OH⁻ absorption spectra of pure lithium niobate crystals

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Abstract. The OH⁻ absorption spectra of congruent pure and nearly stoichiometric lithium niobate crystals have been investigated. Experimental results show that each absorption band consists of three components. The OH⁻ absorption peaks were considered to relate to the stretching vibration of protons located at 336 pm O–O bonds in oxygen triangles nearest to the Li site. The 3466 cm^{-1} absorption peak corresponds to protons directly substituting for Li$^+$ ions; the 3481 and 3489 cm^{-1} peaks are suggested to be associated with protons occupying intrinsic V_{Li}^- defects near Nb_{Li}^{5+} and two different ion environments cause these two absorption peaks.

1. Introduction

Hydrogen is present in nearly all ABO$_3$ compounds; it forms an OH⁻ impurity complex and has an influence on the chemical and physical properties and applications. In LiNbO$_3$, hydrogen has also been found in the form of OH⁻ molecular ions and its role has been extensively studied because of the technological relevance of this crystal, for example, laser-induced optical damage, photorefractive holographic thermal fixing and optical waveguides. On the other hand, because the OH⁻ stretching vibration is sensitive to the change of the environment around the ion, the OH⁻ absorption spectra can be used as a probe for impurities.

The infrared absorption band associated with the OH⁻ stretching vibration in LiNbO$_3$ was first reported by Smith *et al* [1] in 1968. From then on, much work on this subject has been done. For basic understanding of the OH⁻ absorption spectra in LiNbO$_3$, one can see the review papers published by Kovacs and Foldvari [2]. Schirmer *et al* [3] and Cabrera *et al* [4]. As is the case with most properties of LiNbO$_3$, many aspects related to OH⁻ absorption spectra, such as the site occupation of protons, the components of OH⁻ absorption bands and its relationship with the intrinsic defects, are only partly understood.

Recently, Kong *et al* [5] and Engelsberg *et al* [6] have reported that the 'rigid' protons in congruent pure and proton-exchanged LiNbO$_3$ crystals substitute Li$^+$ ions and located at the longest O–O bonds (336 pm in length) in oxygen triangles nearest to the Li site. These results give us great help in understanding the nature of the OH⁻ absorption band. The objective of this paper is to measure the OH⁻ absorption spectra of congruent pure and nearly stoichiometric LiNbO$_3$ crystals, decompose their components and established OH⁻ stretching vibration models for pure LiNbO$_3$ crystals.

2. Experimental procedure

The pure LiNbO$_3$ crystals were grown in air by a balance-controlled Czochralski method along the *c*-axis. One is a congruent pure crystal (sample A) with the composition of

Li/Nb = 48.45/51.55, and the other is a nearly stoichiometric crystal (sample B) obtained by congruent melt composition doped with 6.0 wt.% K_2O. It is reported by Malovichko *et al* [7] that crystals grown in this melt composition are near stoichiometry and K_2O does not enter the crystal lattice. Our other experimental results show the composition of the $LiNbO_3:K_2O$ crystal used in this study is Li/Nb = 49.6/50.4.

The as-grown crystals were cut into about 1 mm plates along the *y*-faces and polished to optical grade. The OH^- absorption spectra were measured by a Nicolet-70l FT–IR spectrometer with the incident light along the *y*-axis. In order to decompose the OH^- absorption bands, a second derivative treatment d^2T/dw^2 (*T*, transmittance; *w*, wavenumber) was employed.

3. Results

Figure 1 shows the OH^- absorption bands of congruent pure and nearly stoichiometric $LiNbO_3$ crystals. From this figure, it is seen that the OH^- absorption bands of these crystals consist of several components and the band shapes are very different. For the congruent pure crystal, the absorption peak appears at about 3481 cm^{-1} and the higher-wavenumbered components have higher intensities. However, the absorption peak appears at about 3466 cm^{-1} for the nearly stoichiometric crystal and the lowest-wavenumbered component has the highest intensity.
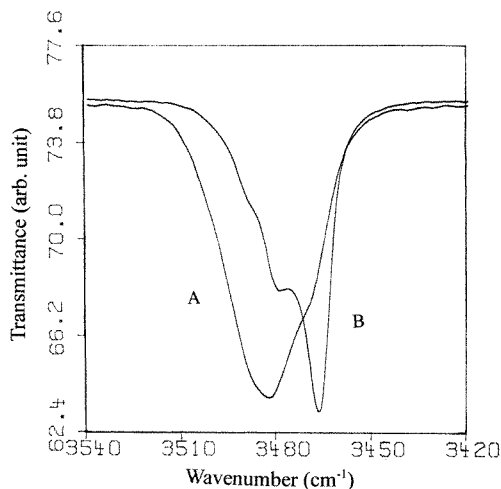

Figure 1. OH^- absorption spectra of $LiNbO_3$: A, congruent pure; B, near stoichiometry.

