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Synthesis, Crystal Structure and Optical Spectra of Europium Borate Fluoride $Eu_5(BO_3)_3F$

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Europium borate fluoride, $Eu_5(BO_3)_3F$, was synthesised as a single-phase crystalline powder starting from europium oxide, europium fluoride and boron oxide at 1370 K. $Eu_5(BO_3)_3F$ crystallises in the space group *Pnma*. Optical spectroscopy (emission and absorption) on $Eu_5(BO_3)_3F$ confirms the presence of Eu^{2+} and delivered no evidence for Eu^{3+}. The vibrational spectra of $Eu_5(BO_3)_3F$ are also reported.

Introduction

Alkaline-earth metal halophosphates, also known as apatites, have the generic molecular formula $M_5(PO_4)_3Y$ (M = Ca, Sr, Ba; Y = F, Cl, Br, OH) and not only form a substantial part of human bones and the mineral deposits of calcium but are also well known for their applications as phosphors[1,2] and laser hosts.[3] Solid-state compounds of the composition M_5X_3Y are therefore normally compared and discussed in terms of the mother compound apatite. In our contribution we shine light on a europium (M = Eu) borate (X = BO_3) fluoride (Y = F) derivative of apatite.

Borate compounds are currently very attractive owing to their wide range of applications.[4] They show high transparency far below the visible spectrum, high chemical stability and, for some of them, crystals with high optical quality. Therefore, alkaline-earth[5,6] and rare-earth fluoride borates like $Ln_3(BO_3)_2F_3$ (Ln = Sm, Eu, Gd)[7] were investigated to study their optical and luminescence properties, which make them good candidates for luminescence applications.[8] Besides $Eu_3(BO_3)_2F_3$, no other europium borate fluorides are known.

Our contribution reports the first crystal-structure determination of $Eu_5(BO_3)_3F$. To the best of our knowledge, this is the first pure europium(II)-containing borate fluoride. Its luminescence and optical properties are discussed on the basis of X-ray structural analysis.

Results and Discussion

Crystal Structure

Europium fluoride tris(borate), $Eu_5(BO_3)_3F$, crystallises in the orthorhombic space group *Pnma* (no. 62), isotypic with that of $Sr_5(BO_3)_3X$ (X = F, Br).[6] The crystal structure of $Eu_5(BO_3)_3F$ is similar to that of apatite[9] and can be understood as a hexagonal packing of columns consisting of face-sharing, distorted Eu octahedra (Eu1 and Eu3, dark grey spheres in Figure 1) along the *a* axis. Within these columns or channels, respectively, the fluoride anions are found. Our X-ray data based structure refinement delivers no evidence for any disorder of the fluoride anions. Between each four channels further Eu atoms (Eu2) are located in a ladder-type arrangement (Figure 1, Eu2: light grey). The borate anions $(BO_3)^{3-}$ occupy two different crystallographic positions. One vertex of the B1 centred borate anions is located in the centre of each ladder segment, forming zigzag chains of borate anions above and below the ladder of Eu2 atoms. Two B2 centred borate anions interconnect two hexagonal channels. Compared with fluoroapatite,[10] the bor-

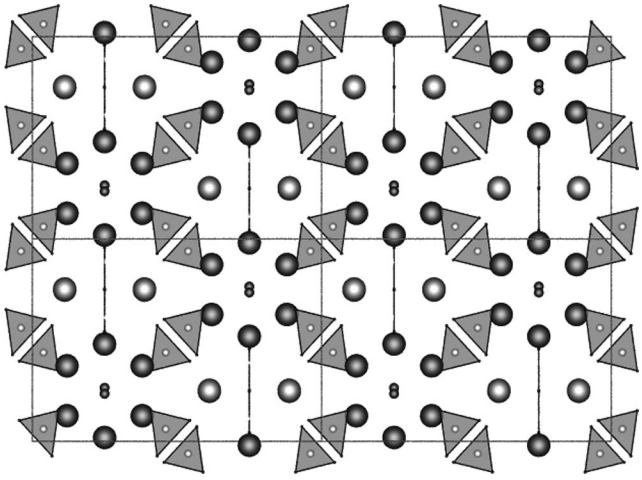

Figure 1. Two unit cells of the crystal structure of $Eu_5(BO_3)_3F$ viewed along the *a* axis. Dark (Eu1 and Eu3) and light grey spheres (Eu2) represent the europium atoms and the light grey triangles the BO_3^{3-} anions. The F atoms (small dark grey spheres) are located within the hexagonal Eu channels.

