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## Infrared Spectroscopy and Tunneling of Protons in Crystals with Hydrogen Bonds

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**Abstract**—Infrared (IR) spectra of a number of crystals with proton conductivity have been investigated. The width of the band gap is determined, and most lines of the IR absorption spectra are identified. A direct proof of the existence of protons, defects  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$ , molecules of adsorbed and crystallization water in the crystals grown in ordinary and in heavy water is also carried out. The transparency of the rectangular potential barrier for protons is calculated, and the possibility of tunneling and translational diffusion of protons in wide-band-gap crystals is shown.

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### INTRODUCTION

High-temperature proton conductors are complex oxide compounds with perovskite structure  $\text{ABO}_3$  (e.g.,  $\text{LaScO}_3$ ). This group includes also zirconates of alkaline earth metals. These groups also include the electrolytes of salts, and have been investigated in sufficient detail. In particular, the proton conductivity in superprotonic phases of these salts at  $T = 460$  K is in the range of  $10^{-3}$ – $10^{-1} \Omega^{-1} \text{cm}^{-1}$  [1]. In the 20th century, dozens of works starting with those of Bjerrum, Hubmann, and Jaccard and ending with Tonkonogov [2], Petrenko and Ryzhkin [3], and others, have been devoted to the study of the proton relaxation and conductivity of hexagonal ice. Their research is based mainly on the analysis of the spectra of dielectric loss, conductivity, and thermally stimulated depolarization currents (TSDCs). More complex crystals with hydrogen bonds began to be explored recently. In particular, ice crystals have been investigated in detail in the thesis of E.A. Aziev (MISiS, 1988) and crystals of mica, talc and crystalline sulfate of copper and calcium in the thesis by V.M. Timokhin (MISiS, 1990).

In this regard, of course, the involvement of other research methods and a broader comprehensive study of the crystallographic structure and optical properties of materials to clarify the features of proton transport and tunneling effect are relevant, these being of major interest both for basic research and to provide theoretical justification and development of new nanotechnologies and methods of diagnosis of crystalline materials.

### EXPERIMENTAL TECHNIQUE

Natural crystals of phlogopite mica  $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$  and muscovite mica  $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$  with a thickness of 5–10  $\mu\text{m}$ , belonging to the monoclinic crystal system  $2/m$  (prismatic point group) and having good electrical insulating properties were studied. We also studied crystals of lithium iodate  $\alpha\text{-LiIO}_3$  grown in NPO Polyus (Moscow) by the method of open evaporation both in  $\text{H}_2\text{O}$  and in  $\text{D}_2\text{O}$ . These crystals belong to the hexagonal crystal system, the  $C_6$  point group, and have unique optical, electrical, piezoelectric, and pyroelectric properties, being widely used in laser technologies and optoelectronics. Samples of lithium iodate with a thickness of 0.5–1 mm were machined from the central part of the growth pyramid.

Transmission spectra were studied using a UV-ViS-NiRCary 5000 spectrophotometer.

The probability of direct allowed transitions does not depend on the photon energy [4]. Taking this into account, the coefficient of absorption for such transitions is expressed by the formula

$$\alpha = A(h\nu - E_g)^{1/2}, \quad h\nu > E_g,$$

where  $E_g$  is the band gap width and

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

is a coefficient that depends on the concentration and effective masses of electrons and holes. It can be seen from this equation that quantity  $\alpha^2$  linearly depends on

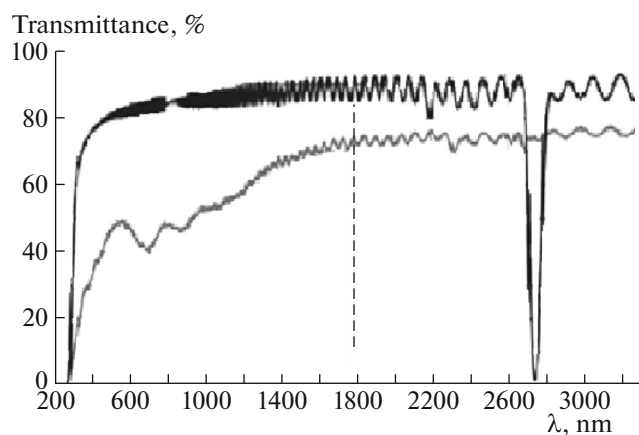


Fig. 1. IR transmittance spectrum of crystals of muscovite (lower) and phlogopite (top).

