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Synthesis, Structure, and Luminescent Properties of the New Double Borate $K_3Eu_3B_4O_{12}$

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Abstract

The study established the formation of the new double borate $K_3Eu_3B_4O_{12}$. The Rietveld refinement of the crystal structure revealed that $K_3Eu_3B_4O_{12}$ crystallises in the monoclinic syngony with unit cell parameters $a = 10.6727(7) \text{ \AA}$, $b = 8.9086(6) \text{ \AA}$, $c = 13.9684(9) \text{ \AA}$, $\beta = 110.388(2)^\circ$ (space group $P2_1/c$). $K_3Eu_3B_4O_{12}$ has a layered structure with $[Eu_8(BO_3)_8]^\infty$ sheets which are almost parallel to the ab plane. These sheets are formed by pentagonal EuO_7 bipyramids, EuO_6 octahedras, and BO_3 triangles attached to them through common vertices. Neighbouring layers are interconnected via pentagonal EuO_7 bipyramids, BO_3 triangles, and potassium cations. The luminescence spectrum demonstrates a noticeable emission band at 611 nm, resulting from the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions.

Keywords: double borates of potassium and rare-earth elements, ceramic technology, Rietveld method, luminescent properties.

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1. Introduction

Over recent years, a lot of attention has been paid to the synthesis of binary and ternary compounds with boron-oxygen groups. They include a great number of phases with functionally relevant (luminescence, nonlinear-optical, etc.) properties [1, 2].

The study of phase equilibria in systems $Rb_2O - RE_2O_3 - B_2O_3$ ($RE = Nd, Eu, Ho$) revealed two families of isostructural double borates: $Rb_3REB_6O_{12}$ [3, 4] and $Rb_3RE_2B_3O_9$ [5]. The present paper continues our systematic research aimed at the identification, preparation, and comprehensive characterisation of double borates

with an alkali metal cation and a rare-earth element in their composition.

The study of the phase formation in $K_2O - Eu_2O_3 - B_2O_3$ resulted in obtaining the $K_3Eu_3B_4O_{12}$ compound, isostructural $K_3Gd_3B_4O_{12}$, for the first time [6].

2. Experimental

Ultra pure K_2CO_3 , Eu_2O_3 , and H_3BO_3 were used for the synthesis. High temperature annealing was conducted in a Naberthern L3/11/P320 programmable laboratory furnace, cooling was carried out inertially in the furnace.

XRD patterns for the synthesised sample were obtained at room temperature using

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a D8 ADVANCE Bruker AXS powder X-ray diffractometer with a Vantec-1 detector (CuK_{α} radiation recording interval $2\theta = 5-100^\circ$, scanning step 0.02076°).

The TOPAS 4.2 software suite was used to analyse the experimental data and to conduct the Rietveld refinement of the obtained compound [7]. All peaks in the $K_3Eu_3B_4O_{12}$ X-ray powder diffraction patterns were indexed satisfactorily by a monoclinic cell (space group $P2_1/c$).

The luminescence spectra were recorded with a SDL-1 (LOMO) double monochromator with $600 \text{ lines/mm}^{-1}$ grating and a FEU-106 photoelectron multiplier, excitation was carried out using a high-pressure 150 WDKSH-150 xenon arc lamp through a MDR-2 monochromator with a diffraction grating of $1200 \text{ lines/mm}^{-1}$. A transparent undoped LiF crystal, used as a substrate for the sample, was fixed in a holder.

The $K_3Eu_3B_4O_{12}$ synthesis was conducted using ceramic technology by stepped annealing of stoichiometric proportions of reagent mixtures.

Calcium carbonate and europium oxide were annealed at 800°C for 24 hours to remove water. The reaction mixture was carefully ground in an agate mortar for better homogenisation, gradually heated to 200 and 600°C at 1°C/min , and incubated for 5 hours at those temperatures. Then, the sample was homogenised and further annealed at $750-850^\circ\text{C}$ for 48 hours (with intermediate grinding every 8 hours of the heat treatment).

