

Synthesis and X-ray structural investigation of undoped borate glasses*

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A series of undoped borate glasses: $Li_2B_4O_7$, $LiKB_4O_7$, LiB_3O_5 , SrB_4O_7 , and $LiCaBO_3$ of high optical quality and chemical purity were obtained from the corresponding polycrystalline compounds using standard glass synthesis under technological conditions developed by the authors. The glasses were obtained by rapid cooling of molten crystalline material, which was heated to 100 K above the melting point to prevent crystallization and to exceed the glass transition point. The X-ray diffraction intensity profiles of the investigated glasses were typical of glassy compounds. The most typical intensity profile, consisting of almost symmetrical peaks, was observed in the case of $Li_2B_4O_7$ and LiB_3O_5 . Substitution and partial substitution of Li atoms by Sr and Ca atoms was accompanied by significant changes in the intensity profiles of the investigated glasses. Pair correlation functions and structural parameters (average interatomic distances and coordination number to oxygen) of the investigated glasses were evaluated and analyzed. Structural peculiarities of the investigated borate glasses are discussed in comparison with structural data available for their crystalline analogs.

Keywords: borate glasses, fabrication, X-ray diffraction, intensity curves, pair correlation functions

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1. Introduction

Anhydrous borate crystals and glasses are characterized by good resistance to the effects of optical [1, 2] and ionizing radiation [3–5]. Moreover, they exhibit high transparency in the vacuum ultraviolet (VUV)-middle infrared (MIR) spectral range [6, 7] as well as good thermoluminescent [8–12], nonlinear optical [13–16], acoustic, piezoelectric, acousto-optic, and piezo-optic [17–20] properties. Therefore, borate crystals are highly attractive materials for the use in quantum electronics, solid state dosimetry, nonlinear optics and acousto-optics. However, growing borate crystals is a very complicated,

lengthy and expensive technological process. Also, the high viscosity of the melt makes the melting of borates difficult. Nevertheless, the ability of boric anhydride (B_2O_3) to polymerize makes possible to obtain borate compounds with different chemical composition in the glassy (or vitreous) state from the corresponding crystalline compounds, in particular Li₂B₄O₇, LiKB₄O₇, LiB₃O₅, SrB₄O₇, LiCaBO₃, etc. Up to now the structure of complex oxide glasses, in particular borate glasses, has not been sufficiently studied, because the direct method for the investigation of glass structure, i.e. extended X-ray absorption fine structure (EXAFS), cannot be applied to light atoms (Li, B, etc.). Therefore, the synthesis and structural investigation of borate glasses with different chemical composition poses an interesting problem from the scientific and practical application points of view.

The structure of different crystalline borates has already been widely investigated by numerous

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authors. In particular, the structural data for crystalline analogs of the investigated glasses: $Li_2B_4O_7$, LiB_3O_5 , SrB_4O_7 , and LiCaBO₃ have been presented in [21-26]. EXAFS investigation [27, 28] has shown that the local structure of oxide glasses (i.e. interatomic distances and coordination numbers to oxygen) is highly similar to the local structure of the corresponding crystals. Therefore, the available structural data for Li₂B₄O₇, LiB₃O₅, SrB₄O₇, LiCaBO₃ crystals [21–26] are cited in Section 3 of this paper in order to compare them with the structural data obtained from X-ray diffraction (XRD) measurements of borate glasses with the same chemical composition.

This paper covers the development of a fabrication method of borate glasses with different chemical compositions, XRD investigation of borate glasses, as well as a comparison of the obtained structural data with corresponding reference data of their crystalline analogs.