Figure 2 shows the OH^- absorption spectra after a second derivative treatment. From this figure, we can find that these absorption bands all consist of three peaks. The locations of all the OH^- absorption peaks are collected in table 1. It is seen from this table that congruent pure and nearly stoichiometric crystals have same components within the experimental deviation, which are about 3466, 3481 and 3489 cm^{-1}.

4. Discussion

How many components constitute the OH^- absorption bands of pure $LiNbO_3$ crystals is a problem discussed by many researchers for a long time. Two-peak, three-peak, four-peak and
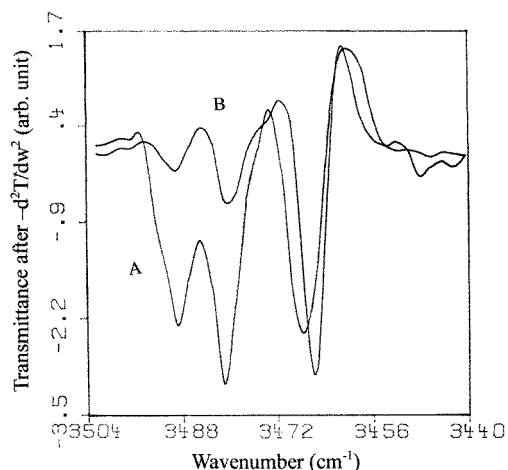
Figure 2. OH$^-$ absorption spectra of LiNbO$_3$ after the second derivative treatment ($-\mathrm{d}^2 T/\mathrm{d}w^2$): A, congruent pure; B, near stoichiometry.

Table 1. The locations of OH$^-$ absorption bands in pure LiNbO$_3$ crystals.

Sample LiNbO$_3$	OH$^-$ band (cm^{-1})	OH$^-$ peaks after second derivative treatment (cm^{-1})		
Congruent pure	3481.1	3466.7	3481.1	3488.7
Near stoichiometry	3465.6	3465.6	3481.0	3488.7

five-peak models have also been proposed [8–11]. Our experimental results strongly support the three-peak model. In decomposing the absorption bands we employed the second derivative method. A component will have a zero point in its first derivation and a peak in the second derivation. In this way, an absorption bands can be decomposed. Some researchers [11] have used Gaussian and Lorentzian functions to fit the absorption bands. In this method one can obtain best fitting results, but it is apparent that more functions can give a more satisfying fitting result and a true absorption peak is not strictly a Gaussian and Lorentzian function because of many crystal defects.

Grone and Kapphan [12] have reported that in the strictly stoichiometric LiNbO$_3$ crystal there is no OH$^-$ absorption band. That is easy to understand: in a perfect LiNbO$_3$ lattice there is no lattice position for the proton to occupy. If the crystal composition is stoichiometric but protons enter the crystal lattice in the crystal growth process, only a very narrow OH$^-$ absorption bands near 3466 cm^{-1} (halfwidth less than 3 cm^{-1}) has been found [13]. For no intrinsic defects, we suggested that this absorption band comes from the OH$^-$ stretching vibration of protons directly substituting for Li$^+$ ions. That is to say the 3466 cm^{-1} absorption band corresponds to the stretching vibration of OH$^-_{Li}$ (this means the proton occupies the Li site). On the other hand, Herrington *et al* have reported that protons locate at O–O bonds in oxygen planes [8]. So, we can deduce that in stoichiometric LiNbO$_3$ crystals protons substitute for Li$^+$ ions and are located at the O–O bonds (336 pm in length) in oxygen planes nearest to the Li site, and their stretching vibration with O^{2-} causes the 3466 cm^{-1} absorption band.

When the composition deviates from stoichiometry slightly, in other words, for composition very near stoichiometry, a narrow OH$^-$ absorption band near 3466 cm^{-1} and a very weak absorption peak near 3480 cm^{-1} due to a small fraction of remaining structural
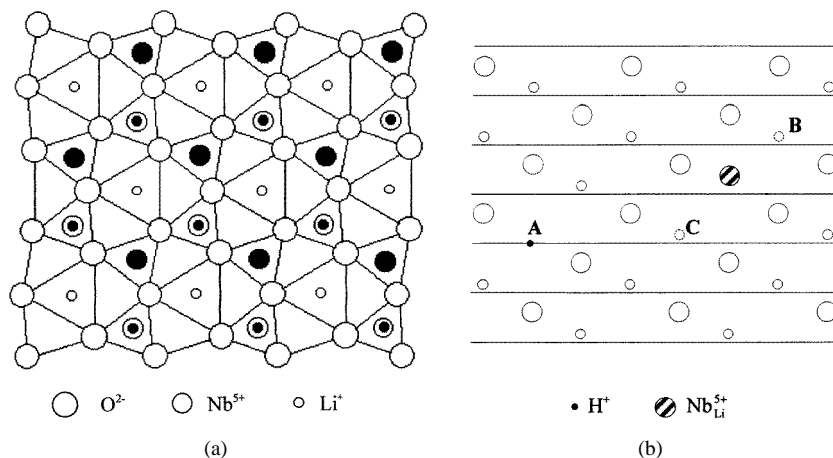
Figure 3. Structural schematics of the LiNbO$_3$ lattice: (a) along an oxygen plane, white Nb^{5+} and Li$^+$ symbols corresponding to ions above the plane, black symbols to ions below the plane; (b) parallel to the *c*-axis.