3. Results and discussion

The synthesised sample of double borate is a dry white powder.

The powder X-ray diffraction patterns were used for the Rietveld refinement of the crystal structure of $K_3Eu_3B_4O_{12}$. The $K_3Gd_3B_4O_{12}$ structure was used to define the positions of atoms for the initial model. They were refined by isotropic approximation with “soft” limitations of the B–O distance and the B–O–B bond angles. The refinement was carried out by gradually adding refined parameters with the constant graphical simulation of the background. The Pearson VII Function was used to describe the shape of peaks. Isotropic displacement parameters (B_{iso}) for the Eu and K atoms were refined separately, while for the O and B atoms they were taken as equivalent.

The refinement process included corrections for the sample preferred orientation and anisotropy broadening of peaks within the model of spherical harmonics [8]. Occupancy refinement of the positions of the disordered oxygen atoms O1, O9, and O9p was not conducted, as the attempts to refine occupancy of the disordered atoms did not contribute to a better description of the x-ray diffraction patterns.

The refinement results for $K_3Eu_3B_4O_{12}$ are shown in Table 1, coordinates of atoms and isotropic displacement parameters are given in Table 2, and calculated and experimental x-ray diffraction patterns with difference curves are shown in Fig. 1.

The structure of the synthesised compound is characterised by the $[Eu_8(BO_3)_8]_\infty$ sheets which are almost parallel to the ab plane. These sheets are formed by pentagonal EuO_7 bipyramids, EuO_6 octahedras, and BO_3 triangles attached to them through common vertices (see Fig. 2). Neighbouring layers are interconnected via pentagonal EuO_7 bipyramids, BO_3 triangles, and potassium cations.

The luminescence centres in the studied phases are the Eu^{3+} [9] ions with intensive red luminescence. All the spectra have the five bands characteristic of transitions in the $4f$ -configuration of the Eu^{3+} ion from the excited metastable

Table 1. $K_3Eu_3B_4O_{12}$ crystallographic characteristics and structure refinement parameters

Space group:	$P2_1/c$
$a, \text{Å}$	10.6727(7)
$b, \text{Å}$	8.9086(6)
$c, \text{Å}$	13.9684(9)
$\beta, ^\circ$	110.388(2)
$V, \text{Å}^3$	1244.90(14)
Z	4
2θ -interval, $^\circ$	8–100
No. of reflections	1295
No. of refined parameters	120
$R_{wp}, \%$	1.77
$R_p, \%$	1.39
$R_{exp}, \%$	1.45
χ^2	1.22
$R_B, \%$	0.55

