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Tetrahedral Triangular 3-D Framework and Europium Luminescence in the Borate $BaBe_2(BO_3)_2$

Kathleen I. Schaffers and Douglas A. Keszler*

Department of Chemistry and Center for Advanced Materials Research, Gilbert Hall 153, Oregon State University, Corvallis, Oregon 97331-4003

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The new compound $BaBe_2(BO_3)_2$ is readily prepared by a solid-state reaction. It crystallizes in the orthorhombic space group *Fddd* ($Z = 8$) in a cell of dimensions $a = 11.725(2)$ Å, $b = 13.004(1)$ Å, $c = 6.286(1)$ Å, and $V = 958.4(2)$ Å^3. Residuals from least-squares refinement with 1689 unique reflections are $R = 0.024$ and $R_w = 0.042$. The structure is composed of two interpenetrating polyhedral frameworks. A beryllium–borate matrix containing dimers of edge-sharing Be-centered tetrahedra linked via regular, planar triangular BO_3 groups is penetrated by a framework constructed from Ba-centered dodecahedra sharing multiple edges. The optical emission characteristics of samples doped with the ions Eu^{2+} and Eu^{3+} are reported.

Introduction

The hydrated beryllium borates Be_2BO_3OH[1] and $Be_2BO_3OH{\cdot}H_2O$,[2] the anhydrous borate fluorides Be_2BO_3F[3] and K_2BeBO_3F,[4] and the alkaline-earth beryllium borates $SrBe_2(BO_3)_2$[5] and $CaBeB_2O_5$[6] are the only reported examples of solid-state oxides containing both beryllium and boron. We have developed an interest in preparing new compounds of this type because of their potential as optical materials; crystals of the type A_2BeBO_3F (A = K, Na), for example, are currently being examined as frequency converters for generation of coherent UV light.[7] To expand and develop the chemistry of these beryllium borates, we have examined phase equilibria in the systems $MO–BeO–B_2O_3$, where M = Ca, Sr, and Ba.

In a recent article we described the structure of the compound $SrBe_2(BO_3)_2$,[5] which contains Sr atoms segregated between layers of interconnected tetrahedra and triangles selectively occupied by Be and B atoms, respectively. Synthesis of the Ba derivative has revealed the existence of a stoichiometric analogue—$BaBe_2(BO_3)_2$—but one that crystallizes in a distinctive three-dimensional structure. We describe here this structure and the luminescence properties of powder samples containing the ions Eu^{2+} and Eu^{3+}.

Experimental Section

Crystals of $BaBe_2(BO_3)_2$ were grown in a Pt crucible from a melt of composition 2:1 $BaBe_2(BO_3)_2$:$LiBO_2$ by mass. The sample was melted at 1303 K and cooled at a rate of 9 K/h to 1098 K and 60 K/h to room temperature. The resulting crystals were physically separated from the crucible; then they were washed with dilute $HNO_3(aq)$ to remove the final traces of flux. A colorless block of approximate dimensions 0.18(1) × 0.2(1) × 0.32(1) mm was selected and mounted on a glass fiber with epoxy for structure analysis. X-ray data were collected with a Rigaku AFC6R single-crystal diffractometer and Mo Kα ($\lambda = 0.710\,69$ Å) radiation. The Laue symmetry was established as *mmm* on the diffractometer. For data collection, three reflections were chosen as standards and measured after each block of 200 data. Crystal and electronic stability were indicated by an overall average intensity decay of only 1.1%. Data of the type $+h$, $+k$, and $+l$ were obtained to $2\theta_{max} = 120°$.

Table 1. Crystallographic Data for $BaBe_2(BO_3)_2$

chem formula	$BaBe_2(BO_3)_2$	fw	272.97
a	11.725(2) Å	space group	*Fddd* (No. 70)
b	13.004(1) Å	T	23 °C
c	6.286(1) Å	λ	0.710 69 Å
V	958.4(2) Å^3	ρ_{calcd}	1.891 g cm^{-3}
Z	8	$R(F_o)^a$	0.024
μ	41.17 cm^{-1}	$R_w(F_o)^a$	0.042

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$.

