Raman scattering in glassy $Li_2B_4O_7$ doped with Er_2O_3

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Abstract. We study Raman scattering spectra for glassy lithium tetraborate with different concentrations of doping erbium ions. Most of the vibrational modes found for the activated $Li_2B_4O_7$:Er_2O_3 glasses in the medium-scale range are caused by mixed and normal modes of compound boron–oxygen, erbium–oxygen and lithium–oxygen structural complexes.

Keywords: glassy lithium tetraborate, Er_2O_3, structural groups, hybridization, tetrahedral groups, trigonal groups, erbium–oxygen groups.

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1. Introduction

Wide-bandgap dielectrics based on lithium tetraborate (LTB) represent materials which are promising for the nonlinear optics, owing to their high damage threshold, radiation stability, transparency in a wide spectral range, nonlinear optical coefficients describing conversion of laser radiation frequency, and Raman scattering intensity. Moreover, these materials are used as superionic conductors in the production of solid electrolytes for the solid-state electric power sources. Knowledge on the correlations of their structure and ionic conductivity, which is largely related to the nature of interactions among superionic complexes in a B_2O_3–Li_2O system, is very important. In this respect, Raman and IR spectroscopies are powerful tools for investigating the structure of the above materials.

In the recent years, a number of works have been devoted to the studies of vibrational spectra of $Li_2B_4O_7$ [1–15]. Except for Refs. [6, 7, 14–16], the rest of the works have dealt with the phonon spectra of LTB single crystals only. As a result, the data on the vibrational spectra of glassy borates are practically missing in the literature. Due to very complicated structures of disordered borate crystals and glasses based on LTB, there are poor results on the vibrational-mode identification for those disordered systems. The structure of $Li_2B_4O_7$ crystals defined for the first time by the authors of Refs. [17, 18], contains eight formula units, i.e. 104 atoms in the primitive unit cell of the space group $I4_1cd$ (C_{4v}^{12}), and the tetragonal unit-cell dimensions are equal to $a = b = 9.477(5)$ Å and $c = 10.290(4)$ Å. Volumetric boron–oxygen complexes [B4O9]6– consist of two flat triangles [BO3] and two tetrahedrons [BO4] with strong covalent binding [10], which are combined by common neighbouring complexes of oxygen atoms in a helix, with its axis parallel to the c axis. This forms a rigid three-dimensional framework through shared oxygen atoms. Lithium cations are located in the channels of this framework along the direction parallel to the optic axis of crystal. The first coordination sphere of lithium atoms includes four nearest oxygen atoms that create a severely deformed tetrahedron. Finally, the chains of lithium–oxygen tetrahedrons are wound about the axis 4I.

Taking into account the fact that the structural complexes in the LTB glasses and single crystals are similar in practice, one can assume that glassy $Li_2B_4O_7$ has a similar structure within the medium-range order scales, with only slightly changed unit-cell parameters, which should introduce some changes in the dynamics of deformed lithium tetraborate structure.

Raman scattering (RS) spectra of glassy materials are believed to provide important data on the short-range order structure. Moreover, they often reveal correlations with the spectra typical for the crystals of similar structure within the medium-range scales covering several coordination spheres. Broad and indiscrete bands usually dominate in the RS spectra of glasses. In addition, RS in glasses is very strong in comparison with the ordinary second-order RS in crystals [19, 20]. In the Raman spectra of glasses, relatively narrow and separated bands characterizing the first-order scattering in crystals can also be observed. It has been shown earlier that disordering in glasses leads to violation of selection rules at $\mathbf{k} = 0$, so that all vibrational modes can contribute to the scattering [19]. On this basis, Shuker and Gammon have concluded [20] that the RS in glasses represents a first-order scattering, being closely related to the vibrational density of states.

Up to date, the Raman spectra for glassy $Li_2B_4O_7$ doped with rare-earth elements have not been given due attention. The aim of the present work is to study experimentally the impurity RS in glassy lithium tetraborate doped with erbium ions which are included in the structure of LTB matrix as triply charged Er^{3+} ions [21].

