



Cyan-emitting LiBaBO₃:Eu²⁺ phosphor: Crystal structure and luminescence property comparison with LiSrBO₃:Eu²⁺



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ABSTRACT

Cyan-emitting LiBaBO₃:Eu²⁺ phosphor was synthesized by solid-state reaction at 800 °C. Structure refinement by Rietveld method reveals that LiBaBO₃ crystallizes in a monoclinic cell, space groups *P*₂₁/*c* or *P*₂₁/*n*. Upon 365 nm excitation, LiBaBO₃:Eu²⁺ shows a symmetric emission band peaking at 496 nm with full-width at half-maximum of 80 nm; when monitoring at 496 nm, a broad excitation band in the UV region (250–420 nm) is observed. The luminescence property of LiBaBO₃:Eu²⁺ is considerably different from LiSrBO₃:Eu²⁺ which holds the same space group. The local structures of the two hosts are compared to explain the different behaviors of Eu²⁺.

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1. Introduction

Phosphor materials play fundamental role in applications such as white light emitting diodes and field emitting displays [1]. Rare earth and transition metal ions generally act as activators doped in phosphors and the fluorescence characteristics of phosphors strongly depend on the activator as well as the host crystal. The divalent europium (Eu²⁺) is the most commonly used dopant owing to the abundant efficient visible color emissions based on 4f–5d transition [2]. The sensitivity of this energy transition in Eu²⁺ to the crystallographic site environment opens possibility to tune the luminescence parameters [3], which falls in the critical industry needs such as tunable correlated color temperature, chromaticity coordinates, and color rendering index (CRI) [4]. Furthermore, to understand the relationship between the luminescence property of the phosphor and the structural property of the host crystal is important in solid state chemistry and solid state lighting [4,5], which can assist the optimization of spectroscopic feature via crystal structure engineering [6].

In this study, the attention is paid to two borate phosphors activated by Eu²⁺, the hosts of which have very similar chemical formula, LiBaBO₃ and LiSrBO₃, but the corresponding phosphors

exhibit different emission features. Earlier, LiSrBO₃:Eu²⁺ has been reported as a blue-light excited yellow-emitting phosphor peaking at 565 nm [7], or red-emitting phosphor peaking at 618 nm [8]. Whereas, LiBaBO₃:Eu²⁺, prepared in our experiment, emits bluish-green light under ultraviolet (UV) irradiation. Although LiSrBO₃ and LiBaBO₃ belong to the same crystal system (monoclinic cell) and space group (*P*₂₁/*n* for LiSrBO₃ [9] and *P*₂₁/*n* for LiBaBO₃ [9] (or *P*₂₁/*c* for LiBaBO₃ [10] in the standard setting)), considerably different luminescence of Eu²⁺ are observed in these crystal lattices. This phosphor family is thus a perfect example for the structure comparison and exploration of the intrinsic structural difference as a source of different luminescence behaviors of Eu²⁺. In this study, firstly, we report the synthesis, crystal structure and photoluminescence property of the LiBaBO₃:Eu²⁺ phosphor, and, then, intend to relate the luminescence difference of Eu²⁺ in the LiBaBO₃ and LiSrBO₃ lattices with their specific structural properties.

2. Experimental

The LiBa_(1-x)BO₃:xEu²⁺ (*x* = 0, 0.005, 0.01, 0.03) powder samples were prepared by sintering stoichiometric mixtures of Li₂CO₃ (A.R.), BaCO₃ (A.R.), H₃BO₃ (A.R.), and Eu₂O₃ (99.99%) for 10 h at *T* = 1023 K in a tube furnace under flowing 5% H₂–95% N₂ reducing gas. Therein, the samples were furnace-cooled before regrinding into fine powders for characterization. The X-ray diffraction (XRD) patterns were recorded on an X-ray powder diffractometer

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(D/max-III A, Rigaku, Japan) by continuous scanning in the 2θ range $10\text{--}90^\circ$, using Cu $K\alpha$ radiation (1.5406 \AA) under operating electric voltage and current of 40 kV and 100 mA, respectively. The acquisition of the XRD patterns which were submitted to profile fitting and Rietveld refinement by TOPAS [11], was in stepwise scanning mode with step size of 0.02° and counting time of 1 s per step. Diffuse reflection spectra of the undoped and Eu^{2+} -doped LiBaBO_3 were measured on a UV–Vis–NIR spectrophotometer (UV-3600, Shimadzu, Japan) attached to an integral sphere and BaSO_4 was used as a reference for 100% reflectance. The room temperature photoluminescence spectra were recorded using a fluorescence spectrophotometer (F-4600, Hitachi, Japan) with a photomultiplier tube operating at 350 V using a 150 W Xe lamp as the excitation source.

