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Synthesis and structural characterization of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$

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Abstract: $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ was prepared by high-temperature solid state synthesis at 900°C in a platinum crucible from lithium carbonate, potassium carbonate, boric acid, and europium(III) oxide. The title compound crystallizes in the orthorhombic space group $Pca2_1$ (no. 29) ($Z=4$). The structure was refined from single-crystal X-ray diffraction data: $a=21.126(2)$, $b=6.502(2)$, $c=17.619(2)$ Å, $V=2420.1(2)$ Å³, $R1=0.0183$ and $wR2=0.0412$ for all data. The crystal structure of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ is isotypic to $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$ featuring isolated BO_3 units and LiO_6 octahedra forming $[\text{Li}_3\text{B}_4\text{O}_{21}]$ units in the ac plane, which are linked by additional BO_3 units. The K^+ and Eu^{3+} cations are arranged in the cavities of the structure.

Keywords: crystal structure; europium lithium potassium borate; solid-state reaction.

1 Introduction

Concerning their wide range of applications, borates have gained remarkable interest in the scientific community. They show a good chemical and thermal stability, high transparency in the UV, and non-linear optical properties [1–3]. Due to their large band gap, borates are possible host structures for luminescent ions, e.g. YBO_3 [4], GdBO_3 [4], GdB_5O_9 [5], $\text{LiRE}_6\text{O}_5(\text{BO}_3)_3$ (RE =rare earth metal) [6], and $\text{Li}_3\text{RE}(\text{BO}_3)_2$ [7] doped with Ce^{3+} , Eu^{3+} , and Tb^{3+} are appropriate phosphors for use in plasma display panels (PDPs). Additionally, there exist several compounds in the ternary system $\text{A}_2\text{O}-\text{RE}_2\text{O}_3-\text{B}_2\text{O}_3$ (A =alkali metal) like $\text{Li}_6\text{Y}(\text{BO}_3)_3$ doped with Yb^{3+} being promising materials for short pulse laser applications [8–10], or Ce^{3+} doped $\text{Li}_6\text{RE}(\text{BO}_3)_3$

($\text{RE}=\text{Gd}$, Y) as an efficient new scintillator material for neutron detection [11].

Just very recently, we reported the synthesis of $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$ [12] in the quaternary system $\text{A}_2\text{O}-\text{A}'_2\text{O}-\text{RE}_2\text{O}_3-\text{B}_2\text{O}_3$ (A , A' =alkali metals). To date, this system exhibits only five other compounds, viz. $\text{CsLi}_2\text{Gd}_4(\text{BO}_3)_5$ [13], $\text{K}_6\text{Li}_3\text{Sc}_2\text{B}_{15}\text{O}_{30}$ [14], $\text{K}_9\text{Li}_3\text{Nd}_3(\text{BO}_3)_7$ [15], and $\text{A}_2\text{LiNd}(\text{BO}_3)_2$ ($\text{A}=\text{Rb}$, Cs) [15]. With the synthesis of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$, we could now extend the list of known compounds in the field of rare earth borates possessing two different alkali cations with another example. In the following, we report the preparation and single-crystal X-ray structure determination of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$. Furthermore, the compound was characterized by infrared and luminescence spectroscopy.

2 Experimental section

2.1 Synthesis

As mentioned above, our synthesis was based on the system $\text{Li}_2\text{O}-\text{K}_2\text{O}-\text{Eu}_2\text{O}_3-\text{B}_2\text{O}_3$ leading to the new compound $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$. The starting materials Li_2CO_3 (99.5%, Alfa Aesar, Karlsruhe, Germany), K_2CO_3 (99.99%, ChemPur, Karlsruhe, Germany), Eu_2O_3 (99.99%, Smart Elements, Wien, Austria) and H_3BO_3 (99.5%, Merck, Darmstadt, Germany) were weighed, finely ground in an agate mortar according to the molar ratio of 3:6:1:7, and filled into a platinum FKS 95/5 crucible (feinkornstabilisiert, 95% Pt, 5% Au, Ögussa, Wien, Austria).