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Table 1. Atomic coordinates the fractional occupation factors (f.o.f.), their respective isotropic displacement parameters/Å^2 for $Eu_5(BO_3)_3[O_{0.0(1)}F_{1.0(1)}]$ with esd values in parentheses; the Wyckoff positions are indicated.

Atom	Wyckoff	f.o.f.	x	y	z	U_{eq}
Eu1	4c		0.21234(6)	1/4	0.48076(4)	0.00861(12)
Eu2	8d		–0.02880(4)	0.38795(2)	0.75272(4)	0.00864(9)
Eu3	8d		0.24893(4)	0.38001(2)	0.12676(3)	0.01158(10)
F	4c	0.92(12)	0.3764(8)	1/4	0.2647(6)	0.020(2)
O	4c	0.08(12)	0.3764(8)	1/4	0.2647(6)	0.020(2)
B1	4c		0.2179(9)	1/4	–0.1120(6)	0.0079(18)
O11	4c		0.3858(8)	1/4	–0.0444(6)	0.0113(13)
O12	4c		0.2159(8)	1/4	–0.2531(6)	0.0103(12)
O13	4c		0.0551(8)	1/4	–0.0381(7)	0.0166(15)
B2	8d		0.3016(9)	0.5388(4)	–0.0609(5)	0.0113(14)
O21	8d		0.2173(6)	0.4556(3)	–0.1035(4)	0.0136(9)
O22	8d		0.4088(6)	0.5900(3)	–0.1516(5)	0.0137(10)
O23	8d		0.2778(6)	0.5685(3)	0.0722(4)	0.0123(9)

Table 2. Anisotropic displacement parameters U_{ij}/Å^2 for the atoms in $Eu_5(BO_3)_3[O_{0.0(1)}F_{1.0(1)}]$ with esd values in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu1	0.0083(2)	0.0092(2)	0.0084(2)	0.000	0.00076(17)	0.000
Eu2	0.00757(15)	0.00900(16)	0.00935(15)	–0.00036(15)	–0.00035(11)	–0.00017(12)
Eu3	0.01506(16)	0.01115(16)	0.00852(15)	–0.00016(12)	0.00099(12)	0.00130(12)
F	0.027(4)	0.021(4)	0.012(3)	0.000	0.007(2)	0.000
O	0.027(4)	0.021(4)	0.012(3)	0.000	0.007(2)	0.000
B1	0.007(4)	0.009(5)	0.008(4)	0.000	0.002(4)	0.000
O11	0.012(3)	0.014(4)	0.008(3)	0.000	–0.003(2)	0.000
O12	0.010(3)	0.008(3)	0.013(3)	0.000	–0.002(2)	0.000
O13	0.016(3)	0.021(4)	0.014(4)	0.000	0.009(3)	0.000
B2	0.012(3)	0.009(3)	0.013(3)	0.000(3)	–0.004(3)	0.004(3)
O21	0.016(2)	0.011(2)	0.014(2)	–0.0035(18)	–0.0040(19)	–0.0018(19)
O22	0.013(2)	0.016(3)	0.012(2)	0.007(2)	0.0010(18)	–0.0032(18)
O23	0.012(2)	0.014(2)	0.011(2)	–0.0022(18)	0.0015(17)	0.0005(19)

ate anions replace the PO_4 tetrahedra. Tables 1 and 2 show the positional and displacement parameters for all atoms. In Table 3, selected interatomic distances and angles are listed. The details of the X-ray data collection are summarised in Table 4.

Table 3. Selected interatomic distances/Å and angles/° in $Eu_5(BO_3)_3[O_{0.0(1)}F_{1.0(1)}]$ with esd values in parentheses.