3. Results and discussion

Figure 1(A) shows the XRD patterns of the $\text{LiBa}_{(1-x)}\text{BO}_3:x\text{Eu}^{2+}$ ($x=0, 0.01, 0.03$) samples as well as the standard pattern of LiBaBO_3 (JCPDS file no. 81–1808). All the diffraction peaks of the as-prepared phosphors can be well matched with the standard

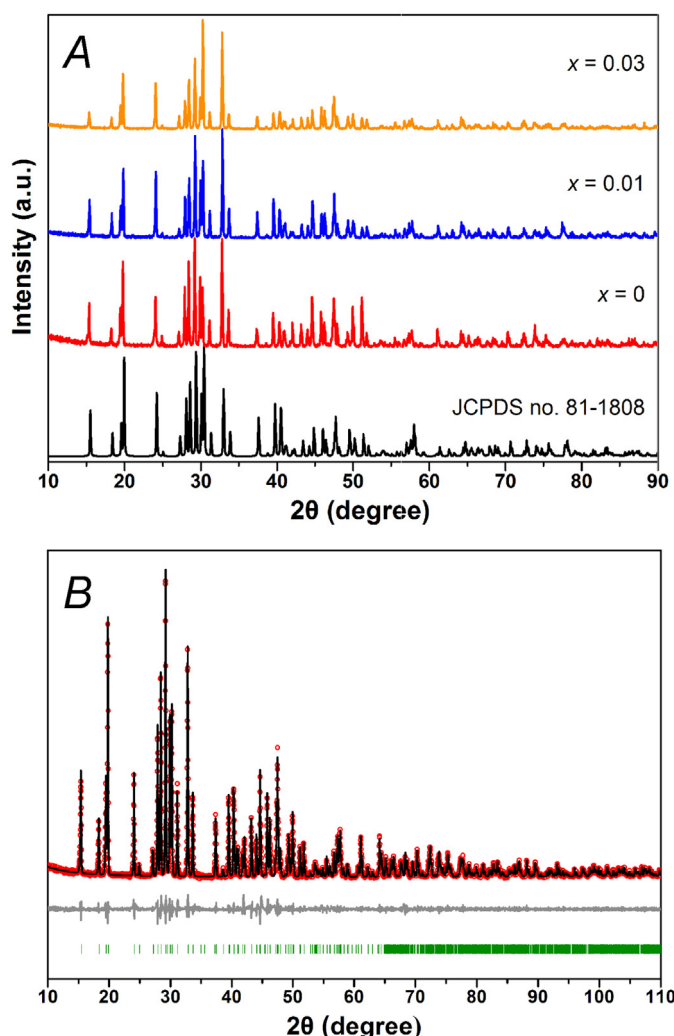


Figure 1. (A) XRD patterns of the $\text{LiBa}_{(1-x)}\text{BO}_3:x\text{Eu}^{2+}$ ($x=0, 0.01, 0.03$) samples. The standard pattern of LiBaBO_3 (JCPDS no. 81–1808) is provided as reference. (B) The observed (red), calculated (black), and difference (gray) XRD profiles of undoped LiBaBO_3 sample with fitting performed by TOPAS. Bragg reflections are indicated with tick marks (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article).