energy  $h\nu$ . The continuation of this line to the intersection with the abscissa axis allows the width of band gap  $E_g$  to be determined on the edge of self-absorption by the method of linear approximation of the transmission optical spectra. For lithium iodate, it was equal to 4.37 eV along the  $Z$  axis ( $C_6$ ) and 4.46 eV along the  $X$  axis, while for muscovite and phlogopite it was 4.31 eV (Fig. 1); i.e., the investigated crystals are wide-band-gap ones, and, for them, the probability of transition of electrons from the valence band to the conduction band at low temperatures is negligibly small.

The absorption spectra of these crystals were investigated by an IFS 66v/S infrared Fourier spectrometer (Bruker).

## EXPERIMENTAL RESULTS AND DISCUSSION

Water molecules possess strong absorption in the IR range of the spectrum [5]. Vibrations at 1595, 3654, and 3700  $\text{cm}^{-1}$  were observed in that work, and lines at

1600, 3630, and 3700  $\text{cm}^{-1}$  were revealed in the spectra of phlogopite and muscovite micas.

In the range of bending vibrations of  $\text{H}_3\text{O}^+$  in silicates and lithium iodate, an intense band is observed, its frequency being in the range of 1650  $\text{cm}^{-1}$ . In addition, there is a bending vibration of the  $\text{H}_3\text{O}^+$  ion in the range of 1120–1150  $\text{cm}^{-1}$  (Fig. 2), which agrees with results of [6]. The absorption bands 1120–1150  $\text{cm}^{-1}$ , which correspond to the activation energy of 0.14 eV, are consistent with the data for hydroxonium ( $\text{H}_3\text{O}^+$ ) obtained from TSDC spectra of silicates [7] and ice [8]. In the IR spectra of lithium iodate (Table 1) and silicates (phlogopite and muscovite, Table 2), the absorption bands at 3240–3620  $\text{cm}^{-1}$  were detected, which correspond to the activation energies of 0.41–0.44 eV [7]; these bands correspond to relaxation of  $VL$  (vacancy +  $L$ -defect) complexes, the probability of appearance of which is five times higher than that of  $VD$  ( $V$ -vacancy +  $D$ -defect) complexes, because the binding energy of paired protons is much higher than the binding energy of an empty valence bond, i.e., proton vacancy.

Single crystals of lithium iodate grown in  $\text{D}_2\text{O}$  exhibit a strong line at 1580  $\text{cm}^{-1}$  (Fig. 3), the intensity of which is two times higher than the intensity of the same line in crystals grown in  $\text{H}_2\text{O}$ . This indicates the occurrence of absorption centers associated with protons and deuterons, which is consistent with the findings of [8] on the transport of protons in H/D exchange in ice.

In [9], it is suggested that the absorption band in the range of 3400 nm is caused by the presence of hydrogen, which corresponds to the wavenumber of 2940  $\text{cm}^{-1}$ . In our case, it is observed in the spectrum of  $\alpha$ - $\text{LiIO}_3$  crystals grown in  $\text{H}_2\text{O}$  along the sixth-order  $Z$  axis ( $C_6$ ) (Fig. 2). However, in crystals grown

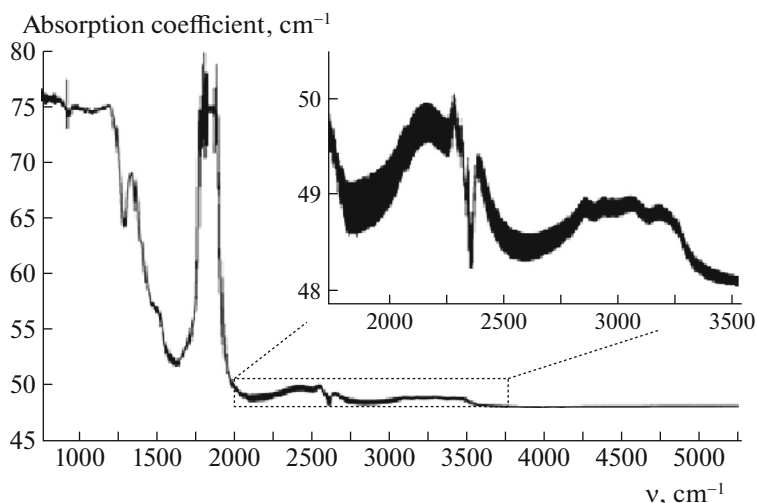


Fig. 2. IR absorption spectrum of  $\alpha$ - $\text{LiIO}_3$  crystals grown in  $\text{H}_2\text{O}$  along the  $Z$  axis.

