Synthesis, structure and Eu$^{2+}$-doped luminescence properties of bromosilicate compound Ca$_3$SiO$_4$Br$_2$

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1. Introduction

The emission and excitation spectra of Eu$^{2+}$ usually consist of broad bands due to transition between the $^8S_{7/2}$ ($4f^7$) ground state and the crystal field components of the $4f^75d^1$ excited state configuration. Therefore, designing and investigating new Eu$^{2+}$ activated phosphors have been boosted by the development of phosphor industry. It is well-known that the silicate compound is a good luminescence host, which can generate plenty of local crystal environments imposed on emission centers [1,2]. Among them, halo-containing silicates based phosphors have great potential due to their low synthesizing temperature, various structures, and excellent chemical and physical stability [3–5].

Considering covalency and anion polarizability arguments, halo-containing hosts would normally be excluded due to the ionic nature when screening for new phosphor compositions. However, the efficient emission due to the minor quenching process from multi-phonon relaxation is expected owing to the low phonon energy in halogen anion. Moreover, more flexible and alternative sites that can be occupied by the doped rare earth ions can be formed in the halo-silicates hosts, which will in turn induce multi-color PL emission originating from different crystal field environment [3–8]. Accordingly, many new phosphor materials have been developed in these years, such as greenish blue emitting Sr$_2$Si$_2$O$_5$Cl$_2$:Eu$^{2+}$ [8–9], blue emitting Ca$_3$Si$_2$O$_5$F$_2$:Eu$^{2+}$ [10], blue/near-white/yellow emitting Ca$_3$Al$_2$(SiO$_4$)$_3$:Cl$_3$:Eu$^{2+}$, Mn$^{2+}$ [11], green emitting Ba$_2$SiO$_4$(F,Cl)$_3$:Eu$^{2+}$ [12], and so on. However, little research concentrates on the bromosilicate phosphors except for the Blasse’s previous work on Ba$_2$SiO$_3$:Eu$^{2+}$ phosphor and our recent work on the (CaO–CaBr$_2$–SiO$_2$):Eu$^{2+}$ phosphor system [13–15]. It is noticed that the detailed crystal structure data for the so-called (CaO–CaBr$_2$–SiO$_2$):Eu$^{2+}$ bromosilicate phosphor is not available [16]. Herein, the crystal structure information of this new bromosilicate compound Ca$_3$SiO$_4$Br$_2$ has been determined by single-crystal X-ray diffraction, the photoluminescence (PL) properties, PL decay curves and the temperature dependent PL behavior were also discussed.

2. Experimental

2.1. Preparation and structural characterization of Ca$_3$SiO$_4$Br$_2$ crystals

The starting materials, CaCO$_3$, CaBr$_2$·2H$_2$O and SiO$_2$ with analytic grade purity (≥ 99.5%), and rare earth oxide activator Eu$_2$O$_3$ (purity grade, ≥ 99.99%) were used as received without further purification. Ca$_3$SiO$_4$Br$_2$ single crystals were grown by the high temperature solution technique with 200% excessive CaBr$_2$ as the flux for crystal growth, and spontaneous crystallization of Ca$_3$SiO$_4$Br$_2$ crystals was obtained by the slow cooling process. The detailed experimental treatment can be found in our previous work [16]. A typical selected flaky-shaped Ca$_3$SiO$_4$Br$_2$ single crystal (dimensions 0.3 × 0.2 × 0.1 mm$^3$) was glued on to a glass fiber and data were collected on a SMART APEX-CCD diffractometer (Bruker AXS, Inc.) equipped with a graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda=0.71073$ Å) at 293 K. The structure...
was solved by the direct method and refined by Bruker SHELXS-97 package of programs.

2.2. Optical properties characterization of Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ crystals

Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ crystal was also prepared by the same flux method mentioned above except for the small addition of 1.5 mol% Eu$_2$O$_3$ and the control of reduction atmosphere. Therefore, room temperature photoluminescence (PL) spectra were recorded by using a JOBIN YVON FL3-21 spectrophotometer with a 150 W xenon lamp. The room temperature decay curves were recorded on the same spectrophotometer and the 370 nm pulse laser radiation (nano-LED) was used as the excitation source. The temperature-dependence luminescence properties were measured on the same spectrophotometer, which was combined with a self-made heating attachment and a computer-controlled electric furnace.

