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Optical Properties of SnS_2 Single Crystals

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Abstract The SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals were grown by the chemical transport reaction method. The indirect optical energy band gap was found to be 2.348, 2.345, and 2.343 eV for the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals, at 6 K respectively. The direct optical energy band gap was found to be 2.511, 2.505, and 2.503 eV for the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals, at 6 K respectively. The temperature dependence of the optical energy band gap was well fitted by the Varshni equation. Two photoluminescence emission peaks with the peak energy of 2.214 and 1.792 eV for SnS_2, 2.214 and 1.837 eV for SnS_2:Cd, and 2.214 and 1.818 eV the SnS_2:Sb were observed. The emission peaks were described as originating from the donor-acceptor pair recombinations.

Key words SnS_2 single crystals, chemical transport reaction method

1. Introduction

A SnS_2 single crystal is a layer type, crystallizes into hexagonal structures, and is grown into the various polytypes 2H, 4H, 6H, and 10H etc. according to growth conditions.[1] A SnS_2 single crystal of a 2H type has the direct and the indirect energy band gap of 2.88 and 2.31 eV,[2] respectively. SnS_2 can be applied to optoelectronic devices in the visible wavelength region, a alkali metal battery and a solar cell.[3] Also, it has attracted interest because of potential applications in optical modulation devices. Thus, the electrical and optical properties of SnS_2 have been studied. Doping impurities in a SnS_2 single crystal could affect its optical properties, and dopants play a significant role in the process of electrical charge compensation. In order to enhance its applicability, the optical and electrical properties of impurity-doped SnS_2 single crystals must be studied, in detail.[4]

This study is purposed to investigate optical properties of a pure SnS_2 single crystal as well as Cd- and Sb-doped SnS_2 single crystals. We grew SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals by the chemical transport reaction method by using iodine as a transport agent. Optical absorption spectra were measured and the optical energy band gap of the single crystals was investigated. Photoluminescence (PL) spectra were measured. The state of the dopants Cd and Sb in the single crystals was investigated.

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2. Experimental Procedure

2.1 A. Crystal growth of SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals

The chemical transport reaction method by using iodine (6 mg/cm^3) as a transport agent was employed to grow SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals. High-purity (99.9999%) Sn and S were used to grow the single crystals as starting materials. SnS_2 single crystals with the stoichiometric composition were grown in the starting material's mole ratio of Sn:S = 1:(2.8~4.0) because of the loss of S from vaporization of sulfur during growing the single crystals. In order to grow SnS_2:Cd and SnS_2:Sb single crystals, metal elements Cd and Sb (purity 99.9999%) of 1.0 mol% as impurities were added to the starting materials. The single crystals were grown by keeping the temperature of the growth and the source zones at 350°C and 600°C for 120 hrs respectively. The single crystals were transparent, showed golden color, and had dimensions of about 12×8×(0.2~0.6) mm^3.

2.2 Measurements

The composition of the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals were examined by the energy dispersive X-ray analysis. In this study, the single crystals satisfying the stoichiometric composition within the error limits of 2% were used for measurements. The X-ray diffraction patterns of the single crystals were measured by using an X-ray diffractometer (Rigaku, DMAX-2400). The crystal structure

of the single crystals was examined by the analysis of the X-ray diffraction patterns.

Optical absorption spectra were measured in the wavelength range of 200~600 nm over the temperature range of 6300 K by using a uv-vis-nir spectrophotometer (Hitachi, U-3501) equipped with a cryogenic system (Janis, SVT-400). Photoluminescence spectra were measured by using a conventional system consisted of a double monochromator (Spex, 1403, f=0.85 m), a photomultiplier tube (RCA, C31034), and a cryogenic system (Janis, SVT-400). The 325-nm line of a He-Cd laser (LiConix, 3650N) was used as an excitation light source. Thermolumi-nescence spectra were measured in the temperature range of 50~300 K and the activation energies were determined by the general order kinetic method.[5)]

3. Results and Discussion

3.1 Crystal structures and optical energy band gaps of SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals

For sulfide semiconductors, metal-excessive single crystals are generally grown because of a higher vapor pressure of sulfur. Thus, in order to grow the single crystals with stoichiometric composition, it is necessary to control the amount of sulfur in starting materials. Namely, the excessive amounts of sulfur should be added to starting materials. We grew the SnS_2 single crystals by using the various mole ratios of Sn:S = 1:2.0 to 1:4.0 in starting materials. Fig. 1 shows the composition of the SnS_2 single crystals as a function of the sulfur mass of starting materials. The composition of the SnS_2 single crystal remained to be a constant above the mole ratio of Sn:S = 1:2.8 in starting materials.