**Table 1.** Lines of the IR absorption spectrum of  $\alpha$ -LiIO<sub>3</sub> crystals

No.	Wave number $\nu$ , cm <sup>-1</sup>	Energy according to IR spectrum, eV	Vibration type
1	550	0.07	H <sup>+</sup>
2	950	0.11	I–O–H
3	1080	0.166	I–O
4	1150	0.143	H <sub>3</sub> O <sup>+</sup> ( $\delta$ )
5	1260	0.157	H <sub>2</sub> O( $\delta$ )
6	1580	0.20	H <sub>2</sub> O, D <sub>2</sub> O
7	1650	0.22	H <sub>2</sub> O( $\delta$ ), H <sub>3</sub> O <sup>+</sup> ( $\delta$ )
8	2200	0.26	H <sub>2</sub> O( $\delta$ ) (crystallographic)
9	2940	0.365	H <sup>+</sup>
10	3240	0.40	OH <sup>-</sup> ( $\nu$ ), $\nu$ L

in D<sub>2</sub>O (Fig. 3) and along the  $X$  axis (Fig. 4), this band is absent because of the anisotropy and translational diffusion of protons only along the  $C_6$  axis. The band

at 3240 cm<sup>-1</sup> can be attributed to vibrations of OH<sup>-</sup>( $\nu$ ) groups and H<sub>2</sub>O molecules (Table 1). Hopping transitions of protons along hydrogen bonds facilitate the formation of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ionization defects. To determine the forms of occurrence of water in minerals from IR spectra, the ranges of frequencies related to the absorption of OH-groups were investigated. The presence of crystalline hydrate water in the investigated crystal is confirmed by the presence in the spectrum of the absorption band of H<sub>2</sub>O ( $\delta$ ).

All examined crystals contain spectral lines with close wavenumbers; thus, the spectra of silicates contain two intense bands with their wavelengths at 10 and 20  $\mu$ m (with the wavenumbers of 833–1250 and 540 cm<sup>-1</sup>) [4, 5, 7, 10], which are characteristic of SiO<sub>4</sub><sup>4-</sup> groups. For muscovite and phlogopite crystals, Si–O bonds are the most significant in the structure. These crystals exhibit an intense band at around 1000 cm<sup>-1</sup> (about 10  $\mu$ m). The replacement of Al ions with Mg ions causes a shift of this band to 1030 cm<sup>-1</sup> in muscovite and to 1050 cm<sup>-1</sup> in phlogopite (Fig. 5). Lithium iodate single crystals exhibit a rather intense band at 1080 cm<sup>-1</sup>, which is observed for crystals that were grown both in H<sub>2</sub>O and in D<sub>2</sub>O. This indicates that strong I–O valence bonds do indeed occur [10].

**Table 2.** Lines of the IR absorption spectrum of crystals of muscovite and phlogopite

No.	Muscovite		Phlogopite		Vibration type
	wavenumber $\nu$ , cm <sup>-1</sup>	energy according to IR spectrum, eV	wave number $\nu$ , cm <sup>-1</sup>	energy according to IR spectrum, eV	
1	430	0.06	430	0.06	Si–O
2	540	0.07	540	0.07	Si–O–H, H <sup>+</sup>
3	610	0.08	640	0.08	Si–O–H
4	750	0.09	730	0.09	OH <sup>-</sup> ( $\delta$ )
5	950	0.11	950	0.11	Si–O–H
6	1030	0.12	1050	0.12	Si–O
7	1120	0.14	1120	0.14	H <sub>3</sub> O <sup>+</sup> ( $\delta$ )
8	1600	0.20	1600	0.20	H <sub>2</sub> O, H <sup>+</sup>
9	1680	0.21	1680	0.22	H <sub>3</sub> O <sup>+</sup> ( $\delta$ )
10	1800	0.22	1800	0.23	H <sub>2</sub> O( $\delta$ ) (adsorption)
11	2020	0.25	2020	0.25	H <sub>3</sub> O <sup>+</sup>
12			3050	0.36	H <sup>+</sup>
13			3240	0.41	OH <sup>-</sup> ( $\nu$ ), $\nu$ L
14	3620	0.42	3650	0.43	H <sub>2</sub> O
15	3760	0.47	3720	0.46	H <sub>2</sub> O (interpackage), $\nu$ L

