Phonon interaction with OH complexes and products of their radiative decomposition in LiF crystals

N A Ivanov¹, L I Bryukvina² and D S Glazunov²
¹Irkutsk National Research Technical University, 83 Lermontov Str., Irkutsk, 664074, Russia
²Irkutsk Division of Institute of Laser Physics SB RAS, 130a Lermontov Str., Irkutsk 664033, Russia

E-mail: ivnik@istu.edu

Abstract. This article deal with study of the vibration spectra of hydroxyl ions and radiation-induced molecular complexes with H-bond in LiF:OH crystals. The IR spectra of the crystals were measured at 300, 80 and 10 K temperatures. The low-temperature behavior of the bands in the 3570–3700 cm⁻¹ region indicates that corresponding vibration energy levels are not associated with phonons. It is shown that the broadening of 3730 cm⁻¹ band with increasing temperature due to phonon interactions, namely, resonant scattering of phonons by vibrations of free hydroxyl. The frequencies of the transverse and longitudinal optical modes of phonons take part in the Fermi resonance splitting of the absorption band of molecular complexes with a strong hydrogen bond in the region of 1800–2300 cm⁻¹ in LiF:Mg, OH crystals. It is determined that the narrow bands in the 3400–3700 cm⁻¹ region can appear in the spectrum of LiF:OH without magnesium ions. It was concluded that narrow bands in the 3400–3700 cm⁻¹ region in γ-irradiated to a dose of 2.58×10⁴ C/kg at T=525 K LiF:OH crystals are caused by an associates of two or more hydroxyl ions or by a complexes with a hydrogen bond OH…O or OH…F.

1. Introduction

The lithium fluoride crystals (LiF) are widely used in dosimetry, in laser physics, as ideal models for studying point defects formed in them under the action of radiation, including high-intensity femtosecond laser pulses [1-7]. The use of LiF crystals is based on the luminescence of radiation-created color centers. The properties of radiation-induced luminescent color centers (CCs) are determined by the impurities of OH⁻ ions and cations deliberately introduced or uncontrollably entered into the crystal during growth [8-15].

It is known that there are several forms of occurrence of hydroxyl ions in LiF, for example: in the form of “free” ions with a band at ν=3730 cm⁻¹ (2.68 μm) and in the form of complexes Mg²⁺–OH⁻ with bands in the 3700–3521 cm⁻¹ (2.72-2.84 μm) [14, 15]. To preserve the electroneutrality of the crystal as a whole, the complexes include a cation vacancy. The main peak of 3571 cm⁻¹ (2.8 μm), in the author's opinion [14, 15], is associated with the most stable form of the magnesium–hydroxyl complex in LiF. However, in [16] it is attributed to the dipoles Mn³⁺–OH⁻ in NaF crystals, in [17] to the Ca(OH)₂ complexes in KCl crystals.
However, not all researchers agree with the interpretation of the vibration bands of hydroxyl ions in the 3570-3700 cm\(^{-1}\) region as belonging to the Me\(^{2+}\)-OH\(^{-}\) complexes. In the IR spectra of LiF:OH crystals grown with an impurity of lithium sulfate [18], a group of bands in the 3573–3728 cm\(^{-1}\) region was observed, which in the authors' opinion [18] are due to OH\(^{-}\)-V\(_{c}\)\(^{-}\) complexes at adjacent lattice sites along the (100). The authors of [18] attributed the most intense band at \(\nu=3573\) cm\(^{-1}\) to the OH\(^{-}\)-V\(_{a}\)\(^{+}\) complex. To clarify the nature of the bands, we have studied the vibration spectrum of hydroxyl in the 3500-3750 cm\(^{-1}\) region.

2. The experimental part

LiF:OH crystals were grown in air by the Kyropoulos method without additional doping with cation impurities, but with the enrichment by hydroxyl ions [19]. Irradiation of the crystals was carried out by gamma radiation from a Co\(^{60}\) source at temperatures from room temperature to 550 K. The IR spectra of the crystals were measured with a Bruker Vertex 70 Fourier spectrometer at 300, 80 and 10 K temperatures.

The content of metallic impurities in the crystal was determined by the method of emission spectral analysis.

3. Experimental results and discussion

3.1. Comparison of IR spectra of LiF:OH crystals measured at 300, 80 and 10 K temperatures

IR spectra of LiF crystals grown in air with enrichment by hydroxyl ions, but without the addition of cation impurities measured at 300 and 80 K are shown in figure 1.

