

Spectral diagnostics of oscillation centers in crystals with hydrogen bonds

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Abstract

Practical application of crystals in optoelectronics and laser engineering requires the directions of optical axes and the types of oscillation centers be known, and this is an important and necessary condition. We have studied the infrared transmittance and absorption spectra of hexagonal lithium iodate α -LiIO₃ crystals grown by open evaporation method in H₂O and D₂O solutions and natural lamellar monoclinic crystals of phlogopite and muscovite. The band gap of the test crystals has been determined from the transmittance spectra. The absorption spectra have provided information on the activation energy and wavelength of the activation centers related to the oscillations of protons, hydroxonium ions H₃O⁺, protium H⁺, OH⁻ groups and HDO molecules. There has been a good correlation between the parameters of infrared spectra, thermally stimulated depolarization current spectra and nuclear magnetic resonance spectra. We have analyzed the possibility of oscillation center diagnostics based on infrared spectra which also allow determining the directions of optical axes. The experimental results confirm the possibility of using IR spectra for determining the type of oscillation centers and the presence of lattice anisotropy in test crystals.

Keywords

diagnostics, infrared spectra, thermally stimulated depolarization currents, oscillation centers, optical axes, anisotropy, nuclear magnetic resonance

1. Introduction

An important task of modern science is to provide nondestructive quality control methods for laser and optical crystals during crystal growth and study of new crystalline materials. The diagnostics of these materials can be considered as a nanotechnological problem since studying the types of oscillation centers implies monitoring the translation diffusion of nanoparticles in crystal nanostructures. Earlier the types of oscillation centers were determined from thermally

stimulated depolarization current spectra (TSDC) [1]. This method however requires low-temperature measurements at 77–350 K which complicates the diagnostics and requires much time. Patented method of determining optical axis positions in crystals that are known to be anisotropic [2] proved to be quite complicated. The mechanism of proton-ion conductivity and dielectric relaxation was studied [3–7] and the study showed the possibility of transportation and translation diffusion of protons in crystal lattice with hydrogen bonds in a wide range of temperatures with the formation of various oscillation centers.

High-temperature super proton conductors based on cesium hydrosulfate crystals CsHSO_4 were studied [5]. The authors assumed a rotation of the whole HSO_4^- anion but this is low probable from the energy viewpoint. The reorientation of the anion occurs most likely due to a tunneling transition of a proton between the oxygen ions inside the tetrahedron. Therefore further studies were required in order to directly confirm the presence of translation diffusion and tunneling of protons along some axes with the formation of oscillation centers. It was first of all to be checked whether the test crystals are wide band gap ones, i.e., whether their band gap is wide enough to exclude the possibility of electron transitions to the conduction band at low temperatures. Another task was to analyze the correlation between the results obtained from infrared (IR) spectra, TSDC and nuclear magnetic resonance (NMR) spectra.

The aim of this work is to analyze the possibility of spectral diagnostics of the types of oscillation centers in crystals with hydrogen bonds and to provide more accurate, streamlined and authentic methods of determining the types of oscillation centers and the directions of optical axes on the basis of IR spectral analysis.

2. Experimental

To provide more accurate, streamlined and authentic spectral diagnostics of the types of oscillation centers and optical axes in crystals with hydrogen bonds carefully polished crystals are placed in an IR spectrometer. Then IR transmittance and absorption spectra are recorded in order to determine the band gap of each crystal. Then the proton component of the oscillation centers is separated. For each spectral band corresponding to a specific oscillation center the activation energy, wavelength and wave number are evaluated. The magnitude of the latter parameters and their presence in a specific direction are the basis for determining the types of oscillation centers and the directions of optical axes. The abovementioned task is achieved due to the use of advanced equipment, careful preparation and polishing of the specimens and significant reduction of time required for the experiment in comparison with the method suggested earlier [1]. Furthermore this diagnostic method allows one to check whether a crystal is anisotropic.