The sample was positioned in an electric resistance furnace (Nabertherm muffle furnace) and heated up to 900°C with a rate of 90°C h⁻¹ and maintained at that temperature for 24 h. After that period, the temperature was lowered to 500°C with a rate of 2°C h⁻¹ followed by switching off the furnace. The product cooled down to room temperature by natural rate.

The product $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ was obtained in form of colorless, air and water resistant crystals. Any effort to synthesize $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ from a stoichiometric mixture of the starting materials failed. The synthesis was only possible with the exact composition and heating process mentioned above.

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2.2 Crystal structure analysis

The powder X-ray diffraction (PXRD) pattern of the reaction product was measured in transmission geometry using a Stoe Stadi P powder diffractometer with Ge(111)-monochromatized $\text{MoK}_{\alpha 1}$ ($\lambda = 70.93$ pm) radiation. The comparison of the experimental and theoretical PXRD pattern simulated from single-crystal data of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ showed that they match well (Fig. 1). However, the experimental PXRD pattern has some additional reflections (marked with red asterisks), which do not belong to $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ and arise from side products, which could not be assigned until now.

For the single-crystal structure analysis, small crystals of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ were isolated by mechanical fragmentation and picked using a polarization microscope. A Bruker D8 Quest Kappa diffractometer with MoK_{α} radiation ($\lambda = 71.073$ pm) was used to collect the single-crystal intensity data at room temperature of 298 K. A multi-scan absorption correction (SADABS-2014 [16]) was applied to the intensity data sets. All relevant details of the data collection and the refinement are listed in Table 1. The orthorhombic space group $Pca2_1$ was derived from the systematic extinctions of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$. The structure solution and parameter refinement were successfully performed with SHELXL-13 [17, 18]. All atoms were refined anisotropically and the final difference Fourier synthesis did not reveal any significant residual peaks. The structural refinement of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ was based on the positional

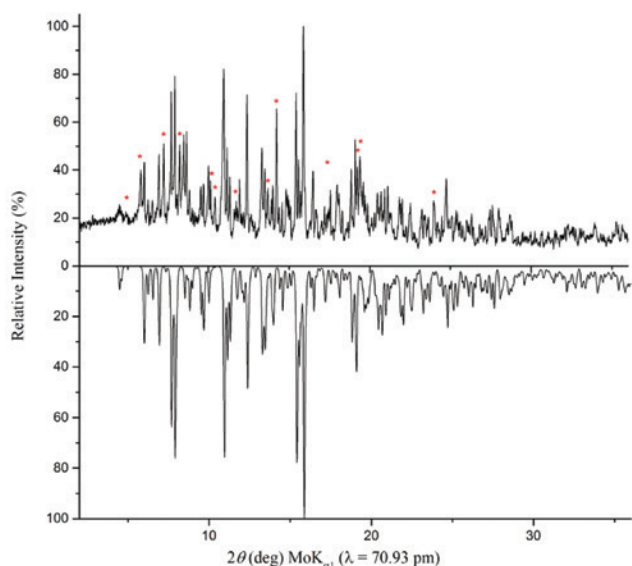


Fig. 1: Top: experimental powder pattern of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$. The reflections marked with red asterisks could not be assigned until now. Bottom: theoretical powder pattern of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$, based on single-crystal diffraction data.

Table 1: Crystal data and structure refinement of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ (standard deviations in parentheses).

Empirical formula	$\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$
Molar mass, $\text{g} \cdot \text{mol}^{-1}$	1731.1
Crystal system	Orthorhombic
Space group	$Pca2_1$ (no. 29)
Powder data	
Powder diffractometer	STOE Stadi P
Radiation; λ , Å	$\text{MoK}_{\alpha 1}$; 0.7093
a , Å	21.153(8)
b , Å	6.497(2)
c , Å	17.601(7)
V , Å ³	2418.9(5)
Single-crystal data	
Single-crystal diffractometer	Bruker D8 Quest Kappa
Radiation; λ , Å	MoK_{α} ; 0.71073
a , Å	21.126(2)
b , Å	6.502(2)
c , Å	17.619(2)
V , Å ³	2420.1(2)
Formula units per cell	4
Calculated density, g cm^{-3}	4.75
Crystal size, mm ³	$0.15 \times 0.10 \times 0.03$
Temperature, K	298(2)
Absorption coefficient, mm^{-1}	18.494
$F(000)$, e	3072
θ Range, deg	2.3–37.9
Range in hkl	$\pm 36, \pm 11, \pm 30$
Total no. of reflections	119 765
Independent reflections	13 059
Reflections with $I > 2 \sigma(I)$	12 844
Data/parameters	13 059/443
Absorption correction	Multi-scan
Goodness-of-fit on F^2	1.072
Final $R1/wR2$ [$I > 2 \sigma(I)$]	0.0176/0.0410
Final $R1/wR2$ (all data)	0.0183/0.0412
Flack parameter (x)	0.025(4)
Largest diff. peak/hole, $e \text{ Å}^{-3}$	4.08/−1.44

