peaks shown in Fig. 5 are assigned to the electron transitions from the ground state $^4A_2(^4F)$ of the Co^{2+} ion to the sub-levels $\Gamma_8 + \Gamma_7$, Γ_8, and Γ_6 at 298 K and the sub-levels Γ_8, Γ_7, Γ_8, and Γ_6 at 5 K.

As shown in Fig. 6, the transition $^4A_2(^4F) \rightarrow {}^4T_2(^4F)$ splits into three and four impurity optical absorption peaks at 298 K and 5 K, respectively. The $^4T_2(^4F)$ state

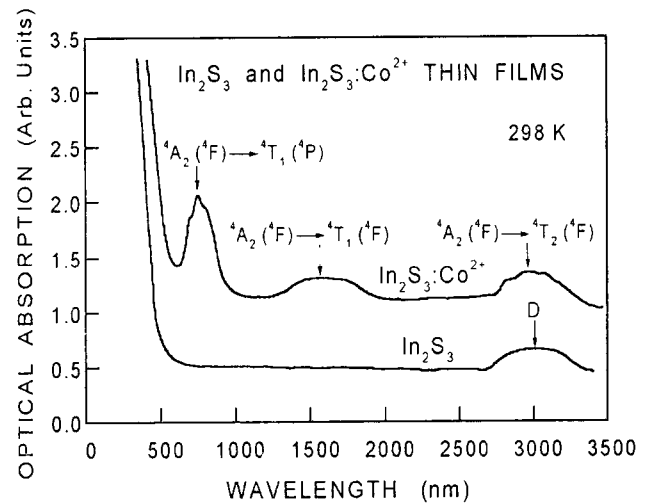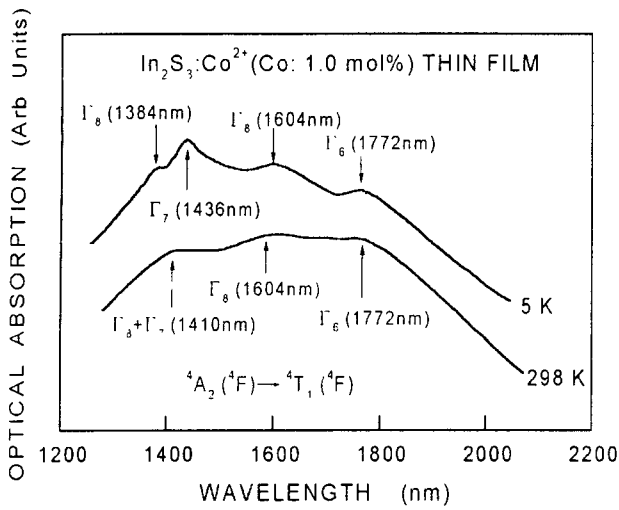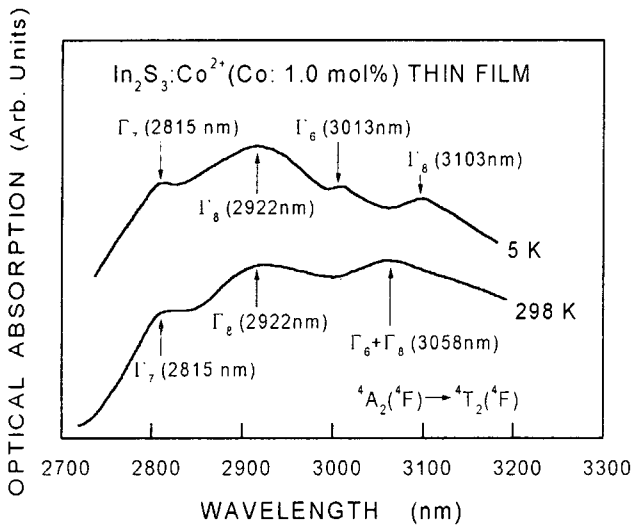Fig. 5. Impurity optical absorption spectra of the β-In_2S_3:Co^{2+} (Co:1.0 mol%) thin films in the wavelength range 1200~2200 nm at 5 K and 298 K.