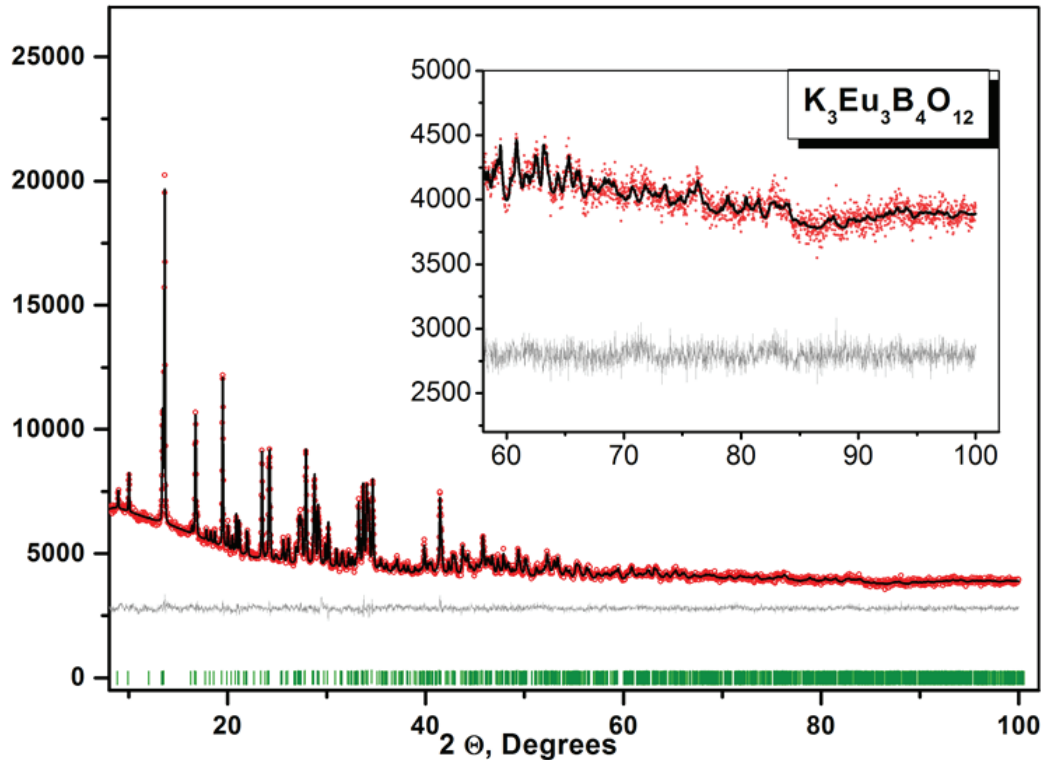


Fig. 1. The measured (circles) and calculated (line), differential, and stroke x-ray diffraction patterns of $K_3Eu_3B_4O_{12}$

Table 2. Fractional atomic coordinates and isotropic displacement parameters (E^2) of $K_3Eu_3B_4O_{12}$

Atom	x	y	z	Occupancy	$B_{iso}, \text{\AA}^2$
Eu1	1/2	0.6925 (8)	1/4	1	0.2 (4)
Eu2	0.7884 (6)	1.3014 (5)	0.2502 (4)	1	1.0 (3)
Eu3	0.6643 (6)	0.9684 (7)	0.1195 (4)	1	1.0 (3)
Eu4	1	0.7648 (8)	1/4	1	1.3 (4)
K1	0.418 (2)	0.357 (2)	0.095 (1)	1	1.5 (6)
K2	0.887 (2)	1.431 (2)	0.042 (1)	1	1.4 (7)
K3	0.798 (2)	0.935 (2)	0.402 (1)	1	1.5 (7)
B1	1/2	1.111 (3)	1/4	1	2.0 (15)
B2	0.737 (2)	0.594 (2)	0.228 (2)	1	2.0 (15)
B3	0.877 (3)	0.758 (3)	0.016 (2)	1	2.0 (15)
B4	0.626 (2)	1.221 (2)	-0.008 (2)	1	2.0 (15)
B5	1	1.101 (3)	1/4	1	2.0 (15)
O1	0.517 (3)	0.960 (2)	0.233 (2)	0.5	0.9 (5)
O2	0.392 (3)	1.156 (2)	0.274 (3)	1	0.9 (5)
O3	0.641 (2)	0.499 (3)	0.236 (2)	1	0.9 (5)
O4	0.854 (2)	0.539 (3)	0.220 (3)	1	0.9 (5)
O5	0.713 (3)	0.751 (4)	0.230 (3)	1	0.9 (5)
O6	0.847 (3)	0.712 (4)	-0.086 (2)	1	0.9 (5)
O7	0.999 (2)	0.721 (4)	0.088 (2)	1	0.9 (5)
O8	0.784 (2)	0.840 (4)	0.042 (2)	1	0.9 (5)
O9	0.502 (6)	1.154 (6)	-0.027 (3)	0.537	0.9 (5)
O9p	0.567 (5)	1.089 (3)	-0.058 (1)	0.463	0.9 (5)
O10	0.628 (3)	1.348 (2)	-0.067 (1)	1	0.9 (5)
O11	0.722 (3)	1.214 (2)	0.089 (2)	1	0.9 (5)
O12	0.891 (2)	1.025 (3)	0.253 (2)	1	0.9 (5)
O13	1	1.254 (2)	1/4	1	0.9 (5)