Table 2. Positional Parameters and Equivalent Displacement Coefficients for $BaBe_2(BO_3)_2$

	x	y	z	B_{eq} (Å^2)^a
Ba	$^5/_8$	$^1/_8$	$^1/_8$	0.713(4)
Be	$^3/_8$	0.2821(2)	$^7/_8$	0.67(6)
B	0.3397(2)	$^1/_8$	$^1/_8$	0.59(4)
O1	0.2227(1)	$^1/_8$	$^1/_8$	0.89(3)
O2	0.3980(1)	0.2141(1)	0.0828(2)	0.73(2)

^{a} $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

The structure was solved and refined by standard procedures with computer programs from the TEXSAN crystallographic software package.[8] After least-squares refinement with isotropic displacement coefficients on each atom, the data were corrected for absorption with the program DIFABS (transmission factors = 0.92–1.28).[9] Refinement with anisotropic displacement coefficients on each atom, a secondary extinction coefficient = 0.326×10^{-6}, and 1689 data having $F_o^2 \geq 3\sigma(F_o^2)$ converged to $R = 0.024$ and $R_w = 0.042$. The final difference electron density map exhibits a maximum peak corresponding to 0.49% of the height of the Ba atom. Crystal data and atomic parameters are summarized in Tables 1 and 2, respectively.

A powder sample was prepared by heating in air a stoichiometric ratio of the reagents BaB_2O_4 and BeF_2 (Cerac, 99.5%). (The reagent BaB_2O_4 was synthesized by heating a 1:1 molar ratio of $Ba(NO_3)_2$ (Aesar, reagent grade):B_2O_3 (Alfa, 99%) at 923 K for 1 h and 1023 K for 12 h.) The borate–fluoride mixture was ground under hexane and heated in an alumina crucible at 923 K for 8 h to hydrolyze the BeF_2 to BeO, followed by heatings at 1023 K for 24 h and 1073 K for 24 h that were interrupted intermittently to grind the samples. The diffraction pattern obtained with a Philips automated powder diffractometer agrees well with a pattern calculated with the computer program LAZY-PULVERIX[9] and the results of the structure determination. Unit cell parameters were also refined from the powder data by selecting 15 peaks in the range $24 \leq 2\theta \leq 60°$; positions were corrected with NIST Si standard 640b. Least-squares refinement with the computer program POLSQ affords the values $a = 11.73(2)$, $b = 13.00(2)$, and $c = 6.292(8)$ Å. These values are

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statistically equivalent to those obtained from the single-crystal data (Table 1), indicating that the crystal chosen for data collection is representative of the bulk material.

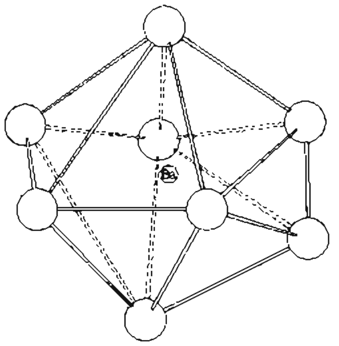
Powder samples of $BaBe_2(BO_3)_2$ nominally doped with 2 mol % Eu^{2+} (Eu_2O_3, Aesar, 99.99%) were prepared according to the method described above, except the sample was heated in a 95%:5% N_2:H_2 reducing atmosphere. An attempt was made to prepare a doped sample containing only Eu^{3+} by heating mixtures in air. Here, a 2 mol % substitution of K atoms for Ba atoms was included in the preparation to compensate for the +3 charge of the lanthanide.

Steady-state room-temperature luminescence and excitation spectra were obtained on a computer-controlled right-angle spectrometer. Light from an Oriel 300-W Xe lamp was passed through a 50-cm water filter, focused onto the slits of a Cary Model-15 prism monochromator, and directed onto the sample. Luminescence was collected at a right angle to excitation, dispersed through an Oriel 22500 $^1/_8$-m monochromator, and detected with a Hamamatsu R636 photomultiplier tube. The signal was collected and amplified with a Keithley Model 602 picoammeter and then converted to a digital signal for computer acquisition. Spectrometer control and data acquisition were achieved with programs written in this laboratory. The excitation spectrum was corrected by employing sodium salicylate as a quantum counter.