The test crystals were optical quality lithium iodate $\alpha\text{-LiIO}_3$ crystals (hexagonal system, point symmetry group C_6) grown by open evaporation method in H_2O and D_2O solutions and natural lamellar monoclinic crystals of phlogopite $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$ and muscovite $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$ micas (monoclinic system, point symmetry group $2/m$, prismatic). The choice of these test materials was not arbitrary: all these crystals have hydrogen bonds. Lithium iodate crystals have unique optical, electrical and piezoelectric properties and are used as short-wavelength radiation frequency doubling crystals in many semiconductor lasers and in optoelectronics. Lamellar phlogopite and muscovite mica crystals are used for the production of electrically insulating materials, e.g. mica paper tape, micanite, micafolium and mica

plastics that are widely used for the fabrication of slot and turn insulation in generators and transformers as well as in microelectronics. Therefore study of these iodate and silicate crystals is an important and timely task since their practical application requires the directions of optical waves and the types of oscillation centers be known.

Lamellar $\alpha\text{-LiIO}_3$ crystals were cut with a diamond disc on an Okamoto machine from the central part of the growth pyramid and cooled with glycerin. The 0.5–1 mm thick plates were manually grinded on grinding glass using suspension of grinding powders and glycerin. The plate sides were parallel accurate to within 0.1 μm . Then the specimens were polished with Goya paste. The 5–10 μm thick natural muscovite and phlogopite mica crystals were separated from the larger druse of crystals. The purity of the these iodate, muscovite and phlogopite crystals was confirmed by microscopic examination and transmittance spectroscopy which proved stably high transmittance in the 500–3000 nm region for $\alpha\text{-LiIO}_3$ and in the 500–3200 nm region for muscovite and phlogopite.

The absorption coefficients were the highest in the direction of the main optical axis $Z(C_6)$ or [0001] and the lowest in the X axis direction which is perpendicular to the main optical axis. The IR transmittance spectra were taken on a UV-Vis-NiR Cary 5000 spectrophotometer (Varian, Australia). The absorption coefficient for allowed direct transitions can be expressed with the formula [8, p. 307]:

$$\alpha = A(h\nu - E_g), \text{ at } h\nu > E_g; \quad (1)$$

$$\alpha = 0, \text{ at } h\nu \leq E_g. \quad (2)$$

where E_g is the band gap, $h\nu$ is the photon energy and A is the coefficient which depends on the concentration and effective masses of electrons and holes as follows:

$$A = \frac{\pi e^2 \left[2m_e^* m_p^* / (m_e^* + m_p^*) \right]^{3/2}}{h^2 c m_e^* \epsilon_r n}. \quad (3)$$

The magnitude of α depends linearly on the photon energy $h\nu$ in the frequency region which is individual for each crystal. Extrapolation of this linear dependence to the crossing with the X axis gives the band gap E_g . It follows from Eqs. (1) and (2) that direct transitions should not cause absorption of quanta with energies lower than the band gap. Therefore the self-absorption edge at the long wave side (low energies) should be very sharp. Indeed, pure lithium iodate single crystals (Fig. 1) as well as phlogopite and muscovite exhibit an abrupt growth of absorption. The band gap was calculated for the self-absorption edge by linear approximation of optical transmittance spectra. The average E_g of the $\alpha\text{-LiIO}_3$ crystals was 4.37 eV along the Z axis and 4.46 eV along the X axis. The wavelength of the absorption edge for the silicates corresponded to 4.31 eV band gap. Therefore electron transitions from the valence band to the conduction band can be disregarded for the test silicates and lithium iodate. This confirms that tunneling and translation diffusion with the formation of oscillation centers are only possible for protons.

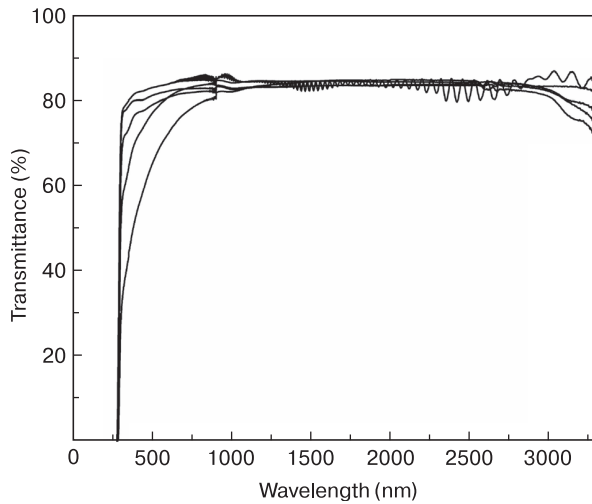


Figure 1. IR transmittance spectrum of α -LiIO₃ crystals in different directions.

