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Synthesis and growth of new rare earth borates $KCaR(BO_3)_2$ (R= La, Pr and Nd)



A.B. Kuznetsov^{a,*}, K.A. Kokh^{a,b}, N.G. Kononova^a, V.S. Shevchenko^a, E.V. Kaneva^c, B. Uralbekov^d, V.A. Svetlichnyi^e, A.E. Kokh^a

^a Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, 630090, Russia

^b Novosibirsk State University, Novosibirsk, 630090, Russia

^c Vinogradov Institute of Geochemistry SB RAS, Irkutsk, 664033, Russia

^d Al-Farabi Kazakh National University, Almaty, 050040, Kazakhstan

^e Tomsk State University, Tomsk, 634050, Russia

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ABSTRACT

Novel KCaR(BO₃)₂ (R = La, Pr and Nd) compounds have been obtained by solid-state synthesis. Specifically, single crystals of KCaNd(BO₃)₂ and KCaPr(BO₃)₂ were grown by using a top seeded solution growth method from the KBO₂ flux. These crystal compounds belong to the orthorhombic system, *Pbca* space group. KCaLa(BO₃)₂ exhibits high transparency in the range of 200–900 nm. Pr and Nd compounds have a strong emission bands that are related to the well-known electron transition of Pr^{3+} (${}^{3}P_{0} \rightarrow {}^{3}H_{6}$ at 630 nm, ${}^{3}P_{0} \rightarrow {}^{3}F_{2}$ at 670 nm) and Nd³⁺ (${}^{4}F_{3/2} \rightarrow {}^{4}I_{1/2} \rightarrow {}^{4}I_{1/2}$ at 1054 nm).

1. Introduction

At present, many research projects are related to the development of more environmentally friendly light sources and luminophores [1-6]. These projects have focused on borates due to their high chemical stability, thermal and radiation stability, wide transparency region and high laser threshold. In addition, borate compounds have diverse chemical compositions and crystal structures due to the ability of boron to form different anionic (BO₃, BO₄) and polyanionic (B₂O₆, B₅O₁₀ etc.) groups [7–11]. According to the anionic group theory [12], the compounds with isolated boron groups (BO₃), (BO₄) exhibit strong potential for use in the range of VIS to deep UV range. To date, the most commonly used crystals that are transparent from IR to deep UV include YAl₃(BO₃)₄ (YAB) ([13] (UV cut-off - 160 nm) and KBe₂BO₃F₂ (KBBF) [14] (UV cut-off - 150 nm) etc. Recently, alkali and/or alkali earth borates with a high concentration of rare earth elements were synthesized and proposed to be efficient phosphor materials. As an example, $RNa_3(BO_3)_2$ (R = Y, La, Nd, Gd) [15] and $Nd_2Ba_3(BO_3)_4$ [16] crystallizing in the R3 space group have a low concentration quenching of rare earth atoms. The existence of these multication borates suggests new complex compounds by replacing part of the Na⁺/Ba²⁺cations, as well as the REE variation. Novel rare earth borates, such as NaBaSc(BO3)2 and NaBaY(BO3)2, have been discovered

in the system R_2O_3 -BaO-Na₂O-B₂O₃ [17]. The consequent substitution of Na→K and of Ba→Sr results in obtaining two new compounds of KBaR(BO₃)₂ [18] and KSrR(BO₃)₂ [19], which crystallize in the $R\overline{3}$ and C2/c space groups, respectively.

In this study, by substituting (Ba^{2+}, Sr^{2+}) atoms into a relatively small atom $(Ca^{2+}, radius = 1.0 \text{ Å} [20], CN = 6)$, we report the synthesis, crystal growth and luminescent properties of a new type compounds $KCaR(BO_3)_2$ (R = La, Pr and Nd). A discussion of the crystal structure and thermal properties of $KCaNd(BO_3)_2$ is given.

2. Experimental section

Crystalline samples of KCaR(BO₃)₂ were prepared by the method of two-stage solid-state synthesis in a Pt crucible. In the first stage, stoichiometric mixtures of pure raw K₂CO₃, CaCO₃, H₃BO₃ and R₂O₃ reactants were heated at 650°C for 5 h to decompose K₂CO₃, CaCO₃, and H₃BO₃. In the second stage, the mixtures were ground in agate mortar, pressed into pellets and heated again at 900°C for 12 h until the powder X-ray method showed no peaks from the initial compounds.