Results and Discussion

A labeled drawing of the contents within the unit cell of the title compound is provided in Figure 1. The structure contains a single crystallographic type of each metal atom (Ba, Be, B) and two types of O atoms. The B atom occupies a distorted O triangle, and the Be atom, a distorted tetrahedron. Adjacent tetrahedra share edges to form Be_2O_6 dimers, and these dimers are bridged by the BO_3 triangles to make the simple and unique three-dimensional framework shown in Figure 2. The Ba atom is positioned in an irregular triangulated dodecahedral site, **1**, within the framework. These dodecahedra share edges and form six-membered rings, **2**, that further condense in three dimensions while interpenetrating the beryllium borate matrix.

The O polyhedron about the Ba atom has D_2 symmetry and is comprised exclusively of O2 atoms. Two types of Ba–O2 interactions are present—four equivalent lengths at 2.915(1) Å and four at 2.797(1) Å.



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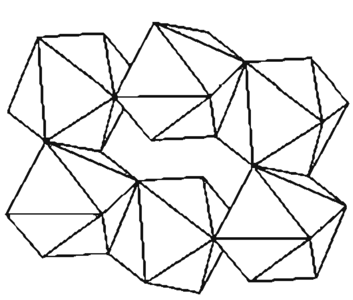
Insofar as the polyhedron may be described as two interpenetrating distorted tetrahedra, each group of lengths corresponds to the distance between the Ba atom and the vertices of one of these tetrahedra.



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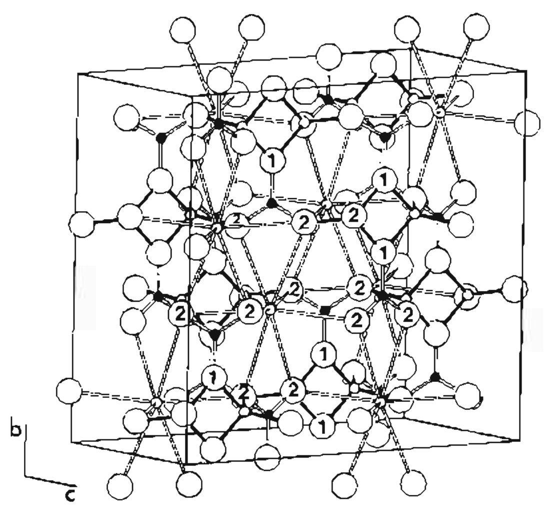
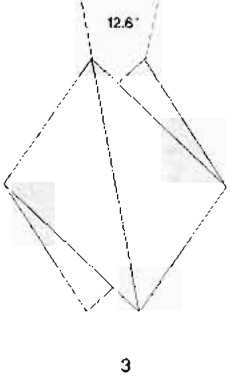


Figure 1. Drawing of the unit cell of $BaBe_2(BO_3)_2$. Small open circles with open bonds are B atoms, small open circles with shaded bonds are Be atoms, small shaded circles with open bonds are B atoms, and large open circles are O atoms.

The distances may be compared with the range of Ba–O distances, 2.644(2)–3.020(2) Å, in the distorted 8-coordinate site of the compound $Ba_2LiB_5O_{10}$[11] and a value of 2.80 Å calculated from Shannon and Prewitt crystal radii.[12] Angles for O2–Ba–O2 range from 48.20(4) to 116.47(3)° (cf. Table 3).

The O environment about the B atom deviates insignificantly from D_{3h} symmetry; the average O–B–O angle is 120.0(2)°, and the distances B–O1 and B–O2 are statistically equivalent.

The distorted tetrahedral environment about the Be atom is characterized by two distances—1.665(3) Å for Be–O1 (×2) and 1.599(2) Å for Be–O2 (×2) with the longer interactions spanning the shared edge of the Be_2O_6 dimer. These lengths are comparable to the average distance 1.63(4) Å observed in $SrBe_2(BO_3)_2$ and the value 1.61 Å computed for a 4-coordinate Be atom. Similar Be-centered dimers have been previously observed in the minerals eudidymite and epididymite ($Na_2Be_2Si_6O_{15}\cdot H_2O$),[13,14] β-BeO,[15] and $SrBe_2(BO_3)_2$. Each of these compounds contains an approximate Be–O–Be–O square with O–Be–O and Be–O–Be angles deviating from orthogonality by no more than 5°. With a Be–O1–Be angle of 93.0(2)° in the Ba compound, a similar square is observed. In the Sr compound the Be···Be separation is 2.35(1) Å, in β-BeO, 2.20 Å, and in the title compound, 2.416(7) Å. The two terminal edges of the tetrahedra in the title compound are also twisted relative to one another by 12.6°, **3**.



