
Hyper-Rayleigh Scattering Characterization of the Movement of Lithium Ions in $\text{Li}_2\text{B}_4\text{O}_7$ Crystals

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Abstract

The integral intensity of hyper-Rayleigh scattering from the bulk of nominally pure ionic conducting $\text{Li}_2\text{B}_4\text{O}_7$ crystals is studied as a function of temperature in the range where a break in the temperature dependence of ionic conductivity expressed in the coordinates $\ln(\sigma_{33}T) = f(1/T)$ is observed. Characteristics of jump-diffusive movement of lithium ions are determined. The movement activation energy for the temperatures $T \geq 400$ K is estimated from the temperature dependences of hyper-Rayleigh scattering intensity. Its value $E_{\text{am}} = 0.46$ eV is close to that obtained from the measurements of temperature dependence of the ionic conductivity.

Key words: hyper-Rayleigh light scattering, ionic conductivity, movement activation energy

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1. Introduction

It is known that lithium tetraborate crystals, $\text{Li}_2\text{B}_4\text{O}_7$ (LB4), are characterized by quasi-one-dimensional ionic conductivity σ_{33} along the channels of structure in [001] direction, caused by the presence of growth defects (vacancies and interstitial atoms) in lithium sublattice in the temperature range 250–700 K. The value of conductivity at 400 K is $\sigma_{33} = 1.6 \times 10^{-5} (\text{Ohm} \times \text{m})^{-1}$ [1,2]. The temperature dependence $\ln(\sigma_{33} \cdot T) = f(1/T)$ shows a break in the vicinity of $T = 390$ K, where the value of activation energy (E_a) decreases from 0.54 eV below 390 K to 0.36 eV above this temperature [2]. In the high-temperature region ($T \geq 700$ K), the ion transport along the directions perpendicular to [001] has been observed [1]. The methods of elastic and inelastic light scattering can be very useful in studying the mechanisms for

temperature migration of ions in ionic conductors. The most important physical parameters characterizing the ionic motion, namely, the activation energies, hopping and vibrational frequencies can be obtained with the light scattering methods. Cooperative scattering with doubling frequency (hyper-Rayleigh light scattering or HRS in short) represents a special interest in this respect, because it possesses a high sensitivity to local symmetry changes induced by defects. The HRS lines observed for crystals seem to arise unquestionably from defects and static distortions of the surrounding host lattices and hopping mobility of the defects on temporal scales [3].

The present work is devoted to studies of the temperature dependences of quasi-elastic hyper-Rayleigh light scattering intensity in the range of temperatures where the ionic

conductivity is observed. The purpose is to determine the characteristics of lithium ion mobility in the channels of structure along the [001] direction.

2. Experiment

The samples of nominally pure LB4 single crystals were grown in the Institute of Physical Optics (L'viv, Ukraine) by the Czochralski method. The sample under study was a rectangular prism of $4 \times 4 \times 10 \text{ mm}^3$ dimensions with its planes perpendicular to [100], [010] and [001] crystallographic directions, respectively. The HRS was excited with the radiation of acousto-optically Q-switched Nd^{3+} :YAG laser ($\lambda = 1.06 \text{ }\mu\text{m}$) having the pulse repetition rate of 8 kHz, the duration of pulses $5 \times 10^{-7} \text{ s}$ and the mean excitation power 200 mW. The measurements were carried out in the Z(YYY)X geometry. The HRS intensity was selected by DFS-12 double monochromator. The useful electric signal was detected with the cooled FEU-79 photo-multiplier tube working in a photon-counting mode with accumulation. The accuracy of the temperature measurements was 0.5 K.

3. Results and discussion

First we have measured the temperature dependence of the integral HRS intensity. Starting from $T = 400 \text{ K}$, a sharp increase in the HRS intensity with increasing temperature was observed, the fact correlating with the increase of ionic conductivity σ_{33} in this temperature range. It is known that in the range of intrinsic conductivity, the character of temperature dependence of the conductivity is determined by the defects formed in a crystal lattice due to a thermal energy. In LB4 crystals, such the defects are Frenkel ones [4] and they are formed in the lithium sub-lattice. The conductivity activation energy (E_a) in this case includes both the energy of defect formation (E_F) and its movement activation energy (E_{am}), i.e. $E_a = 0.5 E_F + E_{am}$. With further increase in temperature, the conductivity is determined by the characteristics