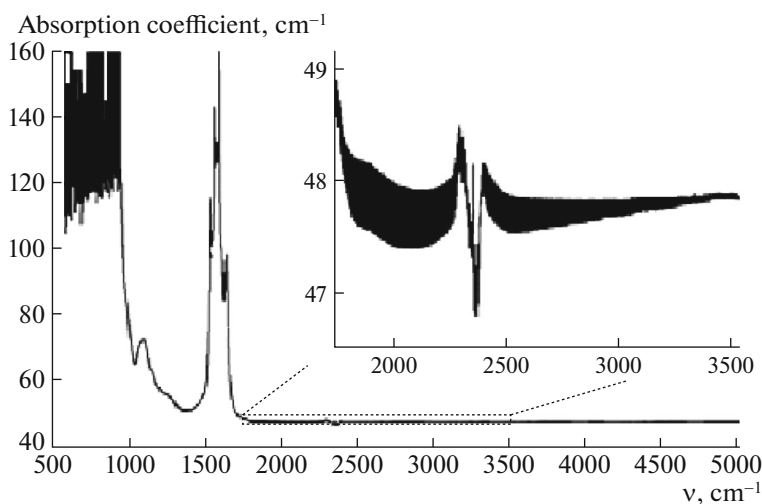


Fig. 3. IR absorption spectrum of  $\alpha$ -LiIO<sub>3</sub> crystals grown in D<sub>2</sub>O along the Z axis.

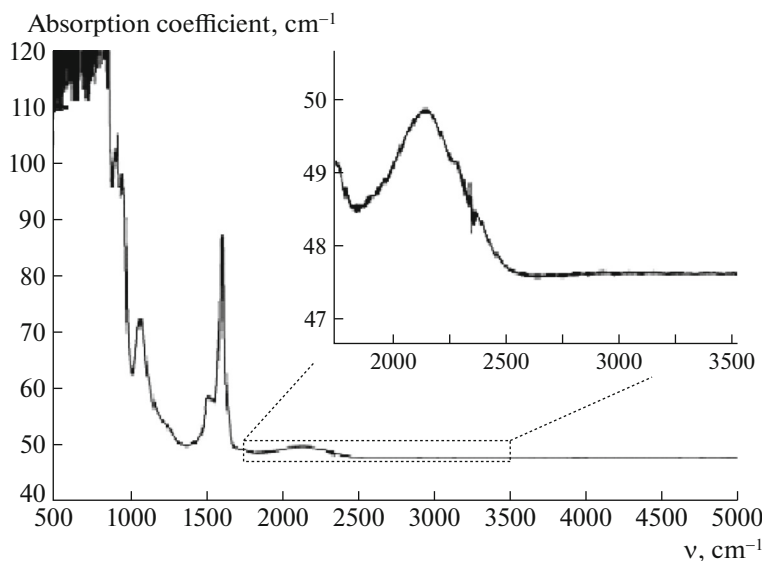


Fig. 4. IR absorption spectrum of  $\alpha$ -LiIO<sub>3</sub> crystals grown in H<sub>2</sub>O along the X axis.

The tunneling of  $\text{HSiO}_4^{3-}$  ions is unlikely and is hardly possible; most probably, rearrangement of protons takes place here. As a result of vibrations of neighboring  $\text{SiO}_4^{4-}$  ions, the potential barrier may be narrowed by tenths of a nanometer, which considerably eases the tunnel transition of a proton between these ions. It is, therefore, quite possible that the bands 950 and 610  $\text{cm}^{-1}$  in the IR spectra of phlogopite and muscovite correspond not to the Si–O vibrations in the  $[\text{SiO}_4]^{4-}$  tetrahedron, but rather to the Si–O–H vibrations in the protonated  $\text{HSiO}_4^{3-}$  anion, which is consistent with conclusions of [11]. Similarly, one can

suggest the occurrence of vibrations of the I–O–H bond in the  $\text{HIO}_3^-$  anion at a frequency of 950  $\text{cm}^{-1}$ .