3. Results and discussion

IR absorption spectra were taken on an IFS 66v/S Fourier spectrometer (BRUKER, Germany). Spectral bands are commonly denoted in spectroscopy with wave numbers in cm^{-1} but this does not allow comparing IR spectra with other spectra where energy is expressed in eV. Using the Planck formula one can obtain the relationship between wave number and energy: $1 \text{ cm}^{-1} = 1.2398 \times 10^{-4} \text{ eV}$. It was assumed that the absorption band near 3400 nm (wave number 2941 cm^{-1}) confirms the probability that hydrogen ions are present [9, p. 275]. This wavelength corresponds to an oscillation center energy of 0.365 eV and this band is actually present in the IR spectra of the silicates and lithium iodate grown in H₂O with iodic

acid HIO₃ addition (this band is absent in neutral crystals) along the sixth order axis C₆. The IR spectrum taken along the Z axis (C₆) (Fig. 2) of the crystal grown in H₂O contained bands at 0.27 eV (hydroxonium ion H₃O⁺), 0.365 eV (proton H⁺) and OH⁻ ions, and that for the crystal grown in D₂O (Fig. 3) did not contain these bands. Furthermore, the IR spectra taken along the X axis (Fig. 4) did not contain bands at energies of above 0.27 eV which would be related to proton and OH⁻ ion oscillations. Thus IR spectrometry can be used for studying anisotropy, determining the directions of main optical axes in crystals and the presence of heavy water. The outburst at 0.29 eV which is resolved in all the spectra of all the crystals is an instrumental feature caused by the presence of nitrogen used for spectrometer chamber cleaning. Free H₂O molecules that are the basis of the hydrogen bond absorb intensely in the IR region and produce three types of oscillations in free state:

- 1595 cm^{-1} band corresponding to a 0.20 eV energy (deformation oscillation δ);
- 3654 cm^{-1} band corresponding to a 0.453 eV energy (symmetrical valence oscillation ν_s);
- 3756 cm^{-1} band corresponding to a 0.466 eV energy (asymmetrical valence oscillation ν_{as}).

In our experiments the silicate crystals only exhibited the bands at 0.20, 0.45 and 0.464–0.470 eV, and lithium iodate only had the 0.195 eV band (Figs 2–6, Tables 1, 2). To obtain information from IR spectra on the state in which bound water is present in the minerals one should study the spectral regions corresponding to OH group absorption.

It was shown [11] that the low-energy edge of KHCO₃ is determined by the OH transitions at 0.372 and 0.186 eV.

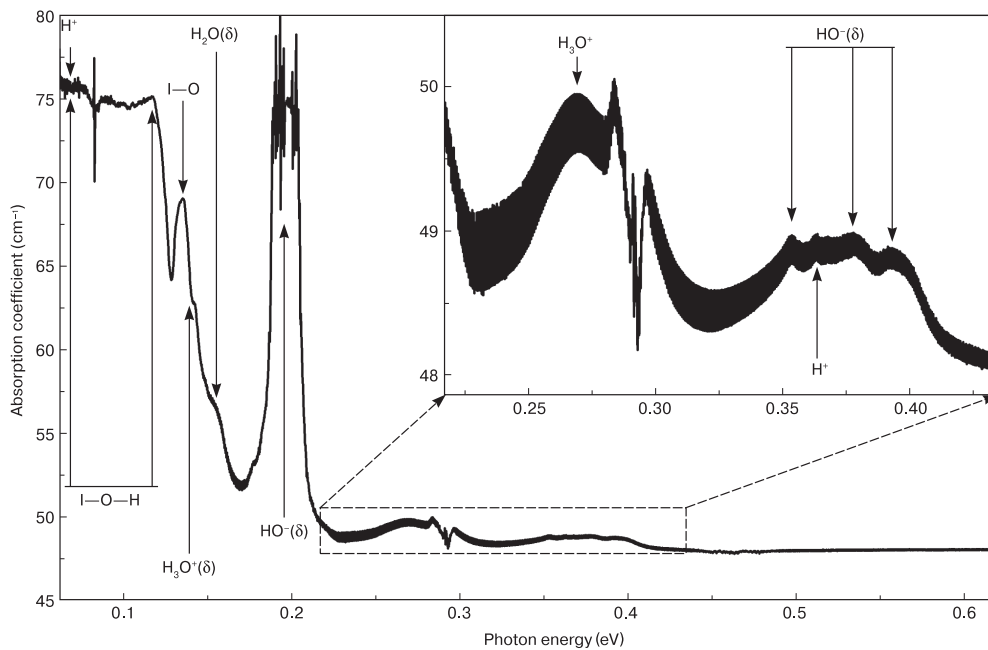


Figure 2. IR absorption spectrum of α -LiIO₃ crystals grown in H₂O, along the Z axis (C₆). Inset shows spectrum fragment.