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The coordination numbers and geometries about each of the two O atoms are normal. Atom O1 occupies a distorted

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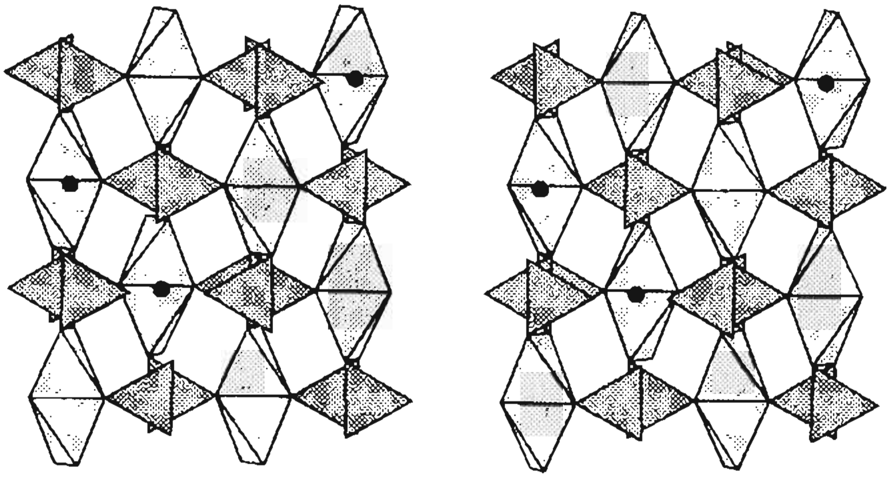

Figure 2. Stereoview of beryllium borate framework. Small filled circles are Ba atoms, lightly shaded polyhedra are BeO_4 tetrahedra, and deeply shaded polyhedra are BO_3 triangles.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $BaBe_2(BO_3)_2$

Ba–O2 (×4)	2.915(1)	O2–Ba–O2	48.20(4)
Ba–O2 (×4)	2.797(1)	O2–Ba–O2	71.00(4)
		O2–Ba–O2	74.37(2)
		O2–Ba–O2	83.25(4)
		O2–Ba–O2	97.83(5)
		O2–Ba–O2	98.58(3)
		O2–Ba–O2	116.47(3)
Be–O1 (×2)	1.665(3)	O1–Be–O1	87.0(2)
Be–O2 (×2)	1.599(2)	O1–Be–O2	106.53(5)
		O1–Be–O2	121.14(6)
		O2–Be–O2	112.9(2)
B–O1	1.372(3)	O1–B–O2	119.9(1)
B–O2 (×2)	1.373(2)	O2–B–O2	120.2(2)

3-coordinate site having bonds to 1 B and 2 Be atoms with the angle Be–O1–B = 133.48(9)°. Again, pairs of O1 atoms from the shared edge of the Be_2O_6 dimer, and the environment of the O1 atom and the Be–O1–B angle differ insignificantly from the O environment and Be–O–T angles (T = Si, B) observed in the structures noted above. Atom O2 is bound by 1 B, 1 Be, and 2 Ba atoms in an irregular 4-coordinate environment.

Emission and excitation spectra (Figure 3) of the Eu^{2+}-doped sample exhibit broad peaks with maxima near 392 and 310 nm, respectively. The wavelength of maximum emission is comparable to those of the polyborates SrB_4O_7 (368 nm),[16] BaB_8O_{13} (400 nm),[17] and SrB_6O_{10} (390 nm)[18] but shorter than those in the Ba compounds $BaGdB_9O_{16}$ (460 nm)[19] and $BaMgAl_{10}O_{17}$ (450 nm).[20] The broad excitation band indicates that the lowest excited state is $4f^65d^1$ rather than $4f^7$. The $4f^7$ excited state would readily be evident by the presence of a sharp peak in the emission spectrum near 360 nm. Such a peak has been observed in numerous fluorides as well as in the doped oxide $BaBe_2Si_2O_7$,[21] where, at room temperature, the f → f transition at 360 nm is superimposed on the broad emission band. Relative to the title beryllium borate, the $4f^65d^1$ levels in the silicate rise in energy because of a weaker crystal field at the Ba site.

