RAMAN AND IR SPECTRA OF ZN-DOPED LITHIUM NIOBATE CRYSTALS

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The congruent grown lithium niobate crystal gives the lithium atom concentration ratio [Li]/([Li]+[Nb]) = 48.6%, which represents a considerable deficit of lithium ions [1]. The most recognized defect model is the Li atom replaced by Nb atom (i.e. Nb_{Li}^{+4}) and four Li vacancies (V_{Li}^{+1}) are created. Raman scattering method has been frequently used to probe the impurity substitution in doped $LiNbO_3$ crystal [2]. We have measure the Raman and IR spectra on a series of congruent grown Zn-doped lithium niobate signal crystals at room temperature (Fig.1) and crystal powders at low temperature (Fig. 2). For different doping concentration samples, Raman spectra clearly show not only the change of vibration Raman shift, but also the variation of the full width at half maximum (FWHM). We interpret the variation of frequency and FWHM for A_1(TO) and E(TO) Raman modes by Force field calculations [3] and the method of full-potential linearized augmented plane-wave [4]. The results revealed from Raman shift and FWHM can determine the substitutive mechanism as Zn doped concentration varies, and it clearly shows three segments in variation of frequency and FWHM as doping concentration increase. The first stage, which has relatively small change in frequency and FWHM, is from 0 to 5 mol. % doping and Nb_{Li}^{+4} are mainly replaced by Zn^{+2} to decrease the number of V_{Li}^{+1}, but increase the impurity content in crystal. The second region, which shows significant decrease of frequency and increase of FWHM, is about 5 to 7.5 mol. %, and we think most of Zn atoms are incorporated into Li sites to increase V_{Li}^{+1}[5]. It has great impact on vibration properties of phonons due to the substitution of Li^+ by Zn^{2+}, which reflected on the Raman lineshapes. Local extreme values for frequency and FWHM are found at 7.5 mol. % that is the optical threshold for $LiNbO_3$:Zn[6]. Raman result is consistent with the results obtained from OH-absorption spectra made by FTIR. From the IR spectra, we find four OH^- absorption bands at 3467 cm^{-1}, 3481 cm^{-1}, 3489 cm^{-1} and 3501 cm^{-1} at doping concentration below 5.3 mol. %. In between 5.3 and 7.5 mol. % Zn doping, mainly two OH^- absorption at 3468 $cm^{-1}$and 3483 cm^{-1} are found, while the band at 3483 cm^{-1} is related to the defect structure of Li^+ replaced by Zn^{+2} only. Above 7.5 mol. % doping, the OH^- bands shift to 3506 cm^{-1} and 3530 cm^{-1}, and signals become rather weak. The OH^- vibration of the highest Zn doped sample are mainly influenced by the rapid reduction of Li vacancies for the self-compensation mechanism as the Zn atoms begin to enter Nb sites [7,8].
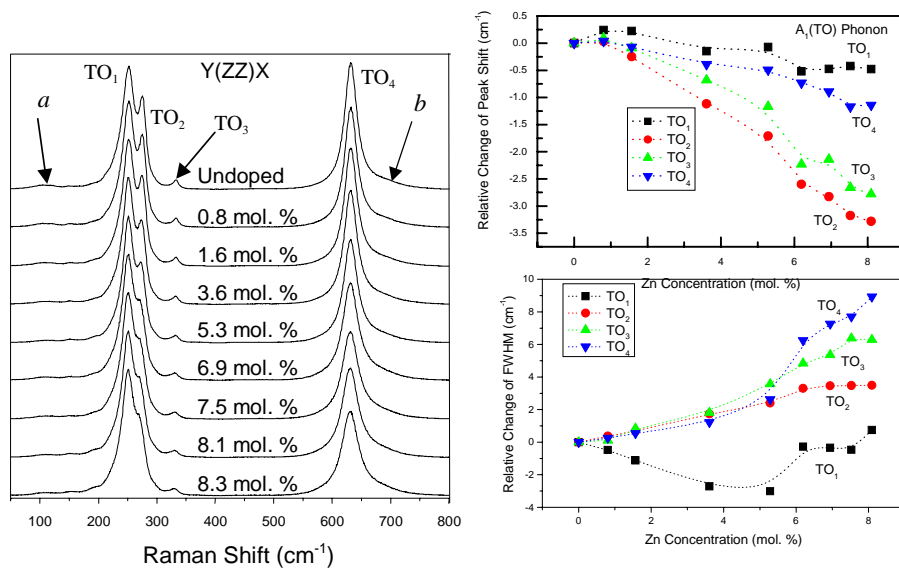
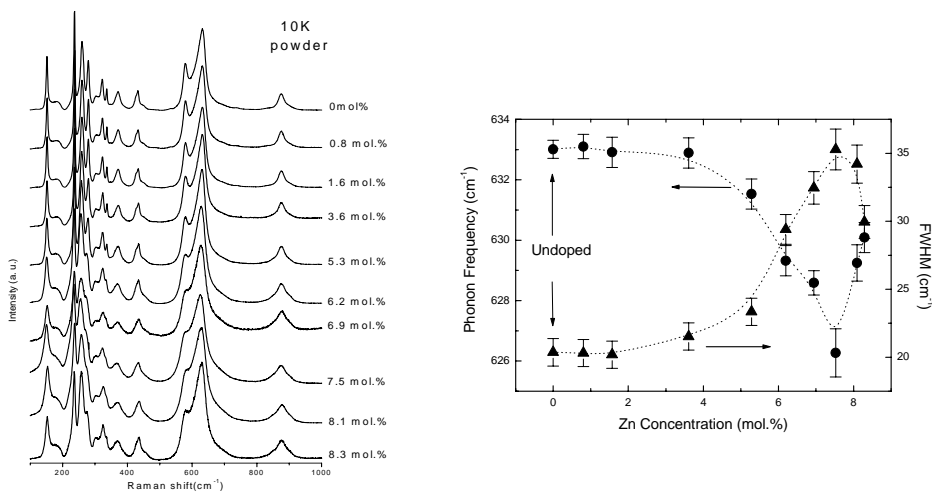Fig. 1. Four $A_1(TO)$ modes of Zn-doped $LiNbO_3$ single crystals.

Fig. 2. Raman spectra of Zn-doped $LiNbO_3$ crystal powders at 10K.

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