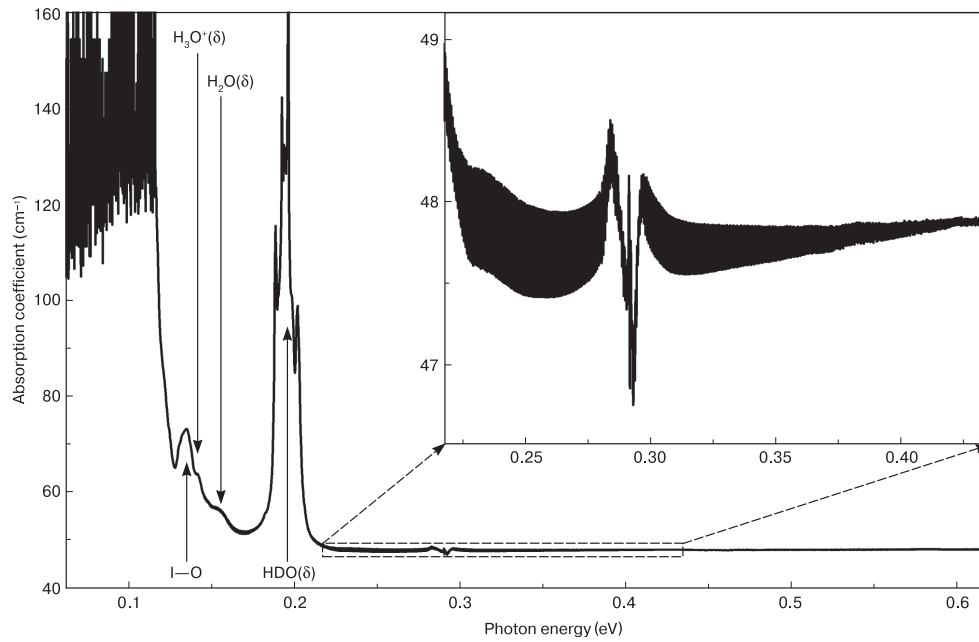


Figure 3. IR absorption spectrum of α -LiIO₃ crystals grown in D₂O, along the Z axis. Inset shows spectrum fragment.

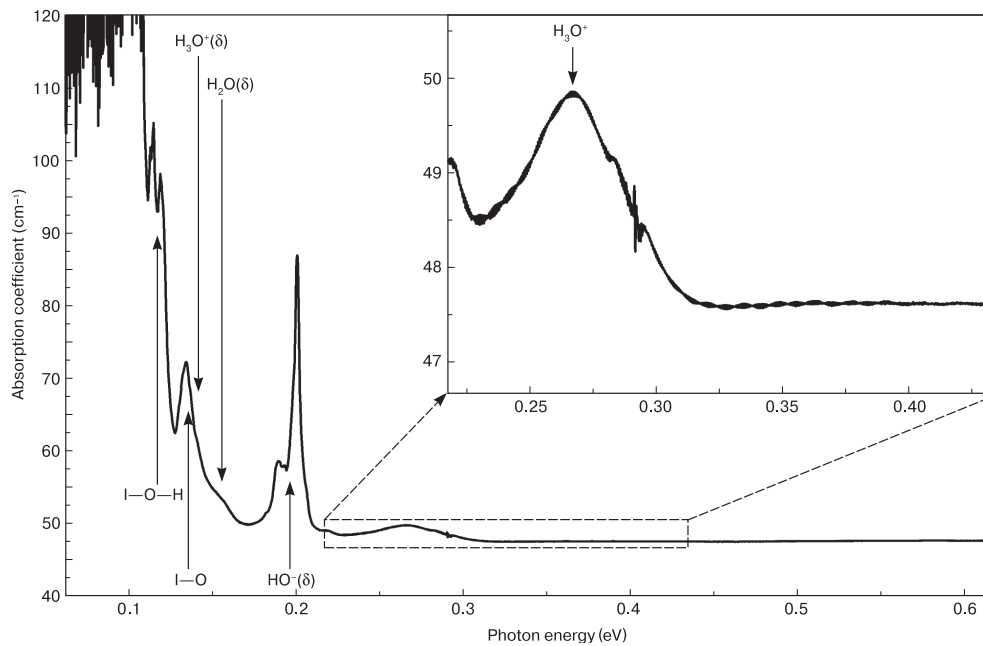


Figure 4. IR absorption spectrum of α -LiIO₃ crystals grown in H₂O, along the X axis. Inset shows spectrum fragment.

