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To the origin of vibrational modes in Raman spectra of $Li_2B_4O_7$ single crystals

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The Raman spectra investigations have been reported at room temperature in the 100–1200 cm^{-1} range for $Li_2B_4O_7$ single crystals with natural Li and B isotopic distribution and for 4 types of single crystals enriched maximally in ^7Li, ^6Li, ^{10}B and ^{11}B isotopes. It has been found that in spectra of $Li_2B_4O_7$ single crystals with natural isotopic distribution, no isotopic splitting takes place; this fact confirms the essentially single-mode behavior of those crystals. The specific modes are subdivided into 5 groups according to their frequency changes: (1) "regular" modes, where the frequency increases at decreasing isotope atomic mass, and vice versa; (2) modes, where the frequency remains insensitive to substitution of isotope; (3) the modes with anomalous behavior, where the frequency decreases at decreasing isotope mass, and vice versa; (4) the modes with frequency changing chaotically at substitution of isotopes; (5) "random" modes observed only in some samples. The origin of the vibrational modes in the Raman spectra of $Li_2B_4O_7$ single crystals is defined in more detail.

Сообщается о результатах исследований при комнатной температуре спектров комбинационного рассеяния монокристаллов $Li_2B_4O_7$ в области 100–1200 см$^{-1}$ с естественным распределением изотопов Li и B и 4-х типов монокристаллов, максимально обогащенных изотопами ^7Li, ^6Li, ^{10}B и ^{11}B. Установлено, что в спектрах $Li_2B_4O_7$ изотопное расщепление не происходит, что свидетельствует про их практически одномодовом поведении. По изотопным изменениям частот колебательные моды разделены на 5 групп: (1) "правильные" моды, частота которых растет об уменьшении атомной массы изотопа и наоборот; (2) моды, частота которых не изменяется со сменой изотопов; (3) моды с аномальным поведением, частота которых изменяется с уменьшением массы изотопа и наоборот; (4) моды с хаотическим изменением частот при замене изотопов; (5) "случайные" моды, которые наблюдались только в отдельных образцах. Предложены уточнения происхождения вибрационных мод в кристаллах $Li_2B_4O_7$.

Many publications are devoted to investigations of the Raman spectra of lithium tetraborate ($Li_2B_4O_7$) single crystal, including 8 references cited in [1] published in 2005 and the works [2–9]. Nevertheless, there is no general concept up to date. First of all, it is to note some discrepancies in positions of the Raman peaks on the frequency scale. Among other problems, there is the identification of the Raman peaks: in this case, some supplements introduced by other authors (see Table 4 in [1]) are added to identification of vibrational modes for this crystal performed in [10] by comparing with spectra of another borate compounds. The mentioned problems are connected both with technological peculiarities in preparation of $Li_2B_4O_7$ single crystals and with very complex structure of $Li_2B_4O_7$ crystal lattice: eight formula units (104 atoms) in the unit cell (space group $I4_1cd$, $a = b = 9.479$ Å, $c = 10.290$ Å), where the voluminous boron-oxygen complexes $[B_4O_9]^{6-}$ (formed by two planar triangles $[BO_3]$ and two tetrahedrons $[BO_4]$ with strong covalent bond) are joined together (by oxygen atoms being common for neighboring complexes) into spirals with the axes parallel to the crystal axis c; these, in turn, form rigid three-dimensional frame by means of common oxygen atoms. Li^+ ions are located in the voids of this frame and, in general, act as the charge compensators [11, 12]. An assumption from [10] can be added that some modes can be caused by the isotopic splitting, i.e. by isotopic effect. In $Li_2B_4O_7$ single crystals with natural isotope distribution, the stable lithium and boron isotopes are in the following proportion: ^6Li — 7.42 %, ^7Li — 92.58 %, ^{10}B — 19 %, and ^{11}B — 81 %. Taking into account that both elements — lithium and boron — belong to light elements, a significant influence on frequencies of some vibrational modes connected with different Li or B isotopes can be expected, that was confirmed by simple theoretical calculations. That is why this work is aimed at investigation of Raman spectra of $Li_2B_4O_7$ single crystals enriched in stable isotopes of ^6Li, ^7Li, ^{10}B and ^{11}B, that will provide to establish the origin of vibrational modes in this crystal more precisely.

