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Optical properties of europium ions in SrB₂O₄ crystal

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Abstract. We investigate absorption, emission and excitation properties of an SrB₂O₄:Eu crystal grown from the melt using the Czochralski method. Eu²⁺ absorption and Eu³⁺ emission spectra are obtained. The five broad absorption bands peaking at 344, 288, 259, 235 and 212 nm correspond to the transitions from the 4f⁷(⁸S_{7/2}) ground state to the excited states of the 4f⁶5d configuration of Eu²⁺. Several zero-phonon lines for the different 4f⁶(⁷F_J) levels of the lowest 4f⁶5d excited state are observed in the absorption spectrum measured at 10 K. The deep-orange luminescence in the 578–640 nm region is due to the transition from the ⁵D₀ excited state to the ⁷F_J (*J* = 0, 1 and 2) states of Eu³⁺. Eu²⁺ does not give rise to luminescence, even at 10 K, because of the photoionization in the excited state, followed by a nonradiative return to the ground state of Eu²⁺. The strong emission due to the ⁵D₀ → ⁷F₀ transition and the existence of different sites of Eu³⁺ for Sr²⁺ are explained by the charge compensation and structural characteristic of SrB₂O₄.

1. Introduction

Optical properties of europium ions in strontium borates, such as SrB₂O₄, Sr₂B₂O₅, SrB₄O₇, Sr₃B₂O₆ and SrB₆O₁₀, have been extensively investigated [1–7]. It is known that Eu²⁺ ion is present together with Eu³⁺ ions in these compounds and that the Eu²⁺ gives rise to a UV–blue luminescence, while the Eu³⁺ gives rise to a red luminescence. Not only Eu²⁺ ions but also Eu³⁺ ions are substituted for Sr²⁺ ions. The ratio of the concentration of Eu²⁺ to that of Eu³⁺ depends on a variety of borates and the preparation conditions of the compounds. For example, Eu³⁺ is easily transformed to Eu²⁺ when a reducing agent, H₂–N₂ or H₂ atmosphere, is used in the process of sample preparation [1, 2, 4–6]. Luminescence due to the Eu²⁺ ions in strontium metaborate, SrB₂O₄, was reported by Machida *et al* [1]. In contrast to their result, Schipper *et al* [6] reported no Eu²⁺ luminescence, but only Eu³⁺ luminescence. As a consequence, Schipper *et al* argued that no Eu²⁺ ion is present in europium doped SrB₂O₄. It has not been established which of these results is correct. The present study clarifies this point. Here we study, for the first time to our knowledge, absorption and luminescence properties of Eu²⁺ and Eu³⁺ in single crystal of SrB₂O₄.

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2. Experimental procedure and results

A single crystal of SrB₂O₄ doped with europium ions was grown from the melt in air by the Czochralski method. No reducing agents were used in the process of crystal growth. 0.5 mol% europium ions were added to the melt. The growth process was similar to that of pure SrB₂O₄ crystal demonstrated in detail [8]. Absorption spectra at room temperature were measured with a Cary-5E spectrophotometer with a resolution of 0.02 nm. In order to obtain 10 K absorption spectra, the white light from a 250 W tungsten halogen lamp was employed. The white light, which passed through the sample, was directly fed into a 75 cm monochromator. Luminescence spectra were obtained by exciting the sample with a third harmonic (355 nm) of a pulsed Nd:YAG laser. Excitation measurement was performed with a 300 W Xe arc lamp passed through a 25 cm monochromator. The sample was placed in a liquid helium flow cryostat for measurements in the variable-temperature region (10–300 K). The luminescence from the sample was collected at right angles to the excitation beam and then sent to a suitably filtered Hamamatsu R928 photomultiplier tube (PMT) attached at the exit slit of a 75 cm monochromator. The slit widths of the 75 cm monochromator were normally set to give a resolution of 0.025 nm. The luminescence and absorption signals from the PMT were read out by a digital oscilloscope or a current amplifier.