In this study, the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals grown by using the starting material's mole ratio of Sn:S = 1:2.8 were used for measurements. The composition of the single crystals is listed in Table 1. The SnS_2 single crystal was 0.031 mol% Sn-excessive. The SnS_2:Cd single crystal was 0.026 mol% Sn-excessive and the composition of the dopant Cd was 0.05 mol%. The SnS_2:Sb single crystal was 0.029 mol% Sn-excessive and the composition of the dopant Sb was 0.02 mol%.

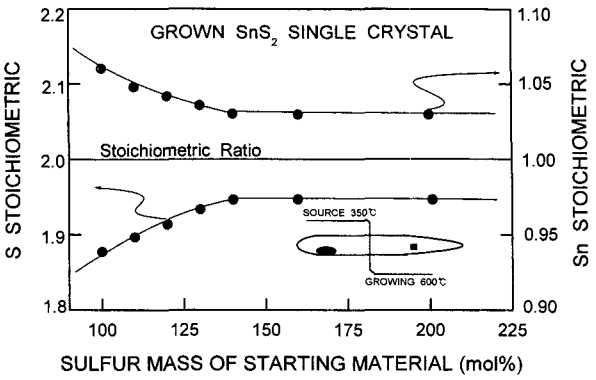

Fig. 1. Sulfur mass of starting materials versus the composition ratio of the SnS_2 single crystals.

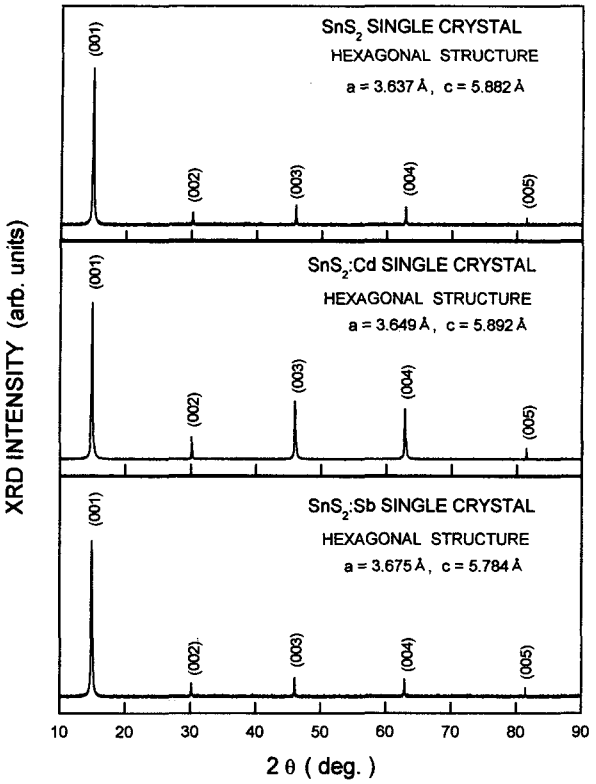

Fig. 2. X-ray diffraction patterns of the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals.

Table 1. Composition of SnS_2, SnS_2:Cd, SnS_2:Sb single crystals

Materials	Start Materials (mol %)			Single crystals (mol %)			Remarks
	Sn	S	Cd, Sb	Sn	S	Cd, Sb	
SnS_2	1	2.8	-	1.031	1.969	-	0.031mol% Sn-excess
SnS_2:Cd	1	2.8	0.1	1.026	1.974	0.05>>	0.026mol% Sn-excess
SnS_2:Sb	1	2.8	0.1	1.029	1.971	0.02>>	0.029mol% Sn-excess

