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Blue photoluminescence of α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+} single crystals

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α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+} single crystals were grown by the two-zone sublimation method. The optical energy gaps of α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+} at 10 K were found to be 3.440 and 3.392 eV, respectively. From the absorption spectra of α-Ga$_2$S$_3$:Fe^{2+}, the crystal field parameter Dq of 345 cm^{-1} and Racah parameters B of 700 and C of 3365 cm^{-1} were obtained for tetrahedral Fe^{2+} ions. From the photoluminescence spectra at 10 K, the blue and red emissions at 424 and 643 nm, respectively, for α-Ga$_2$S$_3$ and the violet and yellow emissions at 400 and 580 nm, respectively, for α-Ga$_2$S$_3$:Fe^{2+} were observed. All the emission lines observed in the photoluminescence spectra were identified. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1609254]

A wide band-gap semiconductor α-Ga$_2$S$_3$ is a promising material for blue-light emitting devices, because of its direct energy gap of about 3.4 eV at 300 K.[1–4] The photoluminescence (PL) properties of α-Ga$_2$S$_3$ have already been studied.[5–7] Aono and Kase reported on the PL emission of undoped and Ag, Cu, and Ge doped α-Ga$_2$S$_3$ crystals obtained by the iodine-transport chemical vapor deposition.[6,7] In the PL spectra of undoped crystals at 96 K, they observed a green emission peak at 520 (2.38 eV) and a broad red band ranging from about 590 to 826 nm with slight peaks at 629 and 725 nm. They described that Ga vacancy causes an electron trap at 0.40 eV (ground state) and at 0.70 eV (excited state) above the valence band. The green emission band has been interpreted as due to the electron transition from the iodine shallow donor to the excited state of the Ga vacancy. In the PL spectra of Ag, Cu, and Ge doped crystals at 94 K, the dominant emission peaks are observed at 496, 514, and 590 nm, respectively. However, any blue emission has not been reported in undoped crystals and also, the impurity optical absorption and PL properties of α-Ga$_2$S$_3$:Fe^{2+} have not yet been studied.

The purpose of this work is to investigate the optical absorption and PL properties of α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+} single crystals grown by the two-zone sublimation method in excess sulfur atmosphere. We present a blue emission for undoped α-Ga$_2$S$_3$. In addition, we perform the first investigation of the PL emission and the absorption structure due to tetrahedral Fe^{2+} ions of α-Ga$_2$S$_3$:Fe^{2+}. In order to clarify the origin of the PL band, the PL data are analyzed in terms of thermally stimulated current (TSC) and photoinduced current transient spectroscopy (PICTS).

α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+} single crystals were grown by the two-zone sublimation method in an excessive sulfur atmosphere. The constituent elements of Ga and S with purity 6N were used as starting materials. For α-Ga$_2$S$_3$ crystals, excessive sulfur of 5 mol % (sample S1), 10 mol % (sample S2), and 15 mol % (sample S3) were added to the starting materials. For α-Ga$_2$S$_3$:Fe^{2+}, excessive sulfur of 15 mol % and and FeS (purity 3N) weighed for Fe to be 1 mol % were added to the starting materials. A stoichiometric mixture was loaded in a quartz ampule, which was evacuated and sealed off under 1×10^{-6} Torr. In order to reduce the growth nuclei, the growth zone was cleaned by keeping the temperature of the growth and source zones at 820 and 600 °C, respectively, for two days. The single crystals were grown by keeping the temperature of the growth and source zones at 820 and 970 °C, respectively, for 25 days. The single crystals of sizes of about $1 \times 5 \times 8$ mm^3 were obtained.

