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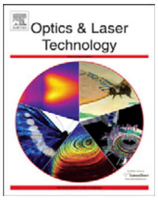

Photorefractive properties of Fe, Zn co-doped near stoichiometric $LiNbO_3$ crystals at moderate intensities (0.5–6 W/cm^2)

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ABSTRACT

Iron and zinc co-doped near stoichiometric lithium niobate (SLN:Fe,Zn) single crystals were grown by the top seeded solution growth technique from Li-rich flux. The Raman scattering analysis confirmed the near stoichiometric composition (Li/Nb ~ 0.98) whereas the birefringence interferometry revealed the optical homogeneity to be better than 5.2×10^{-5}/mm for the grown crystals. Two beam coupling measurements showed the writing time constant to be 26–3.6 s measured in the intensity range 0.5–6 W/cm^2. The slow and fast erasure time constants as obtained from bi-exponential fit are ~22–4 and ~200–24 s, respectively. Interestingly, the fast eraser time is found to be nearly the same as the writing time. The improvement in photorefractive sensitivity (~0.16 cm/J) has been observed. The light induced changes in the refractive index ($\Delta n \sim 5.8 \times 10^{-5}$) are found to be in agreement with the estimated value. The intensity dependent photoconductivity estimated from the two beam coupling experiment is found to vary from $1.12 \times 10^{-11}\ \Omega^{-1}\ m^{-1}$ to $6.20 \times 10^{-11}\ \Omega^{-1}\ m^{-1}$ due to primary defects and from $1.24 \times 10^{-12}\ \Omega^{-1}\ m^{-1}$ to $1.04 \times 10^{-11}\ \Omega^{-1}\ m^{-1}$ due to secondary defects.

1. Introduction

Iron doped lithium niobate ($LiNbO_3$:Fe) is a promising photorefractive (PR) material because of its high diffraction efficiency, long storage time and availability in large size [1–3]. However, large response time, low sensitivity and strong light-induced scattering are limiting factors for its applications [2,4–6]. Moreover, as these crystals are usually grown from Li-deficient congruent melt (Li_2O ~ 48.6 mol%, Li/Nb < 1; CLN:Fe), it contains high concentration of intrinsic defects (Nb_{Li}^{5+} and V_{Li}^{1-}) and disorder that limits its optical and photorefractive properties [4–12]. Defects and imperfection also result in unwanted light induced scattering, which selectively get amplified in the photorefractive process [11,13]. Suppressing these intrinsic defects is therefore essential to improve its optical properties. $LiNbO_3$:Fe crystals grown in stoichiometric form (SLN:Fe, Li/Nb ~ 1) show better photorefractive response time and sensitivity [5,10]. The theoretically estimated response time is of the order of few milliseconds for $LiNbO_3$ crystals [14]. Lin et al. [15] have reported the response time to be ~10 ms for heavily Fe (1 mol% Fe_2O_3) doped CLN crystal. But these crystals have limited practical use as it requires a thin sample ~10 μm owing to the high absorption coefficient ~200 cm^{-1} around 500 nm. Further, response time ~100 ms is reported for highly reduced near-SLN crystals with low diffraction efficiency ~1% [16]. The response time ~0.6 s and 1.5 s have been reported for Fe doped near SLN and CLN crystals, respectively, at power density of 10 W/cm^2 [5]. Because of the near stoichiometric composition, SLN:Fe crystals contain only small concentration of Nb_{Li}^{5+} defects, which can be further reduced by co-doping it with damage-resistant dopant, such as Mg^{2+}, Zn^{2+}, Hf^{2+} etc. [4,7–11]. There are a few reports available on the photorefractive properties of near stoichiometric $LiNbO_3$ crystals co-doped with Fe and Zn, presenting response time ~10–30 s for low power densities ≤1 W/cm^2 [9–11]. As the values are inconsistent and relatively high in comparison to 0.6 s reported for SLN:Fe in Ref. [5], there is a scope for improving the photorefractive parameters such as response time and sensitivity.