Fig. 2 shows the X-ray diffraction patterns of the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals. The diffraction patterns showed the diffraction peaks of (001), (002), (003), (004), and (005) surfaces of a hexagonal structure. From the analysis of the diffraction patterns, the single crystals were found to have a surface parallel to c-axis The lattice constants a and c were found to be a = 3.637Å and c = 5.882Å for the SnS_2 single crystal, a = 3.649Å and c = 5.892Å for the SnS_2:Cd single crystal, and a = 3.675Å and c = 5.784Å for the SnS_2:Sb single crystal. These values agree well with the previously reported values (a = 3.639Å and c = 5.884Å) by Greenway and Nitsche.[6]

3.2 Optical energy band gaps of SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals

Fig. 3 shows the optical absorption spectra of the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals over the temperature range of 6300 K. The abrupt increase of optical absorption appeared near the fundamental absorption edge. The fundamental absorption edge shifted to the shorter wavelength region with decrease of temperature.

The optical energy band gap E_g of a semiconductor can be deduced from the following relation[7]:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (1)$$

where, A is a constant, $h\nu$ the incident photon energy, and α the optical absorption coefficient near the fundamental absorption edge. In eq. (1), n is given by 2 for the direct energy band gap (E_{gd}) and by 1/2 for the indirect energy band gap (E_{gi}).

Fig. 4 shows the value of $(\alpha h\nu)^{1/2}$ plotted as a function of the incident photon energy $h\nu$. The optical absorption coefficient α was calculated from the optical absorption spectra shown in Fig. 3. The indirect energy band gap E_{gi} of the single crystals is the value of $h\nu$ at $(\alpha h\nu)^{1/2} = 0$ by the extrapolation method from eq. (1). The indirect energy band gap E_{gi} at 6 K was found to be 2.348, 2.345, and 2.343 eV for SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals, respectively.

Fig. 5 shows the values of $(\alpha h\nu)^2$ plotted as a function of the incident photon energy hí. The direct energy band gap E_{gd} of the single crystals is the value of $h\nu$ at $(\alpha h\nu)^2 = 0$ by the extrapolation method. The direct energy band gap E_{gd} at 6 K was found to be 2.511, 2.505, and 2.503 eV for SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals, respectively.

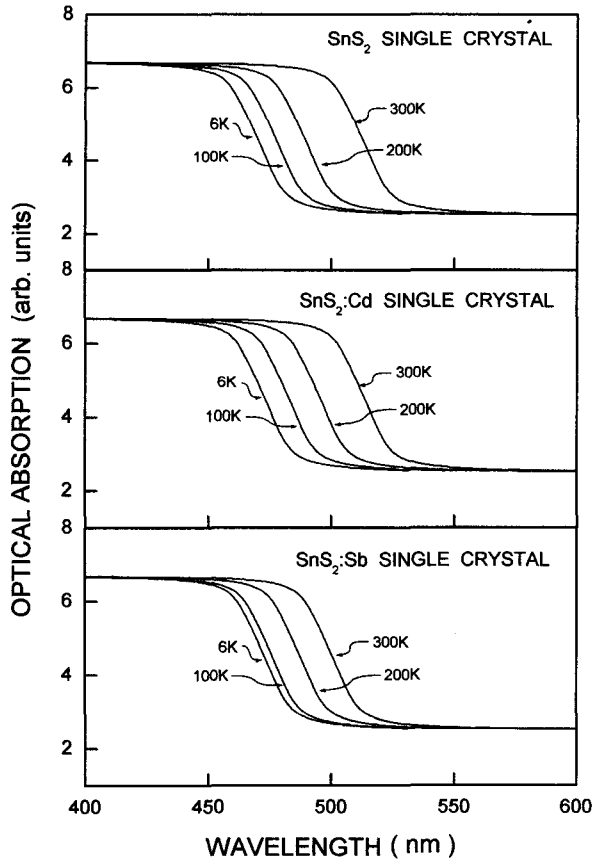

Fig. 3. Optical absorption spectra of the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals.

