Crystal Growth and Polarized Photoluminescence Spectra in Ce-Doped Single Crystal of $SrGa_2S_4$

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Polarized photoluminescence (PL) spectra were measured in single crystal of $SrGa_2S_4$:Ce prepared by chemical vapor transport technique. A PL band with double peaks at 450 and 493 nm showed strong polarization dependence in shapes and intensities between $E \parallel c$ and $E \perp c$ polarizations. The PL spectra have been discussed in the framework of the crystal-field theory by which the two peaks have been assigned to transitions between crystal-field and L-S coupling multiplets of 5d- and 4f-states of Ce^{3+} in D_{4h} symmetry. Polarized PL spectra calculated on the basis of the crystal-field theory show good agreement with the experimental ones. From these results we suggest a possibility of controlling the chromaticity in blue electroluminescent (EL) phosphors using epitaxial films with well-defined growth orientation.

KEYWORDS: $SrGa_2S_4$ thiogallate, Ce rare-earth ions, single crystals, polarized photoluminescence, crystal-field theory, electroluminescent display, chromaticity

1. Introduction

In recent years MGa_2S_4 (M=Sr, Ca, Ba)-type thiogallates have been attracting much interest as new host materials for electroluminescent (EL) displays, among which Ce-doped $SrGa_2S_4$ ($SrGa_2S_4$:Ce) has been known to emit a pure blue light suitable for full color EL display application.[1-4] The ternary compound $SrGa_2S_4$ crystallizes in an orthorhombic structure, the space group being D_{2h}^{24}-Fddd with lattice constants $a = 20.840$ Å, $b = 20.495$ Å and $c = 12.212$ Å[5] or $a = 20.932$ Å, $b = 20.549$ Å and $c = 12.227$ Å,[6] suggesting the presence of strong optical anisotropy in this material. In addition, the ternary compound possesses several nonequivalent cation sites, the Sr atoms being placed in the distorted antiprismatic spacings and the Ga atoms being situated in the regular tetrahedral spacings. No detailed fundamental data of electronic structures and anisotropic optical properties have been reported thus far. It is still under dispute which of these cation sites rare-earth ions prefer to occupy. In order to elucidate these problems, it is necessary to work on well-defined single crystals. However, most of the previous optical and electrical researches on this material have been carried out in powder phosphors or polycrystalline thin films.[1-4,7] We therefore prepared single crystals of $SrGa_2S_4$ doped with Ce by a chemical vapor transport (CVT) technique and measured polarized photoluminescence (PL) spectra for the first time, which have provided important information on the site occupied by the rare-earth ion, as well as the electronic structures relating to the Ce^{3+} ion.

Prior to single-crystal growth experiments, polycrystalline powder of $SrGa_2S_4$ was prepared by a solid-state reaction by sintering a mixture of Ce(1 mol%)-doped SrS and Ga_2S_3 powder at 900°C for 7 days. The polycrystalline powder obtained was analyzed by X-ray diffraction (XRD). The XRD pattern showed a fairly good agreement with the previously reported result of a theoretical calculation.[5] The polycrystalline powder thus obtained was sealed in vacuum in a silica ampoule with an inner diameter of 13 mm and length of 20 cm, together with iodine (10 mg/cm^3 of inner volume of the crucible) as a transporting agent. The ampoule was placed in a two-zone furnace, where the temperature of the source zone was kept at 900°C and that of the growth zone at 700°C. The period of transport was 10 days.

Using these procedures, needle-like single crystals with a typical size of $2-4\times0.1\times0.3$ mm^3 were obtained. All of the Ce-doped crystals obtained were transparent and had several well-developed planes. The XRD analysis was used to determine the crystal axis. The major plane of the resulting crystals was determined to be {100}, which included the c-axis in-plane, while edge planes were indexed as (311) and (3-1 1). The direction of the c-axis was determined from crystal habit. Figure 1 shows an optical micrograph of the crystal, viewed perpendicular to the (100) plane. The angle between two edge planes (311) and (3-1 1) is 118.4° (=59.2° × 2). This value of 59.2° is correcily corresponding to arctan (b/c). Therefore the direction of the c-axis is determined exactly.