In the present work, near-SLN:Fe,Zn crystals have been grown by the top seeded solution growth technique (TSSG). The grown crystals are characterized by optical absorption, Raman scattering and birefringence interferometry. The photorefractive study has been carried out by employing two beam coupling at moderate power densities in the range of 0.5–6 W/cm^2. The improvements in response time and sensitivity are reported. Also, the light induced change in the refractive index and photoconductivity of the grown crystal has been evaluated.

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2. Experimental

Double doped near SLN:Fe,Zn crystals are grown by the top seeded solution growth (TSSG) method from Li-rich melt (58 mol% Li_2O and 42 mol% Nb_2O_5). The concentration of ZnO and Fe_2O_3 in the melt was 1.5 mol% and 0.045 mol% (0.05 wt%) respectively. Starting materials of Li_2CO_3 and Nb_2O_5 of 4N purity are used for the crystal growth experiments. The weighted powders are mixed thoroughly and kept for solid-state reaction at 750 °C for 10 h and subsequently at 850 °C for 15 h. Around 800 g of charge thus prepared is put in to a platinum crucible of 80 mm diameter and 80 mm height. The charge is then homogenized for 24 h before lowering the seed into the melt. Crystal growth workstation and related infrastructure for the growth of SLN crystals were established in-house. The axial temperature gradient is $\sim 10\ ^\circ C/cm$. The growth is initiated using a *Z*-oriented seed. The seeding is done as per the technique described in Ref. [17] to establish the saturation temperature quickly and to minimize the seed loss during seeding. The growth parameters are optimized to get nearly flat interface, core and inclusion free single crystals. Growth rate of 0.5–0.2 mm/h and crystal rotation rates of 20–2 rpm is used.

The phase of the grown crystal is confirmed by the X-ray powder diffraction technique. Transmission spectra are recorded using a Carry 50 spectrophotometer for *z*-cut polished samples of 1 mm thickness. The Li content in these samples was estimated by polarized Raman spectroscopy for $Z(YX)Z$ and $Z(YY)Z$ scattering configurations using a micro-Raman spectrometer (Alpha300SR, Witec Instruments GmbH, Germany) with 488 nm wavelength of Ar-ion laser as excitation source. Optical homogeneity of the SLN:Fe,Zn crystals is investigated by orthoscopic birefringence interferometry, as crystal grown from off-congruent melt tends to exhibit composition variation along the length of the crystal [5]. A collimated parallel He–Ne Laser beam travels through *Y*-cut SLN crystal of dimension $10 \times 10 \times 1.2\ mm^3$ placed between cross polarizes at 45° to the crystal axis. The delay between the ordinary and extraordinary components passing through the polarizer results in formation of interference fringes, revealing the birefringence map of the sample. The corresponding phase delay is given by $\phi = 2\pi\ \Delta nd/\lambda$, where d is the sample thickness and $\Delta n = n_e - n_o$ is the birefringence.

Y-oriented samples of dimension $\sim 10 \times 2.5 \times 8\ mm^3$ are used for the photorefractive studies. The polished samples are reduced in Ar atmosphere at 900 °C for 6 h to increase the donor-to-acceptor ratio (i.e., Fe^{2+}/Fe^{3+}) in the crystals. The photorefractive properties of the near SLN:Fe,Zn crystals are evaluated by the two-beam coupling experiment in transmission geometry at a fixed grating spacing. The side surfaces and peripheries of the samples are short-circuited with conductive silver paste to avoid charge buildup that leads to open circuit voltage and influence the photorefractive process. A 150 mW diode-pumped frequency-doubled $Nd:YVO_4$ laser operating at 532 nm with 2 mm beam diameter is used. The laser beam is split into two extraordinary polarized beams and made to overlap at an angle of 22° in the crystal. The interference pattern of the incident beams results in the formation of index grating ($\sim$720 lines/mm) with period $\sim 1.39\ \mu m$. The grating vector is aligned along the *c*-axis to exploit the major electro-optic coefficient r_{33}. The measurements are carried out at power densities $\sim 0.5–6\ W/cm^2$. The evolution and decay of the grating were monitored by a Bragg angle matched weak HeNe laser (<2 mW, 632.8 nm) beam as a probe. The intensities of diffracted and transmitted beams are measured by photodiodes and recorded in a digital storage oscilloscope.