2. Experimental methods and results

The RS spectra were investigated using an XploRA PLUS (HORIBA Jobin Yvon) Raman spectrometer. A laser with the wavelength $\lambda = 785$ nm was used for exciting the spectra. The spectral resolution was not worse than 1 cm^{-1}. The studies were performed at the temperature $T = 300$ K in the spectral range 70–2000 cm^{-1}.

Glassy $Li_2B_4O_7$ samples were synthesized following the technology described in Refs. [22, 23]. They were doped with erbium oxide Er_2O_3 taken with the concentrations 0, 0.0005, 0.001, 0.005, 0.01 and 0.05 wt %.

The main results for the Raman spectra of glassy LTB doped with Er_2O_3 are shown in Fig. 1. Seven distinct RS bands at 77, 353, 518, 762, 953, 1121 and 1427 cm^{-1} are observed in the spectrum of stoichiometric $Li_2B_4O_7$ (Fig. 1a). Their positions correlate well with the data [6, 7, 14–16, 24] obtained in a limited spectral range (300–1500 cm^{-1}). Moreover, there are additional features in the structure of the above RS bands, which are located at 109, 152, 239, 297, 318, 400, 694, 828, 1086, 1342, 1648 and 1894 cm^{-1}.

For the case of LTB activated with 0.0005 wt % Er_2O_3, the RS structure becomes more complicated. This manifests itself in increasing number of the observed spectral features (see Fig. 1b). In particular, ten intense RS bands are observed in the region 70–600 cm^{-1}. They are located at 77, 110, 152, 239, 297, 318, 380, 433, 478 and 529 cm^{-1}. In the region 600–860 cm^{-1}, we detect an intense band at 762 cm^{-1}, with distinct features seen at 694 and 828 cm^{-1}. This is typical for stoichiometric glassy LTB. In contrast to the stoichiometric composition (Fig. 1a) for which a broad band with the maximum at 953 cm^{-1} is observed in the spectral region

860–1050 cm^{-1}, the spectrum for $Li_2B_4O_7$:0.0005 wt % Er_2O_3 contains a group of closely spaced lines appearing at 936, 953 and 1014 cm^{-1}. Against the background of the spectrum typical for glassy $Li_2B_4O_7$, for which there is a broad diffused band at 1427 cm^{-1} and three modes with the frequencies 1121, 1648 and 1894 cm^{-1}, additional vibrational bands appear for LTB activated with Er_2O_3 in the 1050–2000 cm^{-1} region (Fig. 1b), with the corresponding frequencies being equal to 1086, 1223, 1342 and 1425 cm^{-1}.