parameters of the isotypic compound $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$ [12]. Table 2 lists the interatomic distances. Atomic coordinates and anisotropic displacement parameters are listed in the Tables S1 and S2 of the Supplementary Information. Graphical representations of the structure were produced with the program DIAMOND [19].

Further details of the crystal structure investigation may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the deposition number CSD-433210.

2.3 Vibrational spectra

The transmission FT-IR spectrum of a single-crystal of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ was measured in the spectral range

Table 2: Interatomic distances (Å) in $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ (standard deviations in parentheses).

Li1–O3	1.945(13)	Li2–O2	1.951(10)	Li3–O14	1.989(10)				
Li1–O5	2.119(13)	Li2–O18	1.984(10)	Li3–O10	1.995(11)				
Li1–O16	2.132(15)	Li2–O21	2.103(10)	Li3–O9	2.053(10)				
Li1–O4	2.200(16)	Li2–O6	2.176(10)	Li3–O12	2.074(11)				
Li1–O8	2.381(17)	Li2–O20	2.292(12)	Li3–O19	2.335(13)				
Li1–O25	2.617(15)	Li2–O27	2.937(15)	Li3–O22	2.941(18)				
Ø	2.232	Ø	2.241	Ø	2.231				
B1–O17	1.360(6)	B2–O7	1.364(5)	B3–O22	1.342(6)	B4–O27	1.359(6)		
B1–O25	1.364(6)	B2–O8	1.364(6)	B3–O15	1.379(6)	B4–O11	1.376(5)		
B1–O19	1.396(5)	B2–O20	1.410(5)	B3–O16	1.405(6)	B4–O12	1.395(6)		
Ø	1.373	Ø	1.379	Ø	1.375	Ø	1.377		
B5–O1	1.357(6)	B6–O10	1.365(5)	B7–O9	1.364(5)	B8–O13	1.368(6)	B9–O26	1.363(6)
B5–O4	1.377(6)	B6–O18	1.367(6)	B7–O21	1.379(6)	B8–O14	1.376(6)	B9–O23	1.372(6)
B5–O6	1.402(6)	B6–O5	1.411(6)	B7–O3	1.389(6)	B8–O2	1.384(5)	B9–O24	1.381(6)
Ø	1.379	Ø	1.381	Ø	1.377	Ø	1.376	Ø	1.372
Eu1–O26	2.319(4)	Eu2–O11	2.273(3)	Eu3–O17	2.285(3)	Eu4–O25	2.288(3)	Eu5–O22	2.250(3)
Eu1–O7	2.326(3)	Eu2–O20	2.398(3)	Eu3–O24	2.322(3)	Eu4–O1	2.312(3)	Eu5–O14	2.394(3)
Eu1–O16	2.335(4)	Eu2–O18	2.412(3)	Eu3–O5	2.377(3)	Eu4–O26	2.420(3)	Eu5–O23	2.424(4)
Eu1–O5	2.353(3)	Eu2–O13	2.418(4)	Eu3–O10	2.381(3)	Eu4–O3	2.425(4)	Eu5–O15	2.427(3)
Eu1–O20	2.419(3)	Eu2–O7	2.457(3)	Eu3–O19	2.436(3)	Eu4–O21	2.434(3)	Eu5–O8	2.456(3)
Eu1–O8	2.421(3)	Eu2–O2	2.571(3)	Eu3–O25	2.449(3)	Eu4–O6	2.437(3)	Eu5–O3	2.517(3)
Eu1–O18	2.438(3)	Eu2–O6	2.584(5)	Eu3–O4	2.465(4)	Eu4–O20	2.443(3)	Eu5–O16	2.526(4)
Eu1–O6	2.546(3)	Eu2–O21	2.635(3)	Eu3–O12	2.625(3)	Eu4–O4	2.447(3)	Eu5–O9	2.613(4)
		Eu2–O1	2.657(4)						
Ø	2.387	Ø	2.489	Ø	2.418	Ø	2.401	Ø	2.451
Eu6–O15	2.285(3)	Eu7–O27	2.294(4)	K1–O18	2.770(3)	K2–O8	2.702(4)	K3–O23	2.640(4)
Eu6–O13	2.403(4)	Eu7–O2	2.323(3)	K1–O11	2.777(4)	K2–O4	2.739(3)	K3–O24	2.827(4)
Eu6–O19	2.455(3)	Eu7–O11	2.437(3)	K1–O14	2.802(3)	K2–O7	2.869(4)	K3–O1	2.944(4)
Eu6–O10	2.469(3)	Eu7–O24	2.457(4)	K1–O22	2.840(4)	K2–O3	2.873(4)	K3–O7	2.979(4)
Eu6–O12	2.481(3)	Eu7–O19	2.478(3)	K1–O15	2.859(4)	K2–O25	2.924(4)	K3–O17	3.113(4)
Eu6–O17	2.487(3)	Eu7–O21	2.529(3)	K1–O10	2.864(3)	K2–O17	2.936(4)	K3–O26	3.130(5)
Eu6–O14	2.547(3)	Eu7–O9	2.584(4)	K1–O2	2.870(4)	K2–O5	2.945(4)	K3–O22	3.175(6)
Eu6–O9	2.587(4)	Eu7–O12	2.706(3)	K1–O27	3.047(5)	K2–O16	2.966(4)		
Eu6–O27	2.767(5)	Eu7–O23	2.802(4)			K2–O1	2.997(4)		
						K2–O22	3.065(4)		
Ø	2.498	Ø	2.512	Ø	2.854	Ø	2.902	Ø	2.973