The as-grown SrB₂O₄:Eu crystal was colourless and transparent. The grown crystal had an orthorhombic shape with 6 mm thickness, 12 mm width and 35 mm length. It could be readily separated by mechanical stress into very thin leaves along the (100) plane or fine threads along the *c*-axis. SrB₂O₄ [9] is isostructural with CaB₂O₄ [10] and EuB₂O₄ [11], which consist of chains with slightly puckered infinite (B₂O₄)_{*n*}^{2*n*-} layers extending parallel to a *c*-axis. The cleavage is due to the chain structure of SrB₂O₄. The Sr²⁺ ion is coordinated by eight oxygen ions that belong to four non-equivalent neighbouring chains. Sr²⁺ ions are located in (010) and (020) planes in which no other ion is positioned between neighbouring Sr²⁺ ions. The distance between Sr planes is 6.01 Å. The (B₂O₄)_{*n*}^{2*n*-} layers lie perpendicularly between the Sr planes. The Sr²⁺ ion is surrounded by six nearest neighbours and six next-nearest neighbours in the Sr plane. The distances are 3.89, 4.00 and 4.34 Å to the nearest neighbours and 6.59, 7.20 and 7.39 Å to the next-nearest neighbours. The Sr²⁺ ion has the other eight next-nearest neighbours in the next Sr planes with the distances of 6.41 and 6.87 Å. The ionic radii of Sr²⁺, Eu²⁺ and Eu³⁺ ions are 1.40, 1.39 and 1.21 Å for eightfold coordination of oxygen, respectively [12]. The Eu²⁺ and Sr²⁺ ions have almost the same size. This suggests that the Eu²⁺ ions are undoubtedly substituted for Sr²⁺ ions. When Eu³⁺ ions are introduced into SrB₂O₄, three Sr²⁺ ions are replaced by two Eu³⁺ ions and a vacancy for charge compensation.

Figure 1(a) shows the optical absorption spectra of pure (dashed line) and doped (solid line) crystals at room temperature. The absorption of the pure crystal increases gradually with decreasing wavelength and shows a steep slope from about 250 nm. In the case of the doped crystal we observe the structured strong absorption bands corresponding to the parity allowed electric dipole transition from the 4f⁷(⁸S_{7/2}) ground state to the excited states of the 4f⁶5d configuration of Eu²⁺ in which the background absorption of the host crystal is superimposed. The Eu³⁺ absorption was not observed in the temperature range 10–300 K. This is mainly due to the weak transition probability of the parity forbidden electric dipole transition of the Eu³⁺ ion in comparison with the parity allowed transition of the Eu²⁺ ion. The structured 4f⁶5d configuration of Eu²⁺ consists of five bands with maxima at 29 100, 34 700, 38 600, 42 600, 47 200 cm⁻¹ (corresponding to 344, 288, 259, 235 and 212 nm in wavelength, respectively). This is clear from the spectrum (refer to figure 1(b)) obtained by subtracting background due to the host crystal. The maximum absorption of Eu²⁺ is found at 235 nm. In cubic symmetry, the excited states of the 4f⁶5d configuration consist of doubly degenerate E and triply degenerate