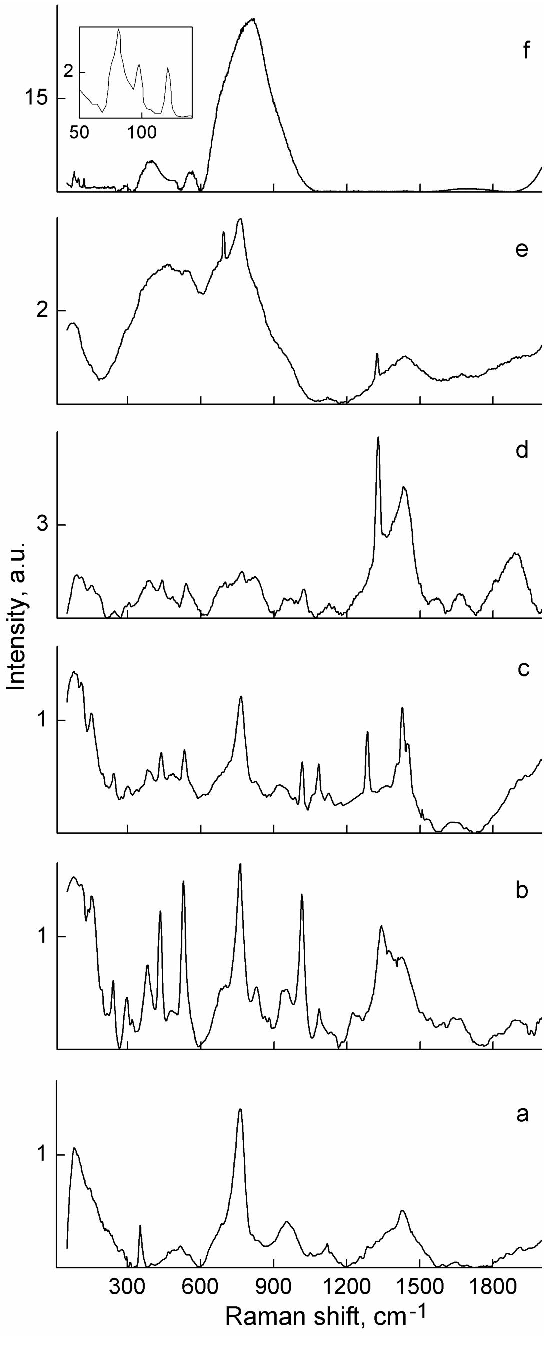

Fig. 1. Raman spectra detected for undopped glassy $Li_2B_4O_7$ (a) and glassy $Li_2B_4O_7$ doped with 0.0005 (b), 0.001 (c), 0.005 (d), 0.010 (e) and 0.050 wt % (f) of Er_2O_3.

When 0.001 wt % of Er_2O_3 is introduced into the LTB matrix (Fig. 1c), the structure of the Raman spectrum does not change significantly in either intensity or frequency positions of the vibrational bands. The exception is the region 1200–1500 cm^{-1} where narrow lines located at 1284, 1423 and 1450 cm^{-1} are clearly visible against the background of a broad band.

When the Er_2O_3 concentration increases up to 0.005 wt % (see Fig. 1e), the intensities of the RS bands in the 1200–2000 cm^{-1} region increase significantly, although their energy positions remain practically unchanged (cf. Fig. 1b–d). In this case broadening of the RS bands is observed within the entire frequency range under study, and a distinct diffused vibrational band appears at 894 cm^{-1}.

The RS spectrum of glassy $Li_2B_4O_7$ transforms substantially with further increase in the activator concentration (up to 0.01 wt % – see Fig. 1d). In particular, we observe redistribution of the spectral intensity at the frequencies 200–1600 cm^{-1} and significant broadening of the vibrational bands in the entire frequency range. Then seven bands located at 77, 468, 544, 694, 762, 1323 and 1450 cm^{-1} are clearly detected in the RS spectrum, along with faint features found at 297, 380, 828 and 953 cm^{-1}.

Finally, we touch upon the RS spectra observed for a notably disordered LTB matrix with the Er_2O_3 concentration equal to 0.05 wt % (see Fig. 1f). Here one detects the vibrational modes at 77, 98, 121, 297, 399, 493 and 560 cm^{-1}, an intense broad asymmetric band in the 600–1100 cm^{-1} region with the maximum located at 809 cm^{-1}, as well as faint features at 694, 762 and 828 cm^{-1}.

3. Analysis of the results

Note that interpretation of the RS lines in the $Li_2B_4O_7$ crystals and glasses in terms of approximate types of movement of the ions and structural groups is quite complicated. The first attempts to identify the modes observed for the LTB structure have been reported in Refs. [1, 6] for the single crystals. According to the type of chemical bonds in the $Li_2B_4O_7$ structure, one can distinguish lithium cations and boron–oxygen frameworks with B_4O_7 as a structural unit. However, these groups are not completely isolated because they create a framework through the bridging links B–O–B due to generalization of O(1) atoms. Thus, a method for assigning vibrational modes in the approximation of molecular crystals [1] can be applied to $Li_2B_4O_7$ only if the vibrations of lithium cations and boron–oxygen frameworks are separated. Unfortunately, the study [25] has shown that even this separation is conditional for the crystals of such a type, because the range of Li–O bond vibrations overlaps with that of internal deformational vibrations of lithium anions. The reason is relatively high natural frequencies of Li–O vibrations in such structures.