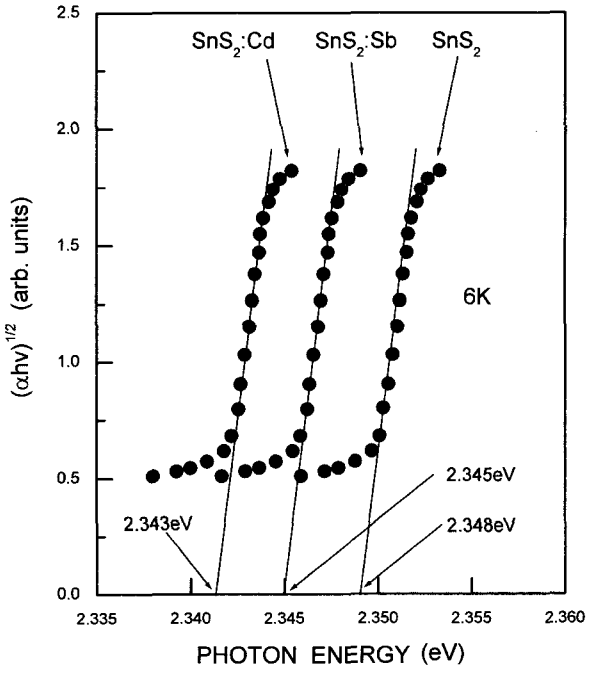

Fig. 4. Plots of $(\alpha h\nu)^{1/2}$ versus photon energy $h\nu$ for the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals.

The values of the indirect and the direct optical energy band gap of the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals were somewhat different from the previously reported values (the indirect gap of 2.07 eV[8] and the direct gap of 2.88 eV[9] for SnS_2). It is thought that the difference of the optical energy band gap is due to the difference of the composition of the SnS_2 single crystal, which occurred from the crystal growth process. Namely, The Sn-excessive SnS_2 single crystals are generally grown. Excessive Sn plays an important role as an impurity. Then, the energy band gap of the SnS_2 single crystals is greatly dependent on the quantity of excessive Sn. By doping Cd and Sn as impurities, the optical energy band gap of the SnS_2:Cd and SnS_2:Sb single crystals was decreased.

The indirect and the direct energy band gaps of the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals were investigated over the temperature range of 6300 K. The optical energy band gap increased with decreasing temperature. Temperature dependence of the indirect and direct energy band gap was well fitted by the Varshni equation[10]

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

where $E_g(0)$ and $E_g(T)$ are the optical energy band gaps at 0 K and T K, respectively, and á and â are constants. The values of $E_g(0)$, α, and β for the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals were obtained from fitting the measured optical energy band gaps by using eq. (2). For the indirect energy band gap, the values were found to be $E_g(0)$ = (2.338~2.342) eV, α= (-6.82×10^{-4} ~ -7.54×10^{-4}) eV/K, and α= (-79.1~-88.2) K. For the direct energy band gap, the values were found to be $E_g(0)$ = (2.499~2.511) eV, α= (-1.86×10^{-3} ~ -6.92×10^{-4}) eV/K, and α= (-134.1 ~ -1087.3) K. These values are listed in Table 2.

3.3 Photoluminescence of SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals

Fig. 6 shows PL spectra of the SnS_2 single crystal. Two PL emission peaks P1 and P2 with the peak energy of

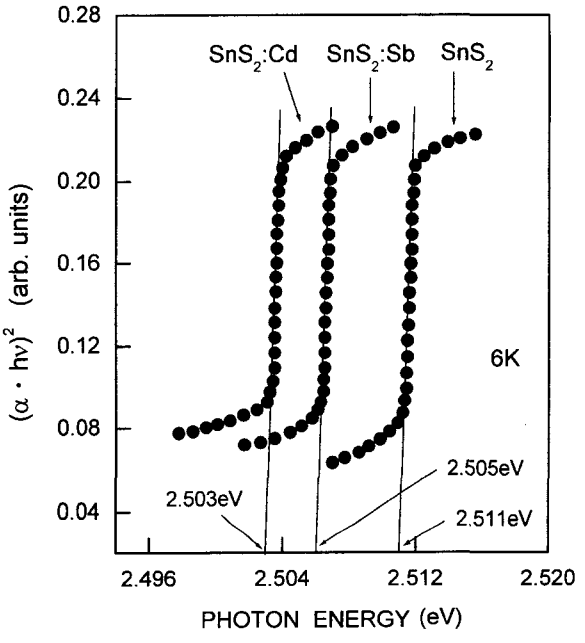

Fig. 5. Plots of $(\alpha h\nu)^2$ versus photon energy $h\nu$ for the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals.