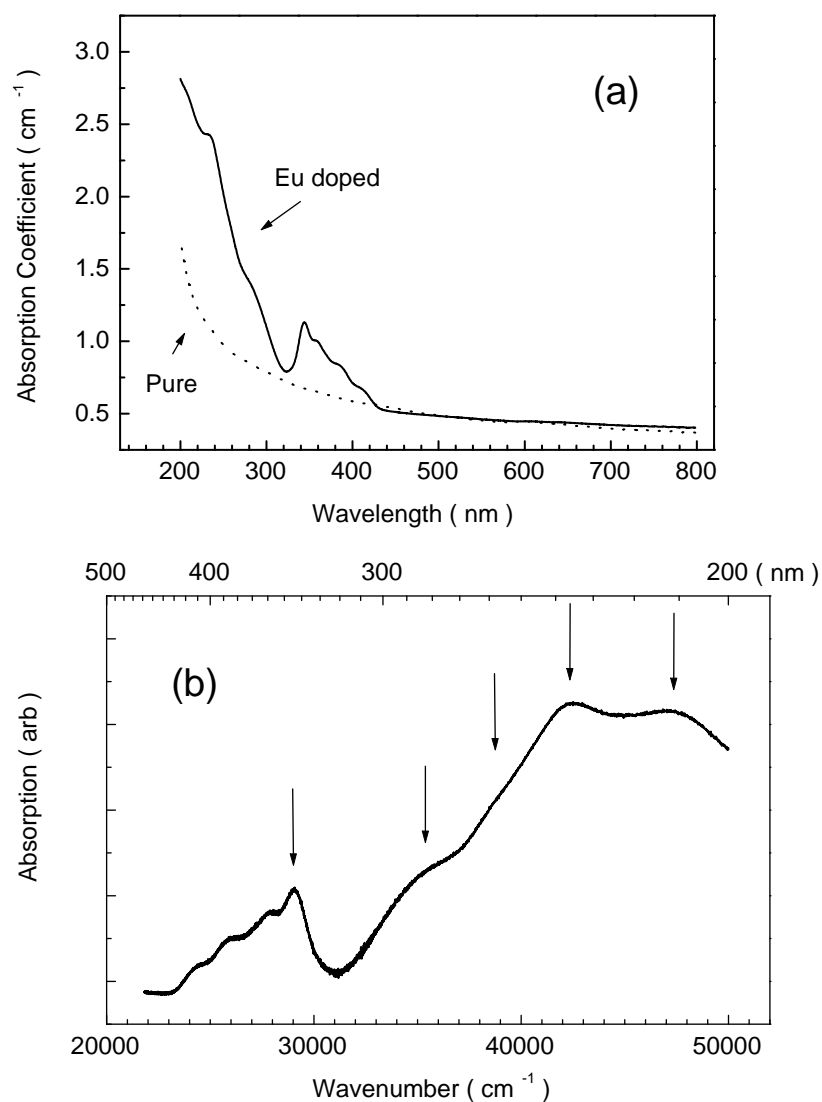


Figure 1. (a) Optical absorption spectra of pure (dashed line) and europium doped (solid line) SrB₂O₄ at 296 K. (b) Extended spectrum of figure 1(a) in the 22 000–50 000 cm⁻¹ (455–200 nm) region. The background due to the host crystal is subtracted. The arrows indicate five bands of the 4f⁶5d configuration of Eu²⁺ with maxima at 29 100, 34 700, 38 600, 42 600, 47 200 cm⁻¹.

T levels. These levels are split completely into five levels by the crystal field acting on the Eu²⁺ ion with the lowest symmetry, C₁, in SrB₂O₄. The separation between the highest and lowest levels is about 18 100 cm⁻¹, which is estimated from the separation between the 212 and 344 nm bands.

The lowest absorption band of the 4f⁶5d configuration extending from about 425 to 325 nm has a characteristic fine structure whereas the higher four bands are unstructured. The fine structure is the result of the weak coupling of the 5d electron with the ⁷F_J states of the 4f⁶ core electrons [13]. The lack of structure of the higher bands is usual because the higher