Average values in bold characters.

of 600–4000 cm^{-1} with a Vertex 70 FT-IR spectrometer (spectral resolution 4 cm^{-1}), which is equipped with a KBr beam splitter, an LN-MCT (Mercury Cadmium Telluride) detector, and a Hyperion 3000 microscope (Bruker, Vienna, Austria). One hundred and twenty scans of the sample were acquired using a Globar (silicon carbide) rod as mid-IR source and a 15× IR objective as focus. During the measurement, the sample was positioned on a BaF_2 window. A correction of atmospheric influences was performed with the software OPUS 6.5.

2.4 Luminescence

The title compound’s emission signal was measured by exciting a single-crystal (exhibiting the above mentioned

unit-cell metrics) with a 460 nm laser (model Sapphire 460/10, 10 mW; COHERENT). The converted light was collected using a multi-mode optical fiber (QP 600-2-VIS/BX; Ocean Optics) and finally detected in a spectrometer (QE 65000; Ocean Optics).

3 Results and discussion

3.1 Crystal structure of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$

As already mentioned, $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ crystallizes isotypically to $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$ [12] in the orthorhombic space group $Pca2_1$ (no. 29) with lattice parameters of $a=21.126(2)$, $b=6.502(2)$, $c=17.619(2)$ Å, $V=2420.1(2)$ Å³, and $Z=4$. The

structure features distorted LiO_6 octahedra, which are connected via planar BO_3 groups, forming $[\text{Li}_3\text{B}_4\text{O}_{21}]$ units in the ac plane (Fig. 2). These units are furthermore connected by additional BO_3 groups, forming tunnels of 12-membered rings along the b axis (Fig. 2). The K^+ and Eu^{3+} cations are arranged in the cavities of the structure (Fig. 3). K(1) is eight-fold, K(2) is 10-fold, and K(3) is seven-fold coordinated by oxygen atoms. Eu(1), Eu(3), Eu(4) and Eu(5) are all coordinated by eight oxygen atoms, whereas Eu(2), Eu(6) and Eu(7) are nine-fold coordinated by oxygen atoms. For a detailed description of the crystal structure, the reader is referred to the description of the isotypic compound $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$ [12]. Below, a comparison of the two isotypic compounds $\text{Li}_3\text{K}_3\text{RE}_7(\text{BO}_3)_9$ ($\text{RE}=\text{Y}, \text{Eu}$) is given.

