Light Scattering in Ionic Conductor $Li_2B_4O_7$ Crystals in the High-Temperature Region

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Abstract

Isofrequency temperature dependences of Rayleigh and hyper-Rayleigh scattering intensities have been measured in isotopically substituted $Li_2B_4O_7$ crystals within a wide temperature range (300–1000 K). The dependences contain two anomalies in the vicinities of 520 and 800 K. The first anomaly is associated with hopping of lithium ions between two non-equivalent positions, with the activation energy of about 0.23 eV. The second one results from the first-order order-disorder phase transition due to the melting of lithium sublattice. The temperature dependence of the relaxation time obtained by analysing quasi-elastic light scattering spectra is satisfactorily described, using the theoretical relation typical for such the phase transitions, with the relevant parameters $T_c = 790$ K and $\Delta = 0.95$.

Keywords: light scattering, ionic conductivity, phase transition

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Introduction

Lithium tetraborate crystals $Li_2B_4O_7$ (LB4) are very promising for applications in acoustoelectronic devices, owing to high values of their pyro- and piezoelectric coefficients [1, 2]. These materials are also used for the higher-order optical harmonics generation in the ultraviolet region [3, 4]. Due to some features of crystal lattice structure, LB4 crystals demonstrate a high conductivity along the crystallographic axis [001] ($\sigma_{33} \sim 10^{-4}$ Ohm$^{-1}\cdot$m^{-1} at 500 K) and may be referred to a group of high-temperature one-dimensional ionic conductors [5]. As a consequence of possible practical applications of this material, the question of temperature stability of its physical properties has been studied in detail for a wide temperature range [5 - 15]. Below the room temperature, the anomalies of physical parameters observed in the vicinity of 235 K [6 - 8] have been described in terms of a phase transition caused by changing lattice translation symmetry [9]. Three intervals containing the anomalies may be distinguished in the high-temperature range (300 – 900 K): (i) a decrease of the conductivity activation energy from 0.54 eV ($T < 390$ K) to 0.36 – 0.39 eV ($T > 390$ K) is peculiar for the vicinity of 390 K [3, 10]; (ii) anomalies of thermoelectric coefficient θ [10] and the real part of dielectric constant ε_{33} [11], as well as a fracture in the temperature dependence of conductivity σ_{11} [12], all occurring at 450 – 700 K, are connected with starting Li^+-ion transfer perpendicular to [001] axis; (iii) frequency-independent maxima of ε_{11} and ε_{33} [11], a peak of the sound absorption for *zz*-mode [13] and anomalies in the optical second harmonics intensity [14] are observed at temperatures higher than 780 K. The results mentioned above, together with the Raman spectroscopy data [15], should testify a possibility of order-disorder phase transition in this temperature interval.

The present work is devoted to studies for the temperature dependences of the elastic and quasi-elastic light scattering (QELS) parameters in the ionic conducting crystals of $Li_2B_4O_7$, which have been undertaken with the purpose of revealing structural changes in the lithium sublattice.

Experimental

The measurements have been performed for single LB4 crystals with various content of the lithium isotopes: LB4-7-10 (^{7}Li – 96%; ^{10}B – 97.3%) and LB4-6-10 (^{6}Li – 95%; ^{10}B – 97.3%). Temperature dependences of the Rayleigh scattering (RS) intensity J_{RS} have been obtained in Y(ZZ)X, Z(YZ)X, Z(YY)X geometries with the excitation by He-Ne laser (632.8 nm, the mean power 1 mW). Temperature dependences of the hyper-Rayleigh scattering (HRS) intensity J_{HRS} have been measured using the excitation by the radiation of Q-switched Nd^{3+}:YAG laser at 1064 nm, with the mean power of 1 W. Non-polarized exciting radiation has propagated along [001] axis and the scattered light detected along [100] axis at the doubled frequency. The spectra of QELS in the range of 3 – 20 cm^{-1} have been excited with the second harmonics of Nd^{3+}:YAG laser at 532 nm. Those measurements have been performed in Y(ZZ)X geometry at 300, 370, 520, 600, 680 and 750 K. The scattered light has been analysed, using a spectrometer based on double monochromator DFS-12. The spectral slit widths in case of the RS, QELS and HRS experiments have been equal to 0.5, 2 and 5 cm^{-1}, respectively. The rates of heating and cooling of samples have been varied within a range of 1 – 4 K/min, with the temperature measurement accuracy of 0.5 K.