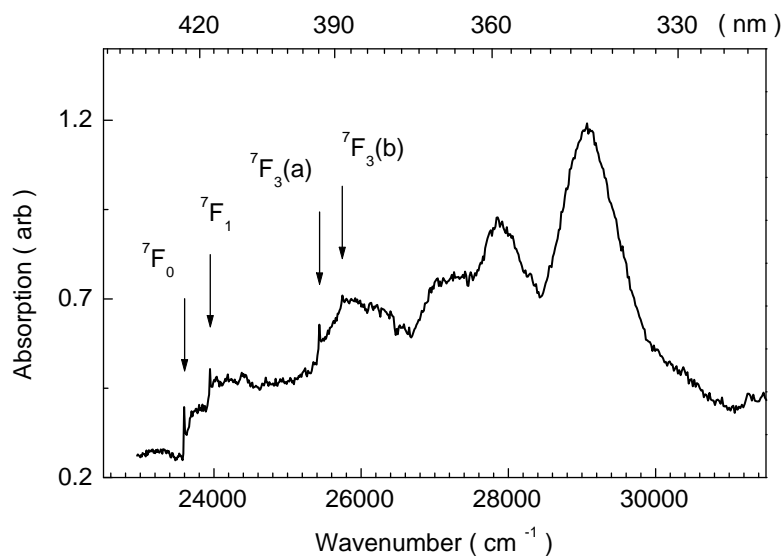


Figure 2. Absorption spectrum in the 22 500–31 500 cm^{-1} region at 10 K. The assignment of the zero-phonon lines for different 7F_J levels of the lowest $4f^6({}^7F_J)5d$ state is indicated in the figure. The two 7F_3 zero-phonon lines are labelled by a and b.

bands vibrationally couple more strongly to the 7F_J states of the $4f^6$ core electrons. The absorption spectrum obtained at 10 K (refer to figure 2) shows better resolved structure. The total width of the 7F_J ($J = 1, 2, 3, 4, 5$ and 6) states is about 5270 cm^{-1} that is similar to the values early reported on the other hosts [12–15] and is in good agreement with the theoretical value of about 5100 cm^{-1} for the splitting of the 7F_J states of the Eu^{3+} free ion [16].

We observe the zero-phonon lines, which are attributed to the transitions from the $4f^7({}^8S_{7/2})$ ground state to the different 7F_J levels of the lowest $4f^6({}^7F_J)5d$ excited state, as indicated by arrows in figure 2. The 7F_0 zero-phonon line, which is the onset of the $4f^65d$ absorption bands, is observed at 423.8 nm. One 7F_1 zero-phonon line and two 7F_3 zero-phonon lines are observed at 417.6, 393.2 and 388.5 nm, respectively. Zero-phonon lines for the 7F_2 level and the higher lying 7F_J levels were not clearly resolved in the absorption spectrum due to the limitations of instrument and temperature variation below 10 K. The assignment of the zero-phonon lines is based on the theoretical splitting of the $4f^6$ configuration of Eu^{3+} . The separation between the 7F_0 and 7F_1 zero-phonon lines is 352 cm^{-1} .

Under the 355 nm excitation the $\text{SrB}_2\text{O}_4:\text{Eu}$ crystal shows a deep-orange luminescence as shown in figure 3(a). The spectrum reveals only emission from Eu^{3+} ions. The Eu^{2+} luminescence was not detected in the temperature range 10–300 K, although the excitation takes place in the $4f^65d$ band of Eu^{2+} (refer to figure 1 and 2). Figure 4 shows the excitation spectrum for the 614.3 nm luminescence of Eu^{3+} at 10 K. We assign the excitation line at 462.5 nm to the ${}^7F_0 \rightarrow {}^5D_2$ transition, while the excitation lines at 392.5 and 400.0 nm to the ${}^7F_0 \rightarrow {}^5L_6$ transition. The broad excitation band appearing in the 355–385 nm region consists of at least three excitation lines and it is overlapped with the $\text{Eu}^{3+}-\text{O}^{2-}$ charge transfer band. These excitation lines are assigned to the transitions from the 7F_0 state to the 5D_4 and 5G_3 states [17]. An excitation line due to the ${}^7F_0 \rightarrow {}^5D_3$ transition is expected to appear between the lines due to the ${}^7F_0 \rightarrow {}^5D_2$ and ${}^7F_0 \rightarrow {}^5L_6$ transitions, but it was not observed clearly, presumably because it was too weak.