3. Results and discussion

3.1. Morphology and structure of Ca$_3$SiO$_4$Br$_2$ crystals

Fig. 1(a) clearly demonstrates the typical Ca$_3$SiO$_4$Br$_2$ crystals, and the inset shows the optical microscope image for a flaky crystal. Colorless, transparent and flaky crystals of Ca$_3$SiO$_4$Br$_2$ with largest size 4 mm × 1 mm × 0.2 mm can be directly isolated from the as-grown products. Accordingly, the optical microscope image in the inset for one typical flaky crystal further testified the character [15]. It is also believed that the observed flaky character of the Ca$_3$SiO$_4$Br$_2$ crystals should be in relation with the crystal growth habits of some inorganic compounds with lameller structure [17,18]. Furthermore, Fig. 1(b) shows the as-grown Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ crystals in the crucible upon the excitation of a 365 nm UV lamp, and the inset shows some selected blue-emitting Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ crystals. Direct observation reveals that flaky crystals of Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ with blue emission upon 365 nm excitation can also be successfully grown, and Eu$^{2+}$ ions can enter the host lattice of Ca$_3$SiO$_4$Br$_2$ compounds and show characteristic blue emission.

The as-obtained Ca$_3$SiO$_4$Br$_2$ crystal was selected to collect reflection data on a SMART APEX-CCD diffractometer, as given in the former experimental section, and the crystal structure was solved by a series of data corrections, Fourier analyses and refinements. Ca$_3$SiO$_4$Br$_2$ crystal belongs to triclinic crystal structure with the space group P-1 (No.2), and the unit cell parameters are as follows, $a = 8.0051(18)$ Å, $b = 8.720(3)$ Å, $c = 11.749(3)$ Å, $\alpha = 69.07(0)^\circ$, $\beta = 89.98(0)^\circ$, $\gamma = 75.46(0)^\circ$, and cell volume $V = 737.88(196)$ Å$^3$, $Z = 3$. As shown in Fig. 2, it gives the Ca$_3$SiO$_4$Br$_2$ framework emphasizing the coordination environments. The detailed structural parameters and atomic coordinates of Ca$_3$SiO$_4$Br$_2$ crystal are also summarized in Table 1. Single-crystal structural analysis reveals that Ca$_3$SiO$_4$Br$_2$ is composed of the alternating layers of CaBr$_2$ and Ca$_2$SiO$_4$, and all Si atoms are tetrahedrally coordinated to O atoms, forming two Si–O–Si bonds and two Si–O–Ca bonds. Especially, the Br atoms exist in the interlayer structure of two adjacent Ca$_2$SiO$_4$ layers, which are bonded with Ca atoms in the two layers. The obtained crystal structure description also testifies the lamellar structure crystal growth mentioned above. The Br atoms have larger radius than that of the O atoms suggesting the instability, so that it can be shifted owing to the interlayer structure, therefore, we can find a large $R$ factor of 0.1374 in Table 1. However, such a structural determination and description is reliable in the present condition. We will also try some work on the crystal structure in the future. It is known that the coordination number and bonded anions play the important role in the effect of crystal field environment of rare earth ions. We can find from Fig. 2 that there are two different Ca$^{2+}$ sites locating in Ca$_2$SiO$_4$ layers and the CaBr$_2$ layers, respectively. Therefore, different Ca$^{2+}$ ion sites in Ca$_3$SiO$_4$Br$_2$ crystal structure can act as the emission centers for the divalent rare earth doping ions, as discussed below.

![Fig. 1](image1.png)  
(a) Typical Ca$_3$SiO$_4$Br$_2$ crystals, and the inset shows the optical microscope image for a flaky crystal; (b) As-grown Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ crystals in the crucible upon the excitation of a 365 nm UV lamp, and the inset shows some selected blue-emitting Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ crystals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

![Fig. 2](image2.png)  
Depiction of the framework of Ca$_3$SiO$_4$Br$_2$ compound emphasizing the layer structure.
Table 1
Summary of refined structural parameters and atomic coordinates of Ca₃SiO₄Br₂ crystal.