![Figure 1. IR transmittance spectra of a LiF:OH crystal measured at 300 K (a) and 80 K (b). The crystal thickness is 6.28 mm.](image)

From the analysis of IR spectra it follows that the intensity of the 3730 cm\(^{-1}\) band increased by 1.21 times and the half-width decreased by a factor of 2 at 80 K compared to 300 K. The intensity of the bands in the 3570-3700 cm\(^{-1}\) region decreased slightly and the half-width did not change. A shift of the bands to the high-frequency region from 5 to 10 cm\(^{-1}\) was observed when the crystal was cooled to 80 K. For example, the 3730 cm\(^{-1}\) band shifted to 3740 cm\(^{-1}\) and the band 3578 cm\(^{-1}\) to 3583 cm\(^{-1}\).
Measurement of the IR spectra at 10 K showed that the intensity of the 3730 cm⁻¹ band increased 1.8 times, and the half-width decreased by a factor of 2.2 (figure 2). The intensity of the bands in the 3570-3700 cm⁻¹ region was decreased slightly, and the half-width was remained practically unchanged.

![IR transmittance spectra of a LiF:OH crystal measured at 300 K (a) and 10 K (b). The crystal thickness is 1.76 mm.](image)

The IR spectra (figure 1 and 2) present a set of lines, which in [15] is assigned to hydroxyl ions perturbed by divalent magnesium and a cation vacancy. However, an impurity of magnesium was not introduced into the melt of lithium fluoride. According to the results of spectral analysis, silicon, magnesium, aluminum and titanium impurities were present in the crystal of ~8×10⁻⁵, ~8×10⁻³, ~10⁻³, and ~4×10⁻⁴, respectively. A similar content of cation impurities is also observed in crystals whose IR spectra contain only the free hydroxyl band at 3730 cm⁻¹. One could question the influence of magnesium on hydroxyl ions, and the formation of magnesium–hydroxyl complexes with bands in the 3570–3700 cm⁻¹ region, because the magnesium concentration in the crystal is comparable to the concentration of silicon and aluminum. In addition, Mg²⁺ ions enter the crystal in the form of Mg²⁺-O²⁻ complexes, due to which the concentration of Mg²⁺-OH⁻,V⁺⁻ complexes (V⁺⁻ – cation vacancy) decreases. However, we believe that the bands in the 3570-3700 cm⁻¹ region belong to complexes with different magnesium-hydroxyl-vacancy structures. This view is supported by the fact that the crystal was grown with the enrichment of the melt with hydroxyl ions and, therefore, hydroxyl ions, rather than oxygen, were embedded in the crystal lattice. Silicon and aluminum ions can form metal-hydroxyl complexes, but may not appear in IR spectra. These facts is confirmed, for example, by the authors of [20] who believe that the spectral lines caused by Me³⁺-OH⁻ complexes can be broadened and shifted and, therefore, are not detectable. If silicon, aluminum and titanium are not detected in the IR spectra of the complexes with hydroxyl, the magnesium ions that enter the crystal in an uncontrolled manner can appear in the IR spectra as magnesium-hydroxyl complexes.

Thus, we believe that the bands in the 3570-3700 cm⁻¹ region may belong to the complexes Mg²⁺-OH⁻,V⁺⁻. This assumption is confirmed by the low-temperature behavior of the bands. Their half-width is practically unchanged, and the intensity even slightly decreases with decreasing temperature to 80 and 10 K. It can be noted that, due to the absence of a strong temperature dependence (figures 1 and 2), the corresponding vibration energy levels are not associated with phonons. These low-energy bands are probably due to hydroxyl ions, which can be associated with impurity centers and possibly with aggregates of two or more hydroxyl ions. All these defects must be located closely with each other to create local areas with defects compressed relative to each other. In this case, according to the authors of [21], the hydroxyl impurities trapped at divalent impurity sites do not scatter the phonons resonantly, since
the presence of Mg\(^{2+}\) in the complexes suppresses the resonance scattering mechanism. The resonance mechanism requires a high lattice symmetry, which decreases in the case of complexes. The weak interaction with phonons of the lattice explains the absence of a temperature dependence of the half-width and the intensity of the bands in the region of 3570-3700 cm\(^{-1}\).

The low-temperature behavior of the free hydroxyl band at 3730 cm\(^{-1}\) demonstrates the reverse trend. The narrowing of the band as the temperature is lowered and the broadening with increasing temperature can be due to phonon interactions, namely, resonant scattering of phonons by vibrations of free hydroxyl. A strong phonon coupling of the energy levels of the free hydroxyl ions with the 3730 cm\(^{-1}\) band is probably due to the fact that the hydroxyl ions are free in the lattice and can undergo large amplitude oscillations or tunneling motions.