Results and discussion

Temperature dependences of the RS intensity, together with the HRS intensity dependence obtained for LB4–6–10 under heating, are presented in Fig. 1. As seen from Fig. 1a and 1b, the RS intensity dependences for the Y(ZZ)X and Z(YZ)X geometries contain two anomalies in the vicinities of 520 and 800 K, which are also observed in the HRS intensity (see Fig. 1d). Both maxima are characterized by a marked difference in the intensity levels “before” and “after” them and the temperature width of about 100 K. The temperature dependences of the RS and HRS intensities during sample cooling have

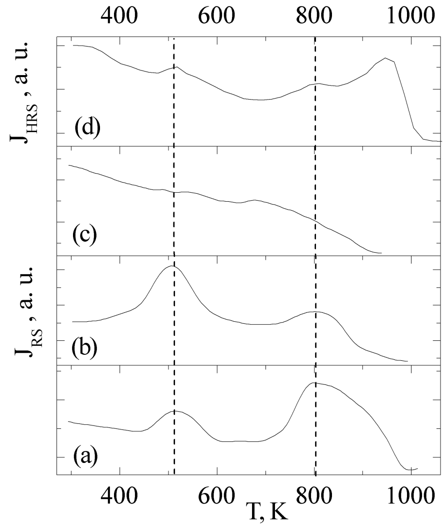

Fig. 1. Temperature dependences of the intensities of Rayleigh scattering in the geometries Y(ZZ)X (a), Z(YZ)X (b), Z(YY)X (c) and hyper-Rayleigh scattering (d) for LB-6-10 crystals measured in the heating run.

lower intensity level and lower maxima temperatures, when compare with those under heating. After each thermal cycle, the RS and HRS intensities return to their initial levels in a few hours. The temperature dependences for LB4–7–10 crystals do not have principal differences and remain similar to those presented in Fig. 1.

Physical properties of LB4 crystals are known to be essentially dependent on the preceding thermal conditions [16]. In case of several successive thermocycles, the high-temperature "wing" of the heating curve $J_{RS}(T)$ in the vicinity of 800 K becomes more structured and tightens towards the high-temperature region. The shoulder at 920 – 950 K appears in the RS intensity dependence already during the second thermocycle. The temperature of this anomaly is close to that of the other maximum in the $J_{HRS}(T)$ dependence occurring at 950 K (Fig. 1d), whose position during thermocycling is quite stable. Different behaviours of the RS and HRS intensities in the region of 840 – 1000 K should be probably due to higher sensitivity of the HRS to the local symmetry changes induced by defects. The position of the maximum at 520 K oscillates within 10 K during several thermocycles. When thermocycling the sample for 12 hours, the maxima are observed at 320 – 420 K. They have a casual, non-systematic character. In order to explain the latter results, one should take into account a sensitivity of temperature dependences of the RS and HRS intensities to the available ill-controlled impurities inside the crystal volume. Such the impurities change essentially the interatomic potential and cause the appearance of various potential wells. As a result of sample cooling performed for the first time, a pinning of mobile ions at these irregular wells occurs, whereas after the second heating happened in a short time they would behave in the other manner.

Light scattering anomalies in superionic conductors in the course of temperature increasing are usually connected with activation of mobile ions and changes in the parameters of their movement through the crystal volume. Estimations of the time of "staying" of mobile ion in the lattice site ($\tau_d \sim 1{,}5\cdot 10^{-10}$ s) and the time of "flighting" between the sites ($\tau_f \sim 5\cdot 10^{-14}$ s) made for LB4 crystals allow one to apply the ion-hopping model. In terms of the model, the hopping rate of the ions is determined by the expression [17]