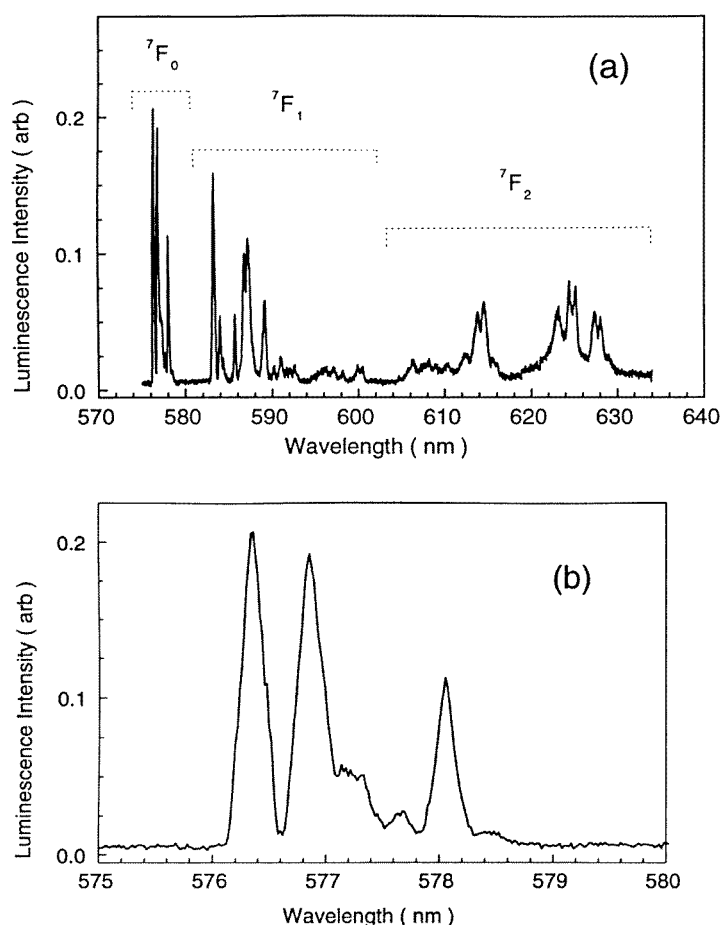


Figure 3. (a) Emission spectrum of Eu³⁺ obtained under the 355 nm laser excitation at 10 K. The transitions from the ⁵D₀ to different ⁷F_{*J*} (*J* = 0, 1 and 2) levels are indicated. (b) Extended emission spectrum of figure 3(a) in the wavelength range from 575 to 580 nm corresponding to the ⁵D₀ → ⁷F₀ transition.

The emission lines in the 575–634 nm region are assigned to the transitions from the ⁵D₀ state to the ⁷F₀, ⁷F₁ and ⁷F₂ states of Eu³⁺ as indicated in figure 3(a). Emission from the energy states higher than ⁵D₀ was not observed due to multiphonon relaxation to the emitting ⁵D₀ state. The relaxation is ascribed to high vibrational frequency in this lattice; especially the (B₂O₄)_{*n*}^{2*n*-} chains give rise to high vibrational energy up to about 1500 cm⁻¹ [18]. It is interesting to note two spectral features in the emission spectrum.

First, a number of lines appear unexpectedly in the spectrum. The ⁷F_{*J*} state of Eu³⁺ is split into 2*J* + 1 levels for C₁ symmetry of Eu³⁺, i.e. the ⁷F₀, ⁷F₁ and ⁷F₂ states split into one, three and five levels, respectively [19]. The excited ⁵D₀ and ground ⁷F₀ states are both singlets well separated from other levels. A single emission line should be identified for the ⁵D₀ → ⁷F₀ transition if the Eu³⁺ ions have a single substitution site for Sr²⁺. Since the excitation into the charge transfer band is not selective, all Eu³⁺ ions present in the crystal are excited. In the spectral region of the ⁵D₀ → ⁷F₀ transition, as shown in figure 3(b), we observe three strong lines at 576.4, 576.9 and 578.1 nm together with at least three weak lines

