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OH^- absorption bands of $LiNbO_3$ with varying composition*

Chen Hong-Jian(陈洪建)[a], Shi Li-Hong(师丽红)[b], Yan Wen-Bo(阎文博)[a]†,
Chen Gui-Feng(陈贵锋)[a], Shen Jun(沈 俊)[a], and Li Yang-Xian(李养贤)[a]

[a] *School of Materials Science and Engineering, Hebei University of Technology, Tianjin* 300130, *China*

[b] *Tianjin Institute of Urban Construction, Tianjin* 300384, *China*

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This paper reports that OH^- absorption bands of lithium niobate crystal have been measured at room temperature, and the band shape depending on the crystal composition has been observed. The OH^- absorption bands are fitted with three Lorentzian peaks by varying position, halfwidth, and height. Nearly constant peak positions (3468, 3481 and 3490 cm^{-1}) are obtained for all samples. It shows that the height and area of the decomposed peaks vary with the Li composition in a complex way. However, the combinations of these fitting parameters show a linear dependence on the composition up to nearly 50 mol%, which is very useful for the composition determination in a wide range. The linear relationships between the parameter combinations and Li composition are also presented quantitatively. In addition, the explanations were given for the excellent composition linearity of parameter combinations.

Keywords: optical materials, Fourier transform infrared, heat treatment, adsorption
PACC: 4270, 7830G

1. Introduction

Lithium niobate ($LiNbO_3$) is an important single-crystal oxide material with many applications, e.g., holographic volume storage, optical image and signal processing, coherent optical amplification, and phase conjugation.[1,2] Hydrogen, presenting as an OH^- impurity complex in this material, often plays a key role in some technical fields, for example, photorefractive holographic thermal fixing and optical waveguides.[3,4] The infrared absorption spectrum, which is one powerful tool used to investigate the OH^- stretching vibration, has become the main subject of much research in recent years. As reviewed by Cabrera and Wöhlecke *et al*,[5,6] OH^-absorption spectra change with the varying Li composition of crystal, because OH^- stretching vibration is sensitive to the environment around H^+. Thus, OH^-absorption spectra are often used as a probe for the crystal composition and lattice defects that affect the environment around H^+.

Bäumer *et al*[7] have studied the OH^- absorption spectrum of lithium tantalate ($LiTaO_3$), which is similar to $LiNbO_3$ in structure. They reported that the composition of $LiTaO_3$ crystal can be determined by two decomposed peaks of the OH^- absorption spectrum. However, two-peak, three-peak, four-peak and five-peak models have also been proposed for the OH^- absorption bands of $LiNbO_3$ crystals.[8−11] The recent experimental results strongly supported the three-peak model.[12−14] In this paper, the OH^- absorption spectra of $LiNbO_3$ crystals with various compositions are measured, and each spectrum is decomposed to three peaks by fitting. A feasible method is suggested for the composition determination in the wide composition range.

2. Experiments

$LiNbO_3$ crystals with various Li compositions were prepared by the vapour transport equilibration (VTE) technique.[15] Starting crystals for VTE processing were grown from congruent melt by the Czochralski method. Congruent composition used in our work was Li/ Nb=48.40:51.60, which was obtained through many times of LN crystal growth. The as-grown crystals were cut into z plates of 1.2 mm thick-

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†Corresponding author. E-mail: yanwenbo@hebut.edu.cn

