

^{11}B and ^7Li MAS NMR of glassy and crystalline borate compounds

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The MAS NMR spectra of the ^{11}B , and ^7Li isotopes in a series of un-doped crystalline and glassy borate compounds with $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 and LiCaBO_3 chemical compositions were investigated and analyzed. The investigated borate glasses of high optical quality and chemical purity were obtained from corresponding polycrystalline compounds using standard glass synthesis technique. The obtained results of MAS NMR spectroscopy show good correlation with X-ray diffraction data for local structure of the cationic sites in borate crystals and glasses with same chemical compositions.

Исследованы и проанализированы спектры MAS ЯМР изотопов ^{11}B и ^7Li в серии нелегированных кристаллических и стекловидных боратных соединений химического состава $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 и LiCaBO_3 . Исследованные боратные стекла высокого оптического качества и химической чистоты, получены из соответствующих поликристаллических соединений с помощью стандартной методики синтеза стекол. Полученные результаты MAS ЯМР спектроскопии хорошо коррелируют с рентгеновскими данными для локальной структуры катионных позиций в боратных кристаллах и стеклах с таким же химическим составом.

MAS ЯМР ^{11}B і ^7Li склоподібних і кристалічних боратних сполук. *М.О.Сергеев, Б.В.Падляк, М.Ольшевський, П.Стемпень.*

Досліджено і проаналізовано спектри MAS ЯМР ізотопів ^{11}B і ^7Li у серії нелегованих кристалічних і склоподібних боратних сполук з хімічними складами $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 і LiCaBO_3 . Досліджувані зразки боратного скла високої оптичної якості та хімічної чистоти, отримано з відповідних полікристалічних сполук за допомогою стандартної методики синтезу скла. Отримані результати MAS ЯМР спектроскопії добре корелюють з даними рентгенівської дифракції для локальної структури катионних позицій у боратних кристалах та склі з таким самим хімічним складом.

1. Introduction

Anhydrous borate compounds (crystals and glasses) are characterized by high resistance to the effects of optical [1, 2] and ionizing radiation [3–5], high transparency in the vacuum ultraviolet (VUV) — middle infrared (MIR) spectral range [6, 7] and ex-

hibit good luminescent, thermoluminescent [8–12], nonlinear optical [13,14] and other interesting properties. Therefore, borate crystals and glasses are very promising materials for quantum electronics, solid state dosimetry, nonlinear optics *etc.*

Practically all borate compounds including $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 , and LiCaBO_3 can be

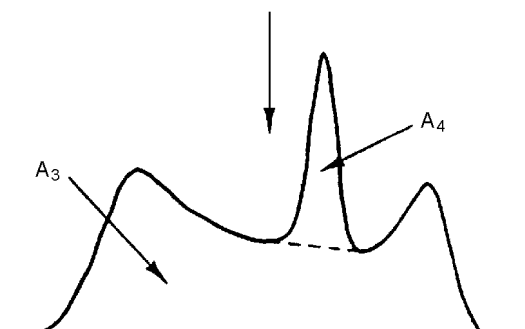


Fig. 1. Method for determining N_4 and N_3 in a ^{11}B NMR spectrum $N_4 = A_4/(A_3 + A_4)$; $N_3 = A_3/(A_3 + A_4)$ [24].

obtained in both crystalline and glassy phases. From technological point of view the glassy (or vitreous) borate compounds are more perspective than their crystalline analogies due to technical difficulty of borate single crystals growth.

The structures of $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 , LiCaBO_3 and other crystalline borate compounds were detailed described in [15–18]. The local structure of cationic sites in the $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 and LiCaBO_3 glasses firstly was investigated in [19] by direct X-ray diffraction (XRD) technique and comparative analysis of the obtained results with referenced data for corresponding borate crystals with the same chemical composition. But, at present time the structural units (or local structure of the cationic sites) in the $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 , LiCaBO_3 and other glassy borate compounds were not satisfactory established and need more detailed investigations by different structural and spectroscopic methods, in particular by nuclear magnetic resonance (NMR) spectroscopy of the ^{11}B and ^7Li isotopes.