The $Li_2B_4O_7$ single crystals have been grown from the melt in air using the Czochralsky technique. To synthesize of $Li_2B_4O_7$ compound enriched in stable isotopes, the following raw materials were used: $^6Li_2CO_3$ with 95 % of ^6Li, $^7Li_2CO_3$ with 96 % of ^7Li, $H_3{}^{10}BO_3$ with 97.3 % of ^{10}B, and $H_3{}^{11}BO_3$ with 99.2 % of ^{11}B (all percentages are expressed as atomic fractions). In such a way, the $Li_2B_4O_7$ single crystals of four isotopic compositions were obtained: I — $^7Li_2{}^{11}B_4O_7$, II — $^6Li_2{}^{10}B_4O_7$, III — $^7Li_2{}^{10}B_4O_7$, and IV — $^6Li_2{}^{11}B_4O_7$. From the grown single crystals, 6×6×7 mm^3 size samples of two types were prepared: 1) with faces oriented along the principal crystallographic axes X, Y, and Z; 2) with side facets turned by 45° about axis Z (axes X' and Y'). The orientation accuracy relatively to the crystallographic axe is not worse than 1°. This permitted to record the Raman spectra in the following geometries: $X(ZZ)Y - A_1(TO)$, $X(YY)Z - A_1(IO) + B_1$, $X'(Y'X')Z - B_1$, $X(YX)Z - B_2$, $Z(YZ)X - E(TO)$, and $X(ZX)Y - E(LO + TO)$. The Raman spectra were taken at room temperature (293 K) in the 100–1200 cm^{-1} range at the accuracy of 1 cm^{-1}. A LGN-402 argon laser (λ = 488.0 nm, P = 150 mW) was used as the excitation source.

As it was expected judging from theoretical calculations, substitution of ^6Li isotope by ^7Li and ^{10}B by ^{11}B in the $Li_2B_4O_7$ single crystal has influenced significantly the Raman spectra. As an example, Fig. 1(a–d) presents the Raman spectra for 4 variants of the isotope composition, recorded in X(ZZ)Y geometry (mode A_1). For comparison, Fig. 1(e) shows the Raman spectrum of $Li_2B_4O_7$ single crystal with natural isotopic distribution recorded in the same conditions and in the same geometry. All observed Raman peaks for the abovementioned geometries and 4 isotopic composition variants are tabulated in our previous work [9].