Compositions of the single crystals were determined by energy dispersive analysis of x-ray (EDAX). The content of the dopant Fe in α-Ga$_2$S$_3$:Fe^{2+} was 0.014 mol %. The x-ray diffraction patterns were measured by x-ray diffractometer (Rigaku, DMAX-2000) and showed the crystals to be monoclinic. Optical absorption spectra were measured by using a uv-vis-nir spectrophotometer (Hitachi, U-3501) equipped with a cryogenic system (APD, SH-4). PL spectra were obtained by using the conventional measurement system consisting of a double monochromator (Spex 1403, $f = 0.85$ m), a photomultiplier tube (RCA, C31034), and a cryogenic sys-
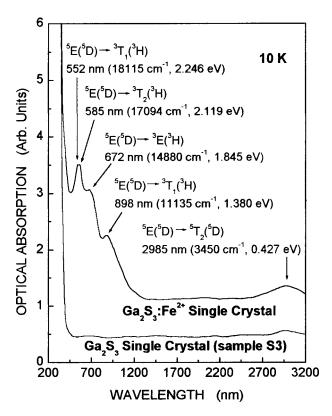
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FIG. 1. Optical absorption spectra of the α-Ga$_2$S$_3$ (sample S3) and α-Ga$_2$S$_3$:Fe^{2+} single crystals in the wavelength range 200–3200 nm at 10 K.

FIG. 2. Proposed energy level scheme of α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+} single crystals at 10 K.

tem (APD, SH-4) over the temperature range of 10–300 K. The 325 line of He–Cd laser (LiConix, 3650N) was used as an excitation source. The TSC and PICTS spectra were obtained by using a conventional measurement system.[8,9] The ohmic contacts for electrical measurements were provided by depositing indium on the surface of the sample.

The optical absorption spectra were measured in the wavelength range 200–3200 nm at 10 K. Typical absorption spectra of α-Ga$_2$S$_3$ (sample S3) and α-Ga$_2$S$_3$:Fe^{2+} are shown in Fig. 1. A rapid rise associated with direct interband transition is observed in high energy region on each sample. The optical energy gap (E_g) of a semiconductor with the direct band structure can be deduced from the relation $(\lambda h\nu)^2 \sim (h\nu - E_g)$,[10] where $h\nu$ is the incident photon energy and λ is the optical absorption coefficient near the fundamental absorption edge. In order to obtain the optical energy gap, $(\lambda h\nu)^2$ vs $h\nu$ curves were plotted, and then the values of E_g were obtained by extrapolation of $(\lambda h\nu)^2 = 0$. The energy gaps of α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+} were found to be 3.440 and 3.392 eV, respectively. These values agree well with those reported by Mushinskii *et al.*[2]

From the optical absorption spectrum of α-Ga$_2$S$_3$:Fe^{2+} (Fig. 1), we observed five impurity absorption peaks at 552, 585, 672, 898, and 2985 nm, which are due to Fe^{2+} ions sited in the T_d symmetry point.[11,12] From the crystal field theory,[13–15] the four higher energy peaks 552, 585, 672, and 898 nm are assigned to the transitions $^5E(^5D) \rightarrow ^3T_1(^3H)$, $^5E(^5D) \rightarrow ^3T_2(^3H)$, $^5E(^5D) \rightarrow ^3E(^3H)$, and $^5E(^5D) \rightarrow ^3T_1(^3H)$, respectively, and the lowest energy peak at 2985 nm is assigned to the transition $^5E(^5D) \rightarrow ^5T_2(^5D)$, as shown in the left part of Fig. 2. The crystal field parameter
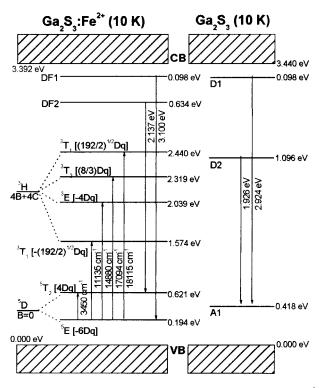
Dq of 345 cm^{-1} and Racah parameters B of 700 cm^{-1} and C of 3365 cm^{-1} were obtained for tetrahedral Fe^{2+} ions.