The solid-state reaction can be represented as follows:

$$K_2CO_3 + 2CaCO_3 + R_2O_3 + 4H_3BO_3 = 2KCaR(BO_3)_2 + 6H_2O + 3CO_2$$

* Corresponding author. *E-mail address:* ku.artemy@igm.nsc.ru (A.B. Kuznetsov).

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Received 19 September 2019; Received in revised form 25 November 2019; Accepted 26 November 2019 Available online 3 December 2019 0022-4596/© 2019 Elsevier Inc. All rights reserved. Crystals of KCaNd(BO₃)₂ with the dimensions $30 \times 30 \times 10 \text{ mm}^3$ with a transparent area of $5 \times 5 \times 5$ mm was grown from the KBO₂ flux (Fig. 1). Briefly, a Pt crucible containing KCaNd(BO₃)₂ and K₂CO₃, H₃BO₃ was heated to 900°C. The charge was held in a melted state for a day to achieve homogenization. Then, the temperature was decreased at the rate of 2 °C day⁻¹ from 800 °C to 770°C and following cooling at the rate of 15 °C day⁻¹ to room temperature. The crystal was extracted from the crucible, and a high-quality crystal was chosen for X-ray analysis. The same procedure was applied for the growth of KCaPr(BO₃)₂.

A high-quality single crystal with the dimensions of 0.293 imes 0.248 imes0.130 mm³ was selected by using a polarizing microscope from the aggregate grown on a Pt-loop. X-ray diffraction data were collected on a Bruker AXS D8 VENTURE dual-source diffractometer with a Photon 100 detector using monochromatized MoKa radiation. Two sets of 12 frames were used for initial cell determination, whereas complete data collections were obtained by several ϕ and ω scans with a 0.5° rotation, 5 s exposure time per frame and a crystal-to-detector distance of 40 mm, at 50 kV and 1 mA. The data collection strategies were optimized by the APEX2 program suite [21], and the reflection intensities were extracted and corrected for Lorentz-polarization correction, which was applied by the SAINT package [22]. A semiempirical absorption correction was applied with the SADABS software [23]. The XPREP software assisted in the determination of the space group and in the calculation of the intensity statistics. The SHELX-2014 software [24] in the WinGX suite [25] was used for the structure solution and refinement. Precise information about the data collection and structural refinement are summarized in Table 1. Crystallographic coordinates and Uiso/equiv parameters are listed in Table 2 and Table 1s.

In addition, powder X-ray diffraction patterns of the KCaR(BO₃)₂ (R = La, Pr, Nd, Tb, Y, Yb) polycrystalline samples were obtained with a Dron Bragg-Brentano diffractometer, using CuK α radiation. The diffraction patterns of the samples with La and Pr were refined by using the Le Bail method [26,27] within the GSAS- II program. The obtained patterns are presented in Fig. 1s. The lattice parameters of KCaR(BO₃)₂ (R = La–Nd) are given in Table 2s. In addition comparison of measured and simulated X-ray powder pattern of KCaNd(BO₃)₂ are given in Fig. 2s.

The chemical composition of the obtained crystals (cations relationship) was determined by X-ray fluorescent analysis using XRF 1800 (Shimadzu, Japan). The results of the analysis are in a good agreement with the formula that was obtained after structural refinement of the crystal (Table 3s).

The thermal properties of the $KCaR(BO_3)_2$ crystals were investigated by the differential scanning calorimetry (DSC) using the scanning



Fig. 1. KCaNd(BO₃)₂ polycrystalline druse.

Table 1

Selected data on single-crystal data collection and structural refinement.