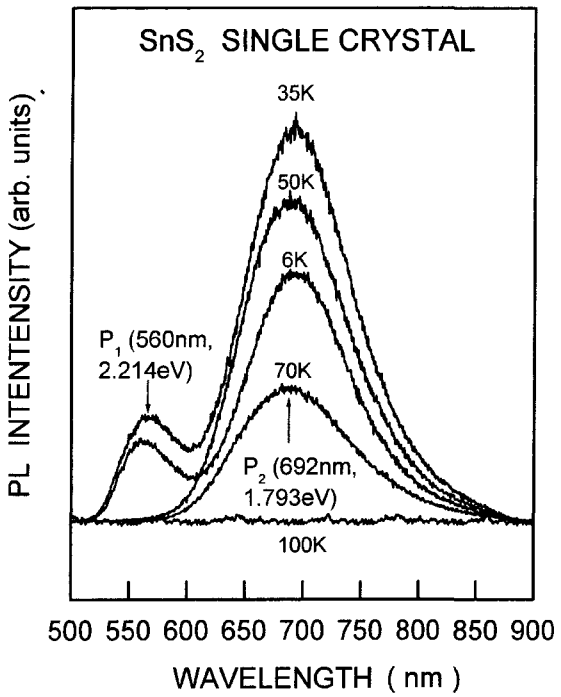

Fig. 6. Photoluminescence spectra of the SnS_2 single crystal.

Table 2. Values of Eg(0), α and β from the Varshni equation

Materials	Eg(0) (eV)		α (eV/k)		β (k)	
	Direct	Indirect	Direct	Indirect	Direct	Indirect
SnS_2	2.511	2.342	-1.86×10^{-3}	-7.54×10^{-4}	-1087.3	-88.2
SnS_2:Cd	2.499	2.338	-8.92×10^{-4}	-7.71×10^{-4}	-128.9	-79.1
SnS_2:Sb	2.502	2.339	-6.92×10^{-4}	-6.82×10^{-4}	-134.1	-84.6

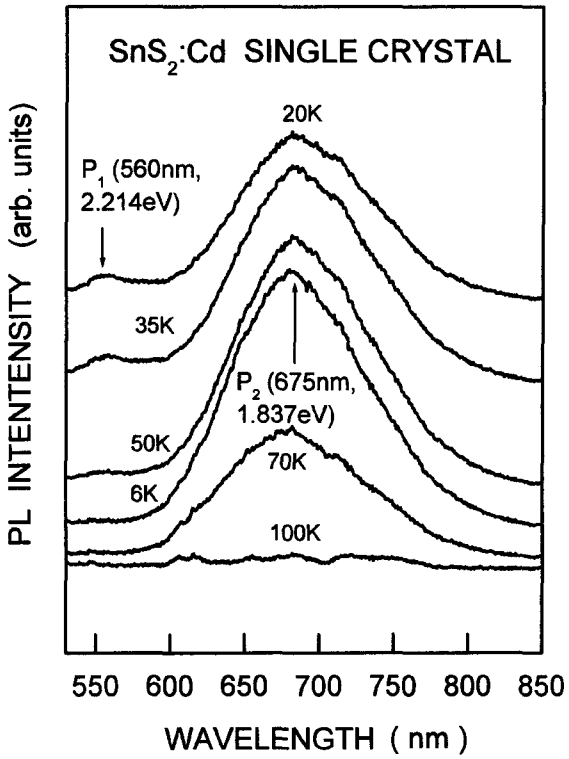

Fig. 7. Photoluminescence spectra of the SnS_2:Cd single crystal.