Eu1–O	2.441(6)–2.752(5) (5×)
Eu2–O	2.467(4)–3.057(5) (6×)
Eu3–O	2.501(4)–2.824(5) (5×)
Eu1, Eu3–F	2.438(6)–2.463(4) (2×)
B–O	1.383(6)–1.392(6) (6×)
O–Eu–O	52.49(13)–160.03(12)
F–Eu–O	72.5(2)–150.4(2)
O–B–O	119.2(5)–121.4(5)

All borate groups consist of boron triangularly coordinated by oxygen atoms. The B–O bond lengths vary in a very small range from 1.386(6) to 1.392(6) Å. The O–B–O angles range between 119 and 121°. The irregular coordination environments of the Eu atoms are shown in Figure 2. The europium atoms are seven- (6 O and 1 F), eight- (7 O and 1 F) and ninefold (only O) coordinated. The Eu1 and Eu3 atoms are surrounded both by oxygen atoms and fluorine atoms [Eu–F 2.438(6)–2.463(4) Å]. The Eu–O bond lengths vary from 2.441(6) to 2.824(5) Å. Both represent typical values for divalent europium compounds.

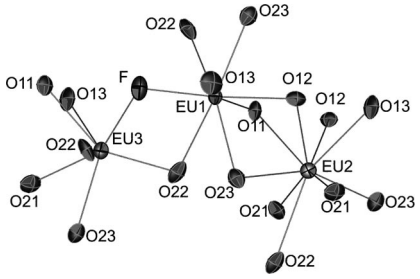

Figure 2. Coordination environments of the Eu atoms. The displacement ellipsoids are drawn at the 90% probability level.

Luminescence of $Eu_5(BO_3)_3F$

Figure 3 shows the excitation and emission spectra of the title compound. The excitation spectrum is characterised by a broad unresolved band that corresponds to a $4f^7 \rightarrow 4f^65d$ absorption of the Eu^{2+} ions. The broad-band emission, also characteristic for 5d–4f transitions in Eu^{2+}, peaking at 418 nm is rather weak. Because $Eu_5(BO_3)_3F$ is a nondoped 100% compound, this is no surprise. Characteristic luminescence bands of Eu^{3+}, which exhibit sharp 4f–4f transitions between 580 and 650 nm, could not be observed. Therefore, there was no spectroscopic indication for the presence of Eu^{3+} in $Eu_5(BO_3)_3F$.

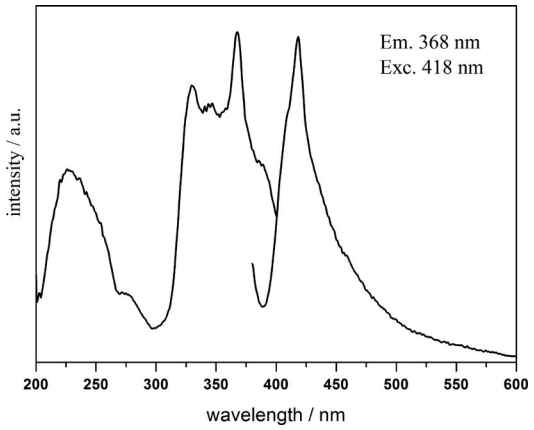

Figure 3. Fluorescence emission (right, excited at 368 nm) and excitation spectra (left, recorded at the emission of 418 nm) of $Eu_5(BO_3)_3F$.

UV/Vis Reflection Spectra

The diffuse reflection spectrum of $Eu_5(BO_3)_3F$ is shown in Figure 4. We observed that the reflection decreases significantly below 600 nm. The characteristic absorption of the europium ions was found in the region between 370 and 250 nm, which is due to the 4f–5d transitions of Eu^{2+}.[11] The measured UV/Vis absorption spectrum is in agreement with the yellow colour of the title compound.

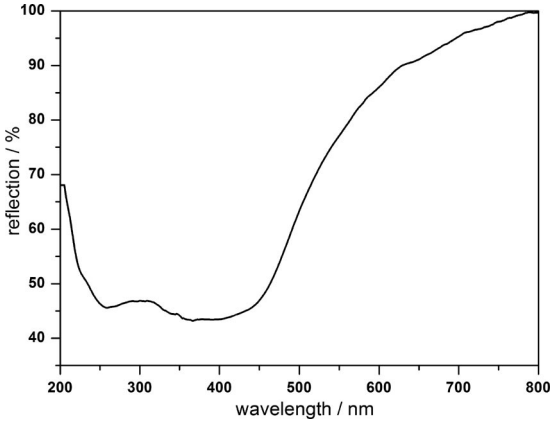

Figure 4. UV/Vis reflection spectra of $Eu_5(BO_3)_3F$.