In the present paper are detailed investigated and analyzed MAS (Magic Angle Spinning) NMR spectra of the ^{11}B and ^7Li quadrupolar nuclei in a series of un-doped crystalline and glassy borate compounds with $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 and LiCaBO_3 compositions. Based on the obtained results of MAS NMR spectroscopy and available referenced structural data for investigated borate glasses and their crystalline analog the main structural units and their proportions in the borate compounds are proposed.

2. Experimental

The un-doped nominally-pure glasses with $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 and LiCaBO_3 compositions of high optical quality and chemical

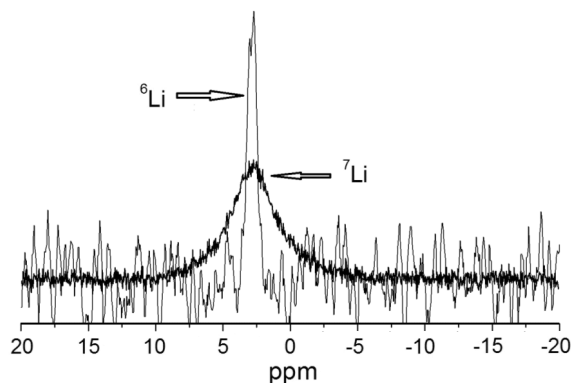


Fig. 2. The MAS NMR spectra of ^7Li and ^6Li in the LiB_3O_5 polycrystalline compound.

purity were obtained in the air from corresponding polycrystalline compounds using corundum crucibles and standard glass technology set-up, described in [19, 20].

The ^{11}B MAS NMR spectra were registered at frequency 128.384 MHz and induction of magnetic field $B = 9.4$ T using a Bruker Avance-400 NMR spectrometer. A 4 mm diameter rotor was filled with a powdered (glassy or polycrystalline) sample and spinning under magic angle with the frequency 14 kHz. A $90-\tau-180-\tau-Acq$ Hahn echo sequence has been employed to investigate the structure of the sample [21–23]. The ^{11}B nucleus has spin $I = 3/2$ and for the selective excitation of the central transition ($+1/2 \leftrightarrow -1/2$), the optimal pulse duration will be equal to the duration of a non-selective $\pi/2$ pulse divided by $(I + 1/2) = 2$ [22]. In our experiments the first radio-frequency pulse $\pi/4 = 1.75 \mu\text{s}$ was used. The recycle delay between acquisitions was 0.5 s and a total of 1024 acquisitions were sufficient to resolve the characteristic borate spectral features for the polycrystalline samples. In the case of some glassy samples it is sufficient to use 100 acquisitions.

In the used magnetic field ($B = 9.4$ T), experimental spectra of ^{11}B of the investigated borate samples contain overlap signals from BO_3 and BO_4 . Symmetric peaks at about 2 ppm are attributed to BO_4 groups and the asymmetric broad peaks are assigned to BO_3 groups [24–28]. The fractions N_4 of the four-coordinated boron (i.e. in BO_4 tetrahedra) and N_3 of three-coordinated boron (i.e. in triangle BO_3 units) was determined using the method proposed by P.J.Bray (Fig. 1) [24].

The ^7Li and ^6Li MAS NMR spectra were obtained at resonance frequencies 155.513 MHz and 58.886 MHz, respec-

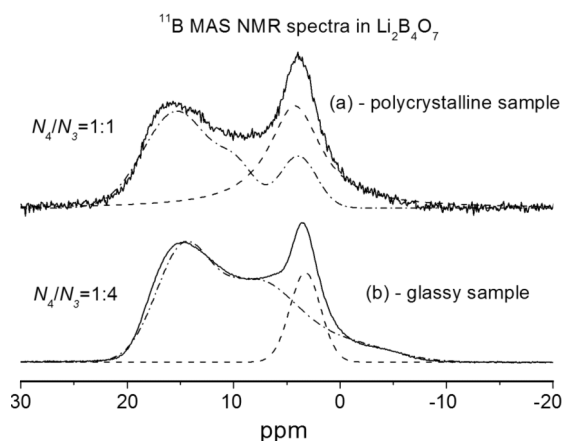


Fig. 3. The MAS NMR spectra of the ^{11}B in the polycrystalline and glassy compounds with $\text{Li}_2\text{B}_4\text{O}_7$; (a) — polycrystalline sample — $N_4/N_3 \cong 1:1$; (b) — glassy sample — $N_4/N_3 \cong 1:4$.