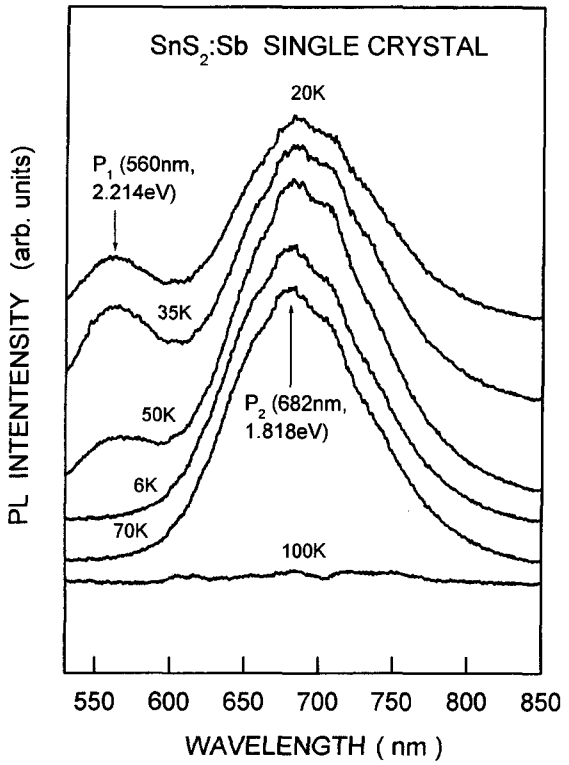

Fig. 8. Photoluminescence spectra of the SnS_2:Sb single crystal.

2.214 and 1.792 eV, respectively, were observed less than 50 K. The emission peak P1 disappeared above 40 K and the emission peak P2 also disappeared above 100 K. In the SnS_2:Cd single crystal, as shown in Fig. 7, the emission peak P1 with the peak energy of 2.214 eV disappeared above 35 K and 6 K. The emission peak P2 of the peak energy of 1.837 eV disappeared above 100 K. In the SnS_2:Sb single crystal, as shown in Fig. 8, the emission peak P1 with the peak energy of 2.214 eV disappeared above 70 K and 6 K. The emission peak P2 of the peak energy of 1.818 eV disappeared above 100 K.

Fig. 9 shows the thermoluminescence spectrum of the SnS_2 single crystal. Thermoluminescence peaks were observed at 100.29 K (D2 peak) and at 178.71 K (A2 peak). The activation energies were determined by the general order kinetic method.[5] The activation energy of the peaks was found to be 0.199 and 0.356 eV for the D2 and A2 peaks, respectively. Similar activation energies were obtained from the thermoluminescence spectra for the SnS_2:Cd and SnS_2:Sb single crystals.

The activation energies obtained from thermoluminescence spectra were also identified from thermally stimulated current spectra.[11] The lattice constants, the optical energy band gaps, and PL peak energies, and the deep levels of the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals are listed in Table 3. Exchanging the polarity of the electric

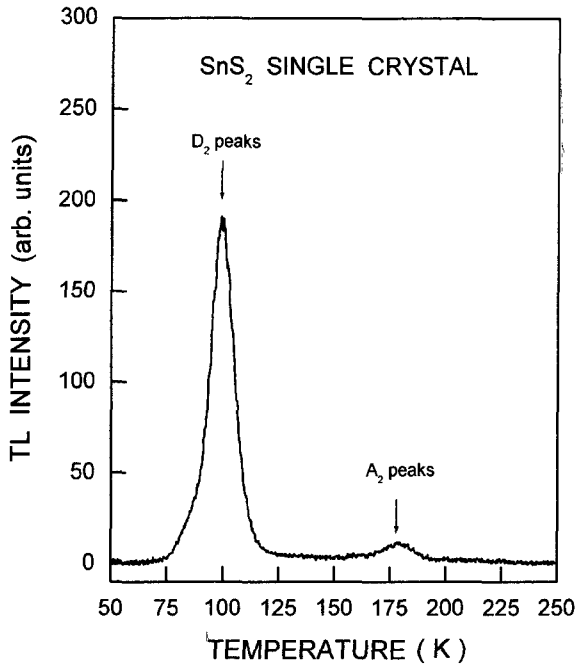

Fig. 9. Thermoluminescence spectrum of the SnS_2 single crystal.

