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journal homepage: [www.elsevier.com/locate/ssc](http://www.elsevier.com/locate/ssc)Synthesis, structure and properties of RbMgBO<sub>3</sub>R.V. Kurbatov<sup>a</sup>, L.A. Solovyov<sup>b</sup>, B.G. Bazarov<sup>a,c</sup>, A.K. Subanakov<sup>a,\*</sup>, J.G. Bazarova<sup>a,c</sup><sup>a</sup> Baikal Institute of Nature Management of the Siberian Branch of the RAS, Ulan-Ude, Russia<sup>b</sup> Institute of Chemistry and Chemical Technology of the Siberian Branch of the RAS, Krasnoyarsk, Russia<sup>c</sup> Buryat State University, Ulan-Ude, Russia

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## ABSTRACT

A double borate RbMgBO<sub>3</sub> was newly synthesized by solid state reactions and the crystal structure were determined from powder X-ray diffraction data. It crystallizes in cubic space group  $P2_13$  ( $a=6.9493(1)$  Å,  $V=335.60(1)$  Å<sup>3</sup>,  $Z=4$ ). RbMgBO<sub>3</sub> was melted at 865.5 °C. The existence of only BO<sub>3</sub> groups was confirmed by IR analysis. The RbMgBO<sub>3</sub> conductivity was measured ( $10^{-6}$ – $10^{-5}$  S/cm).

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## 1. Introduction

The borates include more than 160 mineral species and several hundreds of synthetic compounds. The ability of boron atoms to present in a three- and fourfold coordination defines a large number of anion radicals. The variety of existing and possible structural arrays of borates is of great interest and it is constantly supported by newly discovered compounds with higher performance characteristics. Among the various anionic groups, the planar [BO<sub>3</sub>]<sup>3-</sup> groups are highly attractive for potential second harmonic generation. Because of highly localized valence electrons, low absorption (173 nm), and anisotropic polarizability, some borates are likely to be good candidates for application as birefringent and deep-UV nonlinear optical (NLO) materials. The most recent studies of new noncentrosymmetric borates are presented in a number of studies [1–5].

The phase relationships in the triple-oxide systems M<sub>2</sub>O–MgO–B<sub>2</sub>O<sub>3</sub> (M=K, Rb) was previously investigated [6,7] and the formation of double borates MMgBO<sub>3</sub> (M=K, Rb) was found. Wu and co-authors [8–14] studied M<sub>2</sub>O–M'O–B<sub>2</sub>O<sub>3</sub> (M=Li, Na, K; M'=Mg, Ca, Sr, Ba) systems in searching new optical materials with [BO<sub>3</sub>]<sup>3-</sup> anionic groups. In a previous study [15], the structure and properties of KMgBO<sub>3</sub> were determined. KMgBO<sub>3</sub> crystallizes in cubic chiral space group  $P2_13$ . Effect of SHG produced by KMgBO<sub>3</sub> powder is about one-third of that produced by KDP powder. We

assume to increase a SHG effect by a substitution K to other atoms. The similar system containing monovalent heavy atoms such as Rb, Cs, Ag attracted our attention as a potentially NLO materials. The aim of the present research is to synthesize and study the properties of a double borate RbMgBO<sub>3</sub> in terms of the structure, electrical and thermal characteristics.

## 2. Experimental

Polycrystalline sample of RbMgBO<sub>3</sub> was prepared by a standard ceramic technology. The chemically pure grade Rb<sub>2</sub>CO<sub>3</sub> (99.9%), MgO (99.9%), H<sub>3</sub>BO<sub>3</sub> (99.99%) components were used as initial reagents. The stoichiometric quantities of components were grinded in an agate mortar. The powders were annealed in alumina crucibles in a muffle furnace at 700–750 °C for 80–100 h in the air with intermediate grindings. Phase equilibrium was monitored by X-ray powder analysis at room temperature (D8 diffractometer Bruker AXS, CuK<sub>α</sub>-radiation, Germany).

Powder diffraction data on the analysis of the RbMgBO<sub>3</sub> structure were obtained by PANalytical X'Pert PRO with detector PIXcel and graphite monochromator on CoK<sub>α</sub>-radiation. The sample was prepared by grinding in an agate mortar with addition of octane. The X-ray diagram was taken in the diffraction angle interval of  $2\theta=20$ – $145^\circ$  with increment of  $0.013^\circ$  and total time of 400 s.

