Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Positron lifetime spectroscopy of lithium tetraborate $Li_2B_4O_7$ glass

O. Shpotyuk[a,b,*], V. Adamiv[a], I. Teslyuk[a], A. Ingram[c]

[a] O.G. Vlokh Institute of Physical Optics, 23, Dragomanov str., 79005 Lviv, Ukraine
[b] Institute of Physics of Jan Dlugosz University, al. Armii Krajowej 13/15, Czestochowa 42200, Poland
[c] Opole University of Technology, 75, Ozimska str., 45370 Opole, Poland

ARTICLE INFO

Keywords:
Positron annihilation
Lithium tetraborate
Glass
Crystal
Trapping
Vacancy

ABSTRACT

Free-volume structure of glassy lithium tetraborate $Li_2B_4O_7$ is studied as compared with isocompositional crystal using positron annihilation lifetime spectroscopy in mixed positron-trapping and Ps-decaying modes exploring three-term decomposed positron lifetime spectra. The longest-lived lifetime component in $Li_2B_4O_7$ glass is explained due to low-electron density spaces between neighbouring tetraborate groups, while second component is attributed to positron trapping in lithium vacancy-type complexes. Crystal-to-glass transition in free-volume structure of $Li_2B_4O_7$ is examined with x3-x2-coupling decomposition algorithm. Assuming tight interconnection between atomic-deficient void structure of crystalline and glassy lithium tetraborates, the vitrification from crystalline state is described as expansion of positron-trapping complexes involving singly-ionized lithium vacancies in more spatially-extended positron-trapping sites, this being accompanied by large number of Ps-traps appeared preferentially in boron-oxide network of tetraborate structural units.

1. Introduction

For a long time, since the earliest 1950-s [1–3], the lithium borate glasses of Li_2O-B_2O_3 cut-section have been in sphere of high interests of glass scientists and manufacturers because a number of attractive applications in functional optics [4,5]. From methodological point of glass-forming ability, this quasi-binary system is often accepted as canonical in view of possibility to stabilize isocompositional glass (g) and crystal (c), such as lithium tetraborate (LTB) Li_2O-$2B_2O_3$, i.e. $Li_2B_4O_7$.

The LTB structure is composed by chemically similar atomic entities, which can be considered at the levels of polymerized boron-oxide (B-O) and lithium-oxide (Li-O) sub-systems [4–8]. Nevertheless, an excess of configurational entropy, enthalpy or intrinsic free volume gained under melt quenching is realized in many structural anomalies in vitreous state, when not only atomic-specific arrangement of glass-forming structural blocks, but also atomic-deficient entities incorporated in a nanospace (atomic-accessible or inaccessible nano- and sub-nanometer free-volume voids) are subjects to considerable modification.

In this work, the free-volume structure of glassy g-LTB will be analyzed as compared with the same $Li_2B_4O_7$ single crystal employing the method of annihilating positrons in lifetime measuring mode, the positron annihilation lifetime (PAL) spectroscopy.

2. Experimental

The g-LTB was prepared in ceramics crucible made of corundum (Al_2O_3) from polycrystalline $Li_2B_4O_7$ synthesized by multi-step heating technique as was described in more details elsewhere [5]. The molten polycrystalline material (with melting temperature of 1190 K [3]) was rapidly cooled from homogenized melt kept at 1270 K during 1 h. The mechanical stress accumulated in rapidly-quenched g-LTB was eliminated by annealing at 680–730 K. The vitreous state of the prepared sample was controlled by X-ray diffraction. For PAL measurements, the glass bulk was cut on plane-parallel pieces of nearly ~1 mm in a thickness and carefully polished to a high optical quality. For comparative analysis, we also used crystalline c-LTB sample cut of tetragonal $Li_2B_4O_7$ single crystal grown by the Czochralski technique [9,10].

The PAL spectra were registered with *a fast-fast* coincidence system of 0.230 ns resolution based on two Photonis XP2020/Q photomultipliers coupled to BaF_2 scintillator 25.4A10/2M-Q-BaF-X-N detectors (Scionix, Bunnik, Holland) and ORTEC® electronics (ORTEC, Oak Ridge, TN, USA) [11]. To ensure reliable measurements, each PAL spectrum was recorded at stabilized temperature of 22 °C and relative humidity of *35*% in a normal-measurement statistics (measuring of nearly 1 million of coincidences). The channel width of 6.15 ps allows a total number of channels to be 8000. The radioactive ^{22}Na isotope of low ~50 kBq activity prepared from aqueous solution of $^{22}NaCl$ wrapped by Kapton® foil (DuPont™, Circleville, OH, USA) of 12 μm

* Corresponding author at: O.G. Vlokh Institute of Physical Optics, 23, Dragomanov str., 79005 Lviv, Ukraine.
E-mail address: olehshpotyuk@yahoo.com (O. Shpotyuk).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.06.016
Received 12 March 2017; Received in revised form 2 June 2017; Accepted 12 June 2017

thickness and sealed was used as source of positrons sandwiched between two identical tested samples. The source correction (10% contribution of component with 0.352 ns lifetime, installed due to calibration tests performed with Ni and Kapton® foil) was applied to compensate an input originating from annihilation in a source itself and in covering Kapton® foil.

The measured PAL spectra were processed with LT 9.0 program [12], stabilizing average positron lifetime as a center of mass of full PAL spectrum:

$$\tau_{av}^{\Sigma} = \sum_i I_i \tau_i, \tag{1}$$

where τ_i and I_i denote respectively lifetime and intensity of the corresponding fitting components (the resulting accuracies in their determination were not worse ± 0.005 ns and ± 0.5%).

