The Influence of Point Defects on the Vibrational Spectrum of $Li_2B_4O_7$ Crystal

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Abstract

The Raman and infrared reflection spectra of $Li_2B_4O_7$ crystals doped with potassium, silver and copper ions are measured at 300 K. The damping increase of the Raman lines and the changes in the oscillator strengths for a number of reflection bands are observed in the doped crystals. The results obtained due to theoretical fitting of the spectra are discussed in the framework of heavy isotopic impurity model. The analysis of the experimental and theoretical data has allowed to assume that the potassium and silver ions represent substitution impurities, while the copper ions are probably the interstitial ones.

Introduction

Lithium tetraborate crystals $Li_2B_4O_7$ (abbreviated as LB4) are widely used in acoustoelectronics [1], nonlinear optics [2] and as sensitive elements of dosimetric scintillators [3]. The area of applications of these active dielectric materials may be expanded while embedding different impurity ions into their crystal lattice. However, this way requires comprehensive studies for the physical properties of the modified crystals. To present day, investigations of the influence of potassium (K^+) and silver (Ag^+) impurity ions on the nonlinear optical properties [4] and the Raman spectra [5] of LB4 crystals have been reported. General regularities of the effect of isotopic ^6Li and ^{10}B substitutions on the Raman spectra have been studied, too [6]. Nevertheless, a scantiness of the experimental material presented in these works is evident. Moreover, the detailed theoretical analysis of the corresponding changes observed in the Raman spectra is still absent.

This work is devoted to studies for the vibrational spectra of the doped crystals of $Li_2B_4O_7:K^+$ (abbreviated hereafter as LB4-K), $Li_2B_4O_7:Ag^+$ (LB4-Ag) and $Li_2B_4O_7:Cu^{2+}$ (LB4-Cu) performed using the Raman and the infrared (IR) reflection spectroscopic methods. The aim is to reveal experimentally the impurity effects and interpret them in a proper way.

Experimental

LB4 crystals (the space symmetry group C_{4v}^{12}) were grown with the Czochralski technique. The impurity concentration in the furnace charge was 0.1–0.2%. The samples were rectangular parallelepipeds, whose edges were oriented along the crystallographic directions [100], [010] and [001]. All of the samples had a high enough optical quality.

The Raman spectra were excited using the radiation of second optical harmonic of Nd^{3+}:YAG laser, with the excitation wavelength of 532 nm and the mean radiation power of 100 mW. The spectra of the scattered radiation were recorded with a single channel photon counting system based on cooled FEU-79 photomultiplier (the accumulation time 5 s). Those spectra were analyzed with the aid of double monochromator DFS-12. The spectral width of the monochromator slits was equal to 2 cm^{-1}. The intensity distribution in the spectra was corrected for the spectral dependences of the photomultiplier sensitivity and the reflectivity of diffraction gratings employed in the monochromator. The Raman spectra of the LB4-K and LB4-Ag crystals were obtained in the geometries X(ZZ)Y (the corresponding symmetry of vibrations A_1(TO)) and X(YY)Z (the symmetry A_1(IO)+B_1) within the region of 0–1200 cm^{-1}. The spectra in the geometries Z(YZ)X – E(TO) and X(ZX)Y – E(TO+LO) within the region of 0–1000 cm^{-1} were studied only for LB4-K crystal. The attempts for obtaining qualitative Raman spectra for the LB4-Ag crystals in these geometries failed because of a small scattering efficiency. By this reason, the Raman spectra of LB4-Cu crystals were studied only in the regions of 50–300 cm^{-1} and 450–530 cm^{-1} for the X(ZZ)Y geometry. The spectra for the pure LB4 crystals were taken from the work [7]. All the spectra were obtained under the same conditions and the temperature T = 300 K.

The IR reflection spectra of LB4-K and LB4-Ag crystals were measured in the wavenumber region of 300–2000 cm^{-1}, using IR spectrophotometer Specord M80 with the spectral resolution of 2 cm^{-1}, the photometric accuracy of ±0.2% and the 3 s accumulation time. The incident radiation angle was 20^0. The measurements were carried out for the polarized radiation in the $\vec{E} \perp [001]$ geometry. The spectra in the 60–400 cm^{-1} region were obtained using the non-polarized radiation and Fourier spectrometer LAFS-1000. Then the spectral resolution and the incident radiation angle were 0.2 cm^{-1} and 6^0, respectively. The vibrations of the E symmetry were studied in the both regions.