Formula	$KCaNd(BO_3)_2$
Formula weight	341,04
Space group	Pbca (No. 61)
a(Å)	10.2069(5)
b(Å)	9.0293(4)
c (Å)	13.1634(5)
V(Å ³)	1213.15(9)
Z	8
Calculated density (g/cm ³)	3.734
Absorption coefficient (mm ⁻¹)	10.055
F(000)	1256
θŐ	3.095–45.432
hkl	-20 < h < 20, -18 < k < 18, -20 < l < 26
Measured reflections	49469
Independent reflections	5087
Unique reflections	4443
Reflection with $I > 2\delta(I)$	0.0892
R _{int}	0.0532
R factor (I > $2\delta(I)$)	R1 = 0.0316 wR2 = 0.0536
R factor (all data)	$R1 = 0.0240 \ wR2 = 0.0513$
GOF	1.105
Residual electron density (e $Å^{-3}$)	$Max = 1.571 \ min \ -2.578 \ av = 0.255$

thermal analyzer 449 F1 Jupiter (Netzsch, Germany). Then, 50-mg of powdered KCaR(BO₃)₂ samples were placed in a platinum crucible and heated with argon as a carrier gas from room temperature to 1300°C at the rate of 10 K·min⁻¹. An empty Pt crucible was used as the standard.

Diffuse reflectance spectra of powders of KCaR(BO₃)₂ were recorded at room temperature using a Cary 100 (Varian, Australia) spectrophotometer with a diffuse reflectance accessory in the range of 200–900 nm and by FTIR spectrometer Nicolet 6700 (Thermo Fisher Scientific, USA) in the range of 11000-400 cm⁻¹.

Raman spectra were collected by using a confocal Raman microscope InVia (Renishaw, UK), which is a spectrometer with a spectral resolution of 1 cm⁻¹ equipped with a Leica optical microscope (with 50x objective) and a Peltier cooled Si detector, under 100 mW CW Nd:YAG laser excitation, operating at 532 nm, in the range of 100–3200 cm⁻¹.

High-resolution luminescence spectra of powdered $KCaR(BO_3)_2$ were collected by using an InVia Raman microscope under the excitation with a 785 nm CW diode laser in the range of 800–1100 nm.

3. Results and discussion

Substitution of Ba^{2+} to Sr^{2+} in KBaY(BO₃)₂ resulted in obtaining new compounds being obtained such as $KSrR(BO_3)_2$ crystallizing in the $P2_1/m$ space group [19]. Both compounds are composed by two types of layers that are perpendicular to the c axis and connected by isolated BO₃ triangles. The first layer is formed by RO₆ octahedra, and this structural unit is common for the three cation borates, while the second layer defines the symmetry of the compound and is formed by the polyhedra of alkaline and alkaline earth metals. In the KBaR(BO₃)₂ crystal structure, this layer is formed by Ba and K atoms, having a common nine coordinated position, while the Na, K, Sr, Ba atoms occupy different positions in the KSrR(BO₃)₂, NaBaR(BO₃)₂, KBaR(BO₃)₂ crystal structures (Fig. 2). These features can be explained by their different atomic radii (Na = 1.18 Å, K = 1.55 Å, Ba = 1.47 Å; Sr = 1.31 Å [20]) and coordination number, CN $(CN_{Na} = 8, CN_K = 9, CN_{Ba} = 9, CN_{Sr} = 9)$. Thus, it can be concluded that alkali and alkali earth metal replacements in these compounds result in decreased the symmetry from KBaR(BO₃)₂ ($R\overline{3}m$) though NaBaY(BO₃)₂ $(R\overline{3})$ to KSrR(BO₃)₂ (P2₁/m) (Fig. 3a,b,c.). As a rule, calcium atoms occupy the positions from six- [28-30] to nine-coordinated [31] polyhedra that correlate with its small radius ($Ca^{2+} = 1.0$ Å [20]). Thus, the replacement to Ca²⁺ is likely to form structures with a crystal symmetry between $R\overline{3}m$ and $P2_1/m$.

According to single crystal structural refinement and X-ray diffraction analysis $KCaR(BO_3)_2$ with R = La, Pr and Nd crystallize in the

Table 2

Crystallographic coordinates and Uiso/equiv parameters of the KCaNd(BO₃)₂ crystal structure.