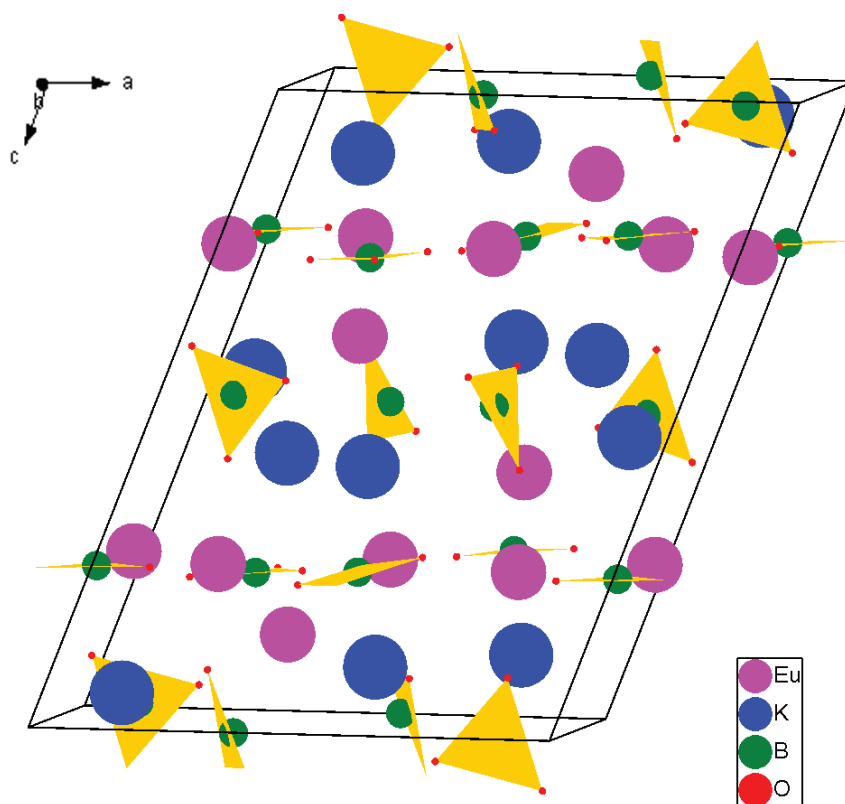


Fig. 2. The crystal structure of $K_3Eu_3B_4O_{12}$

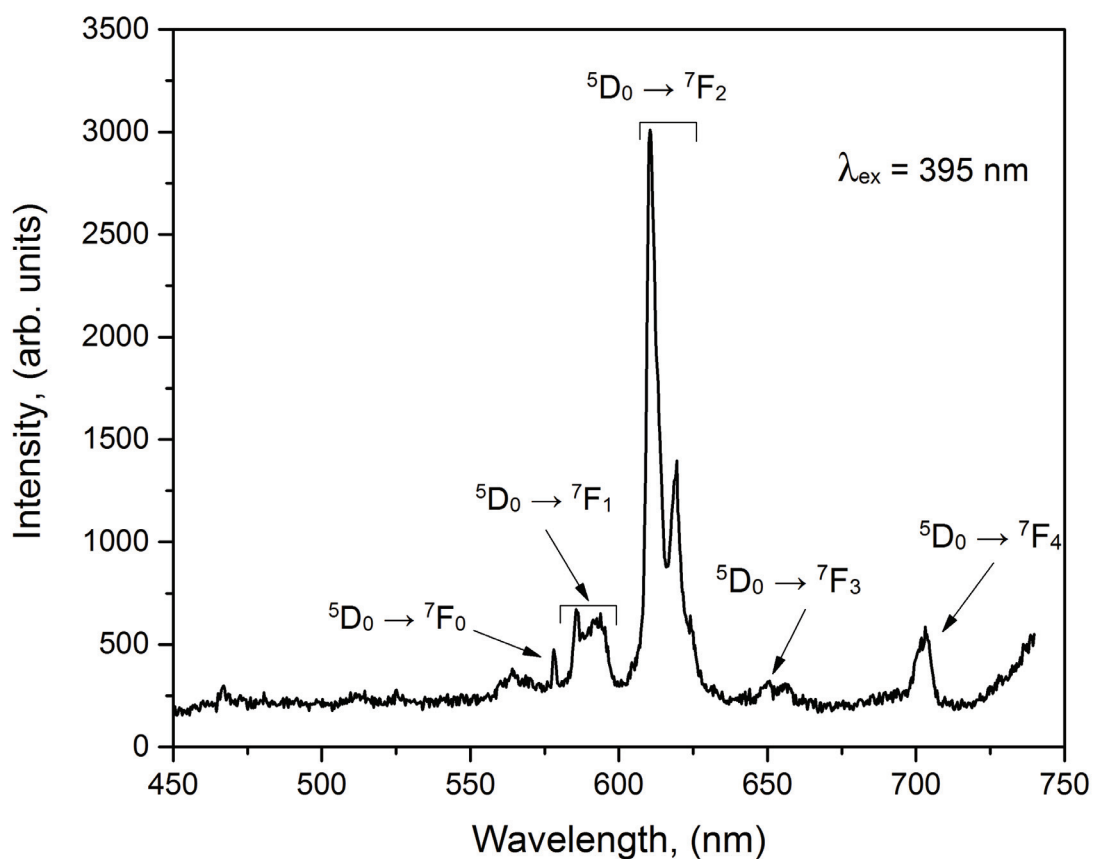


Fig. 3. Luminescence spectra of $K_3Eu_3B_4O_{12}$, excitation wavelength of 395 nm

state 5D_0 to the 7F_1 multiplet components ($J = 0, 1, 2, 3, 4$). Fig. 3 shows the emission spectrum $K_3Eu_3B_4O_{12}$, and Table 3 provides wavelengths of the Eu^{3+} constituent spectra.

When studying the structure of luminescent materials, the $^5D_0 \rightarrow ^7F_2$ transition of $4f$ -configuration of the Eu^{3+} ion is of great interest. The fact that there is only one peak within the range of this transition which is characterised by an insignificant broadening indicates close resemblance of the crystallochemical environment of the four sites of the Eu^{3+} ion in a unit cell. The ratio of maximum intensities of the bands corresponding to the transitions $(^5D_0 \rightarrow ^7F_2)/(^5D_0 \rightarrow ^7F_1)$ is 4.482, which