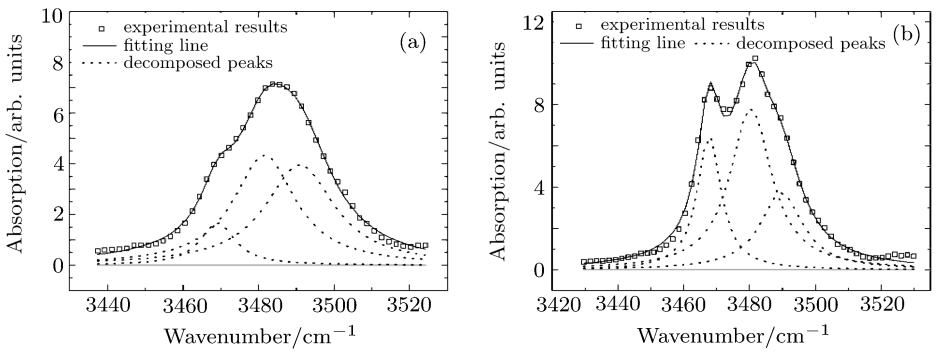
ness. To prepare powder charges with specified compositions for VTE treatment, we used Li_2CO_3 and Nb_2O_5 with a purity of 99.99% for starting chemicals. The powders were mixed, reacted, milled and then reacted to ensure the compositional homogeneity. The reaction crucible containing the crystal and the powder, was positioned within the hot zone of a platinum wound resistance furnace, heated (10 °C/min) to the desired reaction temperature (1150 °C), and maintained at this temperature for a given process duration (140 h). At last, crystal plates were cooled down to room temperature and removed from the furnace. With the rise of the Li composition of the crystal, the depoling temperature will increase. For the congruent lithium niobate crystal, the depoling temperature is about 1170 °C and the stoichiometric crystals depoling temperature is above 1200 °C. After the VTE procedure, we measured the poling of the crystal with charged printing ink. The results showed that the crystals were still single domain ones.

The Li composition of the sample was defined by C_{Li}=[Li]/([Li] + [Nb]). For each sample, the composition was firstly controlled by the specified C_{Li} of powder charges then was further confirmed by the Raman spectrum.[16] The measurement for the width of the Raman lines allows the determination of the composition within an absolute accuracy of 0.05 mol%, which is sufficient to discriminate the different crystals investigated in this paper. We chose the E-mode at 153 cm^{-1} and the A1-mode at 876 cm^{-1} to measure the Raman linewidth. A linear relation was found for both modes with the Li composition (C_{Li}) and the linewidth (Γ) : $C_{Li} = 53.03 - 0.4739\Gamma$ for the 153 cm^{-1} E-mode photon and $C_{Li} = 53.29 - 0.1837\Gamma$ for the 876 cm^{-1} A1-mode photon.[16] A Renishaw microscopic Raman spectrometer with the ability to measure within a very small region (several microns) was used in our experiment. We cut each VTE-treated sample in the middle. In the section, we measured the Raman spectra at different positions along the z axis. In addition, other regions of the sample were also selected for the measurement. The nearly the same Raman linewidth assures the uniformity of Li_2O throughout the sample. The above determination through the Raman line made the results credible enough for our following discussion. Finally, the Li compositions of the samples were determined to be 48.40, 49.50, 49.70, 49.90 and 49.97 mol%, respectively.

The OH^- absorption spectra were measured by a Fourier transform infrared (FTIR) spectrometer with the incident light along the c-axis. The absolute tolerance of this spectrometer is ± 1 cm^{-1} and the relative tolerance is ± 0.5 cm^{-1}. We decomposed the absorption spectrum to three Lorentzian peaks by varying the parameters like position, halfwidth and height.

3. Results and discussion

Figure 1 gives the absorption bands and the peaks fitted by the Lorentzian function for various compositions. We can find that these absorption bands consist of three peaks and the band shape obviously varies with composition. For the congruent sample (48.40 mol% Li_2O), only a broad band can be observed. The spectrum of the sample with 49.50 mol% Li_2O shows a structured band which is made up of three strongly overlapped peaks. With the further increase of the composition, two peaks at higher frequency side weakened gradually.