When identifying the structure of the Raman spectrum for pure glassy $Li_2B_4O_7$ (see Fig. 1a), one has to take into account the features of crystal-chemical structure of lithium tetraborate. According to the structural data [17, 18], lithium ions in the LTB matrix are surrounded by distorted oxygen tetrahedra (with the Li–O distance ranging from 0.197 to 0.214 nm) and octahedra (with the corresponding distance being close to 0.263 nm). By analogy with lithium ions, boron ions are located in a heterogeneous coordination environment. The averaged B–O distance is equal to 0.145 and 0.139 nm respectively for $[BO_4]$ tetrahedron and $[BO_3]$ system. Identification of single-phonon spectra for glassy $Li_2B_4O_7$ has been performed in accordance with the known vibrational frequencies for the structural complexes $[LiO_4]$, $[LiO_3]$, $[BO_4]$ and $[BO_3]$ (see Refs. [5, 7, 8, 12, 14, 15]). A pronounced structure at 77–400 cm^{-1} corresponds to the normal vibrations of $[LiO_6]$ frameworks. There is a superposition of vibrations of $[LiO_4]$ framework groups and $[BO_4]$ tetrahedra in the 400–600 cm^{-1} region. The maxima at 600–800 cm^{-1} are associated with the vibrations of [LiO_4] complexes. The peaks located in the regions of 800–1200 and 1160–1354 cm^{-1} are responsible for the normal vibrations of the same complexes. According to Refs. [5, 6, 14, 24], the modes detected in the region of the broad maximum (954 cm^{-1}) are related to deformations of [BO_4] tetrahedra, whereas stretching of [BO_4] tetrahedra is responsible for the vibration with the frequency 353 cm^{-1}. The frequencies 828 and 953 cm^{-1} correspond to symmetric stretching of [BO_3] group.

In addition, the shoulder of the RS band located at 828 cm^{-1} characterizes the modes of tri-, penta- and diborate groups. The most intense mode seen at 762 cm^{-1} is related to symmetric deformation vibration of [BO_3] complexes. The peculiarity near 694 cm^{-1} corresponds to the vibrations characterizing asymmetric deformations of flat triangles [BO_3] in the $Li_2B_4O_7$ structure. It is due to the vibrations of oxygenic bridges between one tetrahedral and one trigonal boron atoms or between one tetrahedral and two trigonal boron atoms. The faint feature observed in the region of 240–320 cm^{-1} is related to vibrations of [Li–O_6] frameworks, and the maximum at 400 cm^{-1} corresponds to the vibrations caused by symmetric stretching of [BO_4] tetrahedra. The frequencies 518, 953 and 1014 cm^{-1} correspond to the same modes. According to its position, the distinct maximum at 1427 cm^{-1} corresponds to symmetric stretching of flat [BO_3] triangles and vibrations of various borate rings. The shoulder observed at 1086 and the maximum at 1121 cm^{-1} are associated with vibrations of distorted [BO_4] tetrahedra in the structure of glassy lithium tetraborate. Finally, the peculiarities detected at 1648 and 1897 cm^{-1} are caused by the vibrations of B–O bonds.

