Growth and crystal structure of Li₃Ba₄Sc₃B₈O₂₂ borate and its Tb³⁺ doped green-emitting phosphor

A.B. Kuznetsov¹, K.A. Kokha¹,²,³, N.G. Kononova¹, V.S. Shevchenko¹, S.V. Rashchenko¹,², B. Uralbekov⁴, V.A. Svetlichnyi⁴, E.A. Simonova¹, A.E. Kokh¹

¹ Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, 630090, Russia
² Novosibirsk State University, Novosibirsk, 630090, Russia
³ Tomsk State University, Tomsk, 634050, Russia
⁴ Al-Farabi Kazakh National University, Center of Physical-Chemical Methods of Research and Analysis, Almaty, 050040, Kazakhstan

ABSTRACT

A new lithium barium scandium borate (Li₃Ba₄Sc₃B₈O₂₂) was obtained by solid-state synthesis and grown by spontaneous crystallization. Single-crystal X-ray diffraction analysis showed that it crystallizes in the centrosymmetric space group P1 with the cell dimensions a = 5.2230(4) Å, b = 8.5609(6) Å, c = 11.4157(8) Å, α = 73.3750(6)°, β = 78.5020(6)°, γ = 87.0520(6)°, and V = 479.28(6) Å³ and a structure that consists of two layers formed by single [BO₃] and double [B₂O₅] triangles, [ScO₆] octahedra, [BaO₉] polyhedra, and disordered [LiO₄] tetrahedra or squares. The diffuse optical reflection spectrum indicates that Li₃Ba₄Sc₃B₈O₂₂ is transparent in the range of 250–800 nm. Furthermore, an effective green emission centred at 545 nm was observed for the as-prepared Tb³⁺-doped Li₃Ba₄Sc₃B₈O₂₂, making this borate compound a promising host material for engineering light-emitting phosphors.

1. Introduction

Tremendous attention has been given to materials for light-emitting diodes in order to improve their intensity, operation lifetime, size, and environmental friendliness [1–4]. Among these functional materials for light-emitting diodes are borates, which are used as prospective luminesphores and nonlinear crystals. For example, most popular acenitic alkali and alkali earth borates, including Li₂B₂O₃ (LBO) [5], BaB₂O₄ (BBO) [6], and CsLiB₆O₁₀ (CLBO) [7], are used primarily in nonlinear optics. In addition to acenitic borates, many centrosymmetric borates that are doped with or contain rare earth elements (REE), such as YAl₃(BO₃)₄ (YAB) [8] and YCa₄O(BO₃)₃ (YCOB) [9], are used as laser host materials. The ability of the boron atom to form different anions, e.g., BO₃ [5,6] and the polyanions B₅O₁₀ [10–12], B₂O₅ [10–12], and leads to the diverse chemical compositions and crystal structures of borates. Therefore, understanding the relationship between the compound’s crystal structure and its properties is critical for the improvement and development of new functional materials. Among the many reported synthetic borates, the alkali and alkali earth borates are of practical interest as effective host lattices for luminescent materials [13].

In the ternary Li₂O–BaO–B₂O₃ system, three phases (Li₂BaBO₃, Li₂Ba₂B₂O₇, and Li₂BaB₉O₁₅) have been identified [14–17]. According to Ref. [18], Li₂BaB₉O₁₅ exists in two different phases, R3c and R3c. The other anionic groups, B₅O₁₀ and BO₃, are the main building units of Li₂BaB₅O₁₀ and LiBaBO₃, respectively. Such structures provide the separation of active ions that is necessary to decrease the influence of the self-quenching effect. Undoped LiBaBO₃, LiBa₂B₅O₁₅, and LiBaB₉O₁₅ crystals do not have luminescent properties and their use as phosphors is associated with doping. Thus, there is a need to identify compounds that have both a suitable isomorphous position for luminescent dopants and structural motifs that are favourable for efficient excitation.