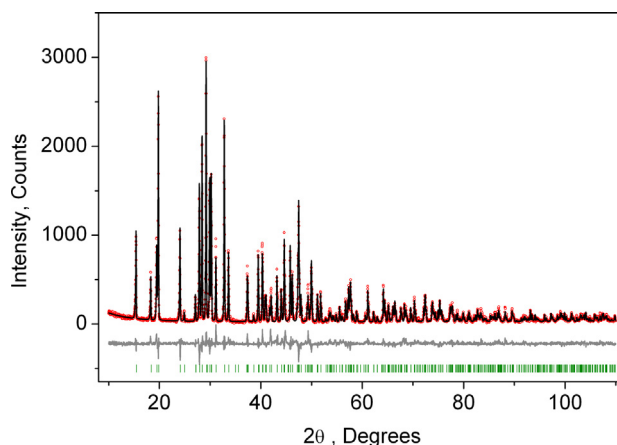


Figure 2. Rietveld refinement of LiBaBO_3 in the space group $P2_1/n$. The observed, calculated, and difference XRD profiles are shown in red, black, and gray, respectively (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article).

pattern, indicating that they are phase pure. To further verify the phase purity and determine the precise cell parameters, the XRD pattern of undoped LiBaBO_3 was subjected to profile fitting by TOPAS. The measured, fitted and difference data are shown in Figure 1(B). All peaks were successfully indexed by a monoclinic cell ($P2_1/c$) with parameters close to the values reported for LiBaBO_3 [10]. The obtained cell parameters are $a=6.48555(11)\text{ \AA}$, $b=7.12765(13)\text{ \AA}$, $c=7.42604(14)\text{ \AA}$, $\beta=117.9316(11)^\circ$, and $Z=4$. Profile fitting of the Eu^{2+} -doped samples reveals that the cell volume ($V_{x=0.005}=303.320(19)\text{ \AA}^3$, $V_{x=0.01}=303.232(17)\text{ \AA}^3$, $V_{x=0.03}=303.155(15)\text{ \AA}^3$) decreases on the Eu^{2+} content increase. This trend suggests the effective incorporation of Eu^{2+} into the host lattice. The Eu^{2+} ions are expected to occupy the Ba site in LiBaBO_3 since the Li^+ effective ion radius ($r_i=0.59\text{ \AA}$, CN=4) [12] (coordination number, CN) is too small for Eu^{2+} ($r_i=1.17\text{ \AA}$, CN=6; $r_i=1.25\text{ \AA}$, CN=8) [12] while the Ba^{2+} site ($r_i=1.42\text{ \AA}$, CN=8) [12] is suitable for Eu^{2+} both in size and valence.

The chemical formula LiSrBO_3 is analogous to that of LiBaBO_3 , and its crystal structure has been reported in space group $P2_1/n$ [9] (a non-standard setting of $P2_1/c$); thus, the two compounds form a crystal family and can be of the same space group. To assist the structural comparison between LiBaBO_3 and LiSrBO_3 , we perform Rietveld refinement of the LiBaBO_3 structure in $P2_1/n$ space group. Figure 2 presented the observed (red), calculated (black), and difference (gray) XRD profiles for this refinement. All peaks were indexed by a monoclinic cell ($P2_1/n$). Crystal structure of pure LiBaBO_3 was taken as starting model for the refinement [10]. Thermal parameters of all ions were refined isotropically and thermal parameters of all O ions have been set to be the same. The main parameters of processing and refinement of the LiBaBO_3 sample are provided in Table 1. In the following, the refined structural data are used to see the local coordination environment of Eu^{2+} in the LiBaBO_3 sample.

The photoluminescence excitation (PLE) and emission (PL) spectra of the $\text{LiBa}_{(1-x)}\text{BO}_3:x\text{Eu}^{2+}$ ($x=0.005, 0.01, 0.03$) phosphors are shown in Figure 3. Upon 365 nm UV light excitation, the PL spectrum exhibits an intense band emission peaking at 496 nm which is attributed to the $5d\text{--}4f$ allowed transition of Eu^{2+} [13]. When emission is monitored at 496 nm, the excitation band is seen to extend from 250 to 420 nm with two local maximums at 300 nm and 353 nm. The emission band is symmetric and relatively broad with a high full-width at half-maximum (fwhm) as $\sim 80\text{ nm}$. In Figure 3(b), the phosphor is seen to emit bright cyan color under the 365 nm UV lamp. The color chromaticity coordinate of the phosphor is calculated from the emission spectrum measured upon 365 nm

Table 1
Main parameters of processing and refinement of the LiBaBO₃ sample.