The occurrence of tunneling transitions with the formation of the protonated  $\text{HSiO}_4^{3-}$  ions (silicates) and  $\text{HIO}_3^-$  ions (iodates) is confirmed by the good coincidence of the activation energies of the maxima of the TSDC spectra [7] and IR spectra (Table 3). Despite the different physical natures of these processes, the transport and translational diffusion of protons and  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions explain the characteristic features of both TSDC spectra and IR absorption spectra of silicates and iodates.

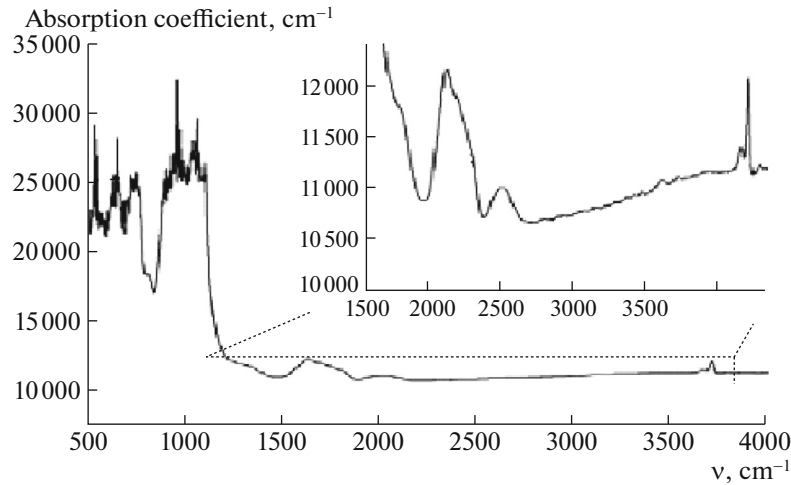


Fig. 5. IR absorption spectrum of phlogopite crystals.

To improve the optical quality of crystals, the iodic acid  $\text{HIO}_3$  is introduced into the solution, the concentration of which can reach 10%. In order to obtain crystals of high quality, the solution with a pH of 1.5 is sufficient. The iodic acid  $\text{HIO}_3$  is a good proton donor; therefore, even at a minimal solution acidity, hydrogen ions are actively incorporated into the growing crystal.

In the NMR spectrum of protons obtained on an AVANCE STM 300 NMR spectrometer (Bruker), a double line was revealed in an  $\alpha\text{-LiIO}_3$  deuterated crystal, indicating the presence of two types of non-equivalent protons, which may belong to  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions [12]. In addition, the translational mobility of protons was determined, which is equal to  $5.1 \times 10^{-5} \text{ m}^2/\text{V s}$ . This is higher than the mobility of  $\text{H}_3\text{O}^+$  ions in ice crystals, which, according to N. Maeno, is  $7.5 \times 10^{-6} \text{ m}^2/\text{V s}$  [13]. This confirms the reality of the

existence of vibrational centers in the IR spectra associated with protons and proton defects.

### A QUANTUM-MECHANICAL APPROACH TO THE EFFECT OF TUNNELING

Upon passage of a freely moving proton to an oxygen ion to form an  $\text{HSiO}_4^{3-}$  protonated anion (in silicates) or  $\text{HIO}_3$  protonated anion (in iodates), this proton with the momentum  $p = k\hbar$  has the kinetic energy

$$E_k = \frac{p^2}{2m_p} = \frac{(k\hbar)^2}{2m_p}. \tag{1}$$

The wavenumber of a proton,  $k = 2\pi/\lambda$ , can acquire an arbitrary, but discrete, value  $k = \pm(\pi/d)n$ ,