The data presented in Figs 3–6 and in Tables 1 and 2 suggest the presence of the 0.365 eV band related to proton oscillation centers and the 0.20–0.12 bands in silicates due to OH centers. This confirms the conclusions made from the TSDC spectra [1, 6].

Of interest is the 1580 cm⁻¹ band (0.195 ± 0.01 eV) in lithium iodate. The absorption coefficient of the crystals grown in D₂O is almost twice as high as that of the crystals grown in H₂O (Figs 2, 3). It was shown [12] that a free D₂O molecule generates the 1460 cm⁻¹ spectral band

(0.181 eV) in the 1550–1350 cm⁻¹ range corresponding to deformation oscillations of semi-heavy water molecules HDO. The 1580 cm⁻¹ band for lithium iodate crystals is in the 1450–1650 cm⁻¹ range, i.e., these ranges overlap. One can therefore assume that in the lithium iodate crystals grown in D₂O this band corresponds to the oscillations of bound semi-heavy water molecules HDO. This method can thus be used for heavy water detection in the test material. In the lithium iodate crystals grown in H₂O this band corresponds to the oscillations of OH⁻ ions.

The region of H_3O^+ deformation oscillations in the silicates and lithium iodate contains a well-resolved band at 0.14 eV [13]. The bands of H_3O^+ valence oscillations at 0.27 eV are very wide and weak. Among the test crystals these bands were observed for the silicates at 0.25 eV (2020 cm^{-1}) and lithium iodate at 0.27 eV (2170 cm^{-1}), but only for those grown in H_2O (Fig. 2 and Table 1). This band is absent in the $\alpha\text{-LiIO}_3$ crystals grown in D_2O (Fig. 3). Thus few if any D_3O^+ absorption centers form in the crystals grown in heavy water. The absorption bands at 0.40–0.45 eV were present in the IR spectra of lithium iodate and the silicates (phlogopite and muscovite, Figs 5, 6 and Table 2). This is in a good agreement with the TSDC spectra of hydroxyl ion OH^- (Table 3) and earlier data [10]. The bands at 0.066 eV (silicates) and 0.068 eV (lithium iodate) agree well with the activation energy of peak 1 (0.07 eV) in the TSDC spectrum (Table 3) generated by the relaxation of $HSiO_4^{3-}$ anions in silicates or HIO_3 in iodates [7] resulting from a tunneling transition of a proton between the oxygen ions. All the crystals contain typical common spectral bands at ~ 10 and $20\ \mu\text{m}$ [10, 14,

15]. Molecules formed by the same chemical groups regardless of the rest of the molecule absorb in a narrow frequency range called characteristic. Thus different silicate compounds should exhibit oscillation spectra containing similar Si–O bands, e.g. 960 cm^{-1} (0.12 eV) [16].

Indeed, the test lamellar silicate crystals exhibited an intense band at 0.12 eV for muscovite (wavelength $\sim 10\ \mu\text{m}$) (Fig. 5) and 0.118 eV for phlogopite (Fig. 6). These bands are characteristic of the strong Si–O bond. Lithium iodate also exhibits intense bands at 0.12 eV ($10\ \mu\text{m}$) that are similar for the crystals grown in H_2O , and D_2O , i.e., there is the strong I–O bond. The $20\ \mu\text{m}$ band (0.062 eV) is the 0.066–0.068 eV for lithium iodate and the silicates.

A proton has not electron shell and is a single-charged particle with a small radius and a low coordination number. Therefore it can easily form protonized oscillation centers. The barrier transparency for protons can be easily evaluated using the formula

$$D = \left[\frac{1}{16} \left(\sqrt{\left(\frac{U_0}{E} - 1\right)^{-1}} + \sqrt{\left(\frac{U_0}{E} - 1\right)} \right)^2 \cdot e^{2\chi d} + 1 \right]^{-1} \quad (4)$$

Table 1. Energy and oscillation centers of IR absorption spectrum of $\alpha\text{-LiIO}_3$ crystals.