The dielectric permittivity and electrical conductivity of the RbMgBO<sub>3</sub> were measured from 400 to 700 °C at 1 MHz by a two-probe technique using a Tesla BM 431E bridge and platinum electrodes.

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IR spectrum was recorded with a Thermo Scientific Nicolet iS10 FT-IR spectrometer using Smart iTR with ZnSe plate in the 600–4000  $\text{cm}^{-1}$  wavenumber range.

Differential scanning calorimetry analysis was carried out using simultaneous thermal analysis STA 449C Netzsch coupled with a quadrupole mass spectrometer (Netzsch QMS 403C) in order to analyze the residual gas stream. The experiment was carried out in Pt crucibles at an Ar+O<sub>2</sub> atmosphere with a heating rate of 10 °C/min from room temperature to 950 °C.

The NLO properties of the RbMgBO<sub>3</sub> and KMgBO<sub>3</sub> compounds were studied by powder second harmonic generation (SHG) technique with the set-up similar to that employed by Kurtz and Perry by Stefanovich S.Yu in Chemical Department of Moscow State University. YAG:Nd-laser was used as source of powerful impulse radiation at wavelength  $\lambda=1.064 \mu\text{m}$  with a repetition rate of 4 impulses per second and a duration of impulses about 10 ns. The reported below SHG signal,  $I_{2\omega}$ , indicates the ratio of second harmonic radiation intensity from a tested sample to that from a reference  $\alpha$ -quartz standard.

### 3. Results and discussion

The crystal structure of double borate was determined and refined by the Rietveld method [16] and the derivative difference minimization method (DDM) [17,18]. The structure determination was made independent from [15]. The diffraction pattern of RbMgBO<sub>3</sub> was indexed using ITO [19] and gave out a cubic unit cell. Space group  $P2_13$  was determined by CheckCell [20]. The refined parameters of elementary cell for RbMgBO<sub>3</sub> are:  $a=6.9493(1) \text{ \AA}$ ,  $V=335.60(1) \text{ \AA}^3$ ,  $Z=4$ . The atomic positions of heavy atoms were found by Patterson synthesis. The position of BO<sub>3</sub> was localized by difference maps of the electron density distribution. 40 F<sub>o</sub> were used. Structure refinement was performed by the DDM method in anisotropic approximation for all atoms with the index of reliability  $R_{\text{DDM}}=3.8\%$ ,  $R_{\text{F}}=1.1\%$ ,  $R_{\text{exp}}=2.95\%$ ,  $\text{GOF}=1.30$ . The peak shape was modeled by Pearson VII function with accounting for anisotropic broadening due to microtensions. Also, the impurity phases of MgO and Mg<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> were introduced in refined model. The experimental, calculated and difference profiles of X-ray graphs of RbMgBO<sub>3</sub> sample after DDM refinement are shown in Fig. 1. The coordinates of the atoms, the equivalent isotropic thermal parameters and basic interatomic distances are given in Table 1.

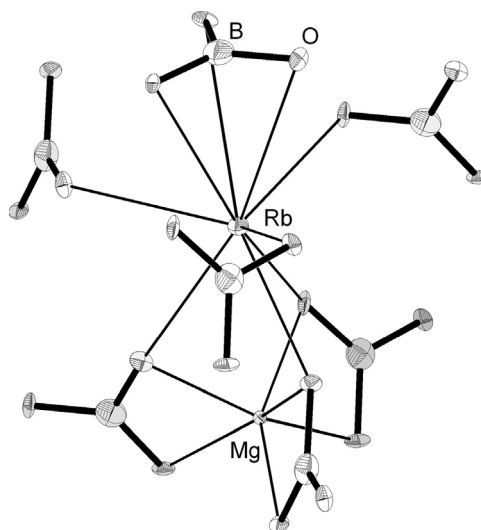
The structure of RbMgBO<sub>3</sub> is different according to the type and symmetry from the structures of known double borates [21], excluding KMgBO<sub>3</sub>. It is a three-dimensional framework consisting

**Table 1**

The coordinates of atoms, the equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) and the main interatomic distances ( $\text{\AA}$ ) in the structure of RbMgBO<sub>3</sub>.