Table 3. Comparative data of TSDC spectra and IR spectra

No. max	TSDC Spectrum of phlogopite	IR spectrum of phlogopite		TSDC Spectrum of lithium iodate	IR spectrum of lithium iodate		Relaxers
	$U_a, \text{eV}$	$\nu, \text{cm}^{-1}$	$U_a, \text{eV}$	$U_a, \text{eV}$	$\nu, \text{cm}^{-1}$	$U_a, \text{eV}$	
1	$0.06 \pm 0.01$	430	0.06	$0.07 \pm 0.02$	550	0.07	Si–O–H, $\text{H}^+$
2	$0.15 \pm 0.01$	1120	0.14	$0.15 \pm 0.03$	1150	0.143	$\text{H}_3\text{O}^+$
3	$0.23 \pm 0.02$	1800	0.22	$0.32 \pm 0.04$	2200	0.26	$\text{H}_2\text{O}$ (crystalline)
4	$0.31 \pm 0.03$	3050	0.36	$0.35 \pm 0.04$	2940	0.36	$\text{H}^+$
5	$0.41 \pm 0.04$	3650	0.43	$0.42 \pm 0.04$	3210	0.40	$\text{OH}^-$
6	$0.49 \pm 0.05$	3720	0.46	$0.48 \pm 0.05$	3240	0.42	$V_L$

where  $n = 1, 2, 3, \dots$ . In this case, the proton should have a certain energy; i.e., its energy must be quantized:

$$E_k = \frac{\hbar^2}{2m_p} \left(\frac{\pi}{d}\right)^2 n^2. \quad (2)$$

It follows from formula (2) that the energy of the proton in a state with  $n = 2$  at the width of the potential barrier of  $d = 0.12$  nm is equal to 0.057 eV. Let us use the solution of the Schrödinger equation for a rectangular barrier of a finite value for the nonrelativistic case. At low temperatures, the kinetic energy of nuclei at the crystal lattice sites is close to zero. In this case, the motion of a proton can be considered in the form of the de Broglie plane wave  $f = A \exp(ikx)$ . In the one-dimensional case, for a rectangular barrier of a finite value, the Schrödinger equation describing the motion of a proton in the periodic field of fixed nuclei allows one to determine the coefficient of transparency of a rectangular barrier [14]:

$$D = \frac{k^2 \chi^2}{(k^2 + \chi^2)^2 \left(\frac{1}{2} \sinh \chi d\right)^2 + k^2 \chi^2}, \quad (3)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} = \frac{2\pi}{\lambda}, \quad \chi = \frac{\sqrt{2m(U_0 - E)}}{\hbar}. \quad (4)$$

After transformations, taking into account that the hyperbolic sine can be expanded in terms of the exponential  $\sinh^2 \chi d = \frac{1}{4} e^{2\chi d}$  with a good accuracy, we obtain

$$D = \left( \frac{1}{16} \left( \frac{k}{\chi} + \frac{\chi}{k} \right)^2 e^{2\chi d} + 1 \right)^{-1}. \quad (5)$$

After substituting (4) into (5), we obtain for the coefficient of transparency

$$D = \left[ \frac{1}{16} \left( \sqrt{\left(\frac{U_0}{E} - 1\right)^{-1}} + \sqrt{\left(\frac{U_0}{E} - 1\right)} \right)^2 e^{2\chi d} + 1 \right]^{-1}. \quad (6)$$

Here, for a proton with energy  $E = 0.057$  eV, barrier height  $U_0 = 0.07$  eV, determined for lithium iodate from the TSDC spectra [7],  $d = 0.12$  nm, and  $m_p = 1.6727 \times 10^{-27}$  kg, we find that  $\chi = 2.501 \times 10^{10}$ ; then,  $e^{2\chi d} = 403.2$  and  $D = 0.0075$ . For the height of the barrier of 0.06 eV (sulfates and silicates), we obtain  $\chi = 1.20 \times 10^{10}$ ,  $e^{2\chi d} = 17.85$ , and  $D = 0.0408$ . For the width of the barrier of  $d = 0.15$  nm at  $U_0 = 0.07$  eV, the transparency of the barrier is  $D = 0.00042$ ; i.e., the transparency of the barrier is strongly dependent on its width and height. Nevertheless, it is a quite discernible value if we take into account a rather high concentra-

tion of proton-containing  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  defects, water molecules  $\text{H}_2\text{O}$ , and protons, which is on the order of  $10^{20}$ – $10^{21}$   $\text{m}^{-3}$ . However, it is necessary to bear in mind that the movement of protons, particularly their tunneling, is closely related to the own, even if they are zero, vibrations of the ions of the “matrix,” which will obviously affect the value of the barrier transparency.