of disordering of the corresponding sub-lattice and depends only on the movement activation energy of defects. Assuming that the intrinsic conductivity takes place in $\text{Li}_2\text{B}_4\text{O}_7$ crystals at the temperatures below 400 K, we can treat a decrease of slope in the $\ln(\sigma_{33}T) = f(1/T)$ dependence with increasing temperature near $T = 390 \text{ K}$ as a transition to conductivity in strongly disordered lithium sub-lattice. Thus, it is possible to estimate the energy necessary to form the Frenkel defects in the lithium sub-lattice as $E_F = 2(E_a - E_{am}) = 0.36 \text{ eV}$. The mechanism of the ionic conductivity is determined by the ratio between the time of “staying” of an ion in the lattice site (τ_u) and the time of “flighting” between the sites (τ_f). The estimation of the specified times within the framework of the diffusion theory of non-interacting particles gives the values of $\tau_u = 4 \times 10^{-8} \text{ s}$ and $\tau_f = 4 \times 10^{-13} \text{ s}$ for the lithium sub-lattice of LB4 crystals. This corresponds to the jump-diffusive mechanism of the lithium ion movement [5, 6]. In contrast to the ionic conductivity, the HRS intensity at any temperature depends on the contribution of crystal lattice defects of various natures, which are characterized by the effective activation energy (E_F^*) and the jump-diffusive movement of the lithium ions [7]. In this case we have

$$I_{\text{HRS}} \sim \exp(-E_a^*/kT).$$

Then the slope of temperature dependence of the HRS intensity in the coordinates $\ln(I_{\text{HRS}}) = f(1/T)$ should be determined by the value $E_a^* = 0.5E_F^* + E_{am}$.

The obtained dependence of the HRS intensity in the specified coordinates is shown in fig. 1. As is evident from fig. 1 that the experimental points in the range of high temperatures can be well approximated by a straight line. The change of the slope occurs near 400 K. The value of E_a^* derived from the measurements of temperature dependence of the HRS intensity amounts to 0.64 eV. Assuming that $E_F^* \approx E_F = 0.36 \text{ eV}$ in the investigated

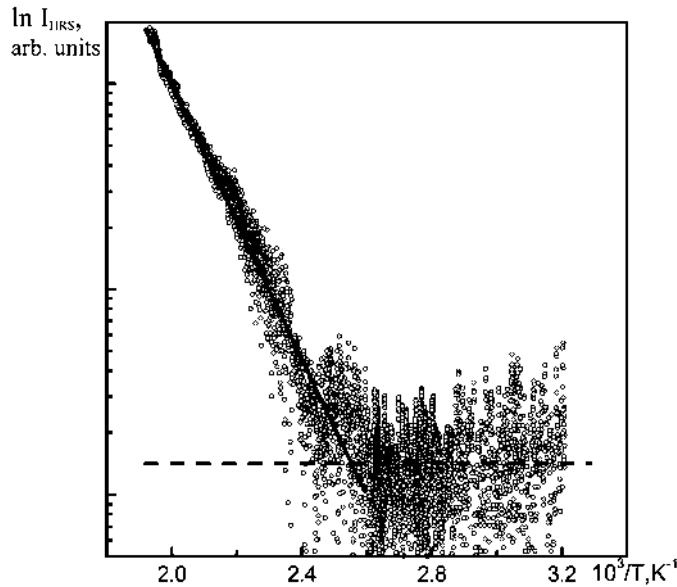


Fig. 1. Temperature dependence of integral intensity of 90° hyper-Rayleigh scattering in the coordinates $\ln I_{HRS} = f(1/T)$.

temperature range, we can get the estimation $E_{am} = 0.46$ eV. This is consistent with the value of $E_a = 0.36$ eV obtained from the temperature dependence of the ionic conductivity.

4. Conclusions

The sharp increase of the HRS intensity with increasing temperature that correlates with the increase of the ionic conductivity σ_{33} in the temperature range above $T = 400$ K is observed. It is revealed that the above increase is caused by both the growth of Frenkel defect concentration and the increase in the hopping frequency of lithium ions along the channels of structure. The jump-diffusive motion of lithium ions in the opposite directions and, as a consequence, the fluctuations of their concentration are the reasons for the fluctuations of nonlinear susceptibility $\chi^{(2)}$. The activation energy of the movement of lithium ions determined from the measurements of temperature dependence of the HRS intensity amounts to 0.46 eV. This estimate is close to the value $E_a = 0.36$ eV

determined from the temperature measurements of the ionic conductivity.

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