In this work, the Li₃Ba₄Sc₃B₈O₂₂ compound was obtained while investigating the effect of substituting Sr with Ba in Sr₃ScLiB₄O₁₀. Li₃Ba₄Sc₃B₈O₂₂ was synthesized by a solid-state reaction and successfully grown using the TSSG method. Powder and single X-ray diffraction and thermal behaviour analyses were performed to investigate the phase transformation. Also, some optical properties are presented, including the Raman spectra and UV–vis–NIR diffuse reflectance spectra (DRS) of the crystal. During the preparation of this manuscript, a report was published on the synthesis of the same compound, Li₃Ba₄Sc₃(BO₃)₄(B₂O₅)₂ [19]; however, there are significant discrepancies between their structural parameters and our results, suggesting that the previous report actually described the compound with different stoichiometry or a different phase modification.
The stoichiometric mixtures of pure raw \( \text{Li}_2\text{CO}_3 \), \( \text{BaCO}_3 \), \( \text{H}_2\text{BO}_3 \), \( \text{Sc}_2\text{O}_3 \), and \( \text{Tb}_2\text{O}_3 \) were heated to 600°C for 5 h to decompose \( \text{Li}_2\text{CO}_3 \), \( \text{BaCO}_3 \), and \( \text{H}_2\text{BO}_3 \). At the second stage, the mixtures were ground in an agate mortar and heated again to 850°C for 12 h until the powder X-ray method showed no peaks that corresponded to the initial compounds. A polycrystalline sample of \( \text{Li}_3\text{Ba}_4\text{Sc}_3\text{B}_8\text{O}_{22} \) with dimensions of \( 0.03 \times 0.08 \times 0.10 \) mm\(^3\) was selected using a polarizing microscope. X-ray diffraction data were collected via a STOE IPDS2T single-crystal diffractometer (image plate detector, graphite-monochromatized MoK\( \alpha \) radiation) using the LeBail method [22,23] in the GSAS-II program.

The crystals’ chemical compositions were measured by X-ray fluorescence analysis using a Cary 100 spectrophotometer (Varian, Australia) with a diffuse reflectance accessory (DRA-CA-301, Labsphere, USA), in the range of 250–900 nm, and a relatively white standard (SRS99-010, Labsphere, USA). The data obtained by DRS are presented in the form of the Kubelka-Munk function (\( F(R) = (1-R)^2/2R \)).

The DRS of powders of \( \text{Li}_3\text{Ba}_4\text{Sc}_3\text{B}_8\text{O}_{22} \) crystals were recorded at room temperature using a Cary 100 spectrophotometer (Varian, Australia) with a diffuse reflectance accessory (DRA-CA-301, Labsphere, USA), in the range of 250–900 nm, and a relatively white standard (SRS99-010, Labsphere, USA). The data obtained by DRS are presented in the form of the Kubelka-Munk function (\( F(R) = (1-R)^2/2R \)).

A high-quality single crystal of \( \text{Li}_3\text{Ba}_4\text{Sc}_3\text{B}_8\text{O}_{22} \) with dimensions \( 5 \times 5 \times 5 \) mm\(^3\) was grown from the \( \text{LiBO}_2 \) flux (Fig. 2).

The structure of \( \text{Li}_3\text{Ba}_4\text{Sc}_3\text{B}_8\text{O}_{22} \) was solved with the unit cell parameters \( a = 5.2230(4) \) Å, \( b = 8.5609(6) \) Å, \( c = 11.4157(8) \) Å, \( \alpha = 73.3750(6)\(^\circ\), \( \beta = 78.5020(6)\(^\circ\), \( \gamma = 87.0520(6)\(^\circ\), and \( V = 479.28(6) \) Å\(^3\)). The relation between Ba and Sc was obtained by X-ray fluorescence analysis and had good agreement with the single-crystal analysis.

Detailed information about the data collection and structure refinement are summarized in Table 1. All structural data and bond valence sums are listed in Tables 1s and 2s. \( \text{Li}_3\text{Ba}_4\text{Sc}_3\text{B}_8\text{O}_{22} \) has a structure that consists of two layers formed by single \([\text{BO}_3]\) and double \([\text{BO}_3]\) bonds.
triangles, ScO₆ octahedra, BaO₉ polyhedra, and LiO₄ disordered tetrahedra or squares (Fig. 3a and b). Let us consider related ternary borates with similar structural units. The structure of Sr₂ScLiB₄O₁₀ is determined by the layered arrangement of the two types of B₂O₅ groups, which differ in terms of their B–O–B angles [24]. The groups alternate in pairs along (101), providing oxygen atoms from different layers for the ScO₆ octahedra. This defines the spatial separation of the 3⁺ cations in the structure. Another compound, LiBaTb₂(BO₃)₃, has a motif of three types of BO₃ triangles. The first type creates ring structures where oxygen atoms surround six vertex polyhedra for Tb, the second type fills interstices between the rings, and the third type is located in their centres of the rings. The peculiarity of the third type of BO₃ triangle is a disordered oxygen [25].