Band #	Wave number ν , cm^{-1}	IR spectrum energy, eV	Oscillation centers
1	550 (HZ)	0.068	I–O–H, H^+
2	970 (HXZ)	0.12	I–O–H
3	1090 (HDXZ)	0.135	I–O
4	1120 (HDXZ)	0.14	$H_3O^+(\delta)$
5	1250 (HDXZ)	0.155	$H_2O(\delta)$
6	1580 (DZ)	0.195	$HDO(\delta)$
7	1580 (HZ)	0.195	$OH^-(\delta)$
8	2170 (HXZ)	0.27	$H_3O^+(\delta)$
9	2850 (HXZ)	0.35	$OH^-(\nu_s)$
10	2941 (HZ)	0.365	H^+
11	3055(HZ)	0.38	$OH^-(\nu_s)$
12	3170 (HZ)	0.40	$OH^-(\nu_s)$

Notations. (H) and (D): crystals grown in light (H_2O) and heavy (D_2O) water, respectively; (Z): direction along the C6 axis; (X): direction perpendicular to the C6 axis.

Table 2. Energy and oscillation centers of IR absorption spectra of muscovite and phlogopite.

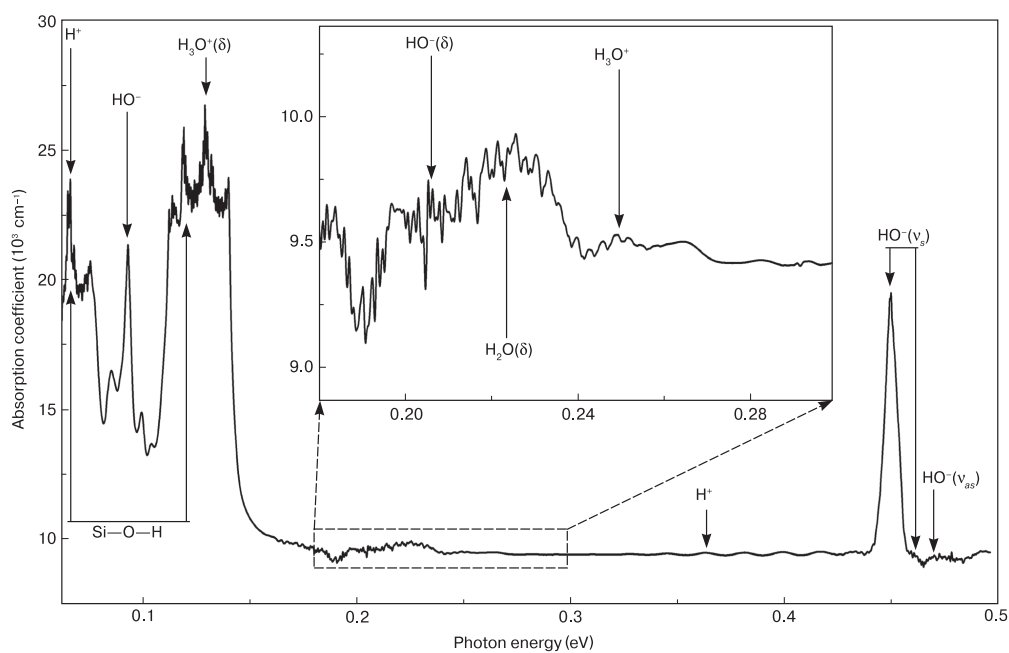
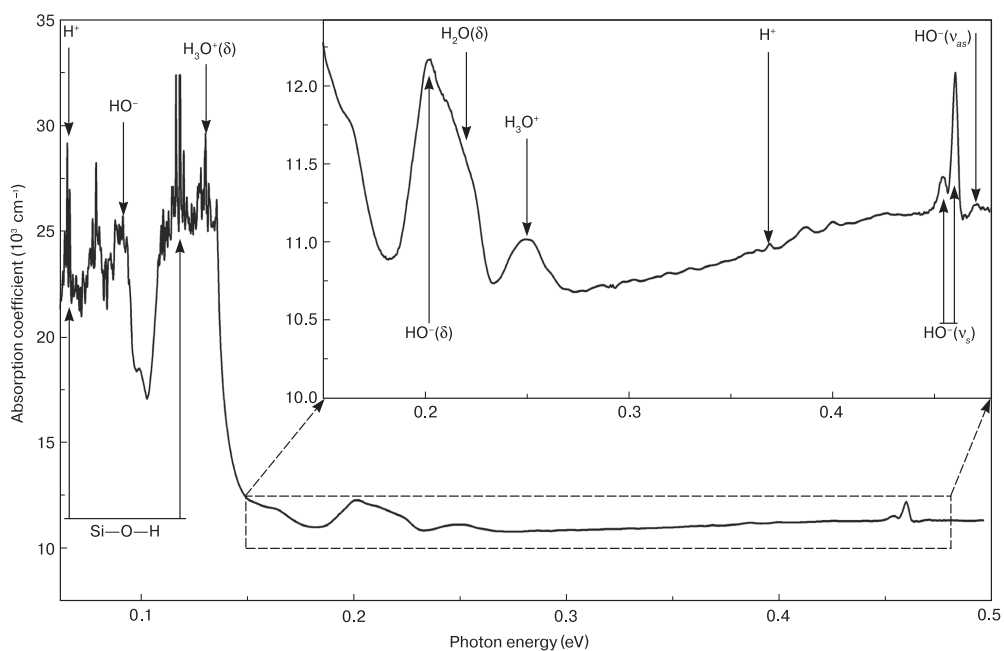
#	Muscovite		Phlogopite		Oscillation centers
	Wave number ν , cm^{-1}	IR Spectrum Energy, eV	Wave number ν , cm^{-1}	IR spectrum energy, eV	
1	530	0.066	530	0.066	Si–O–H, H^+
3	750	0.093	750	0.093	OH^-
4	960	0.12	950	0.118	Si–O–H
5	1070	0.133	1070	0.133	$H_3O^+(\delta)$
6	1680	0.21	1640	0.20	$OH^-(\delta)$
7	1800	0.22	1800	0.22	$H_2O(\delta)$
8	2020	0.25	2020	0.25	H_3O^+
9	2941	0.365	2945	0.365	H^+
10	3640	0.45	3640	0.45	$OH^-(\nu_s)$
11	3740	0.464	3700	0.459	$OH^-(\nu_s)$
12	3800	0.47	3800	0.47	$OH^-(\text{struct.})$ (ν_{as})