tively, and 14 kHz magic angle spinning speed. A free induction decay signals were recorded after application of a single 3 μs radio-frequency pulse. The example of MAS NMR spectra of the ^6Li (nuclear spin $I = 1$, natural abundance — 7.59 %) and ^7Li (nuclear spin $I = 3/2$, natural abundance — 92.41 %) isotopes in the LiB_3O_5 crystalline compound are shown in Fig. 2. The ratio of the ^6Li and ^7Li nuclear quadrupolar moments is ~ 0.02 [25] and, as a result, linewidth of the ^6Li NMR MAS signal are too much less then linewidth of the ^7Li MAS NMR signal. In the present paper are detailed considered the ^7Li MAS NMR spectra only.

3. Results and discussion

In Figs. 3, 4 are presented the ^{11}B MAS NMR spectra obtained for powdered crystalline and glassy samples with $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 chemical compositions.

All observed the ^{11}B MAS NMR spectra contain two peaks corresponding to the BO_3 and BO_4 structural atomic groups. Large differences in the quadrupolar coupling constants between triangular BO_3 groups ($C_Q = e^2qQ/h$) typically about 2.45 to 2.65 MHz) and tetrahedral BO_4 groups (typically $C_Q < 0.85$ MHz) lead to large differences in the linewidth and lineshape of the MAS NMR signals [24–28]. A symmetric peak at about 2 ppm is attributed to the BO_4 groups and an asymmetric broad peak is assigned to the BO_3 groups. The different frequency positions of the MAS NMR signals of the boron-oxygen bonding groups are connected with different ^{11}B isotropic chemical shifts of

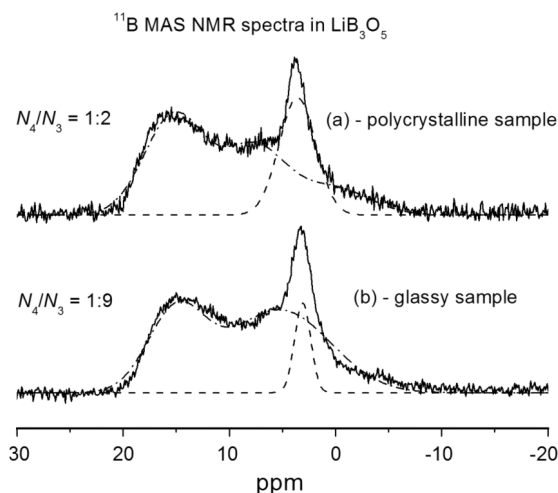


Fig. 4. The MAS NMR spectra of the ^{11}B in the polycrystalline and glassy compounds with LiB_3O_5 ; (a) — polycrystalline sample — $N_4/N_3 \cong 1:2$; (b) — glassy sample — $N_4/N_3 \cong 1:9$.

the BO_3 and BO_4 groups [24, 25]. The lineshape of MAS NMR signal is determined by the second-order quadrupolar shift only, because the dipolar interactions between the magnetic moments of the ^{11}B nuclei are completely averaged [22].

The structure of $\text{Li}_2\text{B}_4\text{O}_7$ crystal contains one magnetically non-equivalent asymmetrical BO_3 group and one magnetically non-equivalent BO_4 group [15, 16] and this is in a good agreement with our NMR data (Fig. 3a). The simulation of the experimental MAS NMR spectrum of the $\text{Li}_2\text{B}_4\text{O}_7$ glass (Fig. 3b) gives the fractions of the BO_4 and BO_3 groups — $N_4/N_3 \cong 1:4$. So the transition $\text{Li}_2\text{B}_4\text{O}_7$ from crystalline to glassy leads to growing of number groups BO_3 .

According to [17] the LiB_3O_5 crystal structure contains two magnetically non-equivalent deforming triangular BO_3 groups and one tetrahedral BO_4 group and this is in a good agreement with our NMR data (Fig. 4a). The deconvolution of the experimental MAS NMR spectrum of the LiB_3O_5 glass (Fig. 4b) gives the fractions of the BO_4 and BO_3 groups — $N_4/N_3 \cong 1:9$. So at the transition LiB_3O_5 from crystalline to glassy grows of number groups BO_3 also.