The structure of the title compound can be described as a combination of LiBaTb₂(BO₃)₃ (Fig. 3c) and Sr₂ScLiB₄O₁₀ (Fig. 3d) motifs. The structure includes layers parallel to (011) which are formed by the BO₃ and B₂O₅ groups. There is a disordering of one oxygen atom in both the BO₃ and B₂O₅ groups, which leads to variations in bond lengths (in the range of 1356(10)-1426(8) Å) in B₂O₅ that are slightly larger than those in Sr₂ScLiB₄O₁₀. The B–O bond lengths in single BO₃ triangles are 1340(14) - 1418(15) Å, which are similar to those observed in other structures of LiBaTb₂(BO₃)₃ borate.

Each Ba atom occupies an irregular nine- (like Sr in Sr₂ScLiB₄O₁₀) or ten-coordinate (like Ba in LiBaTb₂(BO₃)₃) site. The Li atoms occupy disordered positions and surround four O neighbours located at the vertices of a disordered tetrahedron or square. The Sc atom resides in a distorted octahedral environment with bond distances ranging from 2.110 (8) to 2.134 (4) Å. This is comparable to the Sc–O distance (2.120(4) Å) observed in ScBO₃. Sc atoms are well isolated from each other, with the closest distance being 5.215(6) Å, and do not have common O atoms. Therefore, effective luminescence could be expected from this compound.

It should be noted that our structural data differ from the previously-reported data [19]: a = 9.7959(3) Å, b = 10.2519(2) Å, c = 11.5878(3) Å, α = 85.069(2)°, β = 73.362(2)°, and γ = 78.729(2)°.

Fig. 4 Shows a Raman spectrum of Li₃Ba₄Sc₃B₈O₂₂. The vibration modes are complicated by the possible overlap of the different borate groups (B₂O₅ and BO₃), and only those vibration modes that can be attributed to the existence of the borate groups are considered. The isolated planar BO₃ groups have a point group D₃₃ with four normal vibration modes: \( v₁ \)-symmetrical stretch (A₂), \( v₂ \)-the antisymmetric stretch (E), and \( v₄ \)-the in-plane bend (E) at frequencies around 988, 725–820, 1250–1400, and 520–620 cm⁻¹, respectively. In the pyroborate ion B₂O₅, the B–O bonds are not equivalent and there is no symmetry (C₁ point group). It is likely that the peaks with Raman shifts around 954 and 1129 cm⁻¹ are associated with the BO₃ and BO₂ groups in B₂O₅, respectively. These characteristic peaks might indicate the existence of two different borate groups in the structure.

The temperature stability of Li₃Ba₄Sc₃B₈O₂₂ was studied by DSC. The thermal diagram has one endothermic peak of melting at 915°C on the heating curve and two exothermic peaks on the cooling curve at 875 and 860°C (Fig. 1s); this suggests an incongruent type of melting for this compound, which was confirmed by X-ray analysis performed on the melted sample (Fig. 2s). At least three additional phases were identified: Ba₃Sc(BO₃)₉, LiBaBO₃, and ScBO₃.

The unit cell parameters of the obtained doped Li₃Ba₄Sc₂.₈₅Tb₀.₁₅B₈O₂₂ borates were refined by the Le-Bail method (Fig. 3s). The unit cell parameters of Li₃Ba₄Sc₂.₈₅Tb₀.₁₅B₈O₂₂ were: a = 5.2232(4) Å, b = 8.5640(5) Å, c = 11.4209(3) Å, α = 73.362(2)°, β = 78.560(8)°, γ = 87.037(5)°, and V = 479.27(9) Å³. The unit cell parameters of Li₃Ba₄Sc₂.₈₅Tb₀.₁₅B₈O₂₂ were: a = 5.2240 (6) Å, (A₂), \( v₂ \)-the antisymmetric stretch (E), and \( v₄ \)-the in-plane bend (E) at frequencies around 988, 725–820, 1250–1400, and 520–620 cm⁻¹, respectively. In the pyroborate ion B₂O₅, the B–O bonds are not equivalent and there is no symmetry (C₁ point group). It is likely that the peaks with Raman shifts around 954 and 1129 cm⁻¹ are associated with the BO₃ and BO₂ groups in B₂O₅, respectively. These characteristic peaks might indicate the existence of two different borate groups in the structure.