Table 3 shows a comparison of the lattice parameters of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ and $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$. The increase of the lattice parameters corresponds to the increase of the ionic radii from Y^{3+} [1.159 Å for coordination number (CN) eight and 1.215 Å for CN nine] to Eu^{3+} (1.206 Å for CN eight and 1.260 Å for CN nine) [20]. The differences of the lattice parameters also cause an increase of the interatomic distances in $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ compared to $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$, see Table 4. Due to the increase of the lattice parameters and interatomic

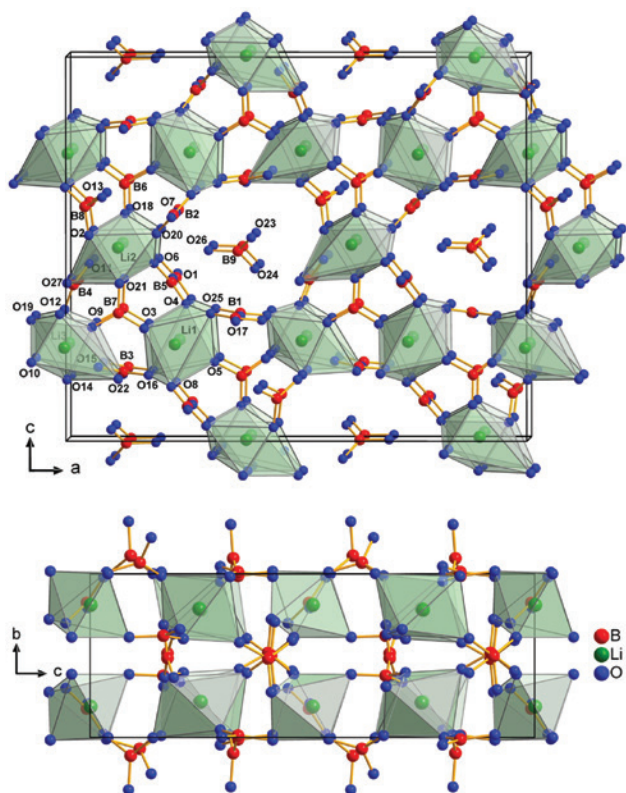


Fig. 2: Top: $[\text{Li}_3\text{B}_4\text{O}_{21}]$ units connected to each other via BO_3 groups along the crystallographic b axis. Bottom: connection of LiO_6 octahedra via BO_3 groups along the a axis.

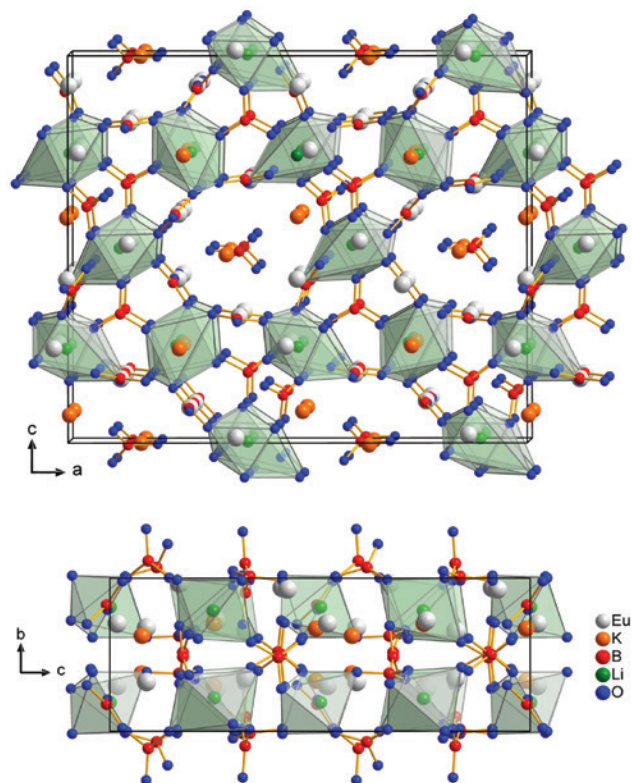


Fig. 3: Top: View of the structure of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ along the crystallographic b axis. Bottom: structure along the a axis.