3. Result and discussion

Fig. 1. SLN:Fe,Zn crystal boule and fabricated PR element.

Fig. 1 shows the photograph of SLN:Fe,Zn (0.05 wt% Fe_2O_3 and 1.5 mol% ZnO) crystal boule (grown by the top seeded solution growth technique using Li-rich melt) and the fabricated element. The grown crystals are of good quality, nearly flat interfaced and light brown in color with the size measuring up to 25 mm in diameter and 30 mm in length. As the crystals are grown from off-congruent melt, only less than 5% of the total charge is crystallized in order to avoid composition variations across the length of the crystal. Fig. 2 shows the Raman scattering spectra of SLN:Fe,Zn, CLN:Fe,Zn, SLN and CLN crystals for the $Z(YX)Z$ and $Z(YY)Z$ scattering configurations (CLN:Fe,Zn, SLN and CLN are included for comparison). The composition of CLN:Fe,Zn crystal is 0.03 wt% Fe_2O_3 and 4 mol% ZnO. The observed Raman peaks are due to E (TO1) (153 cm^{-1}) and A1 (LO) (873 cm^{-1}) phonon modes polarized along the *X* or *Y* direction. The E (TO1) phonon modes represent the vibration of Nb–O bonds and the linewidth of these modes reveals the disorder in the Nb sub-lattice, which is utilized to evaluate the stoichiometry (composition) of the crystal. The stoichiometry (Li content) of SLN:Fe,Zn crystal is evaluated from the linewidth of the 153 cm^{-1} Raman shift peak using the relation c_{Li} [mol%] $\sim 53.03–0.4739\ \Gamma\ [cm^{-1}]$, where Γ is the linewidth of the peak [18]. The stoichiometry is also evaluated from the linewidth of 873 cm^{-1} peak using the relation c_{Li} [mol%] $\sim 53.29–0.1837\ \Gamma\ [cm^{-1}]$ [18]. Referring to Fig. 2, the Raman spectra for both the peaks clearly show that the linewidth of SLN:Fe,Zn appears close to that of SLN crystal and confirms its near stoichiometric composition. The observed linewidth broadening for CLN:Fe,Zn and CLN crystals depicts the structural disorder in the lattice due to the presence of high concentration of intrinsic defects that leads to a deviation from the stoichiometry. The linewidth is estimated from the Lorentz fitting approximation and the values are 6.49, 7.92, 10.72 and 14.70 cm^{-1} (for the 153 cm^{-1} peak), and 20.90, 22.17, 29.08 and 39.07 cm^{-1} (for the 873 cm^{-1} peak) observed for SLN, SLN:Fe,Zn, CLN and CLN:Fe,Zn crystals, respectively. The estimated Li content for SLN:Fe,Zn crystal is $\sim$49.28 mol% Li_2O (Li/Nb$\sim$0.975) and $\sim$49.22 mol% Li_2O (Li/Nb$\sim$0.969) as obtained from the linewidth of 153 cm^{-1} and 873 cm^{-1} peaks, respectively, which is significantly higher than the 46.12 mol% Li_2O (Li/Nb$\sim$0.86) for CLN:FeZn crystal.

Fig. 3 depicts the absorption spectra of near SLN, SLN:Fe,Zn, reduced SLN:Fe,Zn and CLN:Fe,Zn crystals. It shows a shift in UV absorption edge to higher wavelength for SLN:Fe,Zn, reduced SLN:Fe,Zn and CLN:Fe,Zn in comparison to SLN crystal. The observed maximum shift for CLN:Fe,Zn crystal depicts the presence of intrinsic defects that results in a decrease in Li/Nb in this crystal. This is in agreement with the Raman analysis where maximum broadening is observed for the CLN:Fe,Zn crystal