The RS spectra become more complicated when glassy $Li_2B_4O_7$ is doped with Er_2O_3. The structure of the Raman spectra is still similar to that of pure $Li_2B_4O_7$ at the relatively small impurity concentrations, 0.0005–0.005 wt %. With increasing concentration, the maxima of the vibrational modes become somewhat blurred but their positions are not changed (see Fig. 1b–d). A comparison of these spectra with those obtained in non-polarized light for single-crystalline LTB [14] indicates complete coincidence of the vibrational-mode frequencies in the spectral region 80–2000 cm^{-1}. This suggests that activation of glassy $Li_2B_4O_7$ with Er^{3+} ions imposes clustering processes in the disordered matrix. This holds true up to the concentration 0.005 wt % inclusively, for which the structure of glassy $Li_2B_4O_7$ still remains apparently tetragonal within the medium-range scales. The above assumption agrees with the results [26].

For the concentrations of Er_2O_3 mentioned above (see Fig. 1b–d), the Raman spectra consist of separate groups of closely spaced lines. The most intense lines are observed in the regions 70–200, 700–800 and 1300–1500 cm^{-1}. According to Refs. [1–5, 8, 11], the vibrational fundamentals appear at 77–1500 cm^{-1}. The lack of vibrations with the lower frequencies indicates that the glassy matrix becomes more rigid and manifests the features of deformed framework structure of the $Li_2B_4O_7$ glass. This is also evidenced by some differences in the frequency positions of the normal vibrations, if compared with the modes observed in the Raman spectra of the LTB crystals.

The maximum at 1342 cm^{-1} is indicative of vibrations of borate rings and symmetric stretching of flat BO_3 triangles. The normal vibrations of boron–oxygen bonds B–O [12, 15] are responsible for the diffused maxima detected at the frequencies 1648 and 1894 cm^{-1}. The data on the vibrations identification can be obtained using the analysis of characteristic frequencies known for the other compound ions consisting of boron atoms in the tetrahedral and trigonal environments of oxygen atoms. According to Refs. [8, 9, 27, 28], the 900–1050 cm^{-1} region corresponds to symmetric stretching of BO_3 groups (936, 953 and 1014 cm^{-1}), while the 600–900 cm^{-1} region is associated with asymmetric deformations of flat BO_3 triangles (694 cm^{-1}) and vibrations of oxygenic bridges between one tetrahedral and one trigonal boron atom, or between one tetrahedral and two trigonal boron atoms. Note that the vibrations responsible for distorted modes of BO_4 groups are also observed in this frequency region. The intense maximum detected at 762 cm^{-1} results from symmetric deformations of flat BO_3 triangles. Mixed translational (433 and 478 cm^{-1}) and vibrational (528 cm^{-1}) oscillations of lithium ions are observed in the region 400–600 cm^{-1}. In addition, the characteristic lines 200–400 cm^{-1} associated for the vibrational modes of $[LiO_6]$ frameworks are observed in the spectra of lithium borates containing tetrahedral groups $[LiO_4]$. Finally, the vibrations of BO_3 and BO_4 groups in the structure of $[B_4O_7]^{2-}$ cluster as a whole, which lead to deformations of the latter [11], can be attributed to the vibrations in the spectral region 200–300 cm^{-1}.

The frequency region 70–200 cm^{-1} (72, 110 and 152 cm^{-1}) is indicative of ‘external’ modes of the structural complexes included in the glassy $Li_2B_4O_7$ matrix. The normal vibrations of ligands with Er^{3+} ions in the structural complexes of LTB (see Fig. 1b–d) [12] can also contribute to this region.

A further increase in the concentration of Er_2O_3 activator (0.01–0.05 wt % – see Fig. e,f) results in significant transformation of the RS spectra in both their structure and intensity. The vibrational modes detected at the frequencies 1323, 1329, and 1450 cm^{-1} and caused by the oscillations of $[LiO_4]$ clusters still remain in the spectrum for $Li_2B_4O_7$:0.01 wt % Er_2O_3. According to Ref. [5], one deals with a superposition of vibrations of $[LiO_4]$ groups and $[BO_4]$ tetrahedra in the 400–600 cm^{-1} region. Similar to the spectra analyzed above (see Fig. 1a–d), the bands observed at 694 and 762 cm^{-1} can be attributed to the vibrations of oxygenic bridges between one tetrahedral and one trigonal boron atoms (or between one tetrahedral and two trigonal boron atoms) and to the symmetric deformations of flat triangles of $[BO_3]$ groups, respectively.