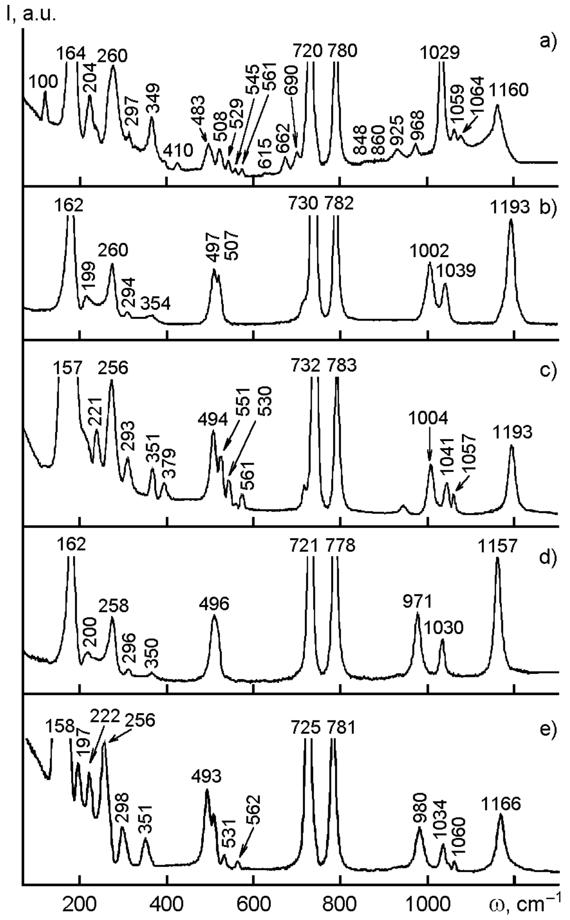

Fig. 1. Raman spectra in $X(ZZ)Y - A_1$ geometry for single crystals: $^7Li_2{}^{11}B_4O_7$ (a), $^6Li_2{}^{10}B_4O_7$ (b), $^7Li_2{}^{10}B_4O_7$ (c), $^6Li_2{}^{11}B_4O_7$ (d) $Li_2B_4O_7$ (natural isotope distribution) (e).

As it is seen from Fig. 1(e), in the Raman spectra of the $Li_2B_4O_7$ single crystals with natural isotopic distribution, some peaks connected with different isotopes Li or B are absent. In other words, explanation of some band pairs as those caused by isotopic splitting proposed in [10] is not confirmed by our results. This fact can be an evidence for purely single-mode behavior of vibrational spectra for the isotopically

Table. Frequencies (cm^{-1}) and origin of vibrational modes active in Raman spectra for $Li_2B_4O_7$ single crystal (the frequency values are given for natural isotope distribution)

		A_1(TO)	A_1(IO) + B_1	B_1	B_2	E(LO + TO)	E(TO)	Interpretation
Group 1	a	725 781 980 1034 1166	667 697 724 968 1032 1165	247 420 491 552 673 731 790 932 977 1039 1087 1172	512 666 782 1032 1162	511 659 685 723 929 968 1142	200 318 516 663 729 933 975 1038 1148	Modes sensitive to changes $^{10}B\leftrightarrow{}^{11}B$ connected with vibrations in (BO_3) and (BO_4) boron-oxygen complexes
	b			173	263	350 378	358 385	Modes sensitive to changes $^{6}Li\leftrightarrow{}^{7}Li$ connected with vibrations in (LiO_4) and (LiO_6) complexes
Group 2			349		102 241 349	106 143 194 319	109 148	Modes connected with plasmons and vibrations of oxygen atoms
Group 3		197 256	378	214 518	482	456		Superposition of internal and librational modes
Group 4		258 298 351 493 507	165 201 262 491	268 306 358	166 411	254 779		Superposition of different another modes

mixed $Li_2B_4O_7$ single crystals, when the frequencies of vibrational modes for crystals of mixed isotopic composition vary continuously from frequency of one pure isotope composition to frequency of another one depending on concentration of isotopes [13].

Consideration of all obtained Raman spectra has shown that various vibrational modes of the $Li_2B_4O_7$ single crystal behave differently at substitution of ^6Li by ^7Li and ^{10}B by ^{11}B. Conditionally, the vibrational modes in these spectra can be subdivided into following groups depending on the frequency changes (Table): (1) "regular" modes where sharply defined and theoretically predictable frequency shifts are observed at substitution of ^{10}B by ^{11}B (Subgroup a), or ^6Li by ^7Li (Subgroup b), the frequency of vibrational mode decreasing at substitution by a heavier isotope; (2) the modes practically insensitive (within the experimental accuracy) to substitution of any isotope; (3) the modes with anomalous behavior (the frequency decreases at decreasing isotope mass); (4) the modes where the frequency changes chaotically at substitution of isotopes; (5) "random" modes observed only for some samples (not included into Table).

