Characteristics of Einstein oscillator, electron-phonon interaction, and band-edge absorption in LiNbO$_3$:In

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Abstract.   Based on the Einstein oscillator model and the Urbach rule, we study the electron-phonon interaction and the band-edge structure of highly doped LiNbO$_3$:In. Significant reduction of the Einstein oscillator energy and the electron-phonon interaction strength appears in highly doped LiNbO$_3$:In compared with the undoped one. The absorption band near to the UV band edge in highly doped LiNbO$_3$:In, which is much stronger than that in the undoped LiNbO$_3$ crystal, may be related to the defect clusters $(O^{2-}\text{-}V_{Li}^-)$ and $(O^{2-}\text{-}In_{Nb}^{2-})$ and the micromechanism of the UV photorefractivity in LiNbO$_3$:In.

It was found that in lithium niobate (LiNbO$_3$, LN) crystal the optical damage in the visible is significantly suppressed by highly In-doping, while the photorefractivity in highly doped LN:In is greatly enhanced in the UV [1, 2]. In this paper, we report on the thermal induced spectra properties of the fundamental band edge and the deep level defect structures of highly doped LN:In.

Congruent LN crystals with In-doping concentrations of 0.0 and 5.0 mol% in melt was prepared and labeled as CLN and CIn5, respectively. Both of the crystals are cut in the form of Y-oriented plates with a thickness of 0.5 mm. The UV band edge absorption spectra in the temperature range from 3.8 K to 973 K were measured for our samples. The band energy gap E_g, defined as the photon energy at which $\alpha = 70$ cm^{-1}, decreases with the increase of temperature, which can be well described by the Bose-Einstein expression $E_g(T) = E_{gBE}(0) - (2a_B)/[exp(E_{pBE}/k_BT) - 1]$, as shown in Fig. 1(a) [3]. The fundamental band gap $E_{gBE}(0)$ has a significant increase in CIn5 and the Einstein oscillator energy E_{pBE} drops abruptly in CIn5 as compared with CLN[4]. The electron-phonon interaction strength weakens dramatically in the CIn5, which would theoretically lead to an increase in the photoconductivity. Note that the photoconductivities of highly doped LN:In are already found to be remarkably enhanced in both visible and UV region [1, 2], this result, therefore, gives a fundamental microscopic picture for the observed optical properties in highly doped LN:In crystals.

The absorption edge tails of both samples at temperatures higher than 400 K are consistent with the widely observed Urbach rule [5]. However, as the temperature goes down below $\sim$ 400 K and the absorption edge shifts towards higher energy, an additional absorption band shows up at the bottom of the absorption edge tail. Typical absorption spectra at a cryogenic temperature of 3.8 K for both samples are shown in Fig. 1(b). It is the appearance of this new absorption band that deforms the Urbach tail at this spectral region. In order to show the true spectral structure of this absorption band, we subtract the Urbach tail from the measured spectra and get $\Delta\alpha = \alpha - \alpha_0 \exp\left[\frac{\sigma}{k_BT^*}(\hbar\omega - \hbar\omega_0)\right]$, where α_0, σ, ω_0 and T^* are calculated
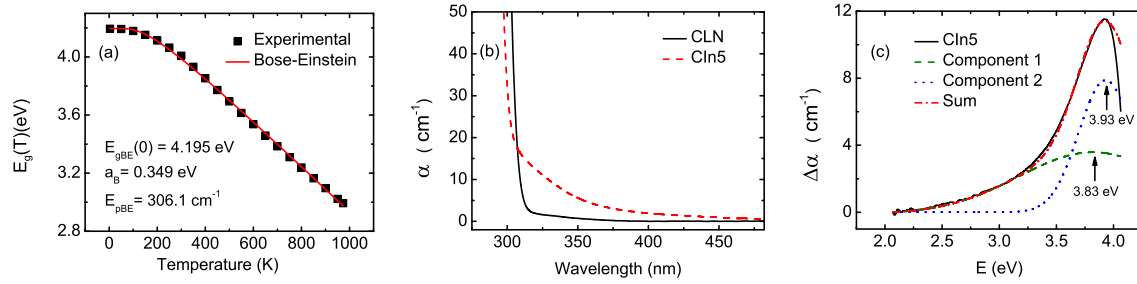
Figure 1. (a) The measured temperature dependence of the band energy gap of CIn5 with the corresponding fitting curves by the Bose-Einstein expression. (b) The absorption spectra of CLN and CIn5 crystals at 3.8 K. (c) The spectral profile of $\Delta\alpha$ measured at 3.8 K for CIn5 with theoretical fit of Gaussian profiles peaked at 3.83 eV and 3.93 eV, respectively

by fitting the remaining spectrum without deformation to the Urbach rule. The the calculated spectral profile of $\Delta\alpha$ measured at 3.8 K for CIn5 is shown in Fig. 1(c). We find that the peak of the absorption band $\Delta\alpha$ of CIn5 is higher than that of CLN [4], which has the same tendency as the enhancement of the UV photorefractivity in highly doped LN:In [2]. Therefore, the corresponding defect centers should be responsible for the photorefraction and the light-induced charge transport process in the UV in highly doped LN:In. Moreover, for CIn5, the absorption band $\Delta\alpha$ at 3.8 K can be decomposed into two Gaussian components peaked at 3.83 eV and 3.93 eV as shown in Figs. 1 (c), while typical result for CLN can be well fitted by a Gaussian spectral profile with its peak energy at 3.83 eV [4]. Just as the existence of defect cluster $(O^{2-}\text{-}Mg_{Nb}^{3-})$ in LN:Mg [4], it is reasonable to suppose that, besides $(O^{2-}\text{-}V_{Li}^{-})$ defect cluster, $(O^{2-}\text{-}In_{Nb}^{2-})$ will also form deep energy levels close to the valence band in the band gap of LN:In. It was found that the two deep energy levels in highly doped LN:Mg are centered at 3.83 eV and 4.03 eV, while in CIn5, one can fit the absorption band of $\Delta\alpha$ by the sum of two Gaussian components centered at 3.83 eV and 3.93 eV. Since In_{Nb}^{2-} has a valence magnitude between V_{Li}^{-} and Mg_{Nb}^{3-}, with respect to the crystal lattice, the two energy levels in highly doped LN:In crystal are closer to each other than those in LN:Mg.

In summary, the UV band edge spectra and the UV photo-sensitive defect centers of highly doped LN:In has been studied. The Einstein oscillator energy and the electron-phonon interaction strength in highly doped LN:In decreased obviously compared with CLN, which could be regarded as the microscopic origin of the significant increase in photoconductivity in highly doped LN:In. A new absorption band at the bottom of the Urbach tail appears in CIn5 at low temperatures, and it is attributed to $(O^{2-}\text{-}V_{Li}^{-})$ and $(O^{2-}\text{-}In_{Nb}^{2-})$ defect clusters, which may determine the band-edge optical properties of highly doped LN:In..

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