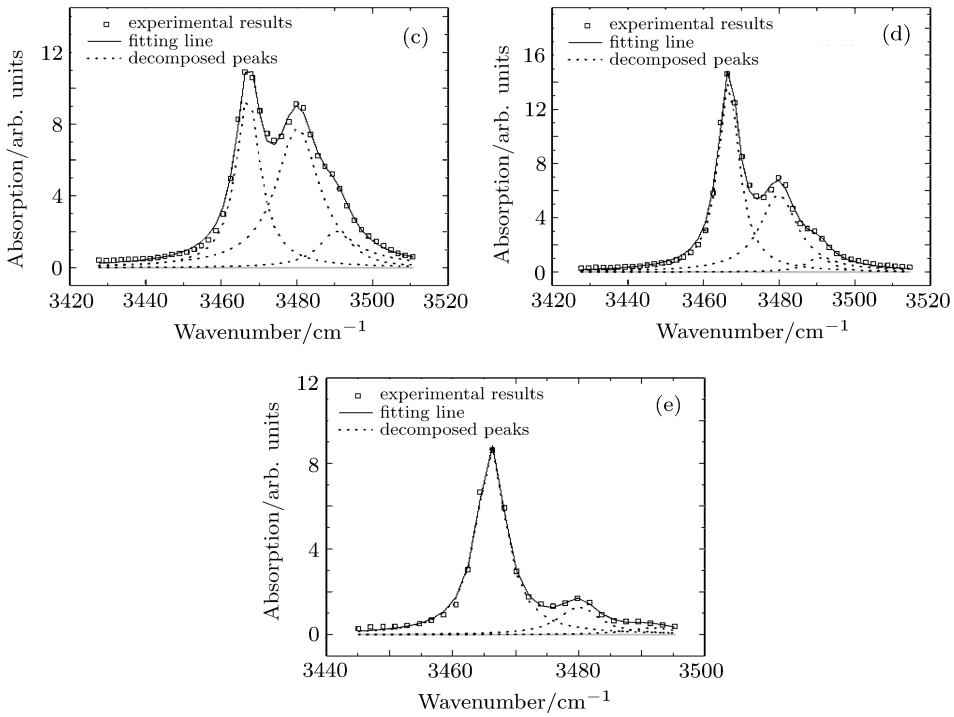


Fig.1. The OH^- absorption bands of $LiNbO_3$ crystals with various compositions and the peaks fitted by the Lorentzian function. Figures (a)–(e) correspond to samples with the composition of 48.40, 49.50, 49.70, 49.90 and 49.97 mol%, respectively.

Figure 2 gives the parameters of the decomposed peaks as a function of the Li composition. In Fig.2(a), the nearly constant positions of about 3468, 3481 and 3490 cm^{-1} are observed for the decomposed peaks in all absorption bands. These peaks are labelled here and later as L, M, and H in the sequence on wavenumber from low to high. The composition dependence on halfwidth was also shown in Fig.2(a). We can see that these peaks gradually narrowed with the increase of Li composition, which may be due to the increase of the lattice perfection.

Figure 2(b) gives the composition dependences for height and area. One can see that they have the same tend to vary with the composition, because parameter height and area are both associated with H^+ concentration in different sites. To explain the results in detail, we must firstly introduce the model about the location of H^+ in the lattice. As suggested in Ref.[13], H^+ always locates at three kinds of Li-vacancy: one is at a perfect crystal lattice and the other two appear around Nb_{Li}^{4+} ions. Different proton sites are associated with different cation environments and induce different decomposed peaks. The H^+ at the perfect crystal lattice corresponds to the decomposed peak L, while H^+ around the Nb_{Li}^{4+} ion corresponds to peaks M and H. With the increase of Li composition, the amount of Nb_{Li}^{4+} ions in crystal decreases, which makes H^+ transfer from the sites around Nb_{Li}^{4+} ions to the sites in the perfect crystal lattice. Thus, we can find from Fig.2(b) that, the height and area of peak L increase and those of peaks M and H decrease when the composition comes up. At the composition of 49.97, the abrupt decrease for peak L is very surprising, and it may be due to the lost of H caused by mild Li diffusion in the VTE treatment required for the high composition. In addition, a small rising trend can be found for peak M in the low composition range, it may be due to the location preference of H^+ at low energy sites (peak M) rather than other sites (peak H).

