# Three-Cation Scandium Borates $R_xLa_{1-X}Sc_3(BO_3)_4$(R = Sm, Tb): Synthesis, Structure, Crystal Growth and Luminescent Properties

A. Kokh[1(✉)], A. Kuznetsov[1], K. Kokh[1,2], N. Kononova[1], V. Shevchenko[1], B. Uralbekov[3], A. Bolatov[3], and V. Svetlichnyi[4]

[1] Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia
a.e.kokh@gmail.com
[2] Novosibirsk State University, Novosibirsk, Russia
[3] Al-Farabi Kazakh National University, Almaty, Kazakhstan
[4] Tomsk State University, Tomsk, Russia

**Abstract.** Complex ortohoborates of rare earth metals with the general chemical formula $R_xLa_{1-x}Sc_3(BO_3)_4$ (R = Sm, Tb) have been obtained by solid state synthesis and spontaneous crystallization. These crystals belong to the huntite family with the space group R32 and for x = 0.5 have unit cell parameters a = 9.823(6), c = 7.975(3) (SLSB) and a = 9.803(3), c = 7.960(4) Å (TLSB).

**Keywords:** Crystal · Borate · Structure · Huntite · Growth · Luminescence

## 1 Introduction

Orthoborates with the general formula $RX_3(BO_3)_4$, where R = Y, Ln; X = Al, Ga, Sc, Cr, Fe are practically important and interesting from the point of view of crystal chemistry objects for research. One of the important properties of these compounds is the ability to form a non-centrosymmetric structure, which is called huntite-like. Such a structure causes, for example, non-linear optical properties.

To understand the formation of the huntite-like structure of three-cation scandoborates, we consider the lanthanum – scandium borate $LaSc_3(BO_3)_4$. The authors (He et al. 1999) distinguish three modifications of this crystal: high-temperature monoclinic with the C2/c space group, medium temperature trigonal with the R32 space group (huntite-like) and low-temperature monoclinic with the Cc space group. As a result of our research (Fedorova et al. 2013) identity of the X-ray patterns of polymorphic modifications high and low was shown.

The stabilization of the huntite-like structure can occur if an additional isomorphic cation is introduced into the $LaSc_3(BO_3)_4$ structure, that was confirmed in (Li et al. 2001) who initiated the new three-cation scandoborate with the huntite-like structure $Nd_xLa_{1-x}Sc_3(BO_3)_4$. Further, in a number of works by adding a third cation


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$R_xLa_ySc_z(BO_3)_4$ nonlinear optical crystals with a stable huntite-like structure were obtained with R = Gd (Xu et al., 2011); Y (Ye et al. 2005) and Lu (Li et al. 2007).

The existence of a huntite-like structure for the boundary members of the REE series suggests the stability of such a structure with the rest of the REE. This paper presents data on the huntite-like structures SLSB and TLSB for systems $R_xLa_{1-x}Sc_3(BO_3)_4$ (R = Sm, Tb).

## 2 Methods and Approaches

Polycrystalline sample of $R_xLa_{1-x}Sc_3(BO_3)_4$ (x = 0–0.5)were prepared by the method of two stage solid state synthesis in a Pt crucible. The stoichiometric mixtures of pure raw $La_2O_3$, $Sc_2O_3$, $H_3BO_3$ and $R_2O_3$(R = Sm, Tb) reactants were heated at 800 °C for 5 h to decompose $H_3BO_3$. At the second stage, the mixtures were grinded in an agate mortar and heated again at 1300 °C for 12 h until the powder X-ray method showed no peaks of initial compounds (Fig. 1).

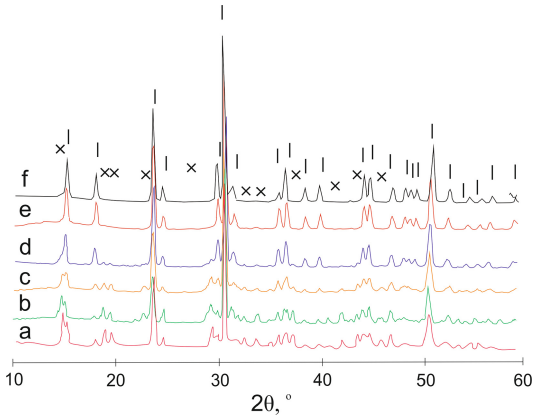



**Fig. 1.** X-ray pattern of $Sm_xLa_{1-x}Sc_3(BO_3)_4$, where x = 0(a), 0.2(b), 0.3(c), 0.4(d), 0.5(e), 1(f). I- huntite (R32), X- monoclinic (C2/c) structure.

Spontaneous crystals of $R_xLa_{1-x}Sc_3(BO_3)_4$with dimensions 30 × 30 × 10 mm with a transparent area of 5 × 5 × 5 mm were grown from $LiBO_2$- LiF flux Fig. 2. A Pt crucible containing $R_{0.5}La_{0.5}Sc_3(BO_3)_4$, $Li_2CO_3$, $H_3BO_3$ and LiF in the molar ratio of 1:1,5:1,5:3 was heated to 1000 °C. The charge was held in a melted state for a day to achieve homogenization. After this stage a platinum wire with a loop was placed in the center of the melt surface and the temperature was decreased to 900 °C. Then the melt was cooled with the 2 °C/day to 850 °C and following cooling at the rate of

15 °C/day to room temperature. The crystal was chosen for x-ray analysis. Powder diffraction patterns were refined using the Rietveld method within the GSAS- II program.