This formula yields the proton transparency of a 0.12 nm wide and 0.06 eV high potential barrier to be 0.0408 [13]. Taking into account that the distance between the oxygen ions in the SiO_4^{4-} tetrahedron is 0.1215 nm and that between the oxygen ion in SiO_4^{4-} and the water molecule is 0.135 nm one can safely state that the rotation of the SiO_4^{4-} tetrahedrons occurs by a tunneling transition of a proton between the oxygen ions inside and between the tetrahedrons which is in agreement with earlier conclusions [17] for hydrates. The oscillations of the adjacent SiO_4^{4-} or IO_3^- ions may make the potential barrier narrower by hundredths of a nanometer which eventually facilitates a tunneling transition of a proton towards these ions. It is therefore plausible that the 530–550 cm^{-1} bands (0.068 eV) are not caused by oscillations of the Si–O groups in SiO_4^{4-} anions but by oscillations of Si–O–H in protonized $HSiO_4^{3-}$ anions which was confirmed earlier [18]. The same is true for I–O–H oscillations in HIO_3 molecules that generate the 970 cm^{-1} band corresponding to 0.12 eV. However these bands in lithium iodate are by almost two orders of magnitude weaker.

The 0.41, 0.462 and 0.45 eV bands of water are attributable to antisymmetrical oscillations of OH groups. Indeed muscovite and phlogopite exhibited well-resolved bands peaking at ~ 0.46 eV in a good agreement with earlier data [19, 20]. The 0.40 eV band caused by OH group oscillations is also present in the IR spectra of the lithium iodate crystals grown in light water. However this band is absent in the IR spectra of the lithium iodate crystals grown in heavy water. This confirms that protons form absorption centers while deuterons do not, because of their low mobility. Figures 1–6 and Table 1 show that study of the type of oscillation centers also allows one to determine the directions of optical axes in crystals.

Table 3. Comparison of TSDC and IR spectra.