Table 3: Comparison of the isotypic compounds $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ and $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$ (standard deviations in parentheses).

Compound	$\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$	$\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$
a , Å	21.126(2)	20.756(8)
b , Å	6.502(2)	6.322(2)
c , Å	17.619(2)	17.413(7)
V , Å ³	2420.1(2)	2284.9(5)

distances, the coordination environment of several cations changes. Table 5 compares the interatomic distances of K(3)–O and of Eu(7)–O in comparison with Y(7)–O on the two compounds, which lead to a change of the CN of K(3) from six to seven, and from eight for Y(7) to nine for Eu(7). All other CNs remain the same as reported in $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$.

In $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$, the K–O distances range from 2.640(4) to 3.175(6) Å, with average values of 2.854 (K1), 2.902 (K2) and 2.973 Å (K3). The distances within the EuO_x polyhedra are between 2.250(3) and 2.802(4) Å, with mean values of 2.387 (Eu1), 2.489 (Eu2), 2.418 (Eu3), 2.401 (Eu4), 2.451 (Eu5), 2.498 (Eu6) and 2.512 Å (Eu7). The average values of the B–O bonds range from 1.372 to 1.381 Å, which fit very well to the literature value of 1.37 Å [21] for common B–O distances in BO_3 groups. The Li–O distances range from 1.945(13) to

Table 4: Comparison of the av. distances (Å) of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ and $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$.

Compound	$\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$	$\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$
Li1–O	2.232	2.204
Li2–O	2.241	2.209
Li3–O	2.231	2.195
B1–O	1.373	1.370
B2–O	1.379	1.375
B3–O	1.375	1.37
B4–O	1.377	1.373
B5–O	1.379	1.379
B6–O	1.381	1.379
B7–O	1.377	1.373
B8–O	1.376	1.374
B9–O	1.372	1.373
RE1–O	2.387	2.347
RE2–O	2.489	2.441
RE3–O	2.418	2.372
RE4–O	2.401	2.350
RE5–O	2.451	2.389
RE6–O	2.498	2.458
RE7–O	2.512	2.409
K1–O	2.854	2.836
K2–O	2.902	2.870
K3–O	2.973	2.884

2.941(18) Å with mean values of 2.232, 2.241, and 2.231 Å for Li(1), Li(2) and Li(3), respectively.

We additionally calculated the bond valence sums for $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ with the bond-length/bond-strength concept (ΣV) [22, 23] and the CHARDI concept (charge distribution in solids, ΣQ) [24]. The results of these

Table 5: Comparison of the interatomic distances (Å) of Eu7, Y7 and K3 in $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ and $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$, indicating the different coordination numbers (CN; standard deviations in parentheses).

Compound			
$\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$		$\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$	
Eu7–O27	2.294(4)	Y7–O27	2.228(4)
Eu7–O2	2.323(3)	Y7–O2	2.271(3)
Eu7–O11	2.437(3)	Y7–O11	2.375(3)
Eu7–O24	2.457(4)	Y7–O24	2.379(3)
Eu7–O19	2.478(3)	Y7–O19	2.435(3)
Eu7–O21	2.529(3)	Y7–O21	2.440(3)
Eu7–O9	2.584(4)	Y7–O9	2.482(3)
Eu7–O12	2.706(3)	Y7–O12	2.658(3)
Eu7–O23	2.802(4)	Y7–O23	3.068(4)
Eu7–O17	4.083(4)		
CN	9	CN	8
K3–O23	2.640(4)	K3–O23	2.618(4)
K3–O24	2.827(4)	K3–O24	2.855(3)
K3–O1	2.944(4)	K3–O1	2.868(4)
K3–O7	2.979(4)	K3–O26	2.948(4)
K3–O17	3.113(4)	K3–O7	2.974(4)
K3–O26	3.130(5)	K3–O17	3.041(4)
K3–O22	3.175(6)	K3–O22	3.346(4)
K3–O27	3.527(5)		
CN	7	CN	6

calculations are listed in Table 6 and correspond well with the expected values of the formal ionic charge of each specific atom.