The obtained results of NMR spectroscopy show good correlation with the XRD data for $\text{Li}_2\text{B}_4\text{O}_7$ and LiB_3O_5 crystals [15–17] and glasses [19].

The structure of LiCaBO_3 crystal contains one magnetically non-equivalent boron atom coordinated by 3 oxygen atoms [18]. The ^{11}B MAS NMR spectrum for polycrys-

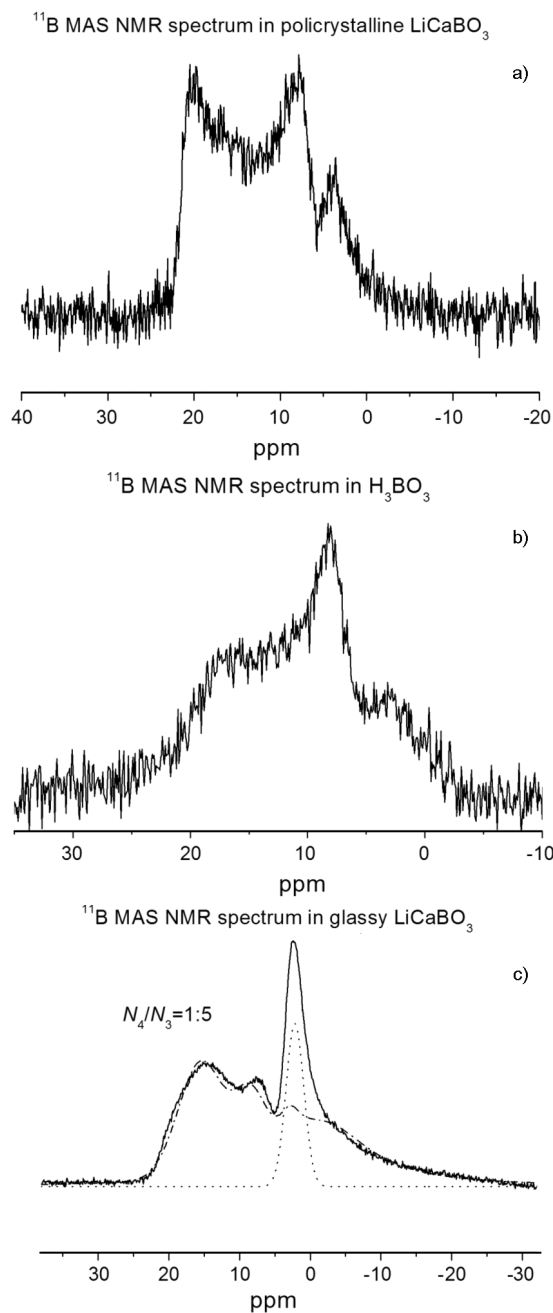


Fig. 5. The MAS NMR spectra of ^{11}B in polycrystalline and glassy compounds with LiCaBO_3 and in boron acid H_3BO_3 ; (a) — polycrystalline sample; (b) — boron acid (c) — glassy sample — $N_4/N_3 \cong 1:5$.

talline LiCaBO_3 agrees with this result (Fig. 5a) and confirms that the structure of the LiCaBO_3 crystal mainly consists of triangular BO_3 units. For comparison in Fig. 5b is presented the ^{11}B MAS NMR spectrum for boric acid (H_3BO_3), which contains the BO_3 groups, only.