Table 3. Wavelengths (nm) of the Eu^{3+} constituent spectra of $K_3Eu_3B_4O_{12}$

$^5D_0 \rightarrow ^7F_0$	$^5D_0 \rightarrow ^7F_1$	$^5D_0 \rightarrow ^7F_2$	$^5D_0 \rightarrow ^7F_3$	$^5D_0 \rightarrow ^7F_4$
578.1	585.6 586.5 590.2 592.6 593.8 596.2	610.4 619.8	650.7 656.5	701.9 703.0

indicates a low symmetry of the Eu^{3+} ion sites in the crystalline structure of $K_3Eu_3B_4O_{12}$ [10]. This agrees with the results of the structural study.

The excitation spectra (see Fig. 4) have bands of europium $4f^6-4f^6$ -transitions from the ground state to the upper levels: $^7F_0 \rightarrow ^5H_5$ (320.0 nm), $^7D_0 \rightarrow ^5D_4$ (363.6 nm), $^5D_0 \rightarrow ^5L_7$ (383.8 nm), $^7F_0 \rightarrow ^5L_6$ (395.5 nm), $^7F_0 \rightarrow ^5D_2$ (466.7 nm). The two narrow resonance bands corresponding to the $^7F_0 \rightarrow ^5L_6$ и $^7F_0 \rightarrow ^5D_2$ transitions are the most intensive.