3.2. IR spectra of \(\gamma\)-irradiated LiF:Mg, OH crystals and the influence of phonon vibrations on them

The significant bond between phonon vibrations with vibrations of molecular complexes in \(\gamma\)-irradiated crystals demonstrates the Fermi resonance splitting of the absorption band of molecular complexes with a strong hydrogen bond in the region of 1800-2300 cm\(^{-1}\) [6]. In [6], the characteristic features of the Fermi resonance splitting of the 1800-2300 cm\(^{-1}\) band in the 2080 cm\(^{-1}\) region (figure 3) were explained by the assumption that the presence of a Fermi resonance \((\nu_s = 2\delta)\) leads to a peak, hole and gap in the \(\nu = 2080\) cm\(^{-1}\) region.

![Figure 3](image-url)

**Figure 3.** The splitting of a band in the region of 1800-2300 cm\(^{-1}\) due to Fermi resonance: 1 – IR transmission spectrum of LiF:OH, Mg (crystal index G7) irradiated by neutrons of 8.7\(\times10^{15}\) n/cm\(^2\) at \(T = 40\) K (a band non-perturbed by Fermi resonance), 2 – IR transmission spectrum of annealed LiF:OH (crystal index 194) (“Evans hole”).

It was noted that the condition \(\nu_s = 2\delta\) is satisfied not precisely: 2080 cm\(^{-1}\)\(\neq 2\times1115\) cm\(^{-1}\) (\(\delta\)-bending vibration). A more thorough analysis carried out by us shows the effect of crystal lattice phonons on the Fermi resonance splitting of the 1800–2300 cm\(^{-1}\) band. The frequencies of the transverse and longitudinal optical modes of phonons were experimentally determined in [22] at \(\nu = 312.5\) and 650 cm\(^{-1}\), respectively. Believing that the bending vibration in the case of the LiF:Mg, OH crystal is 1115 cm\(^{-1}\) [8], we can write the Fermi resonance equation: 2080 cm\(^{-1}\)\(= 1115\) cm\(^{-1}\)\(+312.5\) cm\(^{-1}\)\(+650\) cm\(^{-1}\) = 2077.5 cm\(^{-1}\). Such an equation, in contrast to the equation \(\nu_s = 2\delta\), is completely satisfactory for the Fermi resonance.

3.3. The vibrations of hydroxyl ions in the 3400-3800 cm\(^{-1}\) region in \(\gamma\)-irradiated LiF:OH crystals irradiated at \(T = 525\) K

In the IR spectrum of the unirradiated LiF:OH crystal, there was one band at \(\nu = 3730\) cm\(^{-1}\), which belongs to the hydroxyl ions in the free state in the lattice. Absorption bands corresponding to metal–hydroxyl complexes were not observed. When such a crystal was irradiated to a dose of 2.58\(\times10^7\) C/kg at \(T = 525\) K,
a broad band appeared in the IR spectrum in the region of 3000-3800 cm\(^{-1}\), which had a number of new
peaks (figure 4).

Absorption bands were absent in the 1800-2300 cm\(^{-1}\) region. Absorption bands at \(\nu=3440, 3530, 3688\)
cm\(^{-1}\) in the unirradiated initially grown crystal are absent. In this crystal there are U-centers at \(\nu=1015\) cm\(^{-1}\),
which indicates that a partial radiation damage of hydroxyl ions has occurred. Because of this, complexes
with the H-bond OH…O formed, which according to the Nakamoto diagrams [23], can absorb in the
region of 2800–3800 cm\(^{-1}\). The IR absorption in this region of defects such as O\(_n\)H\(_n\) or water molecules in
irradiated alkali-halide crystals was discussed in [24, 25].

![Figure 4. IR transmittance spectrum of a LiF:OH crystal irradiated at 525 K to a dose of 2.58\times10^4 C/kg.](image)

The maxima that stand out on the background of a wide band of 2800-3800 cm\(^{-1}\) can correspond either
to the association of hydroxyl ions to form a complex, or to complexes with a weak hydrogen bond of the
type OH…O or OH…F. Thus, we see that narrow bands in the 3400-3700 cm\(^{-1}\) region can appear in the
spectrum of LiF:OH without magnesium ions. It can be concluded that they are an associate of two or
more hydroxyl ions, or are a complexes with a hydrogen bond OH…O or OH…F.

This experiment confirms the conclusion that in an unirradiated LiF crystal, complexes of several
hydroxyl ions located in adjacent sites can have the absorption in the 3500-3700 cm\(^{-1}\) region. For such an
arrangement, it is not necessary to have a magnesium ion in the complex. However, to allow several
hydroxyl ions to be located in the neighborhood (their diameter is 2.72 Å, which is larger than the
diameter of the fluorine ion, which is equal to 2.38 Å [14]) cation and anion vacancies at neighboring sites
are needed. Thus, the created complex has a structure different from the LiF lattice.

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