2. Experimental details

2.1. Fabrication and characterization of borate glasses

A series of undoped borate glasses: $Li_2B_4O_7$, LiKB₄O₇, LiB₃O₅, SrB₄O₇, and LiCaBO₃, exhibiting high optical quality and chemical purity, were obtained from the corresponding polycrystalline compounds. For the purposes of solid-state synthesis of polycrystalline compounds, we used the corresponding carbonates (Li₂CO₃, K₂CO₃, CaCO₃, and SrCO₃) and boric acid (H₃BO₃) of high chemical purity (99.99 %) in proportions corresponding to their stoichiometric compositions. Solid-state synthesis of the polycrystalline borate compounds was carried out by multi-step heating. The process can be described, for the example of Li₂B₄O₇, by the following reaction:

 $\begin{array}{rcl} Li_2CO_3 &+& H_3BO_3 & \underline{150\ ^\circ C\ (H_2O)\uparrow} &\rightarrow & Li_2CO_3 \\ +& \alpha\text{-}HBO_2 & \underline{250\ ^\circ C\ (H_2O)\uparrow} &\rightarrow & Li_2CO_3 + & B_2O_3 \\ \underline{600\ ^\circ C\ (CO_2)\uparrow} &\rightarrow & Li_2B_4O_7 + & [Li_2CO_3 + & B_2O_3] \rightarrow \\ \underline{800\ ^\circ C\ (CO_2)\uparrow} &\rightarrow & Li_2B_4O_7 \end{array}$



Fig. 1. Differential scanning calorimetric (DSC) curve for LiKB₄O₇ glass sample.

Borate glasses were obtained by rapid molten polycrystalline material cooling of using high-temperature glass synthesis under technological conditions developed by the authors of this paper. Two types of crucibles, i.e. graphite (C) and corundum ceramic (Al_2O_3) , were used to obtain borate glasses. The method of glass fabrication is essentially different from the technique used for growing crystals. The temperature of the melt during glass synthesis must be higher than the crystallization temperature. The results of an investigation of LiKB₄O₇ using a differential scanning calorimeter (DSC) are presented in Fig. 1. During glass fabrication, the LiKB₄O₇ melt was heated to 1213 K and subsequently kept for 2 h at this temperature (Fig. 1), which is above the melting temperature $(T_{melt} = 1080 \text{ K})$. For the synthesis of remaining borate glasses, the temperature of the melt must also exceed the corresponding melting temperature by at least 100 K. During the fabrication of the investigated borate glasses, their melts were homogenized for 2 h at 1300 K (Li₂B₄O₇ glass), 1280 K (LiB₃O₅ glass), 1500 K (SrB₄O₇ glass), and 1400 K (LiCaBO₃ glass).

The glass samples obtained in both the graphite and corundum crucibles were characterized by significant mechanical stress. The mechanical stress in the obtained glasses was eliminated by annealing in the temperature range of 680–730 K. The distribution of phase differences in the glass samples, which was induced by mechanical stress,







Fig. 2. Distribution of the phase difference inside $Li_2B_4O_7$ glass sample: (a) as-synthesized; (b) annealed at T = 680 K for 12 hrs.

was monitored by a polarimetric technique. Fig. 2 shows the distribution of the phase difference in the same $Li_2B_4O_7$ glass sample, before and after the annealing process. It is evident from Fig. 2 that the values of the phase difference caused by mechanical stress were smaller in case of the annealed glass sample than in the case of the unannealed one.

For X-ray diffraction investigations, we used $Li_2B_4O_7$, LiB_3O_5 , SrB_4O_7 , and $LiCaBO_3$ bulk glass samples. We calculated the diffraction patterns of crystalline compounds on the

basis of reference data for the corresponding crystals [21–26] and compared the simulated profiles with the experimental data obtained for the investigated glasses. The intensity profiles of the nanocrystalline samples (nanoparticles 5 nm in size) were obtained using the DHN/PDS program for powder diffraction, developed in the Institute of Low Temperatures and Structure Research, Polish Academy of Sciences (Wrocław, Poland).

2.2. Experimental methods and equipment

X-ray diffraction studies were carried out using a DRON-3 diffractometer, equipped with a focusing system and a high-temperature chamber. For XRD measurements, Bragg-Brentano focusing geometry was used. Monochromatic Cu K_{α} radiation was selected from the X-ray beam spectrum by means of a graphite single crystal. The variation of the X-ray intensity with the scattering angle was recorded with a step of 0.1° using a scintillation detector, equipped with an electronic system and a computer. The accuracy of the measurements of scattered X-ray intensities was 2 %. The recorded X-ray intensity curves were corrected for incoherent scattering and polarization and normalized to electron units. The scattering intensity curves were Fourier-transformed to obtain the corresponding pair correlation functions and to derive the average interatomic distances in the glass network. In this paper, only the first oxygen coordination shell (local structure) of cations in the investigated glasses is considered and analyzed.