The RS spectrum for glassy $Li_2B_4O_7$:0.05 wt % Er_2O_3 (see Fig. 1f) reveals a number of distinct maxima which, according to their positions (77, 98, 121, 297, 399, 493 and 560 cm^{-1}), should correspond to the spectra of erbium oxide Er_2O_3 of cubic syngony in the region of 70–600 cm^{-1}. They agree well with the data [29–34]. One can distinguish two groups of vibrations in this frequency region of optically active modes (see Fig. 1b–f). The internal vibrations due to the distortions of octahedral $[Er_2O_6]$ clusters are dominant in the first group (above 300 cm^{-1}). In the second group (below 200 cm^{-1}), translational vibrations of the mentioned octahedra and Er^{3+} ions (Er^{3+}–O–Er^{3+} or O–Er^{3+}–O) prevail for the glassy structure of Er_2O_3–$Li_2B_4O_7$ system.

Our results agree with the data of Ref. [26] where, basing on the fine structure of X-ray absorption spectra and the theoretical calculations, it has been shown that hybridization of the triply charged ions of rare-earth elements (Er^{3+} in our case) in the LTB matrix is observed upon activation of glassy lithium tetraborate. Since the borates B_4O_7 are bound by strong covalent links in the $Li_2B_4O_7$ matrix, the Er^{3+} ions occupy, most likely, the positions of Li^+ ions which are bound to basic borates through ionic links [25], thus forming the structural complexes in the system Er_2O_3–$Li_2B_4O_7$ by linking the oxygen atoms with the coordination number 6–8. It should be noted that erbium atoms are heavier than oxygen ones. Then the motion of the oxygen atoms plays a dominant role in the vibrational modes associated with stretching of the Er–O bounds [35].

As in case of the other spectra considered above, a broad diffused maximum observed in the region 600–1000 cm^{-1} (see Fig. 1f) is owing to asymmetric deformations of flat BO_3 triangles (see the feature detected at 694 cm^{-1}) and superposition of the vibrations of oxygen bridges between tetragonal and trigonal boron atoms. Superposition of these vibrations with the vibrations of octahedral $[ErO_6]$ complexes can also make a contribution to this band.

3. Conclusions

We have studied the RS spectra of glassy lithium tetraborate, $Li_2B_4O_7$, which is doped with different concentrations of erbium oxide Er_2O_3. The appropriate vibrational modes are identified and the parameters of all of the detected bands in the RS spectra are determined. The majority of the vibrational modes observed in the RS spectra of glassy $Li_2B_4O_7$:Er_2O_3 are found to belong to the mixed vibrations of different types related to each other by a deformed frame structure within the medium-range order of compound boron–oxygen and erbium–oxygen complexes.

We have shown that, in addition to the above oscillations, the vibrational modes contribute substantially to the scattering. This indicates that the RS in glasses is indeed the first-order scattering process and, in accordance with Ref. [20], it is related to the vibrational density of phonon states. The effect of hybridization of the orbits of triply charged Er^{3+} ions in the $Li_2B_4O_7$ matrix is found to be resulted from the fact that the structure of glassy $Li_2B_4O_7$ becomes clustered and changes from tetrahedral to cubic syngony with increasing Er_2O_3 concentration.

Finally, we have found clear changes in the RS spectra of glassy lithium tetraborate which can provide information on the spectroscopic manifestations of impurity scattering. This can be used when specifying crystallographic parameters of different kinds of borates.