Atom	x	y	z	$U_{\text{eq}}$
Rb	0.1414(9)	0.1414(9)	0.1414(9)	0.012(0)
Mg	0.8594(0)	0.8594(0)	0.8594(0)	0.005(5)
B	0.3982(9)	0.3982(9)	0.3982(9)	0.021(6)
O	0.4027(4)	0.2496(5)	0.5320(4)	0.010(7)
Distances				
Rb–B	3.09(2)	Mg–O <sup>v</sup>	2.114(5)	
Rb–O	3.351(4)	Mg–O <sup>vi</sup>	2.179(5)	
Rb–O <sup>ii</sup>	2.910(4)	B–O	1.390(4)	
Rb–O <sup>iii</sup>	2.840(4)			

Symmetrical positions:  $x+1, y+1, z+1$ ; (ii)  $-x+3/2, -y+1, z+1/2$ ; (iii)  $-x+2, y+1/2, -z+3/2$ ; (iv)  $-x+1/2, -y+1, z-1/2$ ; (v)  $x-1/2, -y+1/2, -z+1$ ; (vi)  $-x+1, y-1/2, -z+1/2$ .

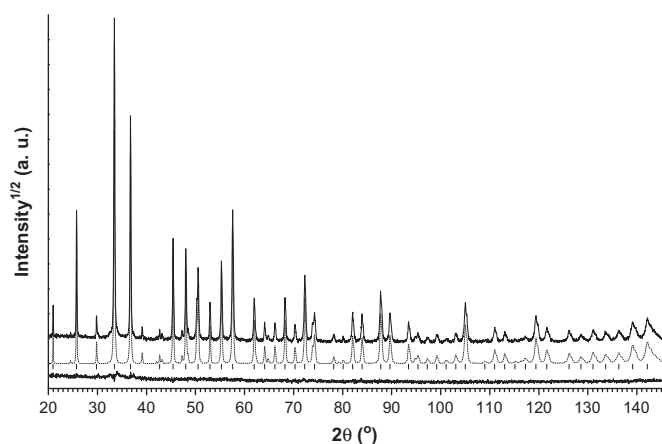


**Fig. 2.** The coordination of atoms in RbMgBO<sub>3</sub> structure.

of triangular BO<sub>3</sub>-groups and distorted MgO<sub>6</sub> octahedrons connected by edges. The Rb atoms, coordinated by nine oxygen atoms (Fig. 2), appear between triangular BO<sub>3</sub>-groups and distorted 1 MgO<sub>6</sub> octahedrons. One of the borate groups is coordinated by the entire plane of O<sub>3</sub> to Rb atom to form a short contact Rb...B and three connections Rb–O, elongated due to the repulsive force between Rb and B atoms (Table 1). The distance K...B is 3.53 Å in KMgBO<sub>3</sub>. The atomic coordinates of RbMgBO<sub>3</sub> in Table 1 insignificantly differ from that of KMgBO<sub>3</sub> [15]. In our opinion this explains by Rb introducing to the structure. All the cavities occupied by Rb atoms form the tunnels directed along the [111] direction and connected among themselves by the «vents» (Fig. 3).

The literary data on double borates of one- and two-valent elements and our experimental data are summarized in Table 2. Note that systems with heavy atoms such as Rb, Cs, Ag, Tl are uninvestigated and, therefore, represent interest for research. The formation of phases at 1:2:1 ratio was found in M<sub>2</sub>O–AO–B<sub>2</sub>O<sub>3</sub> (M=Li, Na, K, Rb; A=Mg, Ca, Sr, Ba) systems, but their anionic frameworks consist only of BO<sub>3</sub>-groups [21]. The space group symmetry of 1:2:1 phase was shown to increase from Li, Na (monoclinic) to K, Rb (cubic). There are large cavities in the structure of MMgBO<sub>3</sub> (M=K, Rb) double borates. These are suitable for the incorporation of other cations, introduced by implantation or ion exchange, similar in ion size and charge. The compounds form a new structure type of double borates (Table 2).

The temperature dependence of the ion conductivity of RbMgBO<sub>3</sub> is shown in Fig. 4. The conductivity gradually increases



**Fig. 1.** The experimental and calculated (dashed line) and the difference diffraction pattern of RbMgBO<sub>3</sub> sample after refining the structure by the DDM method. The peaks of the main phase are shown by the strokes.

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