Fig. 6. Impurity optical absorption spectra of the β-In_2S_3:Co^{2+} (Co:1.0 mol%) thin films in the wavelength range 2700~3300 nm at 5 K and 298 K.

of the Co^{2+} ion sited in T_d symmetry splits into three sub-levels Γ_7, Γ_8, and $\Gamma_6 + \Gamma_8$ due to the first-order spin-orbit coupling effect and four sub-levels Γ_7, Γ_8, Γ_6, and Γ_8 due to the second-order spin-orbit coupling effect. Therefore, the three and four peaks at 298 K and 5 K, respectively, are assigned to the electron transitions from the ground state $^4A_2(^4F)$ to the three and four sub-levels.

The crystal field parameter D_q, the first-order spin-orbit coupling parameter λ, and the second-order spin-orbit coupling parameter p calculated from the transition $^4A_2(^4F) \rightarrow ^4T_1(^4F)$ were 364 cm^{-1}, -242 cm^{-1}, and 260 cm^{-1}, respectively.
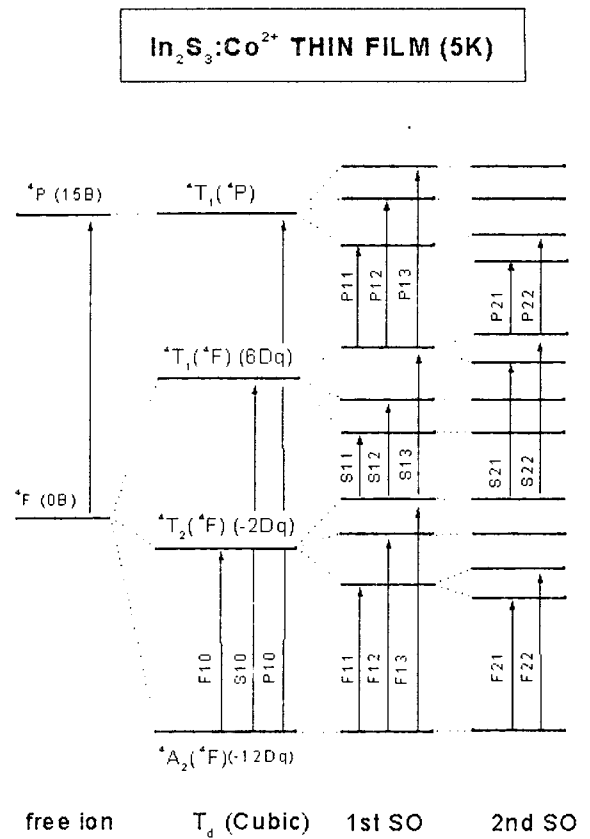

Fig. 7. Energy level splitting and electron transition scheme of the Co^{2+} ion in β-In_2S_3:Co^{2+} thin films.

The Racah parameter B calculated from the transition $^4A_2(^4F) \rightarrow ^4T_1(^4P)$ was 593 cm^{-1}. Comparing these values with $D_q = 390$ cm^{-1}, λ = -185 cm^{-1}, and p = 575 cm^{-1} for a $CuAlS_2$:Co^{2+} single crystal [10], the values obtained here were thought to be reasonable.

The peak positions and peak energies of the impurity optical absorption peaks shown in Figs. 4~6 are listed in Table I . The fine structures corresponding to the peaks, based on the crystal field theory, are also listed in Table I . The electron transition scheme of the Co^{2+} ion in the β-In_2S_3:Co^{2+} thin film, based on the experimental results, is shown in Fig. 7. The values of the crystal field parameter D_q, the first-order spin-orbit coupling parameter λ, the second-order spin-orbit coupling parameter p, and Racah parameter B were calculated using the fine structures and the experimental results listed in Table I. These values are listed in Table II .

Table 1. Peak positions of the absorption bands observed in the β-In$_2$S$_3$:Co^{2+} (Co: 1.0 mole%) thin film at 5 K.