3. Results and discussion

Here, we interpret the XRD structural data obtained for borate glasses basing on two closely related observations. First, the local structure (the first oxygen coordination shell) of cations in oxide crystals and glasses of the same chemical composition is very similar. Second, the coordination numbers to oxygen for cations in the glass network are equal or slightly lower than for the same cations in the lattice of the corresponding crystal. The first observation is based on reference EXAFS data [27, 28], whereas the second – on the well-known experimental fact that the number of oxygen vacancies is larger in the glass than in the corresponding crystal. Therefore, during the analysis of results obtained for each investigated glass sample, the general structural characteristics of the corresponding crystal are also briefly considered.

X-ray scattering intensity curves obtained for the investigated glasses are presented in Fig. 3. A comparison of X-ray diffraction patterns for polycrystalline (1), nanocrystalline (2), and bulk glass (3) samples is shown in Fig. 4. The pair correlation functions for nanocrystalline (1) and glassy (2) borate compounds are presented in Fig. 5. A comparison of the intensity curves (Fig. 4) and pair correlation functions (Fig. 5) for nanocrystalline and bulk glass compounds shows that for all the investigated compounds the local structure of nanocrystals and their corresponding glass is very similar. Even the shoulders on the left-hand side of the principal peaks for Li₂B₄O₇, LiB₃O₅, SrB₄O₇, and LiCaBO₃ nanocrystalline compounds are well-correlated with the corresponding peaks for the bulk glass samples. These data further support the abovementioned observations and allow us to conclude that the distribution of atoms in nanocrystals and glasses displays a high degree of short-range chemical ordering.

The average interatomic distances calculated for the investigated glasses and the corresponding interatomic distances for crystals of the same chemical composition are presented in Tables 1-4. XRD structural data obtained for the investigated glasses and its comparison with the corresponding reference data for their crystalline analogs are discussed below.

3.1. Lithium tetraborate $(Li_2B_4O_7)$ and lithium triborate (LiB_3O_5) glasses

The intensity curves for the obtained $Li_2B_4O_7$ and LiB_3O_5 glasses show closely similar profiles typical of the glassy state, with a relatively sharp first maximum and broad and pronounced second and third maxima (Fig. 3). This indicates the

Fig. 3. X-ray scattered intensity curves for the investigated nominally-pure borate glasses: Li₂B₄O₇, LiB₃O₅, SrB₄O₇, and LiCaBO₃.

dominant contribution of the same structural units to the total atomic distribution in $Li_2B_4O_7$ and LiB₃O₅ glasses. A comparison of the profiles of the intensity curves (see Figs. 3 and 4) for glassy, nanocrystalline, and polycrystalline compounds for each Li₂B₄O₇ and LiB₃O₅ compositions shows good correlation. The pair correlation functions calculated from the corresponding intensity curves for Li₂B₄O₇ and LiB₃O₅ glasses also show similar ordering of the maxima (Figs. 4 and 5). This also indicates that the local environment is identical in the first coordination shell for B and Li atoms in Li₂B₄O₇ and LiB₃O₅ glasses and in their crystalline analogs. As can be seen from Tables 1 and 2, the average interatomic distances (B-O)and Li - O in glasses and crystals of $Li_2B_4O_7$ and LiB₃O₅ are closely similar. The average distance to the nearest-neighbor atoms (r_1) in Li₂B₄O₇ glasses is somewhat larger than in LiB₃O₅ glasses (see Figs. 4 and 5; Tables 1 and 2).

According to [21, 22], the Li₂B₄O₇ crystal structure belongs to the $I4_1cd$ (C_{4v}) space group with the following lattice parameters: a = b= 0.9479(3) nm; and c = 1.0280(4) nm (c = 1.0290(4) nm in [22]). In the structure of Li₂B₄O₇, there are two differently coordinated boron atoms: a threefold-coordinated atom (BO₃)





Fig. 4. Comparison of the diffraction patterns for polycrystalline (1), nanocrystalline (2) and glassy (3) borate compounds: Li₂B₄O₇, LiB₃O₅, SrB₄O₇, and LiCaBO₃.