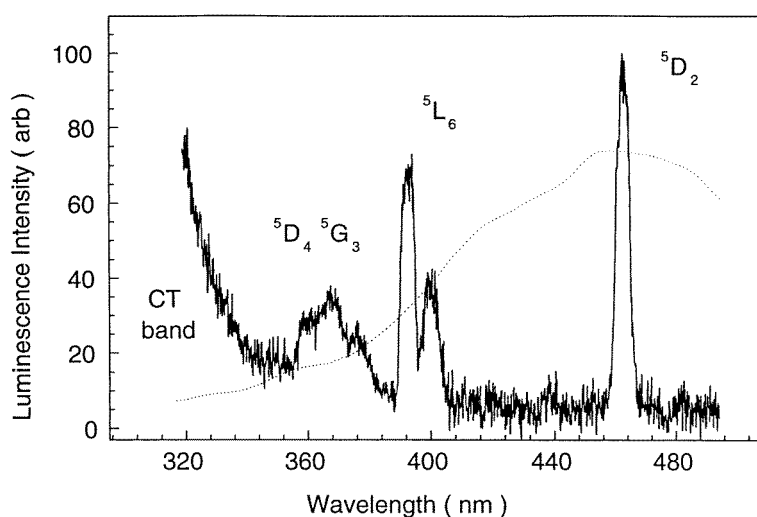


Figure 4. Excitation spectrum (solid line) obtained by monitoring 614.3 nm luminescence of Eu^{3+} at 10 K. The dotted line is the spectral distribution of the lamp output. No correction was performed on the excitation spectrum for the spectral distribution. The entrance and exit slit widths of the 25 cm monochromator were 1 mm. The transitions from the ${}^7\text{F}_0$ ground state are indicated.

in the 576–579 nm region. The occurrence of several ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ peaks indicates the presence of the corresponding different sites of Eu^{3+} for Sr^{2+} in SrB_2O_4 .

Second, the relative peak heights are unusual between the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions. According to the selection rules for rare earth ions with an even number of electrons by Judd–Ofelt theory [20, 21], the electric dipole transition between $J = 0$ and $J' = 0$ is forbidden; $J = 0 \rightarrow \text{odd } J'$ values are weak; $J = 0 \rightarrow J' = 2, 4$ and 6 should be strong. However, we observe strong ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ emission. The ratios of integrated emission intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions to that of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition are estimated to be 0.48 and 1.4, respectively. This behaviour is unusual compared to the emission found in crystals containing Eu^{3+} ions with high symmetry surroundings in which the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition does not appear [22]. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition of Eu^{3+} is often observed in materials containing Eu^{3+} ions with relatively low site symmetries. The breaking down of the selection rules for electric dipole transitions is in relation to the site symmetry, charge transfer band and charge compensation of Eu^{3+} in the SrB_2O_4 crystal as discussed in section 3.

3. Discussion

Although the parity allowed f–d transition on the Eu^{2+} ion is clearly observed in the absorption spectra of the $\text{SrB}_2\text{O}_4:\text{Eu}$ crystal, excitation into this band results in no Eu^{2+} luminescence, even at 10 K. The photoionization process is responsible for the luminescence quenching of Eu^{2+} . The $4f^65d$ excited state of Eu^{2+} lies above the bottom of the conduction band of SrB_2O_4 . The strong coupling of the $4f^65d$ state with the conduction band leads the excited electrons to relax to the bottom of the conduction band, followed by a nonradiative return to the ${}^8\text{S}_{7/2}$ ground state of Eu^{2+} . Luminescence quenching due to photoionization has been reported in several materials such as $\text{InBO}_3:\text{Ce}^{3+}$ [23], $\text{BaGa}_2\text{O}_4:\text{Eu}^{2+}$, $\text{SrGa}_2\text{O}_4:\text{Eu}^{2+}$ [24] and $\text{Lu}_2\text{O}_3:\text{Ce}^{3+}$ [25]. In some cases, although photoionization is taking place, the divalent rare earth ion shows a red

shifted luminescence after excitation. The red shifted emission is attributed to the transition from an impurity trapped exciton level created below the excited state of the impurity ion and the conduction band of host crystal [26, 27].