Figure 3 shows the PL spectra of α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+} in the wavelength range of 300–900 nm at 10 K. For α-Ga$_2$S$_3$, two broad emission peaks at 424 nm

FIG. 3. Photoluminescence spectra of α-Ga$_2$S$_3$ (samples S1, S2, and S3) and α-Ga$_2$S$_3$:Fe^{2+} single crystals in the wavelength range 300–900 nm at 10 K.

TABLE I. Activation energies and capture cross section of deep levels in the α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+} single crystals.

Material	Method	ΔE (eV)[a]	σ (cm^3)[b]	Type
α-Ga$_2$S$_3$	Thermal[c]	0.098		donor
	TSC	0.418	1.21×10^{-16}	acceptor
	PICTS	1.096	1.32×10^{-17}	donor
α-Ga$_2$S$_3$:Fe^{2+}	Thermal[c]	0.098		donor
	TSC	0.634	1.67×10^{-17}	acceptor

[a]Activation energy.
[b]Capture cross section.
[c]Thermal activation energy obtained from the temperature dependence of photoluminescence peak intensity.

(blue emission) and 643 nm (red emission) were observed. The blue emission in α-Ga$_2$S$_3$ has not yet been reported. For α-Ga$_2$S$_3$:Fe^{2+}, two broad emission peaks at 400 nm (violet emission) and 580 nm (yellow emission) were observed. As shown in Fig. 3, the blue emission in α-Ga$_2$S$_3$ showed the highest intensity in the sample S3 (the excessive S of 15 mol %). The positions of the emission peaks in α-Ga$_2$S$_3$:Fe^{2+} are different from ones in α-Ga$_2$S$_3$. The emission intensity in α-Ga$_2$S$_3$:Fe^{2+} was much smaller than that in α-Ga$_2$S$_3$. It could be thought that this is caused by the dopant Fe^{2+}.

In order to identify the transition mechanism of PL emissions, we investigated the deep levels of the crystals. From the temperature dependence of the emission intensity, the thermal activation energy (ΔE) of the blue and violet emission peaks was found to be 0.098 eV. This means that the blue and violet emission peaks are related with a deep level at 0.098 eV below the conduction band for α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+}, respectively. The activation energies and the capture cross section (σ) of deep levels were obtained from TSC and PICTS measurements and were listed in Table I. For α-Ga$_2$S$_3$, two deep levels are located at 0.418 eV above the valence band and 1.096 eV below the conduction band, which are assigned to acceptor and donor levels, respectively. For α-Ga$_2$S$_3$:Fe^{2+}, a deep level is located at 0.634 eV below the conduction band, which is assigned to donor level.

From the above experimental results, the transition mechanism of PL bands can be proposed as follows. The blue and red emissions in α-Ga$_2$S$_3$ are attributed to the elec-

tron transition from the donor levels located at 0.098 eV (D1) and 1.096 eV (D2) below the conduction band to the acceptor level located at 0.418 eV (A1) above the valence band, respectively, as shown in the right part of Fig. 2. The violet and yellow emissions in α-Ga$_2$S$_3$:Fe^{2+} are related to the impurity optical absorption peaks due to Fe^{2+} ions. Their transition mechanism of the emissions are indicated on the left-hand side of Fig. 2.

In summary, we present the optical absorption and PL properties of α-Ga$_2$S$_3$ and α-Ga$_2$S$_3$:Fe^{2+}. For α-Ga$_2$S$_3$:Fe^{2+}, impurity absorption due to the tetrahedral Fe^{2+} was obtained and analyzed. From the PL spectra at 10 K, blue and red emissions for α-Ga$_2$S$_3$ and violet and yellow emissions for α-Ga$_2$S$_3$:Fe^{2+} were observed. Based on the experimental results on deep levels, the transition mechanism of the emissions was identified.

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