| | LiBaBO ₃ |
|-----------------------------|-------------------------|
| Space Group | <i>P2₁/n</i> |
| <i>a</i> (Å) | 6.48591(13) |
| <i>b</i> (Å) | 7.12791(14) |
| <i>c</i> (Å) | 7.21767(15) |
| β (°) | 114.6251(11) |
| <i>V</i> (Å ³) | 303.333(11) |
| <i>Z</i> | 4 |
| 2 θ -interval (°) | 10–110 |
| No. reflns | 382 |
| No. params of refinement | 78 |
| <i>R</i> _{wp} (%) | 14.71 |
| <i>R</i> _p (%) | 10.55 |
| <i>R</i> _{exp} (%) | 9.29 |
| χ^2 | 1.58 |
| <i>R</i> _B (%) | 5.74 |

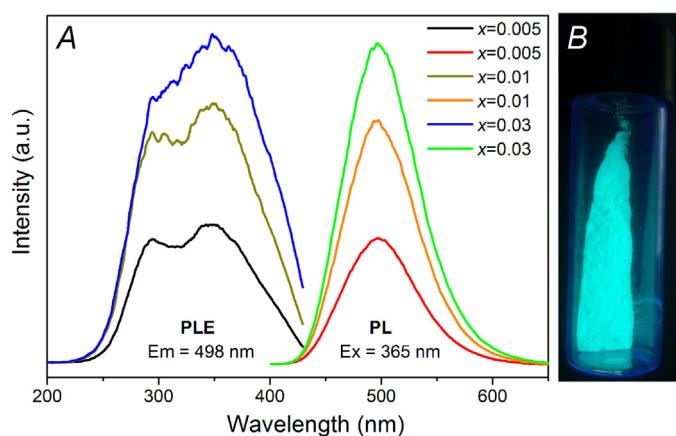


Figure 3. (A) Photoluminescence excitation (PLE) and emission (PL) spectra of the cyan-emitting LiBa_(1-x)BO₃:xEu²⁺ phosphors (*x* = 0.005, 0.01, 0.03). (B) Digital image of LiBa_{0.97}BO₃:0.03Eu²⁺ under 365 nm UV lamp.

excitation, and it is (0.221, 0.693), suggesting that LiBaBO₃:Eu²⁺ can be potentially used as cyan-emitting component for near UV-pumped w-LEDs. Within the investigated doping concentrations, the emission intensity of LiBa_(1-x)BO₃:xEu²⁺ increases at higher Eu²⁺ content, reaching the highest level at *x* = 0.03. In the LiBaBO₃ lattice, only one barium site with 4e symmetry exists, where Ba atom is coordinated with eight O atoms. As expected, just this position is partly occupied by Eu²⁺, forming one coordination environment type for the luminescent center in the host. This is consistent with the symmetric emission band shape.

Figure 4 illustrates the diffuse reflection spectra of pure LiBaBO₃ and Eu²⁺-doped LiBaBO₃ in the range 200–750 nm. The reflection intensity of undoped LiBaBO₃ is about 96% in the range 400–700 nm, and then, it shows a drop to a plateau of ~90%. A remarkable drop starts around 290 nm which corresponds to the band transition in the LiBaBO₃ host lattice. With the introduction of Eu²⁺ ions, the broad absorption in the range of 200–430 nm with two noticeable reflection drops assigned to the 4f⁷ → 4f⁶5d¹ absorption of Eu²⁺ is observed, and this is consistent with the PLE spectra in the same region. In the UV region, LiBa_{0.99}BO₃:0.01Eu²⁺ exhibits bigger absorption in comparison with the undoped sample.

To understand the origin of the observed emission center at 496 nm, the equation proposed by Van Uitert [14] is used to qualitatively analyze the present result. According to his model, the following equation Eq. (1) provides a good fit to the emission peak

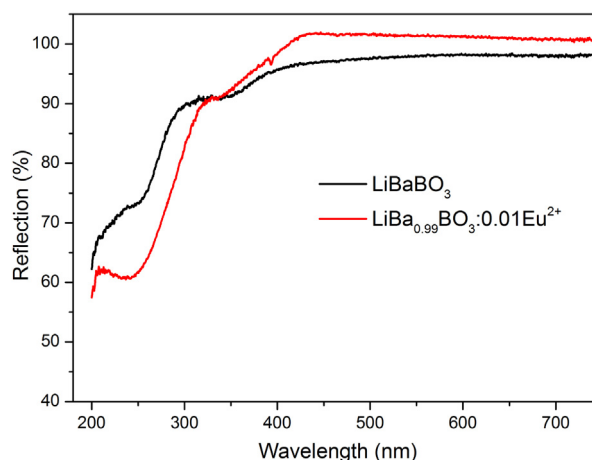


Figure 4. Diffuse reflection spectra of pure and Eu²⁺-doped LiBaBO₃.