Machida *et al* [1] reported Eu²⁺ luminescence in the SrB₂O₄:Eu compound. In contrast, Schipper *et al* [6] observed no Eu²⁺ luminescence and, consequently, argued that no Eu²⁺ ions are present in SrB₂O₄:Eu. They proposed that the Eu²⁺ luminescence observed by Machida *et al* originated from a very small amount of SrB₄O₇:Eu²⁺ which was unexpectedly contained in the process of preparation of the SrB₂O₄:Eu compound. We agree with the fact pointed out by Schipper *et al*. However, by the investigation of the absorption and emission properties, we ascertain the presence of Eu²⁺ together with Eu³⁺ in the SrB₂O₄:Eu crystal. The sample investigated by Schipper *et al* was not a single crystal, but a powder which does not make an absorption measurement possible. They obtained the charge transfer band of Eu³⁺ with the maximum at 230 nm (43 500 cm⁻¹) from the diffuse reflection spectra. In our opinion, they mis-assigned the Eu²⁺ absorption band to the charge transfer band of Eu³⁺. The reason is suggested as follows. In the reflection spectrum, the contributions of the parity allowed f–d transition of the Eu²⁺ ion should not be ignored in comparison with those of the charge transfer transition on the Eu³⁺ ion. Their assignment of the position of the maximum charge transfer band at 230 nm is similar to that of our maximum absorption band peaking at 235 nm as shown in figure 1(b). Pei *et al* [3] reported the value of 257 nm as a maximum charge transfer band of Eu³⁺ in SrB₂O₄, which was obtained by the excitation spectrum of Eu³⁺ luminescence. This is quite different from the result (230 nm) of Schipper *et al*.

There is no report on the zero-phonon lines for transition from the 4f⁷ (⁸S_{7/2}) ground state to the different ⁷F_J levels of the 4f⁶ (⁷F_J)5d excited states of Eu²⁺ except for the MgF₂:Eu²⁺ crystal [28]. The Eu²⁺ ions have only one substitution site for Sr²⁺ in the SrB₂O₄ crystal, because, dissimilarly to Eu³⁺, the charge compensation is not necessary for Eu²⁺ in SrB₂O₄. Splittings of the 4f⁶ (⁷F_J)5d into 2J + 1 lines are expected for the C₁ site symmetry. However, we observe only one ⁷F₁ zero-phonon line corresponding to the splitting expected for a cubic crystal field. The unexpected feature of the splittings was also reported in MgF₂:Eu²⁺ by Lizzo *et al* [28]. The site symmetry of Eu²⁺ substituted for Mg²⁺ in MgF₂ crystal is D_{2h} lower than cubic. Lizzo *et al* explained the absence of non-cubic splitting as follows. The 5d electron in the lowest 4f⁶5d state has its charge density in the direction of the non-cubic distortion. This can shield the 4f⁶ core from the non-cubic crystal field component, so that the splitting of the ⁷F_J states of the 4f⁶ configuration agree with the splitting expected for a cubic crystal field.

The strong emission of the ⁵D₀ → ⁷F₀ transition is allowed by the breakdown of the selection rules by Judd–Ofelt theory. Some mechanisms are able to account for the ⁵D₀ → ⁷F₀ emission. The ⁵D₀ → ⁷F₀ transition occurs when the 4f⁶ states admix into the ⁵D₀ and ⁷F₀ states by the even-parity crystal field perturbation. But this is a third-order effect and is insufficient to explain wholly the strong ⁵D₀ → ⁷F₀ emission [29]. Admixing of the high-lying odd-parity states into the ⁵D₀ and ⁷F₀ states through the crystal field potential leads to the strong ⁵D₀ → ⁷F₀ emission by the breakdown of the closure approximation in the Judd–Ofelt theory. This is the case when the charge transfer band is taken as an admixing excited state [30].