MAPLE values (Madelung Part of Lattice Energy) [25–27] of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ were compared with those received from the summation of the data for the starting

Table 6: Charge distribution in $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$, calculated with the bond-length/bond-strength (ΣV) and the CHARDI (ΣQ) concept.

	Li1	Li2	Li3	Eu1	Eu2	Eu3	Eu4	Eu5	Eu6	Eu7
ΣV	0.88	0.97	0.98	3.43	3.09	3.41	3.34	3.00	3.03	2.99
ΣQ	1.00	0.96	0.98	3.00	2.95	2.97	3.02	3.03	3.01	3.03
	B1	B2	B3	B4	B5	B6	B7	B8	B9	
ΣV	3.02	2.91	2.97	2.95	2.94	2.96	2.93	2.96	2.98	
ΣQ	2.96	2.93	3.04	3.16	3.09	2.81	2.93	2.96	3.17	
	K1	K2	K3	O1	O2	O3	O4	O5	O6	O7
ΣV	1.12	1.15	0.73	–1.98	–2.26	–2.19	–2.1	–2.34	–2.12	–2.27
ΣQ	0.97	0.99	1.02	–2.03	–2.15	–2.10	–1.95	–1.99	–1.84	–2.12
	O8	O9	O10	O11	O12	O13	O14	O15	O16	O17
ΣV	–2.22	–2.12	–2.3	–2.26	–2	–1.9	–2.18	–2.23	–2.12	–2.27
ΣQ	–1.98	–1.99	–2.21	–2.04	–1.85	–1.86	–2.11	–1.974	–1.90	–2.10
	O18	O19	O20	O21	O22	O23	O24	O25	O26	O27
ΣV	–2.3	–2.28	–2.37	–2.24	–2.06	–1.88	–2.08	–2.24	–2.15	–1.79
ΣQ	–2.18	–2.02	–2.05	–2.06	–2.03	–1.78	–1.97	–1.97	–1.94	–1.82

compounds Li_2O [28], K_2O [29], Eu_2O_3 [30] and B_2O_3 [31]. A value of $158777 \text{ kJ mol}^{-1}$ was obtained in comparison to $155254 \text{ kJ mol}^{-1}$ (deviation = 0.03%) calculated from the binary oxides [$1\frac{1}{2} \text{ Li}_2\text{O}$ (5254 kJ mol^{-1}) + $1\frac{1}{2} \text{ K}_2\text{O}$ (3767 kJ mol^{-1}) + $3\frac{1}{2} \text{ Eu}_2\text{O}_3$ ($47574 \text{ kJ mol}^{-1}$) + $4\frac{1}{2} \text{ B}_2\text{O}_3$ ($98659 \text{ kJ mol}^{-1}$)]. The good accordance between the value of the product and the sum of the values of the binary compounds prove the plausibility of the crystal structure solution.

3.2 IR spectroscopy

Figure 4 shows the experimental FT-IR spectra of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ and $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$ [12] in the range between 600 and 4000 cm^{-1} . The absorption bands of the two compounds correspond well with negligible shifts in wavelengths and relative intensities. As already reported for the isotypic compound $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$ [12], an assignments of the vibrational modes can be done based on previous investigations of borates containing trigonal $[\text{BO}_3]^{3-}$ groups [32–36]. The absorption bands between 600 and 800 cm^{-1} could be assigned as deformation and out-of-plane bending of BO_3 groups. The bands in the region from 900 to 965 cm^{-1} are typical for B–O symmetric stretching vibrations. The strong bands observed in the spectral range between 1150 and 1500 cm^{-1} can be related to the antisymmetric B–O stretching vibrations. According to Mak et al. [36] the region between 2100 and 2650 cm^{-1} can be related to combination- and overtone-bands of the BO_3 groups. The absorption peaks in the range of 2800– 3000 cm^{-1} most likely belong to the grease, which was used to fix the crystal on a glass fiber.