The best fitting of PAL spectra was achieved via mixed channels of trapping, occurring due to defect-related positron traps and bound positron-electron (positronium Ps) states. This task can be solved due to multi-component fitting of PAL spectra with three or four negative exponentials. Because of repulsive interaction between positron and atomic nuclei of environment, the positron samples intrinsic regions of minimal positive charge, preferentially negative-charged or neutral free-volume voids.

Under condition of small contribution from third and more higher components in the PAL spectrum (i.e. ignoring Ps decaying channels), the characteristics of positron trapping such as mean $\tau_{av.}$, defect-related τ_d and defect-free bulk τ_b lifetimes, trapping rate in defects κ_d and fraction of trapped positrons η can be parameterized in respect to formalism of two-state model [11,13–17]:

$$\tau_{av.} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}, \tag{2}$$

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}}, \tag{3}$$

$$\tau_d = \tau_2, \tag{4}$$

$$\kappa_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right), \tag{5}$$

$$\eta = \frac{\kappa_d}{\lambda_b + \kappa_d} = \frac{\kappa_d \tau_b}{1 + \kappa_d \tau_b} = \tau_1 \kappa_d. \tag{6}$$

In addition, the τ_2/τ_b ratio can be accepted as a signature of preferential nature of positron traps in terms of equivalent number of monovacancies and $(\tau_2 - \tau_b)$ difference can be ascribed to the character size of these defects [13]. Such two-state trapping model describes positrons annihilating from two distinct states, these being lattice-delocalized and defect-localized states, ignoring back escape of trapped positrons [11,13–17].

In case of stronger input from Ps decaying in the x3-term decomposed PAL spectrum (as it character for crystal-to-glass transition, for instance [11]), the positron trapping can be defined in terms of simple trapping model (STM) assuming two additive positron-trapping inputs from both trapped positrons and o-Ps states [18]. The STM with two types of positron-trapping defects possessing trapping rates κ_{d1} and κ_{d2} defined as

$$\kappa_{d1} = I_2\left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right), \tag{7}$$

$$\kappa_{d2} = I_3\left(\frac{1}{\tau_1} - \frac{1}{\tau_3}\right), \tag{8}$$

allows more correct estimation of defect-free bulk lifetime τ_b related to positron annihilation from the Bloch states:

$$\tau_b = \left(\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} + \frac{I_3}{\tau_3}\right)^{-1}. \tag{9}$$

As to Ps decaying channel, the radius R of free-volume holes responsible for o-Ps atoms annihilating due to “pick-off” with electron from surrounding medium can be calculated like in polymers using empirical Tao-Eldrup equation for the longest positron lifetime τ_3 [19]:

$$\tau_3 = 0.5 \cdot \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1}, \tag{10}$$

The intensity of this component I_3 correlates with content of free-volume holes, which can be considered as specific traps for o-Ps [13], giving a possibility to calculate fractional free volume

$$F_v = C \cdot I_3 \cdot V_f, \tag{11}$$

using empirical constant $C = 0.0018\ \text{Å}^{-3}$ [15]. This process is accompanied by p-Ps annihilation with lifetime $\tau_p = 0.125$ ns and one third intensity $I_p = I_3/3$ [19].

3. Results and discussion

The raw PAL spectra of c-LTB and g-LTB decomposed in terms of minimal statistically weighted least-square deviations between experimental points and theoretical curve built of three single exponentials evolving mixed inputs from positron and Ps trapping are shown in Fig. 1a and b, respectively. The narrow-restricted values of statistical scatter of variance tightly grouped around 0-axis testify that PAL measurements are adequately described by this unconstrained x3-term fitting. The best-fit parameters and numerical values of positron-trapping modes for LTB samples calculated in respect to above formalism of Eqs. (2)–(6) ignoring contribution from third component, as well as Eqs.

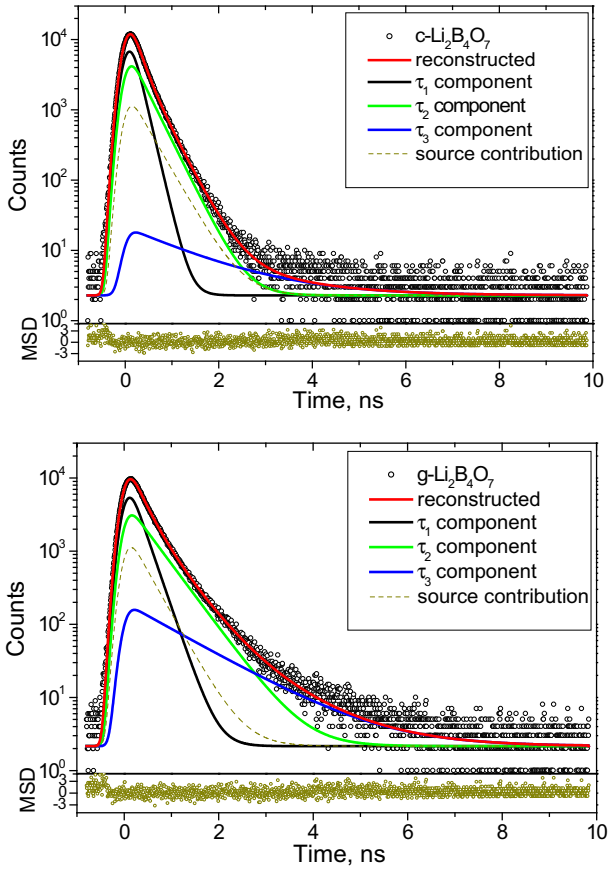

Fig. 1. Raw PAL spectra of c-LTB (a) and g-LTB (b) reconstructed from unconstrained x3-term fitting at background of source contribution (the bottom insets show statistical scatter of variance).