The first group (1) consists in part of fundamental modes connected with vibrations in components (triangle $[BO_3]$ and tetrahedron $[B_4O_9]^{6-}$) of the boron-oxygen complex, as it was proposed in many works, in particular [10]. It is logically to assume that the modes with large frequency shifts at transition from ^{10}B to ^{11}B, reaching 3 %, in particular, 1166 cm^{-1} A_1(TO) for $[BO_4]$, and 980 cm^{-1} A_1(TO) for $[BO_3]$, are connected just with stretching or bending vibrations in these complexes. The calculations have shown that at such mass change of vibrational atoms in the mentioned complexes, the frequency shifts of fundamental vibrations must be of the same order of magnitude. An intense peak near 725 cm^{-1}, observed in all geometries practically at the same isotopic shift about 1.5 % at ^{10}B substitution by ^{11}B, requires additional explanation. The fact that it is connected with $[BO_3]$ group is without doubt because a similar intense Raman peak is observed in $LiBO_2$ crystals [14] where the only $[BO_3]$ boron-oxygen groups are present. Nevertheless, such frequency shift may be caused by a certain vibration type where the influence of boron atom mass on the vibration frequency is weaker. For example, "oblique" phonons can be responsible for this mode [6, 7], the presence thereof becomes quite natural if we look how the [BO_3] groups are oriented in $Li_2B_4O_7$ crystal lattice [11, 12]. Similarly, the other modes from Subgroup (*a*) of Group (1) with weak isotopic frequency shifts are connected obviously with "oblique" phonons or with libration vibrations of the boron-oxygen complex as a whole. As to Subgroup (*a*) of Group (1), the frequency shifts of all modes at ^7Li substitution by ^6Li vary from 2.8 % for 214 cm^{-1} mode to 1.1 % for 358 cm^{-1} one that is several times smaller than the calculated values for [LiO_4] and [LiO_6] clusters. Such a behavior can be explained under assumption that these modes possess the librational character, and the libration axis passes almost through the Li atom.

To explain the origin of modes included into Group (2), the following models can be proposed: 1) 349 cm^{-1} modes of A_1(IO) + B_1type, 349 and 241 cm^{-1} ones of B_2 type, 319 cm^{-1} of E(LO + TO) type, 143 cm^{-1} of E(TO) type can be caused by vibrations of the oxygen atoms located in different positions of $Li_2B_4O_7$ crystal lattice [11, 12]; 2) lower intensity modes in the range <200 cm^{-1}, in particular 102 cm^{-1} of B_2 type, 106 and 194 cm^{-1} of E(LO + TO) type and 109 cm^{-1} of E(TO) type can be referred to collective excitations — plasmons (similarly to the low-frequency modes in $LiBO_2$ Raman spectra [14]) that can be confirmed by negative values of real part of permittivity $\varepsilon_1(\nu)$ in this region [15]. Both these models agree well with independence of the frequency peak on the lithium or boron isotope type. Although the existence of purely oxygen vibrational modes in $Li_2B_4O_7$ crystals had not been considered till today, their existence can be assumed in this case owing to the frame structure of $Li_2B_4O_7$ crystal lattice where oxygen atoms occupy 4 nonequivalent positions with different bond ionicity [11, 12].

As to group (3) with anomalous frequency shifts under interchange of Li and B stable isotopes, similar cases had been observed in organic crystals at hydrogen substitution by deuterium and were explained in such a way that internal vibrations of CH_3 group in these crystals mix with librations of whole molecules, resulting in energy redistribution between the vibrations which causes the frequency "repelling" towards higher frequencies, although the vibrational atom mass increases [16]. Similar frequency mixing for the modes of different types and origins, including acoustic ones, occurring in $Li_2B_4O_7$ crystal, is no doubt the reason for appearing of modes referred to group (4). But at the present investigation stage, it can hardly be said how a specific mode is connected with such anomalous behavior-overtones, mixing of modes, or some other mechanisms, as considered, for example, in [17, 18]. For this purpose, it is necessary to examine precisely the temperature dependences of intensity and half-width for all Raman peaks together with detailed theoretical calculations of various cluster models and with accounting for their spatial orientation in the $Li_2B_4O_7$ unit cell. For example, taking the results [19] for the temperature dependences of some Raman peaks for $Li_2B_4O_7$ and ignoring the frequency difference, the peaks 350 cm^{-1} E(LO + TO) and 358 cm^{-1} E(TO) can be interpreted as manifestation of the same E(TO) type mode, because these disappear simultaneously at temperatures above 400 K.