References

1. Paul G L and Taylor W, 1982. Raman spectrum of $Li_2B_4O_7$. J. Phys. C: Solid State Phys. **15**: l753–1764.
2. Furusawa S, Tange S, Ishibashi Y and Miwa K, 1990. Raman scattering study of lithium diborate ($Li_2B_4O_7$) single crystal. J. Phys. Soc. Japan. **59**: 1825–1830.
3. Burak Ya V, Dovhiy Ya O and Kityk I V, 1990. Longitudinal-transverse splitting of phonon modes in $Li_2B_4O_7$ crystals. Zhurn. Prikl.Spectr. **52**: 126–128.
4. Adamiv V T, Berko T J, Kityk I V, Burak Ja V, Dzhala V I, Dovgij Ja O and Moroz I E, 1992. On phonon spectra of the borate monocrystals. Ukr. Fiz.Zhurn **37**: 368–373.
5. Berko T J, Dovgij Ja O, Kityk I V, Burak Ja V, Dzhala V I and Moroz I E, 1993. Raman spectra of lithium tetraborate monocrystals. Ukr. Fiz.Zhurn. **38**: 39–43.
6. Lopez T, Haro-Poniatowski E, Bosh P, Asomoza M, Gomez R, Massot M and Balkanski M, 1994. Spectroscopic characterization of lithium doped borate glasses. J. Sol-Gel Sci. and Technol. **2**: 891–894.
7. Li Y and Lan G, 1996. Pressure-induced amorphization study of lithium diborate. J. Phys. Chem. Solids. **57**: 1887–1890.
8. Dergachev M P, Moiseenko V N and Burak Ya V, 2001. Raman scattering in $Li_2B_4O_7$ crystals with impurities. Opt. Spectrosc. **90**: 604–607.
9. Vdovin A V, Moiseenko V N, Gorelik V S and Burak Ya V, 2001. Vibrational spectrum of $Li_2B_4O_7$ crystals. Phys. Solid State. 43: 1584–1589.
10. Burak Ya V, Trach I B, Adamiv V T and Teslyuk I M, 2002. Isotope effect in the Raman spectra of $Li_2B_4O_7$ single crystals. Ukr. Fiz.Zhurn. **47**: 923–928.
11. Gorelik V S, Vdovin A V and Moiseenko V N, 2003. Raman and hyper-Rayleigh scattering of light in lithium tetraborate crystals. Preprint of the Lebedev Physics Institute of Russian Academy of Sciences, No 13, Moscow.
12. Elalaoui A E, Maillard A and Fontana M D, 2005. Raman scattering and non-linear optical properties in $Li_2B_4O_7$. J. Phys.: Condens. Matter. **17**: 7441–7454.
13. Burak Ya V, Adamiv V T and Teslyuk I M, 2006. To the origin of vibrational modes in Raman spectra of $Li_2B_4O_7$ single crystals. Function Mater. **13**: 591–595.