Results and discussion

The Raman and the IR reflection spectra of LB4-K and LB4-Ag crystals do not contain new bands. Notice that the appearance of the latter could have testified the existence of localized vibrational states. Therefore, our results confirm experimentally the theoretical estimations [5]. According to this work, the impurity vibrations must not appear in the Raman and IR reflection spectra at the present impurity concentrations. In our case, the existence of the impurity ions causes rather the changes in the damping and the intensities of the bands. The regions of the Raman and IR reflection spectra, that demonstrate obviously these facts, are presented in Fig. 1 and 2.
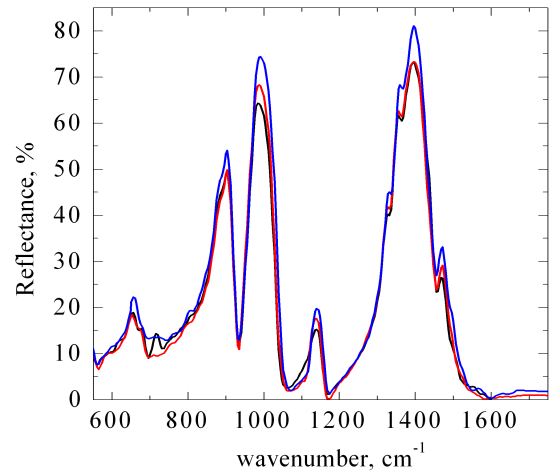
In order to obtain quantitative characteristics of the observed changes, we have fitted the Raman spectra, using the model of weakly interacting oscillators [5]. The data referred to the phonon modes and the Raman intensities have been obtained. The oscillator parameters of the phonon modes have been also determined from the IR reflection measurements on the basis of dispersion analysis (DA) method [8], using the initial values of the parameters determined for the pure LB4 crystals [9]. Taking into account that many bands overlap in the obtained spectra, resulting in a nontrivial definition of the band parameters, we have chosen special requirements for the fitting results. Namely, we have supposed that the changes in the damping $\Delta\gamma = \gamma - \gamma_0$ not less than 1 cm^{-1} and the relative changes in the integral intensity of the Raman lines $(J_0 - J)/J_0$ not less than ±0.15 should be correct. The difference from the oscillator strength values calculated for the reflection band in the pure crystal with the
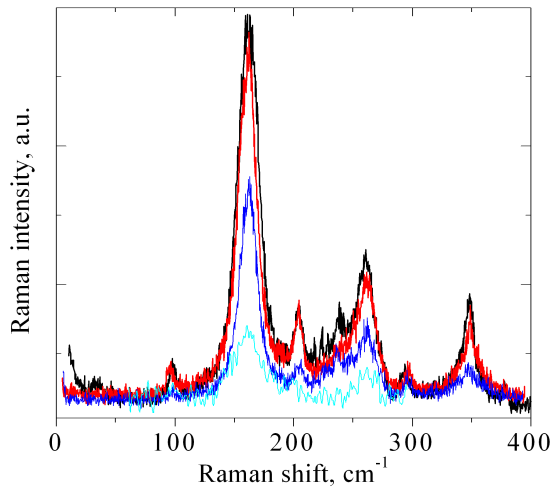
Fig. 1. The A_1(IO)+B_1 symmetry Raman spectra for the pure LB4 (black line) [7], LB4-K (red), and LB4-Ag (blue) and LB4-Cu (cyan; multiplied by the factor 3) crystals.

Fig. 2. The E symmetry IR reflection spectra for the pure LB4 (black line) [9], LB4-K (red) and LB4-Ag (blue) crystals.

DA and the Kramers-Kronig techniques [9] has served as a reliability criterion for the relative change in the oscillator strength $\delta S = (S - S_0)/S_0$ occurred while passing from the pure crystal to the doped one. Here, γ_0 and γ mean the damping parameters, J_0 and J the integral intensities of the Raman lines and S_0 and S the oscillator strengths of the reflection bands observed in the spectra of the pure and doped crystals, respectively.