The situation is more complicated with the modes of Group (5), because these appear only in some crystals and are of low or very low intensity independent on the observed sample. Local vibrations within limits of isolated crystal lattice defects, in particular impurities, might be a reason for appearance of such random peaks in individual Raman spectra for some samples. Such model is quite valid for low intensity peaks, for example, 531 and 562 cm^{-1} ones of A_1(TO) type observed only in the $Li_2B_4O_7$ single crystals of two isotopic compositions: $^7Li_2{}^{11}B_4O_7$ and $^7Li_2{}^{10}B_4O_7$. But single peaks of moderate intensity, for example, 1028 and 1043 cm^{-1} of E(LO + TO) type ones for the same isotopic compositions, had been observed, too. Those may originate from resonance effects.

The main conclusion of this work is that the assignment of vibrational modes in $Li_2B_4O_7$ crystal is much more complex as it had been considered before. That is why in Table 4 [1], the identification of vibrational modes needs a more detailed study. For example, vibrational modes 378 cm^{-1} of E(LO + TO) type and 385 cm^{-1} of E(TO) type must be connected unambiguously with the lithium atoms but not the boron ones, as it had been considered previously, while the mode 780 cm^{-1} of B_2 type is to be ascribed to boron atoms but not to complexes [LiO_4]. Similarly, the modes 194 cm^{-1} of E(LO + TO) type, 197 cm^{-1} of A_1(TO) type, 493 cm^{-1} of A_1(TO) type, and 201 cm^{-1} of

$A_1(IO) + B_1$ type, as well as 205, 702 and 856 modes of B_2 type, and all other belonging to the 5th Group must be excluded from the group of fundamental vibrations. These modes cannot obviously belong to fundamental ones, both translational and librational, judging from their frequency behavior at the isotopic substitution, and it is necessary to use more complex models to identify those modes. Therefore, it should be stated that almost a half of the modes observed in the $Li_2B_4O_7$ single crystal Raman spectra belong to mixed vibrations, and it is necessary to take this into account when determining the origin of any specific mode. The consideration of the results obtained has shown also that in the Raman spectra of $Li_2B_4O_7$, no isotopic splitting takes place that confirms their purely single-mode behavior.

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До походження вібраційних мод у Раманівських спектрах комбінаційного розсіювання монокристалів $Li_2B_4O_7$

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Повідомляється про результати досліджень при кімнатній температурі спектрів комбінаційного розсіювання монокристалів $Li_2B_4O_7$ в області 100–1200 $см^{-1}$ з природнім розподілом ізотопів Li і B і 4-х типів монокристалів максимально збагачених ізотопами ^7Li, ^6Li, ^{10}B і ^{11}B. Встановлено, що у спектрах $Li_2B_4O_7$ ізотопного розщеплення не відбувається, що свідчить про їх практично чисто одномодову поведінку. За ізотопними змінами частот коливні моди розділені на 5 груп: (1) "правильні" моди, частота яких зростає при зменшенні атомної маси ізотопу і навпаки; (2) моди, частота яких не міняється із зміною ізотопів; (3) моди з аномальною поведінкою, частота яких зменшується із зменшенням маси ізотопу і навпаки; (4) моди з хаотичними змінами частот при заміні ізотопів; (5) "випадкові" моди, які спостерігалися тільки в окремих зразках. Запропоновано уточнення походження вібраційних мод у кристалах $Li_2B_4O_7$.