Polarized photoluminescence (PL) spectra were mea-

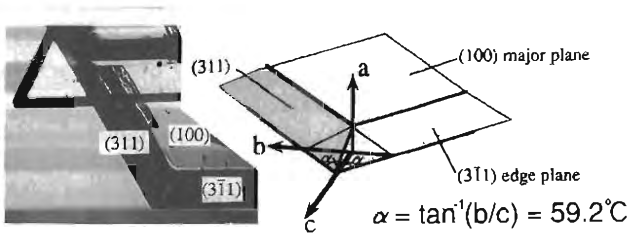

Fig. 1. An optical micrograph of $SrGa_2S_4$ single crystal, viewed perpendicular to the (100) plane, showing a process of c-axis determination.

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sured in the temperature range between 75 K and 300 K. The 325-nm line of the He–Cd laser (10 mW power) was employed as an excitation source, with the samples being put into an Oxford Instruments continuous-flow cryostat. The emitted PL was polarized by a Glan-Thomson prism polarizer to align the direction (E) of the transmission axis to 0° ($E \parallel c$) and 90° ($E \perp c$) with the crystal c-axis, with each of the polarized spectra being referred to in the following text as π- and σ-spectrum, respectively. The emitted PL was dispersed by a JASCO CT-25C monochromator with a focal length (FL) of 25 cm and a 1200 groove/mm grating blazed at 750 nm, and detected by a Hamamatsu R928 photomultiplier (PM). To avoid the polarization problem of the monochromator, the polarized light was passed through a Kogakugiken achromatic quarter wave plate, the direction of the transmission axis of which was set at 45° from the plane of incidence to make circular polarization.

Figure 2 shows polarized PL spectra of the $SrGa_2S_4$:Ce single crystal measured at 75 K, 170 K and 290 K. An emission band with two well-resolved peaks labeled A and B at 450 nm and 493 nm, respectively, was observed at 75 K. The maximum PL intensity in $\sigma(E \perp c)$ polarization was stronger by a factor of two than that in $\pi(E \parallel c)$ polarization. This polarization dependence holds throughout the temperature range of measurement. The ratio of the emission intensity of A band to that of B band (A:B) is different for σ and π polarizations. The A:B ratio for σ polarization gradually increased as the temperature was increased; A:B=100:75 (75 K), 100:79 (170 K) and 100:89 (290 K), while that for π polarization remained approximately constant; A:B=100:39 (75 K), 100:40 (170 K) and 100:41 (290 K).

The emissions of A band and B band have been attributed to the transitions from the 5d (T_{2g}) state to the 4f($^2F_{5/2}$) and 4f($^2F_{7/2}$) states, respectively. Peters and Baglio have shown that the Ce^{3+} ion can substitute for Sr^{2+} site in $SrGa_2S_4$ phases, the charge compensation being satisfied by sodium ions.[5] As described earlier the Ga ions are surrounded by a regular arrangement of sulfur tetrahedron. If the rare-earth ion occupies the Ga site (Td) no polarization dependence can be expected, which is inconsistent with the experiment. We therefore assume that the Ce^{3+} ion can substitute for Sr^{2+} site, where the charge compensation is satisfied by the introduction of cation vacancies in our case.

In $SrGa_2S_4$ crystals, Sr cations occupy sites surrounded by square antiprimatic sheets consisting of sulfur ions.[6] Since atomic distances of Sr-S in three inequivalent Sr sites take almost the same value of 3.1 Å, we can neglect the slight difference of these three sites and assume a symmetry surrounding the Sr ion sites as D_{4h}. We therefore assume the site symmetry of the Ce^{3+} ion occupying the Sr site to be D_{4h}.