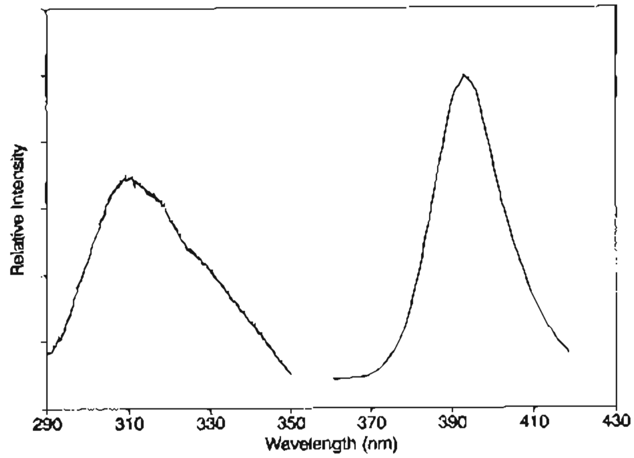

Figure 3. Room-temperature excitation (left) and emission (right) spectra of Eu^{2+}:$BaBe_2(BO_3)_2$. For excitation λ_{em} = 400 nm, and for emission λ_{ex} = 325 nm.

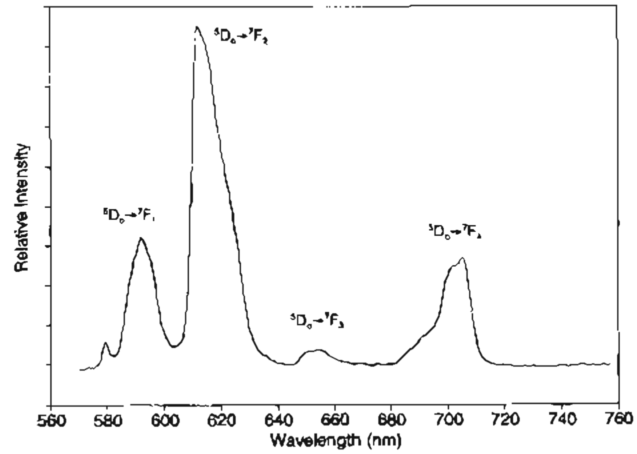

Figure 4. Room-temperature emission spectrum of Eu^{3+}:$BaBe_2(BO_3)_2$ (excitation wavelength = 394 nm).

The breadth of the excitation band (Figure 3) is dictated by the crystal-field splitting of the d levels, and under D_2 symmetry these levels transform as 2a, b_1, b_2, and b_3. At sufficiently low temperatures, the splittings among these levels may be resolved. Overall, the optical results indicate that the beryllium borate matrix is comparable to other rigid polyborate hosts that efficiently produce luminescence when doped.

When illuminated with a UV lamp, the powder doped nominally with Eu^{3+} exhibits an unusual luminescence that appears pink to the eye—typically Eu^{3+}-doped compounds luminesce to give red to orange-red colors. To explain this result, a room-temperature emission spectrum was obtained, and a portion is shown in Figure 4. The relative intensities of the magnetic-dipole transitions ${}^5D_0$

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$\rightarrow {}^7F_1$ and the electric-dipole transitions ${}^5D_0 \rightarrow {}^7F_2$ appear to be consistent with the substitution of Eu^{3+} onto the Ba site. Although the site symmetry is D_2, the ligands are distributed in an approximately centrosymmetric manner about the Ba atom. The peaks in the spectrum, however, are considerably broadened relative to those commonly observed in spectra of Eu^{3+}-doped samples. This broadening could arise from a highly inhomogeneous distribution of the ion in the beryllium borate matrix. Such a distribution could result from a charge compensation of the Eu^{3+} ion by substitution of Be^{2+} on B^{3+} sites, but it may be that some of the Eu^{3+} ions have precipitated in a secondary, impurity phase. At higher energies the emission spectrum is identical to that of the Eu^{2+}-doped sample; hence, the combination of both Eu^{2+} and Eu^{3+} in the sample produce the pink emission. The ready reduction of Eu^{3+} to Eu^{2+} by heating the sample in air certainly reflects the relatively high acidity of the beryllium borate host, which should stabilize lower oxidation states.

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Supplementary Material Available: Tables listing complete crystallographic and data collection information and anisotropic displacement coefficients (2 pages). Ordering information is given on any current masthead page.