BAND	In$_2$S$_3$:Co^{2+} Units: nm	In$_2$S$_3$:Co^{2+} Unit: cm^{-1}	Fine structure	Assignment
F10	2962	3376	$10Dq$	$^4A_2(^4F) \rightarrow {}^4T_2(^4F)$
F11	3058	3270	$10Dq - \frac{9}{12}\lambda_1$	$\rightarrow \Gamma_6 + \Gamma_8$
F12	2922	3422	$10Dq + \frac{3}{6}\lambda_1$	$\rightarrow \Gamma_8$
F13	2815	3552	$10Dq + \frac{15}{12}\lambda_1$	$\rightarrow \Gamma_7$
F21	3103	3222	$10Dq - \frac{9}{12}\lambda_1 - \frac{1}{2}p_1$	$\rightarrow \Gamma_8$
F22	3013	3318	$10Dq - \frac{9}{12}\lambda_1 + \frac{1}{2}p_1$	$\rightarrow \Gamma_6$
S10	1527	6549	$18Dq^*$	$^4A_2(^4F) \rightarrow {}^4T_1(^4F)$
S11	1772	5643	$18Dq^* - \frac{15}{4}\lambda_2$	$\rightarrow \Gamma_6$
S12	1604	6234	$18Dq^* - \frac{3}{2}\lambda_2$	$\rightarrow \Gamma_8$
S13	1410	7092	$18Dq^* + \frac{9}{4}\lambda_2$	$\rightarrow \Gamma_8 + \Gamma_7$
S21	1436	6962	$18Dq^* + \frac{9}{4}\lambda_2 - \frac{1}{2}p_2$	$\rightarrow \Gamma_7$
S22	1384	7220	$18Dq^* + \frac{9}{4}\lambda_2 + \frac{1}{2}p_2$	$\rightarrow \Gamma_8$
P10	754	13268	$15B + 12Dq^*$	$^4A_2(^4F) \rightarrow {}^4T_1(^4P)$
P11	790	12658	$15B + 12Dq^* - \frac{3}{2}\lambda_3$	$\rightarrow \Gamma_7 + \Gamma_8$
P12	749	13351	$15B + 12Dq^* + \lambda_3$	$\rightarrow \Gamma_8$
P13	700	14285	$15B + 12Dq^* + \frac{5}{2}\lambda_3$	$\rightarrow \Gamma_6$
P21	806	12406	$15B + 12Dq^* - \frac{3}{2}\lambda_3 - \frac{1}{2}$	$\rightarrow \Gamma_8$
P22	774	12910	$15B + 12Dq^* - \frac{3}{2}\lambda_3 + \frac{1}{2}$	$\rightarrow \Gamma_6$

Table 2. Values D_q, λ, p, B, and optical transition energies od Co^{2+} ion in the β-In$_2$S$_3$:Co^{2+} (Co: 1.0 mole%) thin film at 5 K (Units: cm^{-1}).

ITEM	In$_2$S$_3$:Co^{2+}	Other works CdIn$_2$S$_4$:Co^{2+} *	Other works CdAlS$_2$:Co^{2+} **
$^4A_2(^4F) \rightarrow {}^4T_2(^4F)$	3376		
Dq	338		
λ_1	-141		
P_1	96		
$^4A_2(^4F) \rightarrow {}^4T_1(^4F)$	6549		6940
Dq*	364	296	390
λ_2	-242	-133	-185
p_2	260		240
$^4A_2(^4F) \rightarrow {}^4T_1(^4P)$	13268		12845
B	596	618	575
λ_3	-407		-396
p_3	504		547

4. CONCLUSION

β-In$_2$S$_3$ and β-In$_2$S$_3$:Co^{2+} thin films were produced using the spray pyrolysis method. The indirect energy band gap at 298 K was found to be 2.32 eV for β-In$_2$S$_3$ and 1.814 eV for β-In$_2$S$_3$:Co^{2+} (Co: 1.0 mol%). The direct energy band gap at 298 K was found to be 2.67 eV for β-In$_2$S$_3$ and 2.17 eV for β-In$_2$S$_3$:Co^{2+} (Co: 1.0 mol%). Impurity optical absorption peaks due to the Co^{2+} ion in the β-In$_2$S$_3$:Co^{2+} thin films were observed. It is believed that these impurity optical absorption peaks are assigned to the electron transitions between the energy levels of the Co^{2+} ion sited in the T$_d$ symmetry point.

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