The most significant changes in the phonon damping that happen for the LB4-K, LB4-Ag and LB4-Cu crystals are presented in Table. The parameters of the phonon modes and the Raman intensities (the frequency Ω_0, the damping γ_0 and the integral intensity J_0) have been extracted from the Raman spectra for the pure crystals. Here the integral intensity value J_0 implies a "weight" (in percents) of each of the mentioned band, when compare to the most intensive band in the corresponding spectrum. The data obtained due to analysis of the IR reflection spectra are presented in brackets. The last column contains both the summary of the experimental data [6,10,11] and the theoretical calculation results obtained after solving secular equation with the aid of the GF-matrix technique [12]. The initial set of the force constants necessary for forming the matrix of dynamic

coefficients has been determined using the transportation equations [13]. The pairs of frequencies for each of the normal vibrations of the BO$_4$ group correspond to longer ($r = 1.50$ Å) and shorter ($r = 1.45$ Å) B–O bonds in the tetrahedrons present in the crystal structure of LB4 [14]. As seen from Table, the largest $\Delta\gamma$ values in the 50–300 cm^{-1} region are observed for the LB4-Cu crystals. For the region of 450 – 530 cm^{-1}, the mean $\Delta\gamma$ value in this crystal is smaller, being equal to 4 cm^{-1}. As for the changes in the integral intensity, a decrease in the J parameter with increasing mass of the impurity ion is observed for the majority of the Raman lines, except for the 400–550 cm^{-1} region in the Raman spectra of LB4-K and LB4-Ag crystals [5].

The changes in the oscillator parameters determined from the IR reflection spectrum for the LB4-K crystal are negligible, when compare with the corresponding parameters of the pure crystal (see Fig. 2). They are inside the limits of the criteria mentioned above. However, the δS increase for the LB4-Ag crystal remains appreciable for the following TO-LO vibrations: 660 and 664 cm^{-1} ($\delta S = 0.71$), 884 and 924 cm^{-1} ($\delta S = 0.12$), 898 and 892 cm^{-1} ($\delta S = 0.31$) and 1325 and 1334 cm^{-1} ($\delta S = 0.45$). Moreover, the corresponding values of the dielectric

Table. Changes in the vibration damping parameter $\Delta\gamma$ caused by the impurity ions embedded in the LB4 crystal lattice.

Frequency Ω_0, cm⁻¹ – phonon symmetry	γ_0, cm⁻¹	J_0, %	$\Delta\gamma$, cm⁻¹			Assignment experimental / calculated frequencies, cm⁻¹
			$_+$	Ag⁺	Cu²⁺	
99 – B_1	5	1	1	8		
100 – E(TO)	11	19	2 (5)	(6)		$\boldsymbol{T'}$(B₄O₇)²⁻
157 – A_1(TO)	20	73	1	2	12	
162 A_1(IO)	15	100	1	1		$\boldsymbol{R}$(B₄O₇)²⁻
202 A_1(IO)	10	12	0	5		
237 B_1	17	15	3	2		
255 – A_1(TO)	16	31	0	5	13.5	$\boldsymbol{R'}$(BO₃) + $\boldsymbol{R'}$(BO₄)
262 A_1(IO)	11	40	0	3		
338 – A_1(TO)	16	12	1.5	3		
348 – A_1(IO)	12	22	8	16		$\boldsymbol{\nu_2}$(BO₄): 360 – 460 / 374, 418
350 – E(TO)	17	14	0 (0)	(6)		
658 – E(TO+LO)	7	21	1 (4)	(4)		$\boldsymbol{\nu_4}$(BO₃): 540 – 650 / 660 $\boldsymbol{\nu_4}$(BO₄): 490 – 630 / 571, 604
723 – E(TO)	9	58	5 (4)	(14)		$\boldsymbol{\nu_1}$(BO₄): 740 – 900 / 766, 778
970 – A_1(IO)	21	7	1	2		
1055 – B_1	9	6	2	2		$\boldsymbol{\nu_1}$(BO₃): 930 – 990 / 895
1080 – B_1	18	8	2	3		$\boldsymbol{\nu_3}$(BO₄): 890 – 1085 / 1257, 1362
(1325) – E(TO)	(14)		(1)	(3)		
(1347) – E(TO)	(11)		(2)	(5)		$\boldsymbol{\nu_3}$(BO₃): 1330-1440 / 1376

permeability ε_∞, which have been determined as fitting parameters for the 1600–2000 cm⁻¹ region in the IR reflection spectrum, are also different. The ε_∞ value for the pure crystal is equal to 2.45, while $\varepsilon_\infty = 2.15$ for the LB4-K and $\varepsilon_\infty = 2.65$ for the LB4-Ag.