Fig. 5. Pair correlation functions for nanocrystalline (1) and glassy (2) borate compounds: $Li_2B_4O_7$, LiB_3O_5 , SrB_4O_7 , and $LiCaBO_3$.

Bond lengths in Li ₂ B ₄ O ₇	Glass	Crystal [22]		Crystal [21]	
	Distances, d [nm]	Distances, d [nm]		Distances, d [nm]	
B-O	0.165	Trigonal BO ₃ group	Tetragonal BO ₄ group	Trigonal BO ₃ group	Tetragonal BO ₄ group
		0.1355	0.1453	0.1349(10)	0.1448(10)
		0.1371	0.1506	0.1384(10)	0.1507(10)
		0.1374	0.1502	0.1386(10)	0.1497(10)
			0.1454		0.1454(10)
Li-O	0.279	0.2170		0.197(2)	
		0.1967		0.202(2)	
		0.2027		0.207(2)	
		0.2080		0.214(2)	
				0.263(2)	
				0.285(2)	
				0.288(2)	

Table 1. Average interatomic distances for Li₂B₄O₇ glass, obtained from pair correlation functions and precise interatomic distances for the corresponding crystal.

Table 2. Average interatomic distances for LiB₃O₅ glass, obtained from pair correlation functions and precise interatomic distances for the corresponding crystal.

Bond lengths in LiB ₃ O ₅	Glass	Crystal ([23], T = 20 C)		
	Distances, d [nm]	Distances, d [nm]		
B-O	0.144	BO ₃ group BO ₄ gr		BO ₄ group
		0.13486	0.13564	0.1460
		0.1367	0.1369	0.1461
		0.1396	0.1391	0.1483
				0.1489
Li-O	0.250	0.1979		
		0.2005		
		0.2013		
		0.2180		

Table 3. Average interatomic distances for SrB_4O_7 glass, obtained from pair correlation functions and precise interatomic distances for the corresponding crystal.

Bond	lengths	in	Glass	Crystal [24]	
SrB ₄ O	7				
			Distances, <i>d</i> [nm]	Distances, d [nm]	
	B-O		0.140	0.137(4)	0.153(6)
				0.147(5)	0.148(6)
				0.150(6)	0.150(9)
				0.155(9)	0.138(6)
	Sr-O		0.262	0.273(7)	
				0.247(3)	
				0.268(4)	
				0.279(4)	

triangles), with B-O distances between 0.1349 and 0.1386 nm; and a fourfold-coordinated atom (BO₄ tetrahedra), with B-O distances between 0.1448 and 0.1507 nm [21]. According to [21], the Li atoms in Li₂B₄O₇ crystal are fourfold-coordinated by close oxygen atoms, with Li-O distances in the range of 0.197-0.214 nm. However, if one takes into account next-neighbour oxygen atoms located 0.263, 0.285, and 0.288 nm away from the Li atom, it can be concluded that the coordination number of Li varies between 4 and 7, depending on the chosen Li – O distance threshold. In particular, the coordination number to oxygen equals 5, 6 and 7 for the Li-O distances up to 0.263, 0.285 and 0.288 nm, respectively (Table 1). Such a statistical distribution of the Li – O distances

Table 4. Average interatomic distances for LiCaBO₃ glass, obtained from pair correlation functions and precise interatomic distances for the corresponding crystal.

Bond lengths in LiCaBO ₃	Glass	Crystal [26]
	Distances,	Distances,
	d [nm]	d [nm]
B-O	0.149	0.13699(15)
		0.13844(12)
		0.13835(12)
Ca-O	0.258	0.23726(9)
		0.24075(7)
		0.24750(7)
		0.23606(7)
		0.25122(7)
		0.23637(7)
		0.24412(7)

for different coordination numbers (N = 4-7) is an evidence of the so-called positional disorder in the Li₂B₄O₇ crystal lattice.