From (4), the de Broglie wavelength of a proton that has passed through the barrier must be

$$\lambda = \frac{2\pi\hbar}{\sqrt{2mE}} = \frac{2 \times 3.14 \times 1.055 \times 10^{-34}}{\sqrt{2 \times 1.673 \times 10^{-27} \times 0.057 \times 1.6 \times 10^{-19}}} = 0.12 \text{ nm}.$$

On the other hand, the de Broglie wavelength can be expressed in the form

$$\lambda = \frac{h}{m_p v} = \frac{h}{\sqrt{2m_p E_k}} = \frac{h}{\sqrt{2m_p \frac{\pi^2 \hbar^2}{2m_p d^2} n^2}} = \frac{2d}{n}.$$

The solution of the Schrödinger equation has a physical meaning not at arbitrary energy values, but only when the width of the potential barrier is on the order of the de Broglie wavelength. That is, the width of the barrier for  $n = 2$  must be equal to  $d = n\lambda/2 = 0.12$  nm, which agrees well with the spacing between the oxygen ions of 0.1215 nm in the  $\text{SiO}_4^{4-}$  tetrahedron, between the oxygen ion in  $\text{SiO}_4^{4-}$  and water molecule of 0.135 nm, and between 0.14-nm tetrahedra in silicates. In addition, the proton falling on the electronic shell of the oxygen atom forms the  $\text{OH}^-$  groups and reduces its size from  $r(\text{O}_2^-) = 0.14$  nm to  $r(\text{OH}^-) = 0.137$  nm.

A barrier of a parabolic shape can be approximated by a set of barriers of a rectangular shape, and the transparency coefficient can be expressed by the formula [14]

$$D = D_0 \exp \left( -\frac{2}{\hbar} \sqrt{2m} \int_{x_1}^{x_2} \sqrt{(U(x) - E)} dx \right).$$

However, here, the dependence of the shape of the potential barrier is more complex; for example,

$$U(x) = \lambda_0 (x^2 - d^2)^2,$$

where  $\lambda_0 = \frac{m\omega^2}{8d^2}$  is a constant parameter and  $d$  is the barrier width. In this case, with increasing proton energy, it occurs closer to the top, where the width of the barrier is smaller, leading to a significant increase in the transparency of the barrier. Consequently, a rectangular barrier gives the lower limit value of the transparency.

## CONCLUSIONS

Investigations of the IR spectra allowed us to determine the width of the forbidden zone and to identify spectra and confirmed the existence of the proton-ion mechanism of dielectric relaxation and electrical conductivity. This allowed us to study translational diffusion and tunneling of protons in a series of wide-bandgap crystals. In considering the mechanism of translational diffusion of protons, it is necessary to take into account that, at low temperatures, the diffusion process takes place precisely in  $\text{HIO}_3$  or  $\text{HSiO}_4^{3-}$  protonated anions, but not in  $\text{IO}_3^-$  or  $\text{SiO}_4^{4-}$  and in layers containing water molecules and defects and complexes associated with them. In the relaxation process of protonated anions, the passage of a proton from one oxygen ion to another within and between anions occurs both through thermoactivation transitions and through tunneling. The tunnel transition of the proton through hydrogen bonds in the investigated crystals is in good agreement with the conclusions of papers [8, 15, 16], where various aspects of the tunneling and dynamics of protons in a network of hydrogen bonds of ice at low temperatures are considered.

In the process of research, a number of technologies and methods of diagnostics were developed having both basic and applied importance, for example:

—the physical bases of the technology of obtaining and diagnostics of proton conductors and semiconductors of  $n$ - and  $p$ -types [17]; and

—a method of the temperature diagnostics of the appearance of the tunnel effect in dielectrics and electrical-insulating materials [18] and other methods and techniques.

Thus, in the present work, one of the fundamental practical problems of identification and revision of the IR absorption spectra of a number of crystals with hydrogen bonds is solved and the probability of tunneling of a proton through a potential barrier is shown,

which is of great importance in the development of new electrical-insulating and laser materials.

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