In Ref.[14], the OH^-absorption spectrum of $LiTaO_3$ was also decomposed to three peaks, where the halfwidth of the low decomposed peak was found to remain unchanged regardless of the hydrogen concentration. Moreover, the linear relationship between this parameter and crystal composition was sug-

gested to be suitable for composition determination. In present works, the halfwidth of peak L also exhibits fair linearity in the composition range below 49.9 mol%, but the linearity becomes bad if the datum point for 49.97 mol% is considered. It should be noticed that the highest composition used in Ref.[14] is only 49.8 mol%. Therefore, the determination method by using the halfwidth of peak L is likely to be invalid for high composition.

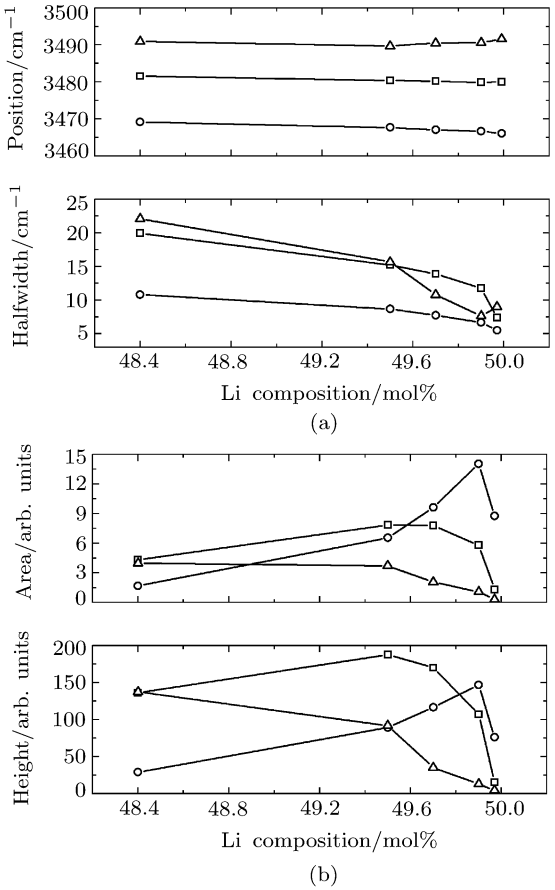


Fig.2. The position, halfwidth (a) and area, height (b) for each decomposed peak as a function of Li composition. Circles, squares and triangles denote the experimental results of the peaks L, M and H, respectively.

The parameters height and area can also be used for composition determination. But their composition dependences are very complicated, as shown in Fig.2(b). Moreover, these parameters are usually in proportion to hydrogen concentration in crystal. Therefore, none of them can alone be used to determine the crystal composition. However, if these parameters are combined in some form, the case may be different. Based on the model about the H^+ location, peaks M and H are associated with Nb_{Li}^{4+} concentration. Therefore, their height and area should be in reverse proportion to the composition and in proportion to the hydrogen concentration. For peak L, its height and area are only in proportion to the hydrogen concentration. Thus, the parameters can be combined in the following forms: A=(Area$_M$+Area$_H$)/Area$_L$ and H=(Height$_M$+Height$_H$)/Height$_L$. By using these combinations, the influence of hydrogen concentration on the composition determination can be canceled. Figure 3 gives the dependences of these combinations on the Li composition. We can see that their dependences show excellent linearity even when the composition is very close to 50 mol%. By linear fitting, the quantitative relationships between parameter combinations (A and H) and the Li composition were obtained as follows: $A = 291.3 - 5.823 \times C_{\mathrm{Li}}$ and $H = 148.0 - 2.957 \times C_{\mathrm{Li}}$.

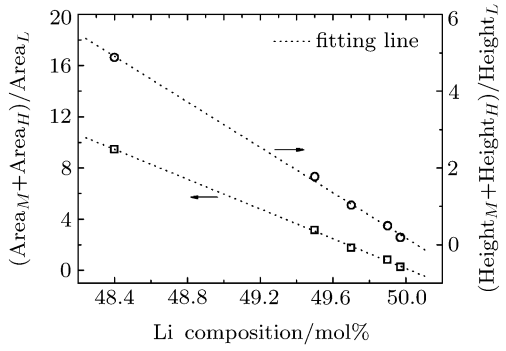


Fig.3. The combination A=(Area$_M$+Area$_H$)/Area$_L$ and H=(Height$_M$+Height$_H$)/Height$_L$ as a function of Li composition.