<table>
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<tr>
<th>Formula weight</th>
<th>Crystals system</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume (Å³)</th>
<th>Z</th>
<th>Density (calculated) (g cm⁻³)</th>
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<td>1488.490</td>
<td>Triclinic</td>
<td>P-1 (No. 2)</td>
<td>6.907(0)</td>
<td>6.720(3)</td>
<td>7.149(3)</td>
<td>737.88 (1 9 6)</td>
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<tr>
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<th>z</th>
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<td>0.60576</td>
<td>0.83180</td>
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<td>0.0265</td>
<td>01(2i)</td>
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<td>0.87653</td>
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Fig. 3. UV–vis diffuse reflectance spectrum, PLE (λem=468 nm and 515 nm), and PL (λem=353 nm) spectra of as-grown Ca₃SiO₄Br₂:Eu²⁺ crystals powders and the dotted lines denote the Gaussian fit of the PL spectrum.

3.2. Luminescence properties of Ca₃SiO₄Br₂:Eu²⁺ crystals

Fig. 3 shows the diffuse reflectance spectrum (DRS), photoluminescence excitation (PLE, λem=468 nm and λem=515 nm) and photoluminescence (PL, λem=353 nm) spectra of as-grown Ca₃SiO₄Br₂:Eu²⁺ crystals powders. There is a wide and large absorption band (with the absorption edge at 450 nm) in the UV–vis DRS, as shown in Fig. 3. As a comparison, the PLE spectra for different monitoring wavelengths (λem=468 nm and λem=515 nm) have the similar broad band between 250 and 450 nm except for the intensities, which both correspond to the 4f–5d transition of Eu²⁺ ions. The difference in the spectral profiles for the two excitation spectra also indicates that there are different Eu²⁺ emission centers in this host. Furthermore, the obtained results indicate that Ca₃SiO₄Br₂:Eu²⁺ has excellent near ultraviolet (UV) excitation and absorption properties, which in turn means that this kind of phosphor will be a promising candidate as the light-conversion phosphors for white light-emitting diodes (w-LEDs). As also given by the emission spectrum in Fig. 3, Ca₃SiO₄Br₂:Eu²⁺ shows a broad band with a peak at 469 nm upon 353 nm UV excitation. Accordingly, the Stokes shift can be determined from the energy of the zero phonon line (Ezp), which is taken as the point of intersection between the normalized excitation and emission bands [19,20]. In the present Ca₃SiO₄Br₂:Eu²⁺ phosphor, the overlap of the excitation and emission spectra occurs at about 438 nm (2.83 eV), as shown in Fig. 3. The Stokes shift is twice the energy difference between Ezp and the emission energy. The emission of Eu²⁺ in Ca₃SiO₄Br₂ host is a broad band peaking near 469 nm (2.64 eV). Therefore, the Stokes shift of the Eu²⁺ emission is 0.48 eV. Furthermore, the emission band appears to be asymmetric on the long wavelength side, and the dotted line in Fig. 3 denotes the Gaussian fit of the PL spectrum with maxima at 468 and 515 nm, respectively. From the previous crystal structure description, Ca₃SiO₄Br₂:Eu²⁺ phosphors have two different cation sites in the lattice. Then, two Eu²⁺ emission centers ((Eu(1) and Eu(2))) are formed in Ca₃SiO₄Br₂:Eu²⁺.

As shown in Fig. 4, the PL decay curves of Eu²⁺ emission monitored at different emission centers, 468 nm (a) and 515 nm (b), for as-grown Ca₃SiO₄Br₂:Eu²⁺ crystals powders under excitation at 370 nm.

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As shown in Fig. 4, the PL decay curves of Eu²⁺ emission monitored at different emission centers, 468 nm and 515 nm, of as-grown Ca₃SiO₄Br₂:Eu²⁺ crystals powders were obtained under the excitation at 370 nm. Both of the two decay curves can be well fitted by the double-exponential equation given by [21,22]

$$I(t) = I_0 + A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2) \tag{1}$$

where $I_0$ and $I$ are the luminescence intensities at time 0 and $t$; $A_1$ and $A_2$ are constants; $t_1$ is the time; $t_1$ and $t_2$ are the lifetimes for the exponential components, respectively. The fitting results are shown in Fig. 4. Furthermore, the average decay lifetimes ($\bar{t}$) can be calculated as the following Eq. (2)