The temperature stability of Li₃Ba₄Sc₃B₈O₂₂ was studied by DSC. The thermal diagram has one endothermic peak of melting at 915°C on the heating curve and two exothermic peaks on the cooling curve at 875 and 860°C (Fig. 1s); this suggests an incongruent type of melting for this compound, which was confirmed by X-ray analysis performed on the melted sample (Fig. 2s). At least three additional phases were identified: Ba₃Sc(BO₃)₉, LiBaBO₃, and ScBO₃.

The unit cell parameters of the obtained doped Li₃Ba₄Sc₂.₈₅Tb₀.₁₅B₈O₂₂ borates were refined by the Le-Bail method (Fig. 3s). The unit cell parameters of Li₃Ba₄Sc₂.₈₅Tb₀.₁₅B₈O₂₂ were: a = 5.2232(4) Å, b = 8.5640(5) Å, c = 11.4209(3) Å, α = 73.362(2)°, β = 78.560(8)°, γ = 87.037(5)°, and V = 479.27(9) Å³. The unit cell parameters of Li₃Ba₄Sc₂.₈₅Tb₀.₁₅B₈O₂₂ were: a = 5.2240 (6) Å,
Li$_3$Ba$_4$Sc$_3$B$_8$O$_{22}$.Tb$^{3+}$ presented in Fig. 5 (green line) allows us to attribute to the well-known electronic transitions of Tb$^{3+}$ [26]. Transparent in the range of 250–800 nm is almost the PLE could be attributed to the $^7F_6 \rightarrow ^5D_{2}$ transition. In addition, the long-wavelength band at 480 nm in the range of compositions and temperatures. According to our single-crystal X-ray diffraction data, Li$_3$Ba$_4$Sc$_3$B$_8$O$_{22}$ crystallizes in the centrosymmetric space group P-1, with cell dimensions $a = 5.2230(4)$ Å, $b = 8.5609(6)$ Å, $c = 11.4157(8)$ Å, $\alpha = 73.3750(6)^\circ$, $\beta = 78.5020(6)^\circ$, $\gamma = 87.0502(6)^\circ$, and $V = 479.28(6)$ Å$^3$. In addition, the diffuse optical reflectance and luminescent properties of powdered Li$_3$Ba$_4$Sc$_3$B$_8$O$_{22}$.Tb$^{3+}$ were studied. This compound might be considered an effective narrowband luminescent material. For example, its selective excitation ability and visual transparency make it suitable for use in markers in recognition systems and document security.

4. Conclusions

The primary crystallization field of the Li$_3$Ba$_4$Sc$_3$B$_8$O$_{22}$ compound in the LiBO$_2$–Li$_3$Ba$_4$Sc$_3$B$_8$O$_{22}$ system was studied. The LiBO$_2$ solvent allowed us to grow high-quality Li$_3$Ba$_4$Sc$_3$B$_8$O$_{22}$-based crystals in a wide range of 300–800 nm. According to our single-crystal X-ray diffraction data, Li$_3$Ba$_4$Sc$_3$B$_8$O$_{22}$ crystallizes in the centrosymmetric space group P-1, with cell dimensions $a = 5.2230(4)$ Å, $b = 8.5609(6)$ Å, $c = 11.4157(8)$ Å, $\alpha = 73.3750(6)^\circ$, $\beta = 78.5020(6)^\circ$, $\gamma = 87.0502(6)^\circ$, and $V = 479.28(6)$ Å$^3$. In addition, the diffuse optical reflectance and luminescent properties of powdered Li$_3$Ba$_4$Sc$_3$B$_8$O$_{22}$.Tb$^{3+}$ were studied. This compound might be considered an effective narrowband luminescent material. For example, its selective excitation ability and visual transparency make it suitable for use in markers in recognition systems and document security.

Conflicts of interest

Authors declare no conflict of interests. On behalf of the authors Konstantin Kokh.

Acknowledgements

This work was supported by Russian Foundation for Basic Research (RFBR) project #18-32-0001, Russian Science Foundation project (RSF) project #19-42-02003 in the part of structure refinement, project GF MES RK * New rare-earth borates: synthesis, crystal-chemical features, optical properties (IRN AP05130794), and state assignment of IGM SB RAS.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jlumin.2019.116755.

References