Generally, band halfwidth is related to phonons in crystal and band may be broadened due to the coupling of the incident light and phonons produced in the lattice. Because Li deficiency usually induces the lattice distortion and increases the phonon concentration, the band halfwidth can be indirectly associated with the Li composition. However, there are other factors to affect the phonon concentration in crystal, for example, the residual stress depending on the annealing history. Thus, the linearity of Li composition with the halfwidth may be disturbed in the sensitive range with high composition. By contrast, the distribution of H^+ in different sites is directly connected with the Nb_{Li}^{4+} concentration (e.g. the Li composition) and cannot be easily affected by other factors. Thus, the determination method through parameter combinations exhibits better reliability than that by using only the halfwidth parameter. In further work, we will investigate the validity of this method for iron-doped nearly stoichiometric lithium niobate crystals.[17]

4. Conclusion

In this paper, we measured the OH^- absorption spectra of $LiNbO_3$ crystals with various compositions, and adopted the three-peak model to decompose the spectra. Nearly constant peak positions (3468, 3481 and 3490 cm^{-1}) are obtained for all samples. It was shown that the height and area of decomposed peaks vary with the composition in a complex way. But the combinations of these fitting parameters were found to keep linear with composition up to nearly 50 mol%, which is very useful for the composition determination in a wide range. In addition, the quantitative relationships between the parameter combinations and crystal composition are also presented in this paper.

References

[1] Mizuuchi K and Yamamoto K 1992 *Appl. Phys. Lett.* **60** 1283

[2] Günter P and Huignard J P 1989 *Photorefractive Materials and Their Applications* (Heidelberg: Springer-Verlag) p1

[3] Vormanm H, Weber G, Kapphan S and Kratzig E 1981 *Solid State Commun.* **40** 543

[4] Jackel J L, Fraser D B, Denton R T and Rich T C 1982 *Appl. Phys. Lett.* **41** 607

[5] Cabrera J M, Olivares J, Carrascosa M, Rams J, Müller R and Diéguez E 1996 *Adv. Phys.* **45** 349

[6] Wöhlecke M and Kovács L 2001 *Crit. Rev. Solid State* **26** 1

[7] Bäumer C, David C, Betzler K, Hesse H, Lengyel K, Kovács L and Wöhlecke M 2004 *Phys. Stat. Sol.* (a) **201** R13

[8] Herrington J, Dischler B, Rauber A and Schneider 1973 *J. Solid State Commun.* **12** 351

[9] Kovács L, Szalav V and Capelletti R 1984 *Solid State Commun.* **52** 1029

[10] Jovanovic A, Kapphan S and Wöhlecke M 1987 *Cryst. Lattice Defects Amorph. Mater.* **15** 137

[11] Kovács L, Wöhlecke M, Jovanovic A, Polgar K and Kapphan S 1991 *J. Phys. Chem. Solids* **52** 797

[12] Kong Y, Zhang W, Chen X, Xu J and Zhang G 1999 *J. Phys.: Condens. Matter* **11** 2139

[13] Yan W, Kong Y, Shi L, Xie X, Li X, Xu J, Lou C, Liu H, Zhang W and Zhang G 2004 *Phys. Stat. Sol.* (a) **201** 2013

[14] Shi L, Kong Y, Yan W, Liu H, Li X, Xie X, Zhao D, Sun L, Wang Z, Xu J, Sun J, Chen S, Zhang L, Huang Z, Liu S, Zhang W and Zhang G 2006 *Mater. Chem. Phys.* **2** 229

[15] Bordui P F, Notwood F G, Bird C D and Carella J T 1995 *J. Appl. Phys.* **78** 4647

[16] Wöhlecke M, Corradi G and Betzler K 1996 *Appl. Phys.* B **63** 323

[17] Li X C, Kong Y F, Wang L Z and Liu H D 2008 *Chin. Phys.* B **17** 1014