Peak #	TSDC spectrum of phlogopite	IR spectrum of phlogopite	TSDC spectrum of lithium iodate		IR spectrum of lithium iodate	Oscillation centers	
	U_a , eV	ν , cm^{-1}	U_a , eV	U_a , eV	ν , cm^{-1}		U_a , eV
1	0.06 ± 0.01	530	0.066	0.07 ± 0.02	550	0.068	Si–O–H, H^+
2	0.15 ± 0.02	1070	0.133	0.15 ± 0.02	1120	0.14	H_3O^+
3	0.23 ± 0.02	1800	0.22	0.30 ± 0.03	2850	0.35	H_2O
4	0.31 ± 0.04	2945	0.365	0.35 ± 0.04	2941	0.364	H^+
5	0.41 ± 0.04	3640	0.45	0.42 ± 0.04	3170	0.40	$\text{OH}(\nu_s)$

**Figure 5.** IR absorption spectrum of muscovite crystals. Inset shows spectrum fragment.**Figure 6.** IR absorption spectrum of phlogopite crystals. Inset shows spectrum fragment.

To grow high-quality lithium iodate laser crystals one should add iodic acid HIO_3 with $\text{pH} = 1.5$ to the growth solution. Iodic acid is a good donor of protons which penetrate into the growing crystal even at very low solution acidities. In our experiments the absorption bands at 2941 cm^{-1} (0.365 eV) caused by proton oscillations were well resolved. The presence of tunneling transitions with the formation of protonized HSiO_4^{3-} anions (silicates) and HIO_3 (iodates) is confirmed by the good agreement between the activation energies of peak 1 in the TSDC spectrum (0.07 eV) and in the IR spectrum (Si–O–H band, 0.066 eV) for the silicates, and between the TSDC spectrum and the IR spectrum (I–O–H band, 0.068 eV) for lithium iodate (Table 3). The TSDC peak at 0.23 and 0.3 eV [1, 6] caused by H_2O ion relaxation also agrees well with the IR spectra. Despite the different physical origins of the TSDC and IR spectra the agreement of the activation energies indicates that the TSDC peaks and the IR spectral bands of oscillation centers are generated by the same relaxers.

The NMR proton spectrum of the deuterized $\alpha\text{-LiIO}_3$ crystal taken on a BRUKER AVANCE III TM 300 spectrometer contained a resolvable twin band. It suggests the presence of two types of nonequivalent protons which may pertain to H_3O^+ and OH^- ions [21]. These oscillation centers are not observed in every crystal with hydrogen bonds. For example the NMR proton spectrum of NH_4SeO_4 crystals contains a single band [22]. Furthermore NMR spectra allowed determining the translation mobility of protons to be $5.1 \times 10^{-5} \text{ m}^2/(\text{V} \times \text{s})$. This is far greater than the H_3O^+ ion mobility in ice crystals which is $7.5 \times 10^{-6} \text{ m}^2/(\text{V} \times \text{s})$ according to N. Maeno [23]. This suggests a high probability of the formation of proton oscillation centers in the test crystals. The NMR proton band halfwidth temper-

ature dependence contained 0.054 and 0.31 eV activation energies which are close to the 0.066 and 0.365 eV bands in the IR spectra. This is an additional confirmation that crystals with hydrogen bonds contain oscillation centers formed by protons and proton defects.

4. Conclusion

The conclusions made from IR spectroscopic studies are in a good agreement with TSDC and NMR spectra. Thus IR spectra can be used as an independent tool for determining the directions of optical axes and the types of oscillation centers in most crystalline materials. Wide band gap crystals with hydrogen bonds grown in H_2O and D_2O solutions proved to contain protons in the mobile phase. The crystals contain absorption centers related to H^+ ions and OH^- , H_3O^+ , H_2O , Si–O–H and I–O–H groups and semi-heavy water molecules HDO. Their activation energies and directions of main optical axes were determined. The types of oscillation centers were clarified for a number of spectral bands. The experimental results confirm the possibility of using IR spectra for determining the type of oscillation centers and the presence of lattice anisotropy in test crystals.

These IR spectral studies solve a fundamental research and technical problem of determining the types of oscillation centers in the design of optical and laser crystals and the development of reliable processes and diagnostic methods for the production and operation of crystals, e.g. for laser navigation of ships, laser location, security alarms, laser welding and cutting of metals, opto- and microelectronics etc.

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