Table 3. Lattice constants, optical energy gaps, emission peaks and deep levels of SnS_2, SnS_2: Cd, SnS_2: Sb, single crystals

Materials	Lattice constant (Å)		Energy Gaps (eV)		Emission Peaks (nm/eV)		Deep Level (eV)			
	a	c	Ei	Ed	P1	P2	D1	D2	A1	A2
SnS_2	3.637	5.882	2.348	2.511	560/2.214	692/1.793	0.019	0.199	0.115	0.356
SnS_2 :Cd	3.649	5.892	2.343	2.503	560/2.214	675/1.838	0.02	0.197	0.109	0.308
SnS_2 :Sb	3.675	5.784	2.345	2.505	560/2.214	681/1.822	0.019	0.197	0.112	0.326

field applied to the sample illuminated in proximity to a contact in the TSC measurement, the type of the deep levels A1, A2, D1, and D2 were determined. The deep levels A1 and A2 were acceptor levels and the deep levels D1 and D2 were donor levels.

Considering that the indirect optical energy band gap of the SnS_2 single crystal is 2.348 eV at 6 K, the donor levels are located at 0.019 and 0.199 eV, and the acceptor levels are located at 0.155 and 0.356 eV, we can suggest the energy band model of the SnS_2 single crystal as shown in Fig. 10. Then, the emission peak P1 with the peak energy of 2.214 eV in Fig. 6 can be assigned to the donor-acceptor pair emission due to the radiation recombination between the donor level D1 with the activation energy of 0.019 eV and the acceptor level A1 with the activation energy of 0.115 eV. The emission peak P2 with the peak energy of 1.792 eV can be assigned to the donor-acceptor pair emission due to the radiation recombination between the donor level D2 with the activation energy of 0.199 eV and the acceptor level A2 with the activation energy of 0.356 eV. Similarly,

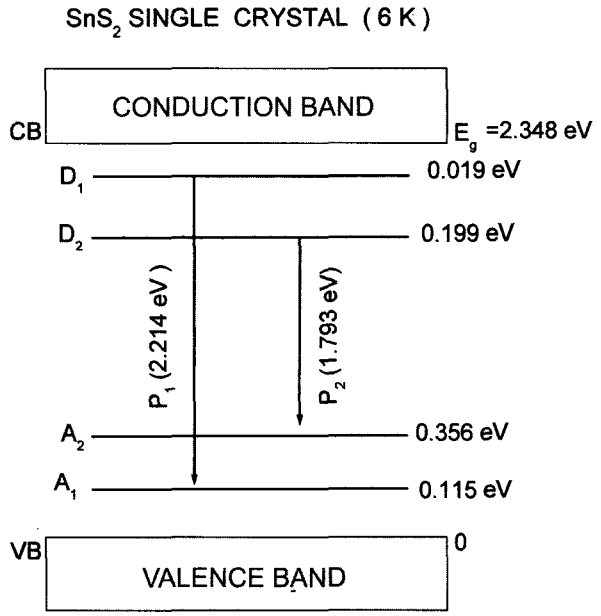

Fig. 10. The tentative transition model of photoluminescence processes in the SnS_2 single crystal.

the PL transition mechanism of the SnS_2:Cd and SnS_2:Sb single crystals can be described by using the energy band model shown in Fig. 10.

4. Conclusion

The SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals were grown by the chemical transport reaction method by using iodine as a transport agent. The single crystals with stoichiometric composition were grown in the starting material's mole ratio of Sn:S = 1:(2.84.0) because of the loss of S from Vaporization of sulfur during growing the single crystals. The indirect energy band gap at 6 K was found to be 2.348, 2.345, and 2.343 eV for the SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals, respectively. The direct energy band gap at 6 K was found to be 2.511, 2.505, and 2.503 eV for SnS_2, SnS_2:Cd, and SnS_2:Sb single crystals, respectively. The temperature dependence of the indirect and direct energy band gaps was well fitted by the Varshni equation over the temperature range of 6300 K. Two photoluminescence emission peaks with the peak energy of 2.214 and 1.792 eV for the SnS_2 single crystal, 2.214 and 1.837 eV for the SnS_2:Cd single crystal 2.214 and 1.818 eV for the SnS_2:Sb single crystal were observed. Based on the optical energy band gaps and the activation energies obtained from thermoluminescence spectra and thermally stimulated current spectra, the emission peaks were assigned to the donor-acceptor pair recombinations.

Acknowledgement

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