On the basis of the results presented above and reference data for $Li_2B_4O_7$ crystals [21, 22], we claim that the boron atoms in Li₂B₄O₇ glass are, in general, fourfold-coordinated (BO₄ tetrahedral units) with an average B - O distance of 0.165 nm, with a certain proportion of threefold-coordinated B atoms (BO₃ triangular units) with shorter B-Odistances also present, as evidenced by shoulders in a dominant first peak in the intensity curves and pair correlation functions, which corresponds to BO_4 tetrahedral units (Figs. 4 and 5). The local environment of Li atoms in Li₂B₄O₇ glass also consists of oxygen tetrahedral units with an average Li-O distance of 0.279 nm. This is in a good agreement with the corresponding distances in the first coordination shell of the Li atoms in Li₂B₄O₇ crystal (see Table 1).

According to [23], the structure of crystalline lithium triborate (LiB₃O₅) belongs to the space group *Pna*2₁. The following lattice parameters were obtained at room temperature: a = 0.8444 nm, b = 0.7378 nm, c = 0.5146 nm. In the structure of LiB₃O₅ crystal, two of the three boron atoms were threefold-coordinated by oxygen, with B–O distances in the range of 0.13486–0.13960 nm for one of the B atoms and in the range of 0.13564-0.1391 nm for another one. The remaining boron atoms were fourfold-coordinated by oxygen with a B-O distance in the range of 0.1460 to 0.1489 nm. Lithium atoms were fourfold-coordinated by oxygen, with Li-O distances in the range of 0.1979-0.2180 nm.

According to the experimental data obtained for LiB₃O₅ glasses (Figs. 3-5 and Table 2) and reference structural data for LiB₃O₅ crystals [23], we can conclude that the structure of LiB_3O_5 glasses mainly consists of triangular (BO₃) units with an average B-O distance of 0.144 nm. A certain proportion of boron atoms in LiB₃O₅ glasses are fourfold-coordinated with larger average B-O distances ($d_{B-O} > 0.144$ nm), as evidenced by a shoulder in the first peak in their intensity curve and pair correlation function (Figs. 4 and 5). For the same reason, we can state that the local environment of the Li atoms in LiB₃O₅ glasses also consists of oxygen tetrahedra with an average Li-O distance of 0.250 nm. The obtained average B-O and Li-O distances in the LiB₃O₅ glass network show satisfactory correlation with corresponding distances in the BO_3 , BO_4 and LiO_4 structural units in the LiB_3O_5 crystal lattice (see Table 2).

The average B-O and Li-O distances for BO_4 and LiO_4 tetrahedral units in $Li_2B_4O_7$ and LiB_3O_5 glasses are larger than the corresponding distances for BO_4 and LiO_4 tetrahedra in their crystalline analogs (see Tables 1, 2). This behavior is characteristic of oxide compounds [27, 28].

3.2. Strontium tetraborate (SrB₄O₇) glasses

Intensity curve profiles observed for SrB_4O_7 glasses are significantly different from those of lithium tetraborate (Li₂B₄O₇) and lithium triborate (LiB₃O₅) glasses (Figs. 3, 4). In this case, the first two peaks are almost equal in height and are shifted towards larger wave vectors (*s*). These first two peaks are especially well-resolved in the pair correlation function of SrB_4O_7 (Fig. 5). The atomic distribution in the SrB_4O_7 glass is significantly different from that of Li₂B₄O₇ and LiB₃O₅ due to the increase in atomic radius when going from Li to Sr.

According to reference data [24, 25], strontium diborate $SrO \cdot 2B_2O_3$ (or SrB_4O_7) crystallizes in the rhombic system (space group $-Pnm2_1$) with the following unit cell parameters: a = 1.0711 nm, b = 0.4427 nm, c = 0.4235 nm. The SrB₄O₇ lattice is formed by two types of fourfold-coordinated BO_4 complexes (tetrahedra). The B-O bond lengths lie in the range of 0.137-0.155 nm and 0.138-0.161 nm for B1 and B2 atoms, respectively. The presence of only BO₄ tetrahedra is characteristic of the SrB₄O₇ crystal lattice, while in the other borate crystalline compounds, for example in $Li_2B_4O_7$ crystal, the polyanions are formed by both boron-oxygen tetrahedra and boron-oxygen triangles [21, 22]. The Sr-O distances in SrB₄O₇ crystal are in the range of 0.273-0.339 nm. The coordination number to oxygen for the Sr atoms depends on the Sr-O distances and equals 4 when the radius of the first coordination shell is less than 0.290 nm (see Table 3).