In the following, we interpret the experimental polarized PL spectra in terms of the selection rules of the spin-allowed electric dipole transition between 5d and 4f states. The 4f orbitals of the Ce^{3+} ion incorporated in the crystal lattice are electrically screened by $5s^25p^6$ electrons, whereas the 5d orbitals are affected by a crystal field by which the 5d level is split into the E_g and T_{2g} by

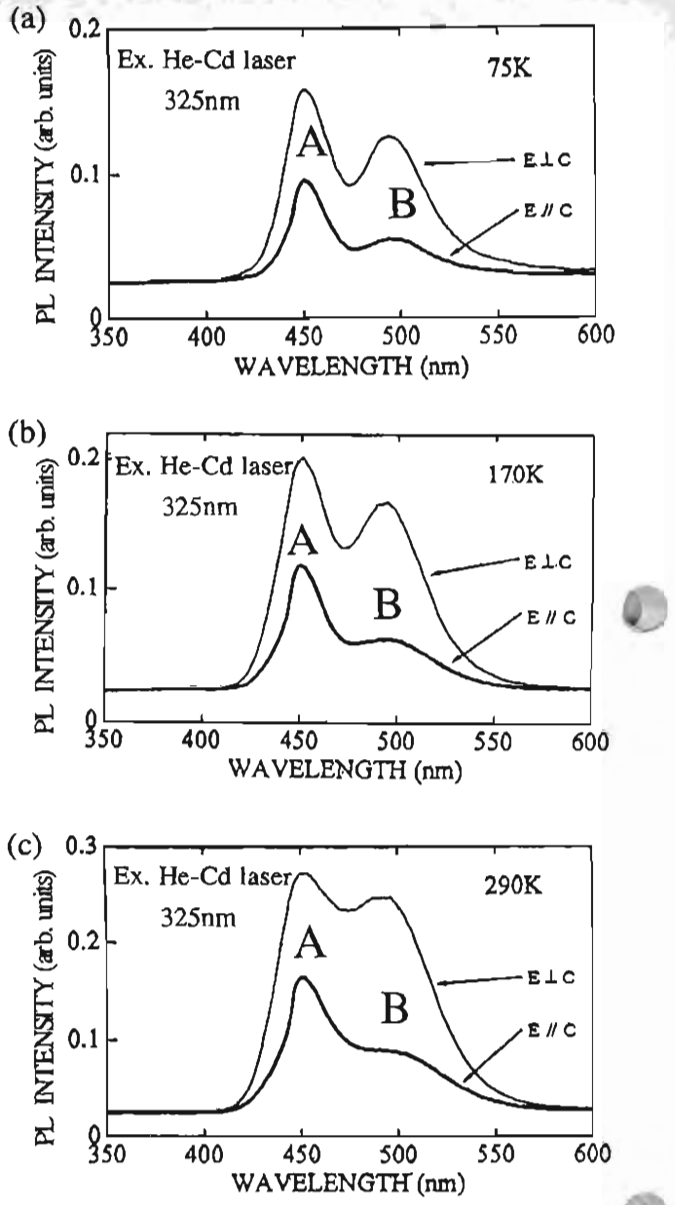

Fig. 2. Polarized PL spectra of $SrGa_2S_4$:Ce single crystal at temperatures (a) 75 K, (b) 170 K and (c) 290 K.

the cubic crystal field. The 4f level is split by spin-orbit interaction into LS-coupling multiplets $^2F_{7/2}$ and $^2F_{5/2}$ which in turn are split into respective substrates Γ_6, Γ_7, Γ_8 and Γ_7, Γ_8 by the cubic crystal field (Oh), and the Γ_8 sublevel is further split by the tetragonal crystal field (D_{4h}) into Γ_6 and Γ_7 sublevels. On the other hand, the T_{2g} states of 5d electrons are split into Γ_4 and Γ_5 due to a low symmetry component (D_{4h}) of the crystal field. The spin-orbit interaction further lifts the degeneracy of these levels into one Γ_6 and two Γ_7 states.