and/or excitation edge data of most divalent and some trivalent rare earth elements including Eu²⁺ and Ce³⁺:

$$E = Q \left[1 - \left(\frac{V}{4} \right)^{1/V} \cdot 10^{-n-ea-r/80} \right] \quad (1)$$

here *E* is the position of the *d*-band edge in energy for a rare-earth ion (for example, Eu²⁺) (cm⁻¹), *Q* is the position in energy for the lower *d*-band energy for free ions (obtained from spark data; and 34 000 cm⁻¹ for Eu²⁺), *V* is the valence of the cation activator (for Eu²⁺, *V* = 2), *n* is the number of anions in the immediate shell about this cation, *r* is the radius of the host cation replaced by the activator ion (in Å), and *ea* is the electron affinity of the atoms that form anions (in eV). The value of *ea* changes when Eu²⁺ is introduced into different anion complexes; here, *ea* is determined as 1.60 for an oxide host from statistical analysis [14]. The calculated energy position of the Eu²⁺ *d*-band edge in the eight-coordinated Ba²⁺ site (*r*_i = 1.42 Å, CN = 8) of LiBaBO₃ is 19 752 cm⁻¹ (506 nm), which almost perfectly corresponds to the measured emission peaking wavelength of Eu²⁺ in LiBaBO₃ (496 nm).

If Ba in LiBaBO₃ is completely substituted by Sr, the obtained LiSrBO₃ crystallize in the same space group *P2₁/n*. Interestingly, the photoluminescence property of Eu²⁺ in these two monoclinic hosts is considerably different. In 2010, Wang et al. [7] has reported LiSrBO₃:Eu²⁺ as a yellow-emitting phosphor which can be effectively excited by ultraviolet (360 and 400 nm) and blue (425 and 460 nm) light, and exhibits a yellow color emission centered at 565 nm. Afterwards, in 2012, Zhang et al. [8] also reported LiSrBO₃:Eu²⁺ but as a red-emitting phosphor which can be excited by the 460 nm blue light and exhibits a broad-band emission peaking at 618 nm. Thus, the emission of Eu²⁺ in LiSrBO₃ does exhibit a big red-shift effect in comparison with that in LiBaBO₃. To evaluate the contradictory results in earlier studies, Eq. (1) is used to calculate the Eu²⁺ emission wavelength in LiSrBO₃. There is only one Sr²⁺ site in the lattice which is coordinated with seven oxygen atoms, and the calculated energy position of the *d* band of Eu²⁺ in the seven-coordinated Sr²⁺ site (*r*_i = 1.21 Å, CN = 7) is 17 723 cm⁻¹ (564 nm). The calculated red shift value is similar with the reported value (565 nm) in Ref. [7] and much smaller than that (618 nm) in Ref. [8].

As is known, the absorption and emission spectra of free rare earth ions are different from those appear when they are doped in the crystal structure where the influence of crystal field and lattice vibration is felt. Thus, the crystal structure of the host plays a crucial role in determining the luminescence spectra of the optically active impurity ions such as Eu²⁺. This is recognized as ligand field theory (in general) and crystal field theory (in the case of an ordered