Lable	х	у	Z	Occupancy	Uiso/equiv
Nd1	0.12594(2)	0.24434(2)	0.21668(2)	0.8790(5)	0.00775(3)
Nd2	-0.08723(2)	0.09144(2)	0.39214(2)	0.1210(5)	0.00755(4)
Ca1	-0.08723(2)	0.09144(2)	0.39214(2)	0.8790(5)	0.00755(4)
Ca2	0.12594(2)	0.24434(2)	0.21668(2)	0.1210(5)	0.00775(3)
КЗ	0.15414(3)	-0.06292(4)	0.90308(2)	1	0.01922(6)
04	-0.03848(10)	-0.15442(11)	0.44619(7)	1	0.01167(15)
05	0.01928(9)	-0.00393(10)	0.24328(7)	1	0.01081(14)
O6	-0.28356(11)	0.17878(14)	0.45425(7)	1	0.0180(2)
07	-0.25153(9)	-0.02108(12)	0.28556(7)	1	0.01242(16)
08	-0.12496(8)	0.26028(10)	0.25851(9)	1	0.01009(16)
09	0.11498(10)	0.23389(13)	0.39248(7)	1	0.01341(18)
B10	0.12986(12)	-0.08821(15)	0.23238(10)	1	0.00718(18)
B11	0.12522(11)	0.23840(15)	0.49615(9)	1	0.0078(2)



Fig. 2. Crystal structures of a)NaBaR(BO₃)₂, b)KBaY(BO₃)₂, c) KSrR(BO₃)₂ and d) KCaR(BO₃)₂.

orthorhombic space group *Pbca*. The double layered crystal structure of these compounds is shown in Fig. 3. It can be seen that all boron atoms possess only one environment that forms isolated BO₃ triangles, which are oriented perpendicular to the *c* axis and along the *c* axis for layers A and B, correspondingly (Fig. 3a and b). The average B–O distances are equal to 1376 Å, which is similar to KBaR(BO₃)₂ (1,3816 Å), NaBaY(BO₃)₂ (1,3590 Å) and KSrR(BO₃)₂ (1,3760 Å). Layer A consists of isolated RO₉ polyhedra connected to each other through BO₃ triangles (Fig. 3c). However, REE atoms occupy octahedral positions in other



Fig. 3. Crystal structure of KCaR(BO₃)₂.

structures of alkali and earth alkali borates. Disordered CaO₆ octahedra and KO₈ polyhedra form chains along the *b* axis and connect to BO₃ triangles (Fig. 3d). It should be noted that the substitution between R³⁺ and Ca²⁺ in both RO₉ and CaO₆ positions were revealed in the structure of KCaNd(BO₃)₂.

The structures of NaBaSc(BO₃)₂, NaBaY(BO₃)₂ (Fig. 2a.), KBaY(BO₃)₂ (Fig. 2b.) and KSrY(BO₃)₂ (Fig. 2c.) consist of AO₃ layers, where A is a large cation (alkaline and alkaline earth metals). The basis of AO₃ is a flat BO₃ groups occupying one of two positions. The layers are interconnected by octahedrally coordinated cation (M). Each [A(BO₃)] layer forms one M cation position (rare earth cation). This all leads to the formation of a two–layer {[A(BO₃)]–M - [A(BO₃)]} sandwiches, which are held together by slightly displaced 2 + cations. It can be concluded that the features of the distribution of A-cations in the structure determine the cell metric and symmetry of the compounds. On the other hand, the AO₃ layers in KCaR(BO₃)₂ are formed by nine coordinated cations Ca^{2+} or K⁺ with eight coordination (Fig. 2d.). Thus the compound KCaR(BO₃)₂ has an inverted structure with respect to KSrY(BO₃)₂.

Since the structure is highly complicated, vibrations of BO₃ group are described only in IR and Raman spectra based on the data of [32]. These polyhedra have oscillation active modes v_2 and v_4 in IR; v_2 , v_3 and v_4 in Raman; v_1 , v_2 , v_3 and v_4 both in IR and Raman. IR spectra for as-prepared KCaR(BO₃)₂ crystals are shown in Fig. 4a. The spectra have two main modes, v4 (stretching) and v2 (bending), which corresponded to the vibrations of the BO₃ groups (v4: 1208 1379 cm⁻¹, v2: 734, 782 cm⁻¹). Raman spectra are given in Fig. 4b. The strong bands in the ranges of 1335, 1525, 937, 710, 786 and 628 cm⁻¹ are likely correspond to BO₃



Fig. 4. IR (a) and Raman (b) spectra of KCaR(BO₃)₂.

asymmetric stretching, stretching, out-of-plane bending and bending vibration, respectively. Bands, which are likely to correspond to the vibrations of CaO₆ and RO₉ octahedra locate, in the range 124-300 cm⁻¹.