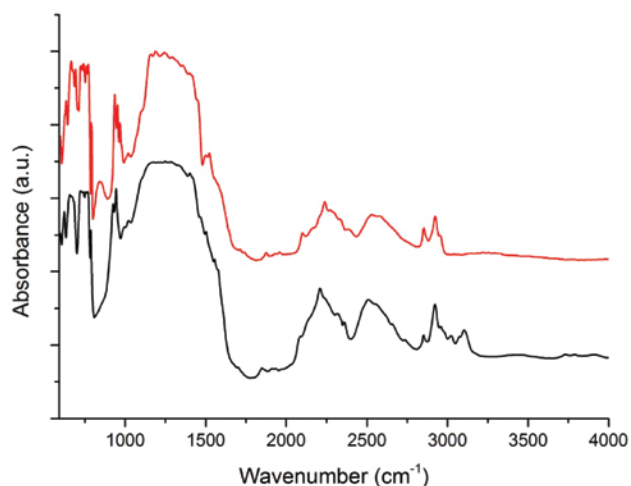


Fig. 4: FT-IR absorbance spectra of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ (black) and the isotypic compound $\text{Li}_3\text{K}_3\text{Y}_7(\text{BO}_3)_9$ (red).

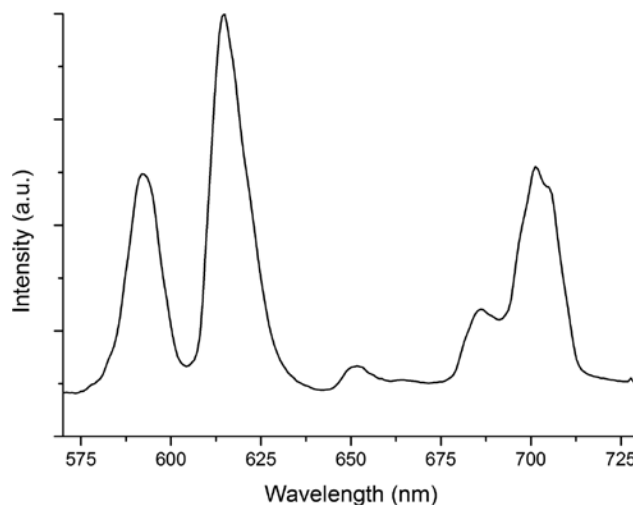


Fig. 5: Luminescence spectrum of a single-crystal of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$, obtained on excitation at 460 nm.

3.3 Luminescence

Figure 5 shows the title compound's emission signal on excitation at 460 nm. The profile can be assigned to typical Eu^{3+} luminescence regarding the transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 0-4$). From the relative intensities, one can conclude that there is no inversion symmetry around the Eu^{3+} activator ion which is in good agreement with the results of the crystal structure determination. To our astonishment, concentration quenching of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ was not observed. Ortner et al. also reported this phenomenon in the europium borate $\text{Eu}[\text{B}_6\text{O}_8(\text{OH})_5] \cdot \text{H}_3\text{BO}_3$ [37], which could be expected due to the fact that the shortest Eu–Eu distance is $4.459(1) \text{ \AA}$. Obviously an Eu–Eu distance of $3.556(2) \text{ \AA}$ in $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ does not lead to concentration quenching of the Eu^{3+} activator ion.

4 Conclusions

This report contains the description of the synthesis and crystal structure of the new mixed alkali rare earth borate $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$. Furthermore, the compound was characterized by infrared and luminescence spectroscopy. With the successful synthesis of $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$, this class of compounds could be extended by an additional example.

5 Supporting information

Additional crystallographic data for $\text{Li}_3\text{K}_3\text{Eu}_7(\text{BO}_3)_9$ (atomic coordinates and anisotropic displacement parameters) are

given as Supporting Information available online (<https://doi.org/10.1515/znb-2017-0146>).

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