disorder have been found [12]. When the crystal composition deviates from stoichiometry a little more, just as our sample B, a strong 3466 cm^{-1} absorption peak, a medium 3481 cm^{-1} peak and a weak 3489 cm^{-1} peak appear. As composition deviating from stoichiometry will induce intrinsic effects, it is suggested that the 3481 and 3489 cm^{-1} absorption peaks are related to protons near intrinsic defects. Because the number of protons near intrinsic defects is smaller than that of point defects caused by protons directly substituting for Li$^+$ ions. the intensity of the 3481 and 3489 cm^{-1} absorption peaks is lower than that of 3466 cm^{-1}. When the composition is near congruent, just as for our sample A, the situation is contrasting. It has been reported by Kong *et al* [5] that in congruent pure LiNbO$_3$ crystals protons substitute for Li$^+$ ions and are located at the longest O–O bonds (336 pm in length) in oxygen triangles nearest to the Li sites. So, the OH$^-$ absorption peaks in congruent pure LiNbO$_3$ also corresponds to the stretching vibration of OH$_{Li}^-$ in 336 pm O–O bonds.

Now, the intrinsic defects of congruent pure LiNbO$_3$ are still under discussion. The Li-vacancy model [14] and Nb-vacancy model [15] have been proposed mainly. Recent experimental results show the Li-vacancy model is more reasonable [16–18], so it was used in the following discussion. According to the Li-vacancy model, there are about 1 mol% Nb$_{Li}^{5+}$ and 4 mol% V$_{Li}^-$ point defects in a congruent LiNbO$_3$ lattice. The different OH$^-$ absorption peaks of congruent pure and nearly stoichiometric LiNbO$_3$ crystals illustrate that the ion environment around the protons has changed. For the 3466 cm^{-1} absorption peak, only protons substitute for Li$^+$ ions; no other nearly point defects are induced. As to the 3481 and 3489 cm^{-1} peaks. four Li vacancies are around an (Nb$_{Li}^{5+}$)$^{4+}$, and it is unavoidable that the OH$_{Li}^-$ stretching vibration near these V$_{Li}^-$ is affected by Nb$_{Li}^{5+}$ ions. Figure 3 shows the structural schematics of LiNbO$_3$; figure 3(a) is along an oxygen plane and figure 3(b) parallel to the *c*-axis. Position A denotes the situation where a proton directly substitutes for an Li$^+$ ions in a perfect LiNbO$_3$ lattice. When an Li$^+$ ion is substituted by an Nb^{5+} ion, four V$_{Li}^-$ should appear around this Nb$_{Li}^{5+}$ ion for electric balance. It is seen from figure 3(b) that the nearest positions for V$_{Li}^-$ to occur are positions B and C. Figure 3(a) shows that there are three B and three C positions suitable for V$_{Li}^-$ to occur. The four V$_{Li}^-$ to electrically match Nb$_{Li}^{5+}$ should appear at these six positions, two B and two C, three B and one C or one B and three C. Figure 3(b) also shows that the ions environments of B and C have little difference. The oxygen triangle below B is less affected

by Nb_{Li}^{5+} than that above C, however, the distance between B and Nb_{Li}^{5+} is shorter than that of C. It seems that position B is more affected by Nb_{Li}^{5+} than position C and that the 3489 cm^{-1} absorption peak corresponds to position B and 3481 cm^{-1} to C.

5. Summary and conclusion

The OH$^-$ absorption spectra of congruent pure and nearly stoichiometric LiNbO₃ crystals have been measured. There are three components for each absorption band. The 3466 cm^{-1} peak is considered to relate to the stretching vibration of OH$^-$ for protons directly substituted for Li$^+$ ions and located at 336 pm O–O bonds in oxygen triangles nearest to the Li site, and the 3481 and 3489 cm^{-1} peaks are also due to OH$^-$ in 336 ppm O–O bonds but protons are suggested to occupy V_{Li}^- near Nb_{Li}^{5+} and two different ion environment around V_{Li}^- cause these two absorption peaks.

Acknowledgments

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