14. Voronko Yu K, Sobol A A and Shukshin V E, 2013. Raman spectroscopy study of the phase transformations of LiB_3O_5 and $Li_2B_4O_7$ during heating and melting. Inorganic Mater. **9**: 923–929.
15. El Batal F H, El Kheshen A A, Azooz M A and Abo-Naf S M, 2008. Gamma ray interaction with lithium diborate glasses containing transition metals ions. Opt. Mater. **30**: P. 881–891.
16. Yadav A K and Singh P, 2015. A review of the structures of oxide glasses by Raman spectroscopy. RSC Adv. **5**: 67583–67609.
17. Krogh-Moe J, 1962. The crystal structure of lithium diborate, Li_2O–$2B_2O_3$. Acta Cryst. **15**: 190–193.
18. Krogh-Moe J, 1968. Refinement of the crystal structure of lithium diborate, Li_2O–$2B_2O_3$. Acta Cryst. B. **24**: 179–181.
19. Lorösch J, Couzi M, Pelous J, Vacher R and Levasseur A, 1984. Brillouin and Raman scattering study of borate glasses. J. Non-Cryst. Sol. **69**: 1–25.
20. Shuker R and Gammon R W, 1970. Raman-scattering selection-rule breaking and the density of states in amorphous materials. Phys. Rev. Lett. **25**: 222–225.
21. Kustov E F, Bandurkin E A, Muravyev E N and Orlovsky V P. Electronic spectra of compounds of rare-earth elements. Moscow: Nauka (1981).
22. Danilyuk P S, Puga P P, Gomonai A I, Krasilinets V N, Volovich P N and Rizak V M, 2015. X-Ray luminescence and spectroscopic characteristics of Er^{3+} ions in a glassy lithium tetraborate matrix. Opt. Spectrosc. **118**: 924–929.
23. Danilyuk P S, Popovich K P, Puga P P, Gomonai A I, Primak N V, Krasilinets V N, Turok I I, Puga G D and Rizak V M, 2014. Optical absorption spectra and energy levels of Er^{3+} ions in glassy lithium tetraborate matrix. Opt. Spectrosc. **117**: 759–763.
24. Massot M, Haro E, Oueslati M, Balkanski M, Levasseur A and Menetrier M, 1989. Structural investigation of doped lithium borate glasses. Mater. Sci. Eng. B. **3**: 57–63.
25. Lazarev A N, Mirgorodsky A P and Ignatiev I S. Vibrational spectra of complex oxides. Silicates and their analogues. Moscow: Nauka (1975).
26. Kelly T D, Petrosky J C, McClory J W, Adamiv V T, Burak Y V, Padlyak B V, Teslyuk J M, Lu N, Wang L, Mei W N and Dowben P A, 2014. Rare earth dopant (Nd, Gd, Dy, and Er) hybridization in lithium tetraborate. Frontiers in Phys. (Condens. Matter Phys.). **2**: 1–10.
27. Nakamoto K. IR spectra and Raman spectra of inorganic and coordination compounds. Moscow: Mir (1991).
28. Moiseenko V N, Vdovin A V and Burak Ya V, 1996. The efficiency of Raman scattering in $Li_2B_4O_7$ crystals. Opt. Spectrosc. **81**: 565–567.
29. McDevitt N T and Davidson A D, 1966. Infrared lattice spectra of cubic rare earth oxides in the region 700 to 50 cm^{-1}. J. Opt. Soc. Amer. **56**: 636–638.
30. Schaack G and Koningstein J A, 1970. Phonon and electronic Raman spectra of cubic rare-earth oxides and isomorphous yttrium oxide. J. Opt. Soc. Amer. **60**: 1110–1115.
31. Tomar R, Kumar P, Kumar A, Kumar A, Kumar P, Pant R P and Asokan K, 2017. Investigations on structural and magnetic properties of Mn doped Er_2O_3. Solid State Sci. **67**: 8–12.
32. Lejus A M and Michel D, 1977. Raman spectrum of Er_2O_3 sesquioxide. Phys. Stat. Solidi (b). **84**: K105–K108.
33. Tucker L A, Carney F J, McMillan P, Lin S H and Eyring L, 1984. Raman and resonance Raman spectroscopy of selected rare-earth sesquioxides. Appl. Spectrosc. **38**: 857–860.

34. Yan D, Wu P, Zhang S P, Liang L, Yang F, Pei Y L and Chen S, 2013. Assignments of the Raman modes of monoclinic erbium oxide. J. Appl. Phys. **114**: 193502-1–193502-7.
35. Abrashev M V, Todorov N D and Geshev J, 2014. Raman spectra of R_2O_3 (R – rare earth) sesquioxides with C-type bixbyite crystal structure: A comparative study. J. Appl. Phys. **116**: 103508.

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Анотація. *Вивчено спектри комбінаційного розсіяння склоподібного тетраборату літію з різними концентраціями легуючих іонів ербію. Більшість вібраційних мод, знайдених для активованих стекол* $Li_2B_4O_7{:}Er_2O_3$ *у середньомасштабному діапазоні, обумовлено змішаними та нормальними модами складних структурних комплексів бор–кисень, ербій–кисень і літій–кисень.*