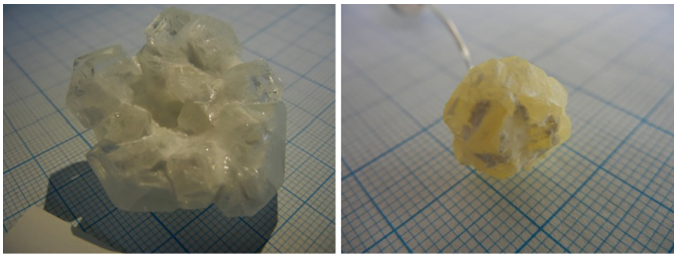


**Fig. 2.** Crystals grown from $LiBO_2$-LiF flux: TLSB (left) and SLSB (right)

The chemical composition of obtained crystals was measured by X-ray fluorescent analysis using XRF 1800 (Shimadzu, Japan). The results of the analysis are conformed with the formula obtained after crystal structure refinement: (Table 1)

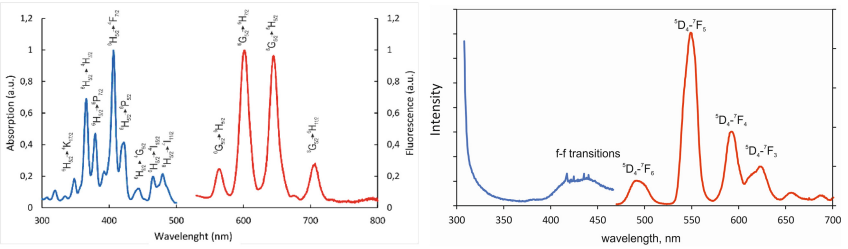
**Table 1.** Composition of TLSB and SLSB based on X-ray fluorescent elemental analysis

| Composition of the $Tb_xLa_ySc_z(BO_3)_4$ | | Ratio of Tb/La |
|---|---|---|
| Starting melt | $Tb_{0.5}La_{0.5}Sc_3(BO_3)_4$ | 1 |
| Center | $Tb_{0.22}La_{0.78}Sc_3(BO_3)_4$ | 0.28 |
| Edge | $Tb_{0.24}La_{0.75}Sc_{2,99}(BO_3)_4$ | 0.32 |
| Composition of the $Sm_xLa_ySc_z(BO_3)_4$ | | Ratio of Sm/La |
| Starting melt | $Sm_{0.5}La_{0.5}Sc_3(BO_3)_4$ | 1 |
| Center | $Sm_{0.32}La_{0.69}Sc_{2,98}(BO_3)_4$ | 0.46 |
| Edge | $Sm_{0.35}La_{0.68}Sc_{2,97}(BO_3)_4$ | 0.52 |

## 3 Results and Discussion

**Structure.** According to Rietveld refinement both SLSB and TLSB crystalize in the trigonal space group R32 with unit cell parameters: a = 9.823(6), c = 7.975(3) (SLSB) and a = 9.803(3), c = 7.960(4)Å (TLSB). The structure framework is composed of the R, La atoms, Sc atoms and B atoms occupy trigonal prisms, octahedra and planar triangle of oxygen, respectively. The isolated (R, La)$O_6$ trigonal prisms alternate along the c-axis with BO3 triangle that are perpendicular to the c-axis. $ScO_6$octahedra link to each other along the edge and form twisted chain along c, which separate (R, La)$O_6$ prisms as well. The discrepancies between refined diffraction spectra with model calculations can be explained by crystal cleavage along {202} and {113}.

**Luminescence.** Typical excitation and luminescence spectra of SLSB are shown on Fig. 3(a). The strongest excitation peak of samarium crystal corresponds to $^6H_{5/2} \rightarrow {}^4F_{7/2}$ transition located at 407 nm. Whereas luminescent spectrum of SLSB has some peaks corresponding to$^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2 и 11/2) and located at 566, 602, 645 and 708 nm.




a b

**Fig. 3.** Luminescent properties of (a) SLSB, (b) TLSB

On Fig. 3(b) TLSB excitation and luminescence spectra are shown with a wide strip at 300 nm corresponding to$^4F$ - $^5D$ transition. Luminescent spectra consist of 5 peaks at 490, 505, 585 and 640 corresponding to$^5D_4$ - $^7F_J$ (J = 6, 5, 4, 3) transitions.

## 4 Conclusions

The formation of a huntite structure in systems $R_xLa_{1-x}Sc_3(BO_3)_4$, (R = Sm, Tb), as well as the dependence of the compositions stable in the required structure depending on the production method is shown. The spectral characteristics confirm the potential of using crystals as luminescent materials.

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