Theoretical analysis of the influence of point defects on the vibrational spectra in crystals with simple structure has been performed in a number of works [15,16]. The crystal defects result in chaotic breaking of the amplitude and phase of the atomic displacement wave. As a consequence, they cause spatial decay of this wave at the distances $l \sim (N_{\mathrm{imp}})^{-1/3}$, where N_{imp} denotes the impurity concentration [15]. This may be considered as a process of phonon scattering by defects, leading to decrease in the phonon life time. In accordance with [16], the optical vibration frequencies become complex $(\Omega_j(\mathbf{q}) = \Omega'_j(\mathbf{q}) + i \cdot \Omega''_j(\mathbf{q}))$ due to the existence of point defects. In this case, the plane wave of atomic displacements is determined by

$$u(\mathbf{r},t) = u_0 \cdot \exp[i \cdot (\mathbf{q} \cdot \mathbf{r}) - i \cdot \Omega'_j(\mathbf{q}) \cdot t] \times$$
$$\times \exp[-\Omega''_j(\mathbf{q}) \cdot t] \quad , \quad (1)$$

where $\Omega''_j(\mathbf{q}) = 1/\tau = \gamma$ and τ is the time of vibration decay. Considering the perturbation of acoustic spectrum by heavy isotopic impurities [16], the following regularities have been theoretically obtained for a long-wave vibrations with $q << 2\pi(N_{\mathrm{imp}})^{1/3}$:

(1) significant increase in the vibration damping for heavy impurities should appear at quite small concentrations $N_{\mathrm{imp}} \leq (M/\Delta M)^2$, where $\Delta M = M_{\mathrm{imp}} - M >> M$ and M and M_{imp} are the masses of the initial and the impurity ions, respectively;

(2) impurity ions with greater masses should give rise to higher increase of the damping $(1/[\Omega'_j(\mathbf{q}) \cdot \tau] \sim N_{\mathrm{imp}} \cdot (\Delta M / M)^2)$.

One can see from Table that the mentioned theoretical regularities are well satisfied by the vibrations belonging to the 100–500 cm⁻¹ region. According to [6], many vibrations from this region have a complex character, due to their

mixing with lithium ion translations. It is especially characteristic of the 338 cm^{-1} vibration, which reveals a single-mode behaviour with substituting of [6]Li for [7]Li. Significant changes in the damping $\Delta\gamma$ are also observed for the lines assigned to translational vibrations of $(B_4O_7)^{2-}$ complex (99 and 100 cm^{-1}) and internal vibrations of BO_4 group (350 and 723 cm^{-1}). Concerning the first pair of lines, some authors assign them to lithium plasma vibrations [6]. Mixing of the second pair of vibrations with the lithium ion translations could be confirmed by the fact that the nearest environment of the lithium ions consists of oxygen atoms of BO_4 tetrahedrons [14]. The changes occurring in the high-frequency region do not allow us to make any definite conclusion, due to a small intensity of the Raman lines.

Finally, in what the impurity influence on the scattering efficiency concerns (see Fig. 1), the latter has in general to cause a decrease in the Raman lines intensity, owing to decaying character of the displacement waves and a dispersion of their wavevectors within the range $|\Delta q| \sim 2\pi(N_{imp})^{1/3}$ [15].

Conclusion

Thus, a comparison of the results of theoretical analysis with the experimental data enables one to assume that the lithium ions are substituted with the potassium and silver ones. The conclusion about the location of these impurity ions in the interstices made by us earlier on the basis of spectral intensity redistribution observed in the 400–550 cm^{-1} region [5] has not been proved by the more detailed analysis of the Raman spectra presented here. This fact testifies a highly intricate character of the vibrations referred to this region, whose interpretation is complicated enough due to strong overlapping of lines in the X(YY)Z scattering geometry. The results obtained for the LB4-Cu crystals (here the damping changes are more essential than those occurring in the LB4-Ag crystals) and combined with the presented theoretical analysis do not

allow to assert for sure that the lithium ions are substituted with the copper ones, whose mass is smaller than the silver ion mass. The observed increase in the damping parameter may be caused by arrangement of the copper ions in interstices and, just as well, by the other charge state of these ions. According to [15,16], such the defects should result in appearance of delocalized vibrations and so affect mainly the low-frequency region. Besides, the charge state of Cu^{2+} ions has to make the most profound effect on the polar vibrations. This effect is experimentally proved.

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