Vibrational Spectroscopy

Figure 5 shows the infrared and Raman spectra of the title compound. The only characteristic bands of the BO_3 group are expected in the range below 1600 cm^{-1}.[12] The strongest peaks (1381 and 1272 cm^{-1}) in $Eu_5(BO_3)_3F$ can be assigned to the $\nu_{as}(BO_3)$ vibration of the B–O bonds. A very weak but relatively sharp band is observed at 952 cm^{-1}, attributable to $\nu_s(BO_3)$ stretching vibrations. The out-of-plane bending is observed near 769 cm^{-1}. At 591 cm^{-1}, middle in-plane bending modes are detected. All bands observed in the range from 1500 to 500 cm^{-1} in the Raman spectra correspond to typical B–O group vibration modes of non-condensed borate anions. The strongest emission at 1362 cm^{-1} originates from B–O asymmetric stretching and at 917 cm^{-1} symmetric stretching vibration. No significant vibrations could be detected above 1600 cm^{-1}.

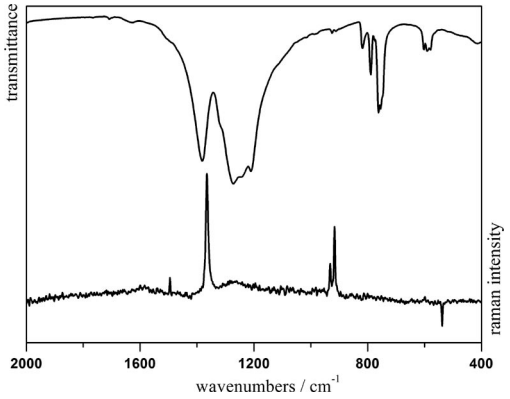

Figure 5. Infrared und Raman vibrational spectra of $Eu_5(BO_3)_3F$.

Thus, the observed frequencies in the spectra correspond very well with the expected values and our structure model.

Conclusion

In this contribution we presented the first borate fluoride of europium(II). The optical spectra gave no evidence for the presence of Eu^{3+} in $Eu_5(BO_3)_3F$. As no other elements could be identified, the overall composition is $Eu_5(BO_3)_3F$. Furthermore, our structure model based on single-crystal structure analysis based on X-ray diffraction data was confirmed by the vibrational spectra.

Experimental Section

Synthesis: Mixtures of Eu_2O_3 (35.4 mg, 0.101 mmol, ChemPur, 99.99%), EuF_3 (8.4 mg, 0.040 mmol, ChemPur, 99.9%) and B_2O_3 (7 mg, 1 mmol, ChemPur, 99.9%) were pulverised and filled in boron nitride crucibles. In general, the reducing conditions in a boron nitride crucible are sufficient for the reduction of Eu^{3+} to Eu^{2+}. The complete reaction was carried out under constant argon flow by applying the following temperature program: Heating up to 1370 K with a rate of 30 $K\,h^{-1}$, holding this temperature for 60 h and then rapidly cooling down to room temperature. We obtained 39.6 mg of the yellow coarsely crystalline product; on a few crystals adhesive white BN from the crucible material was found. The chemical composition of carefully selected single crystals of $Eu_5(BO_3)_3F$ was checked by energy dispersive X-ray spectroscopy (EDX). No other elements than those expected could be identified. The phase purity of the assorted sample was confirmed by powder X-ray diffraction (Figure 6).

Crystal Structure Determination: Single-crystal X-ray diffraction data were collected with a Rigaku Spider Image-Plate diffractometer by using Mo-K_α radiation (λ = 0.71073 Å) at room temperature and corrected for absorption by applying a multiscan correction.[13] The crystal structure of $Eu_5(BO_3)_3[O_{0.0(1)}F_{1.0(1)}]$ was solved by direct methods by using the SHELXTL program package[14] in space group *Pnma* (no. 62) and refined with anisotropic displacement parameters for all atoms.