$$\bar{t}^* = (A_1 t_1^2 + A_2 t_2^2)/(A_1 t_1 + A_2 t_2) \tag{2}$$

The result show that the average decay time of the two thresholds corresponding to 468 nm and 515 nm are determined to be 0.60 and 0.72 μs, respectively. The lifetime of the Eu²⁺ ion is
usually in the range of 0.2–2 μs, and the shorter decay time can be found in the present Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ systems. Furthermore, the double-exponential decay behaviors for the two emission centers also supports that the emission spectra are an overlap of the shorter and longer wavelength emission bands, consistent with the fact that the emission spectra are originated from two different Eu$^{2+}$ emissions as mentioned above [23].

Fig. 5(a) shows the temperature dependent emission spectra (normalized at 20°C) of as-grown Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ crystals powders excited by 353 nm in the range of 20–270°C, and the inset shows the relative emission intensity as a function of temperature in order to clarify this variation. It is found that the integrated intensity continuously decreases with increasing temperature, showing a typical thermal quenching behavior. With increasing temperature up to 120°C, the normalized emission intensity is decreased to 41.9% of the initial value, which indicates that the as-prepared Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ samples have relatively poor thermal stability, and some ongoing work for the practical application will be developed for this novel phosphor system.

Srivastava and Dorenbos [19] have systematically analyzed and proposed that the thermal quenching of Eu$^{2+}$ (4f–5d) luminescence should be explained in terms of three mechanisms: (1) Thermal quenching by level crossing between the curves of the 4f5d level and lower energy 4f states in a configuration coordinate model; (2) Thermal quenching by the promotion of the electron in the 4f5d level to the host lattice conduction band states (photoionization); and (3) Thermal quenching by the promotion of the electron in the 4f5d level to the impurity trapped excitation state, in which the electron is located in the host lattice while the hole is trapped on the rare earth ion. In our case, if we can exclude the effect of energy migration of different Eu$^{2+}$ ions, the thermal quenching of the Eu$^{2+}$ emission should come from process (2), viz. photoionization process. As reported in our previous work, the present Eu$^{2+}$ doping concentration (3 mol%) is very low [13]. So we can propose that the thermal quenching of the Eu$^{2+}$ emission in the Ca$_3$SiO$_4$Br$_2$ host is due to photoionization. Accordingly, considering that the probability of thermal activation is strongly dependent on the temperature, the relationship between emission intensity and the given temperature has been investigated, which can be deduced according to the following equation [24,25]

\[ I_T = \frac{I_0}{1 + c \exp \left( - \frac{\Delta E}{kT} \right)} \]  
(3)

where $I_0$ is the initial emission intensity, $I_T$ is the intensity at different temperatures, $\Delta E$ is activation energy of thermal quenching, $c$ is a constant for a certain host, and $k$ is the Boltzmann constant ($8.629 \times 10^{-5}$ eV). Therefore, Fig. 5(b) plots the relationship of $\ln(I_0/I_T)$–1 versus 1000/T of the Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ powders, which is linear with a slope of $-4.33$. The activation energy $\Delta E$ was calculated to be 0.374 eV based on Eq. (3). $\Delta E$ is related to the energy gap between the lowest energy 4f$^5$5d$^1$ excited level of Eu$^{2+}$ and the bottom of the conduction band, which is connected with thermally activated energy transfer processes. It is found that the activation energy of thermal quenching in Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ is higher than that in its counterpart compounds, Ca$_3$SiO$_4$Cl$_2$:Eu$^{2+}$ ($\Delta E=0.159$ eV) [26].

4. Conclusions

In summary, we have obtained and studied the new bromo-silicate Ca$_3$SiO$_4$Br$_2$ crystal. The crystal structure characters have been discussed preliminarily, which can be used to explain the asymmetry emission band. The luminescence of Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ upon the 365 nm UV lamp gives a broad emission band centered at 469 nm with some asymmetry on the long wavelength side. The double-exponential decay behaviors for the two fitted emission centers further support that there are two different Eu$^{2+}$ sites in Ca$_3$SiO$_4$Br$_2$. The activation energy of thermal quenching in Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ is calculated as 0.374 eV. The above results indicate that Ca$_3$SiO$_4$Br$_2$:Eu$^{2+}$ is a good candidate for blue component in w-LEDs.

Acknowledgments

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