$$\nu = 1/\tau_d = \nu_0 \exp(-E_a / k_B T), \qquad (1)$$

where ν_0 is the "attempt frequency" and E_a the activation energy. The maximum at 520 K is not strongly sensitive to the effect of impurities mentioned above and is caused by the ion hoppings between the regular lattice positions. According to [17], the slopes of the RS intensity dependence plotted in the coordinates $\ln J_{RS}$ vs. $10^3/T$ would determine the activation energy of the mobile ions. The calculations for Y(ZZ)X and Z(YZ)X geometries carried out in such a way give the corresponding values 0.22 – 0.24 eV. This result is satisfactorily correlated with the activation energy estimations (0.2 eV) made in frame of the model of double-well potential [10]. The existence of two non-equivalent positions for the Li^+ ions has been also proved by the NMR spectra studies [18].

Further temperature increase results in intensification of the hopping movement, with subsequent melting of the lithium sublattice. Character of evolution of the maximum at 820 K in the RS is typical for the order-disorder phase transitions of a first order. To obtain more detailed information about the phase transition parameters, we have studied the QELS spectra. The instrumental profile has been subtracted from the measured spectra, and the final spectra have been fitted by the response function of the relaxation type,

$$J(\Omega,T) = \left[n(\Omega,T)+1\right]\frac{I_R \Omega \tau_R}{1+\Omega^2 \tau_R^2}, \qquad (2)$$

where I_R denotes a constant proportional to the strength of the relaxator, τ_R the relaxation time and $[n(\Omega, T) + 1]$ the Bose-Einstein factor. Both I_R and τ_R have been chosen as fitting parameters. The temperature dependence of the relaxation time is shown in Fig. 2. For the analysis of the obtained results near T_c, a theoretical dependence typical for the order-disorder phase transition has been used [19]:

$$\tau_R \sim \tau_d \left|\frac{T_c - T}{T_c}\right|^{-\Delta}, \qquad (3)$$

where τ_d is determined by Eq. (1) at ν_0 = 400 cm^{-1} (the typical frequency of Li–O vibrations in LB4 crystals [20]) and E_a = 0.23 eV. The most satisfactory correlation between the experimental data and Eq. (3) is observed for the values of T_c = 790 K and Δ = 0.95 (see Fig. 2). The obtained results enable one to classify the anomalies of the RS and HRS intensities in the vicinity of 800 K as a consequence of the first-order phase transition at T_c = 790 K of order-disorder type. The existence of the second high-temperature maximum of the HRS intensity at 950 K and essential width of the anomaly in the RS may testify that the phase transition has a complex character, due to metastability of lithium sublattice and its high sensitivity to the available impurities.

Conclusion

The studies performed by us have allowed to establish a change of the activation energy of Li$^+$ ions in the vicinity of 520 K and a fact of existence of the first-order phase transition of order-disorder type at T_c = 790 K, which is caused by melting of the lithium sublattice. The phase transition characteristics are defined by the effects of fluctuation stabilization due to the defects.

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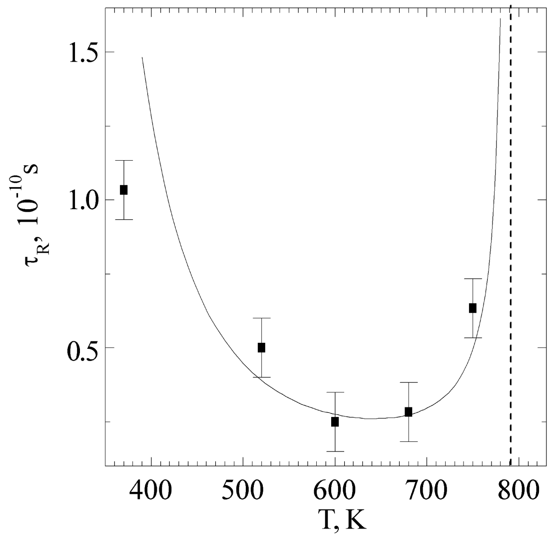

Fig. 2. Temperature dependence of the relaxation time τ_R for LB4-6-10 crystals. Data points are extracted from the QELS spectra and solid line represents the theoretical dependence (see text).

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