Because EDX revealed the presence of fluorine in the compound, we checked very carefully on which sites in the crystal structure

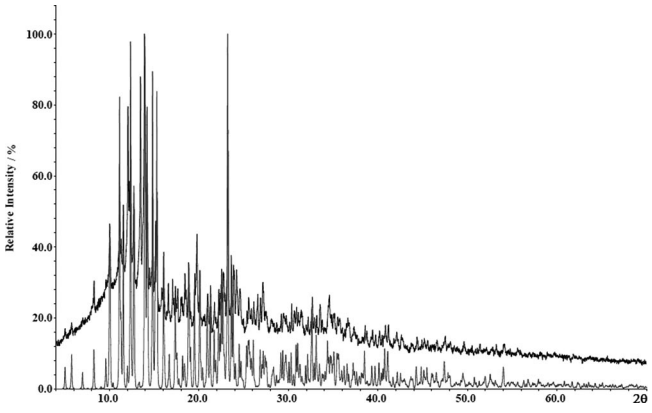

Figure 6. Observed (black) and calculated (grey) X-ray powder diffraction pattern (Mo-K_α radiation) of $Eu_5(BO_3)_3F$.

oxygen may be replaced by fluorine. Therefore a mixed refinement on each O site starting from "$Eu_5(BO_3)_3O$" was performed. Only on the sites within the hexagonal Eu channels (see structure description) could F be refined with reasonable thermal displacement factors. The fractional occupation factor amounts for F to 1.0(1) and for O to 0.0(1). Thus a small contribution of oxygen may be localised on this channel position. This is very important, as any deviation from one fluorine atom per formula unit calls for the presence of Eu^{3+} ions in the structure. We addressed and clarified this topic by UV/Vis and fluorescence spectroscopy, which delivered no evidence for the presence of Eu^{3+} in our sample (see above). Accordingly, we used the composition $Eu_5(BO_3)_3F$ throughout the manuscript.

The relevant crystallographic data and further details of the X-ray data collection are summarised in Table 4. Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-421537.

Powder X-ray Diffraction: X-ray powder diffraction data of $Eu_5(BO_3)_3F$ were collected in Debye–Scherrer geometry with a STOE Stadi P diffractometer by using Mo–K_α radiation (linear PSD detector, with steps of 0.5, acquisition time: 200 s/step) at room temperature. The observed intensities are in very good agreement with the calculated diffraction pattern based on the single crystal data (Figure 6).

Vibrational Spectroscopy: An FTIR spectrum was measured at room temperature by using a Bruker IFS 66v/S spectrometer. The samples were thoroughly mixed with dried KBr (ca. 1 mg sample, 300 mg of KBr). Raman spectra were recorded with a Bruker FRA 106/S module with a Nd–YAG laser (λ = 1064 nm) with scanning range from 4000 to 400 cm^{-1}.

Luminescence Spectroscopy: Luminescence spectra were recorded at room temperature with a Perkin–Elmer LS55 fluorescence spectrometer equipped with a Xe discharge lamp (equivalent to 20 kW for 8 μs duration) and a gated photomultiplier with modified S5 response. The spectra have been corrected for excitation and emission.

UV/Vis Spectroscopy: The optical reflection spectrum for $Eu_5(BO_3)_3F$ was recorded by using a UV/Vis spectrophotometer (Cary 300 Scan, Varian) and is shown in Figure 4. The spectrum was obtained from 200 to 800 nm at a scan rate of 100 nm min^{-1}.

Table 4. Crystallographic data for $Eu_5(BO_3)_3[O_{0.0(1)}F_{1.0(1)}]$.

M / g mol^{-1}	955.1
Crystal shape	needles
Temperature / K	293(2)
Radiation (λ / Å)	Mo-K_α (0.71073)
Crystal colour	yellow
Crystal system	orthorhombic
Space group	*Pnma* (no.62)
a / Å	7.2249(13)
b / Å	14.124(3)
c / Å	9.8591(18)
V / $Å^3$	1006.1(3)
Z	4
$\rho_{x\text{-ray}}$ / g cm^{-3}	6.306
μ / mm^{-1}	30.76
F(000)	1644
h	$-9 \rightarrow 9$
k	$-18 \rightarrow 18$
l	$-12 \rightarrow 12$
$T_{min.}$, $T_{max.}$	0.4166, 0.8228
R_{int}, R_σ	0.0679, 0.0222
$2\theta_{max.}$ / °	60.0
Measured reflections	21926
Independent reflections	1199
Observed reflections [$F_o^2 \geq 2\sigma(F_o^2)$]	1056
R_1, wR_2	0.027, 0.038
GooF	1.082
Parameters collected	93
Min., max resid. electron dens. / e $Å^{-3}$	–1.000, 1.258
w^{-1}	$\sigma^2 F_o^2 + (0.0118P)^2 + 6.8408P$
P	$(F_o^2 + 2F_c^2)/3$

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