Based on the obtained results (Figs. 3-5 and Table 3) and SrB₄O₇ crystal structure data [24, 25] we conclude that the structure of SrB₄O₇ glasses consists of BO₄ tetrahedra with an average B-O distance of 0.140 nm. Two types of BO₄ tetrahedra with similar B-O distances, which are characteristic of the SrB₄O₇ crystal lattice are unresolved in the intensity curve and pair correlation function of SrB₄O₇ glass. For the same reasons, the Sr atoms are stabilized in the SrB₄O₇ glass network in the sites with coordination numbers to oxygen N = 4 with an average Sr-O distance of 0.262 nm (see Table 3).

3.3. Lithium-calcium triborate (LiCaBO₃) glasses

Changes similar to those of SrB_4O_7 glass, only less pronounced, are observed in lithium-calcium triborate (LiCaBO₃) glass, where the divalent Ca partially substitutes univalent Li. Particularly, the intensity curve of the LiCaBO₃ glass also shows two maxima, however, they are located at comparatively smaller wave vectors (Figs. 3 and 4). In other words, the intensity curves of $LiCaBO_3$ glass are observed to have an intermediate character, relative to the intensity curves of Li- and Sr-containing glasses. A similar tendency is observed for the behavior of the pair correlation function (Fig. 5).

According to [26], the structure of LiCaBO₃ crystal is characterized by an orthorhombic unit cell (space group – *Pbca*) with the following lattice parameters: a = 1.3227 nm, b = 0.61675 nm, c = 0.60620 nm. The boron atoms are coordinated by 3 oxygen atoms and the B – O distances are equal to 0.13699, 0.13844, and 0.13835 nm. The Ca atoms are coordinated by 7 oxygen atoms and the Ca – O distances lie between 0.23606 and 0.25122 nm. The Li atoms are coordinated by 5 oxygen atoms and the Li – O distances lie between 0.2004 and 0.2226 nm.

On the basis of the obtained results (Figs. 3-5 and Table 4) and LiCaBO₃ crystal structure data [26] we infer that the boron atoms in the LiCaBO₃ glass network form triangular BO₃ units with an average B-O distance of 0.149 nm. The Ca atoms are located in sites with coordination numbers N = 6-7 with an average Ca-O distance of 0.258 nm. The Li atoms are located in sites with coordination numbers N = 4-5 with an average Li-O distance below 0.258 nm. The obtained B-O and Ca-O average interatomic distances in LiCaBO₃ glass show good correlation with corresponding distances in its crystalline analog (Table 4).

4. Conclusions

In this paper the results of XRD investigation of nominally-pure borate glasses: $Li_2B_4O_7$, LiB_3O_5 , SrB_4O_7 , and $LiCaBO_3$, obtained by a high-temperature synthesis technique are presented for the first time. The obtained intensity curves and pair correlation functions for all investigated borate compounds show their classical glass structure. The distributions of atoms in the nanocrystalline clusters and glasses are characterized by a high degree of short-range chemical ordering. The average interatomic distances for cations in their

first (oxygen) coordination shell in all investigated glasses were derived from the analysis of pair correlation functions and from the comparison with corresponding interatomic distances in borate crystals with identical chemical compositions. The obtained average interatomic distances for the main structural units of the all investigated glasses demonstrate good correlation with corresponding distances for structural units in their crystalline analogs. The coordination numbers to oxygen of the cations (indicative of short-range order) in the investigated borate glasses are closely similar to the corresponding coordination numbers for their crystalline analogs. The obtained results can be used in future work, devoted to the study of local structure of the impurity paramagnetic and luminescence centers in the cationic sites of the borate glass network.

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