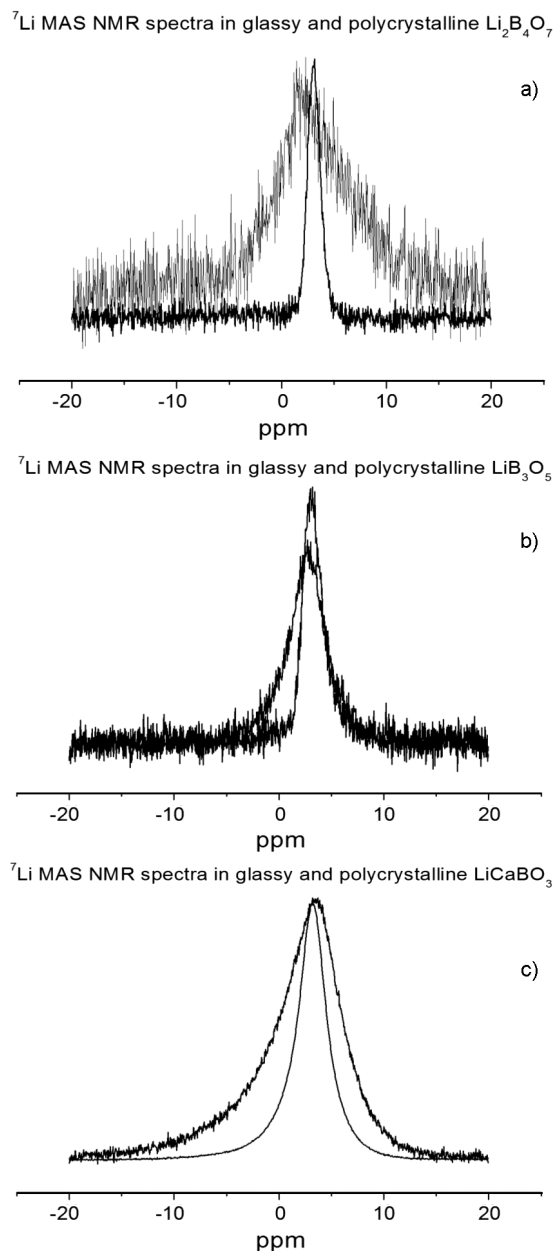


Fig. 6. The MAS NMR spectra of ^7Li in the glassy and polycrystalline compounds with $\text{Li}_2\text{B}_4\text{O}_7$ (a), LiB_3O_5 (b) and LiCaBO_3 compositions (c). Narrow symmetrical MAS NMR lines of ^7Li nuclei refer to the glassy compounds.

As it follows from Fig. 5c in the LiCaBO_3 glass the peak nearly ~ 2 ppm is observed in the ^{11}B MAS NMR spectrum. This peak indicates the presence in the LiCaBO_3 glass fourfold-coordinated tetrahedral (BO_4) groups. So, on the basis of obtained results (Fig. 5c) we infer that the boron atoms in the LiCaBO_3 glass network form not only triangle BO_3 units, but also fourfold-coordi-

nated tetrahedral BO_4 groups. The obtained NMR results show satisfactory agreement with the XRD structural data for LiCaBO_3 crystal [18] and glass [19].

In Fig. 6 are presented the ^7Li MAS NMR spectra obtained for powdered crystalline and glassy samples with $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 and LiCaBO_3 chemical compositions. Sufficiently narrow symmetrical MAS NMR line of ^7Li nuclei in polycrystalline and glass $\text{Li}_2\text{B}_4\text{O}_7$ confirms that the main structural units in lithium tetraborate compound are LiO_4 group. From Fig. 6 it follows that the linewidths of MAS NMR spectrum of the ^7Li nuclei in glassy samples are smaller than corresponding linewidths in their crystalline analogy. This indicates that the average interatomic Li–O distances in the LiO_4 group in the glassy samples are somewhat larger than that in the polycrystalline compound. These results coincide with results obtained in [19].

4. Conclusions

The MAS NMR spectroscopy of the ^{11}B quadrupole nuclei in a series of un-doped crystalline and glassy borate compounds with $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 and LiCaBO_3 chemical compositions allows determining the main structural units: triangular BO_3 and tetrahedral BO_4 atomic groups and their proportions in the structure of crystals and glasses. Based on the analysis of the ^7Li MAS NMR spectra it was shown that the LiO_4 structural units dominate in the $\text{Li}_2\text{B}_4\text{O}_7$, LiB_3O_5 and LiCaBO_3 crystalline and glassy borate compounds. The obtained results of NMR spectroscopy show good correlation with the XRD structural data for investigated crystalline and glassy borate compounds. The obtained NMR results and corresponding referenced structural data allow concluding that the local structure of the cationic sites (main structural units) in the oxide glasses and their crystalline analogies is closely similar.

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