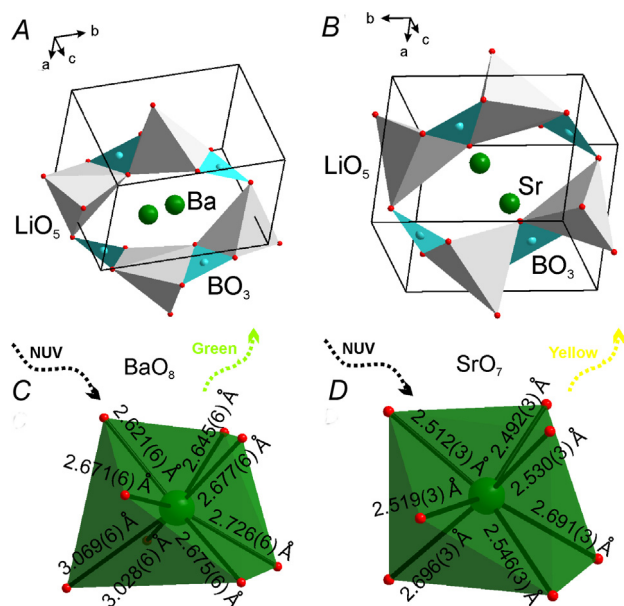


Figure 5. Crystal structures of (A) LiBaBO₃ (in $P2_1/n$ space group) and (B) LiSrBO₃ (in $P2_1/n$ space group), and coordination of (C) Ba²⁺ in LiBaBO₃ and (D) Sr²⁺ in LiSrBO₃.

periodic lattice) [15,16]. As assumed from the literature [17], the coordination number, polyhedron size and crystal field splitting are the main intrinsic factors governing specific emission spectra of Eu²⁺ in local structure. Thus, the structures of LiBaBO₃ and LiSrBO₃ are compared regarding with the local environment of Eu²⁺ in them. Figure 5 presents the unit cells of the two borate compounds (both in $P2_1/n$ space group) and the coordination environment of Ba and Sr atoms. The independent part of the LiBaBO₃ unit cell consists of one Ba²⁺, one Li⁺, one B⁵⁺ and three O²⁻ ions. LiSrBO₃ relate to the same space group (with cell parameters of $a=6.480$ Å, $b=6.480$ Å, $c=6.840$ Å, $\beta=109.41^\circ$ and $Z=4$) [9] and has the same number of ions in the independent part. In both compounds, the BO₃ joins alternately to the distorted square pyramids LiO₅ by edges forming a ring [18], but orientations of the polyhedra are different, which leads to different coordination of Ba/Sr ions (Figure 5C and D). The Sr atoms are seven-coordinated by O atoms with average bond length (Sr–O) of 2.569(3) Å, forming mono-capped distorted trigonal prisms of SrO₇ while the Ba is eight-coordinated by O atoms with average bond length (Ba–O) of 2.764(6) Å, and the BaO₈ polyhedron can be described as a distorted square anti-prism. One can see that the main difference between Ba site in LiBaBO₃ and Sr site in LiSrBO₃ is the number of coordinating O atoms and the size of the formed polyhedron, which induces the large difference between the Stokes shifts of the observed Eu²⁺ emission.

The influence of coordination and size of polyhedron on the luminescence of Eu²⁺ can be also expressed as different crystal field splitting effects. According to the statistical results from Dorenbos [19], Eu²⁺ in a site with fewer coordinated anions relates to a longer emission wavelength. The crystal field around Eu²⁺ has been suggested to obey the relation [20]:

$$D_q = \frac{ze^2r^4}{6R^5} \quad (2)$$

where D_q is the measurement of the energy-level splitting, R is the bond length, z is the charge or valence of the anion ($O_z=2$), e is the charge of an electron, and r is the radius of the d wave function ($r=1.00$ Å). When Eu²⁺ substitutes the Ba²⁺ in LiBaBO₃, the distance between Eu²⁺ and O²⁻ is longer than that in LiSrBO₃ where Sr²⁺ is substituted, and the magnitude of the crystal field increase, resulting in the decreasing 5d band of Eu²⁺. Finally, the emission wavelength of Eu²⁺ in LiSrBO₃ should be red-shifted in reference to that in LiBaBO₃.

4. Conclusions

The cyan-emitting phosphor LiBaBO₃:Eu²⁺ has been successfully synthesized at $T=1023$ K by the high-temperature solid state reaction method. It shows broad absorption band in the UV light range (250–420 nm) which well matches with the characteristic emission of a near UV-light emitting diode chip. An intense cyan visible emission with a symmetric band curve peaking at 496 nm is observed when the phosphor is excited by 365 nm UV light. Analysis of the ion radius and valence suggests Eu²⁺ occupies the Ba site in LiBaBO₃ which forms distorted square anti-prism (BaO₈) together with eight coordinating O atoms. The LiBaBO₃ and LiSrBO₃ hold the same space group but they are not isostructural. The considerably different photoluminescence emission of LiBaBO₃:Eu²⁺ and LiSrBO₃:Eu²⁺ originates from the specific structural properties regarding the number of coordinating oxygen atoms and the polyhedron size.

Acknowledgements

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