4. Conclusions

Thus, a ceramic technology and stepped annealing were used to synthesise a new double borate of potassium-europium $K_3Eu_3B_4O_{12}$. According to the results of the Rietveld refinement of the crystal structure, the synthesised phase is isostructural to the $K_3Gd_3B_4O_{12}$ compound and crystallises in the monoclinic syngony with unit cell parameters $a = 10.6727(7)$ Å, $b = 8.9086(6)$ Å, $c = 13.9684(9)$ Å, $\beta = 110.388(2)^\circ$ (space group P2/c).

Luminescent properties of $K_3Eu_3B_4O_{12}$ were studied. Luminescence is due to optical

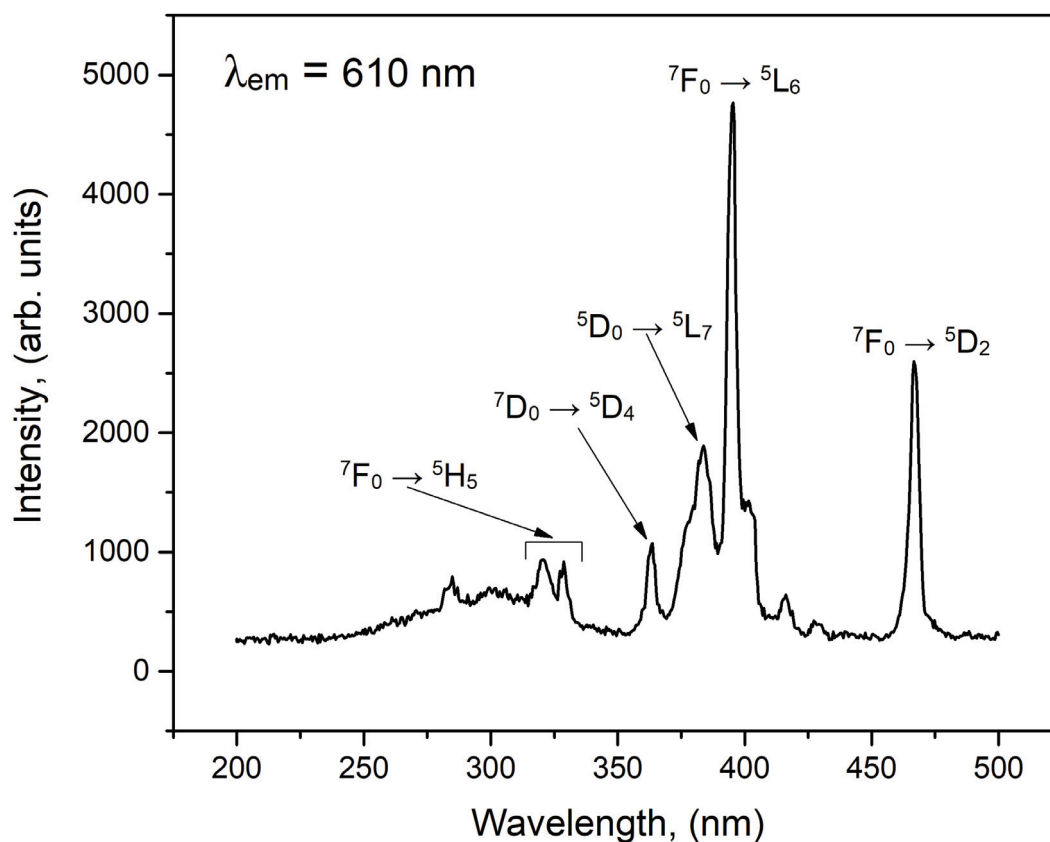


Fig. 4. The excitation spectra of $K_3Eu_3B_4O_{12}$, emission wavelength of 610 nm

transitions in the 4f-configuration of the Eu^{3+} ion. The brightest luminescence of a bright red monochromatic colour is seen in the ${}^5D_0 \rightarrow {}^7F_2$ electric dipole transition band, which is convenient for the production of screen luminophores with colours of high contrast.

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Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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