The thermal stability was studied by examining the DSC diagram of KCaNd(BO₃)₂ (KCaPr(BO₃)₂), which is represented in Fig. 3s. The diagram shows one endothermic peak of melting at 1120 (1104) °C on the heating curve and 2 exothermic peaks on the cooling curve at 1098 (1085) and 1070 (1050) °C, which, in turn, proves that decomposition of the compounds occurs before full melting. Different X-ray data of KCaPr(BO₃)₂ before and after DSC (Fig. 4s) confirm the incongruent nature of the compounds.

Absorption spectra of KCaR(BO₃)₂ in the UV-VIS-NIR ranges are shown in Fig. 5 (green line). The samples demonstrate that typical absorption bands in the range of 200–900 nm correspond to the presence of Pr³⁺ and Nd³⁺, while the sample with La³⁺ has no peaks in 200–900 nm range. The observed peaks are assigned to well-known electron transitions for Pr³⁺: electronic transitions from the fundamental to the lower excited states, ³P₂, ³P₁+¹I₀, ³P₀, and ¹D₂. It should be noted that an additional wide peak (350–400 nm) on the PLE spectra of KCaPr(BO₃)₂ corresponds to the energy transfer. This peak correlate to the promotion of the orbital redistribution of the charge density transmission from ²p (O²⁻) to ³p (Ca²⁺) or to ³p (K⁺) state. The strong transfer band also possibly owes to the charge imbalance caused by trivalent Pr³⁺ ions partly replacing divalent Ca²⁺ sites in the KCaPr(BO₃)₂ [33]. Crystals containing Nd³⁺ have the peaks that are associated with well-known electron transitions (in more detail ⁴I_{9/2} \rightarrow ⁴G_{7/2}, ⁴C_{1/2}, ²K_{13/2} at



Fig. 5. Absorption (F(R) – function) (green line) and photoluminescence emission for $\lambda_{ex} = 450 \ (Pr^{3+})$, 650 (Nd³⁺) nm (red line) and photoluminescence excitation for $\lambda_{em} = 785 \ (Pr^{3+})$, 820 (Nd³⁺) nm (blue line) spectra of KCaR(BO₃)₂. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The photoluminescent emission spectra of the obtained crystal borates are shown on Fig. 5. (red line) Photoluminescent emission spectrum of the KCaPr(BO₃)₂ powder exhibits characteristic emissions that are attributed to the transitions in Pr³⁺ ions: luminescence lines in the 500–800 nm range, which arise due to emission Pr³⁺ ³P₀ \rightarrow ³H₅, ³H₆, ³F₂, ³F₃ and³F₄ transitions (~530, 630,670, 723 and 740 nm). Samples of KCaNd(BO₃)₂ have a strong emission band that is related to the well-known electron transition ⁴F_{3/2} \rightarrow ⁴I_{9/2} at 875 nm, which can be used for the laser, operating in a quasi-three-level scheme, and the classical emission band for a quasi-four-level scheme lasers with ⁴F_{3/2} \rightarrow ⁴I_{11/2} transition near 1054 nm [34].

4. Conclusion

New rare earth borates with the composition KCaR(BO₃)₂, that crystallize in the *Pbca* space group have been synthesized, and single crystals of KCaNd(BO₃)₂ and KCaPr(BO₃)₂ were grown from the KBO₂ flux. Their crystal structure of these compounds may be represented as double-layered. Layer A consists of isolated RO₉ polyhedra that are connected to each other through BO₃ triangles, while layer B is formed by disordered CaO₆ octahedra and KO₈ polyhedra. The diffuse optical reflectance and luminescent properties of the powdered KCaNd(BO₃)₂ and KCaPr(BO₃)₂ samples were studied and may be considered to be effective narrowband luminescent materials in the visible and near-IR range.

Author contributions section

A.B. Kuznetsov; Data curation, Writing- Original draft preparation, K.A. Kokh; Supervision, N.G. Kononova; Methodology, V.S. Shevchenko; Formal analysis, E.V. Kaneva; Investigation, B.Uralbekov; Funding acquisition, V.A. Svetlichnyi; Investigation and A.E. Kokh: Project administration

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.jssc.2019.121091.

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