The energy level diagrams of 4f and 5d configurations in the Ce^{3+} ion discussed above are illustrated in Fig. 3. According to ref. 8, it is described that in the case of 5d ions surrounded by hexahedron of anions like the present case, T_{2g} comes above E_g. However the preliminary calculation based on this assumption cannot reproduce the polarization-dependent spectrum observed in the experiment. We therefore assumed that energy level of the T_{2g} state lies below the E_g state as shown in Fig. 3.

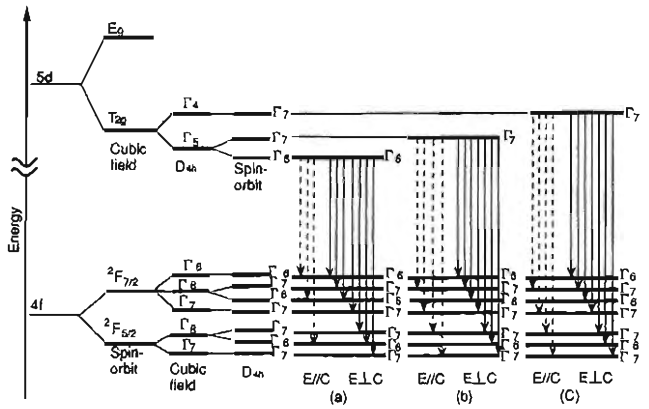

Fig. 3. Energy level diagrams of the Ce^{3+} ion in D_{4h} symmetry. Transitions for three cases of initial state (a) $5dT_{2g}\Gamma_5\Gamma_6$, (b) $5dT_{2g}\Gamma_5\Gamma_7$ and (c) $5dT_{2g}\Gamma_4\Gamma_7$ are shown, where solid and dashed arrows represent $\sigma(E \perp c)$ and $\pi(E \parallel c)$ polarizations, respectively.

Since relative energy positions of the Γ_6 and Γ_7 states cannot be determined only by symmetry considerations, we show three cases. In this figure, transitions are shown for the three cases of initial state (a) $5dT_{2g}\Gamma_5\Gamma_6$, (b) $5dT_{2g}\Gamma_5\Gamma_7$ and (c) $5dT_{2g}\Gamma_4\Gamma_7$. Electric dipole-allowed transitions for $\sigma(E \perp c)$ and $\pi(E \parallel c)$ polarizations are shown by solid and dashed arrows, respectively. Using Wigner-Eckart's theorem, we made a rough estimate of polarization-dependent spectra as shown in Fig. 4, details of which will be published later. In Fig. 4, we show calculated spectra for the cases (a), (b) and (c). In this calculation, energy splitting in the $^2F_{7/2}$ and $^2F_{5/2}$ states is neglected. The half-width of the simulated spectra is suitably selected to give the best fit to the observed spectra; full width at half maximum (FWHM) of lines is 180 meV. Rough features of the observed polarized spectra can be reproduced by the case (a) in which the $5dT_{2g}\Gamma_5\Gamma_6$ state is the lowest excited state: the simulated PL intensity ratio A:B is 100:54 for $\sigma(E \perp c)$ polarization and the ratio of σ:π is 100:62, which is in fair agreement with the observed polarization ratio. The calculated A:B ratio for σ-polarization is quite different from observed spectra if one assumes $5dT_{2g}\Gamma_5\Gamma_7$ or $5dT_{2g}\Gamma_4\Gamma_7$ as the initial state, as in (b) or (c).

A qualitative explanation of the temperature dependence of the emission intensity ratio (A:B) for $E \perp c$ can be given in terms of the Boltzmann distribution in higher excited state $5dT_{2g}\Gamma_5\Gamma_7$ or $5dT_{2g}\Gamma_4\Gamma_7$. Higher temperatures bring about an increased contribution from the transitions originating from the higher excited states ($5dT_{2g}\Gamma_5\Gamma_7$ or $5dT_{2g}\Gamma_4\Gamma_7$) compared to those originating from the lower state ($5dT_{2g}\Gamma_5\Gamma_6$).