The site symmetry of Eu³⁺ in SrB₂O₄ is the lowest, C₁. It is noted that the ⁵D₀ → ⁷F₀ transition is often observed in the materials in which the site symmetries of Eu³⁺ are relatively low [22]. The charge compensation for trivalent ions substituted for divalent ions gives rise to a distortion of the site symmetry allowing a stronger interaction of the ⁵D₀ and ⁷F₀ states with the charge transfer band of Eu³⁺ [30, 31]. In the case of SrB₂O₄, the crystal has a plane structure of Sr²⁺ in which no other ions are positioned between the neighbouring Sr²⁺ ions. This lowers the shielding effect of the neighbouring oxygen ions for interaction between the

Eu^{3+} ion and the neighbouring vacancy in the Sr plane. The Eu^{3+} ion in SrB_2O_4 thus strongly experiences the neighbouring vacancy in comparison with an isolating Eu^{3+} ion in the other compounds. This causes a larger distortion of the site symmetry and then results in a stronger emission of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition of Eu^{3+} in the SrB_2O_4 crystal.

The existence of different sites of Eu^{3+} for Sr^{2+} is also explained by the plane structure of Sr^{2+} in SrB_2O_4 . The charge compensation and plane structure of Sr^{2+} give rise to a number of Eu^{3+} pairs in SrB_2O_4 . The main pairs are composed of two Eu^{3+} ions with a central vacancy which replace three Sr^{2+} ions in the Sr plane. There exist three types of main pair as follows: $\text{Eu}^{3+}(\text{I})$ -vacancy- $\text{Eu}^{3+}(\text{II})$, $\text{Eu}^{3+}(\text{II})$ -vacancy- $\text{Eu}^{3+}(\text{I})$ and $\text{Eu}^{3+}(\text{III})$ -vacancy- $\text{Eu}^{3+}(\text{III})$, where $\text{Eu}^{3+}(\text{I})$, $\text{Eu}^{3+}(\text{II})$ and $\text{Eu}^{3+}(\text{III})$ designate the Eu^{3+} ions located at the nearest neighbour positions beside a vacancy corresponding to the three kinds of nearest neighbour of Sr^{2+} with the Sr-Sr distances of 3.89, 4.00 and 4.34 Å, respectively. The angle of $\text{Eu}^{3+}(\text{I})$ -vacancy- $\text{Eu}^{3+}(\text{II})$ and $\text{Eu}^{3+}(\text{II})$ -vacancy- $\text{Eu}^{3+}(\text{I})$ is 177.4° while that of $\text{Eu}^{3+}(\text{III})$ -vacancy- $\text{Eu}^{3+}(\text{III})$ is 180° . The former two pairs are approximately located in the direction of (302) and (30 $\bar{2}$) axes and the last pair is located in the direction of the (001) axis. We suggest that the three strong lines in the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition appearing in figure 3 are due to the three kinds of vacancy-associated Eu^{3+} site (i.e. vacancy- $\text{Eu}^{3+}(\text{I})$, vacancy- $\text{Eu}^{3+}(\text{II})$ and vacancy- $\text{Eu}^{3+}(\text{III})$). The weak emission lines are attributed to Eu^{3+} sites originating from the other combination between a vacancy and two Eu^{3+} ions in the nearest and next-nearest neighbour positions. We will discuss in detail the different sites of Eu^{3+} and energy transfer between Eu^{3+} ions in pairs in the SrB_2O_4 crystal by site selection laser spectroscopy elsewhere.

In conclusion, by the absorption, excitation and emission measurements, we have shown that both Eu^{2+} and Eu^{3+} ions are contained in the SrB_2O_4 crystal. Luminescence spectra reveal that there are several substitution sites of Eu^{3+} due to the crystal structure and charge compensation in the SrB_2O_4 crystal.

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