Observation of polarization-dependent PL spectra in $SrGa_2S_4$:Ce leads to a proposal of a practical application, i.e., a possibility of changing the chromaticity of emission by the use of a polarizer, since the emitted light in the $\pi(E \parallel c)$ spectrum is close to pure blue in the Commission International de l'Eclairage (CIE) color coordinates, whereas that in the $\sigma(E \perp c)$ spectrum is close to blue-green. We may be able to apply the proposal to EL display devices if we can grow an epitaxial single-crystalline

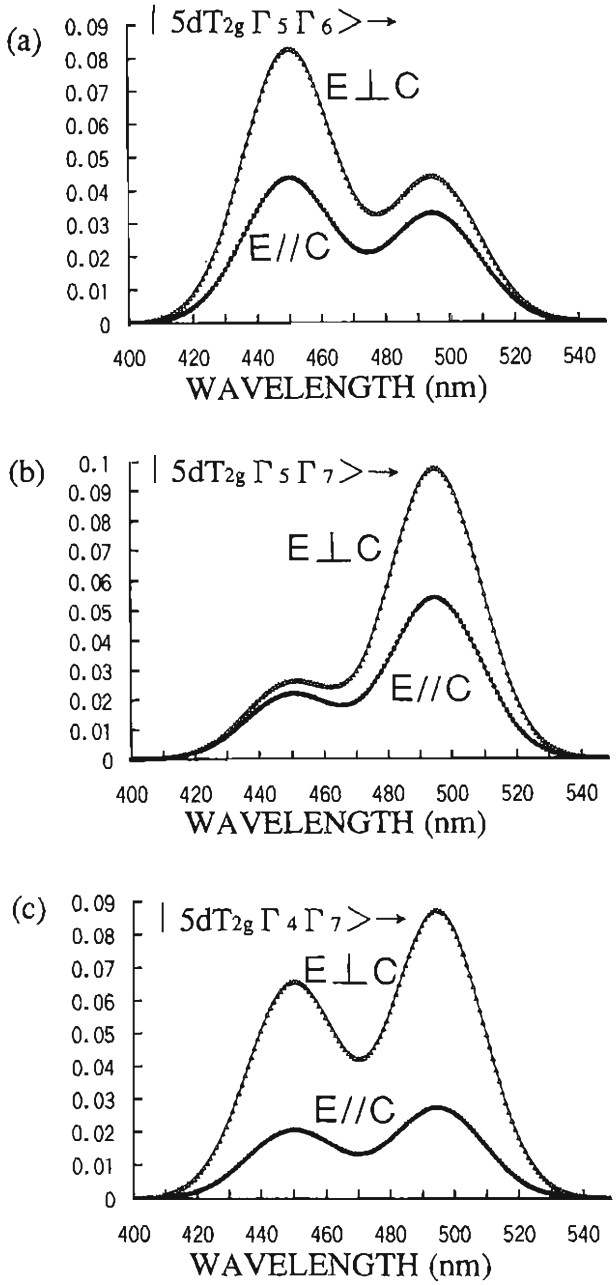

Fig. 4. Spectra simulated by two Gaussian lines with intensities given by the calculation using Wigner-Eckart's theorem assuming (a) $5dT_{2g}\Gamma_5\Gamma_6$, (b) $5dT_{2g}\Gamma_5\Gamma_7$ and (c) $5dT_{2g}\Gamma_4\Gamma_7$ for as the initial state of transitions.

film with an in-plane c-axis orientation. We believe that control of c-axis orientation is possible if suitable substrate materials are selected, since most of the polycrystalline thin films prepared by MBE, sputtering and other techniques show {100} preferred orientation.

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