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Green-induced infrared absorption in MgO doped LiNbO₃

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Green-induced infrared absorption (GRIIRA) was investigated by a photothermal technique for undoped and Mg-doped LiNbO₃ crystals that have different Li/Nb ratios. Threshold effect on GRIIRA was found, threshold MgO concentrations being the same for GRIIRA and photorefraction. We suggest that GRIIRA is associated with the formation of the small polaron that is located on Nb antisite defect. The remarkable decrease of GRIIRA in Mg:LiNbO₃ can then be attributed to the elimination of this intrinsic defect, Nb in Li, following the incorporation of Mg on Li sites. For nonlinear optical applications, LiNbO₃ doped with MgO at concentrations over threshold has a combined advantage of having almost no GRIIRA and photorefraction. © 2001 American Institute of Physics. [DOI: 10.1063/1.1359137]

In recent years there has been increasing interest in the use of quasi-phase-matched (QPM) nonlinear crystals¹ for a variety of frequency conversion applications. Periodically poled lithium niobate (PPLN) has been demonstrated to give efficient second-harmonic generation² and optical parametric oscillation³ in both the cw and the Q-switched regimes. However, the performance of high power operating PPLN-SHG devices has been limited by material issues such as photorefractive beam distortion and green-induced infrared absorption (GRIIRA).⁴ It has been demonstrated that the former problem can be solved by either high temperature device operation or MgO doping to the LiNbO₃ crystal, however, the latter problem still remains to be investigated. Defect models of the phenomena of green-induced infrared absorption have not been developed. Recently we reported that photorefractive in LiNbO₃ was completely eliminated by the doping of small amounts of MgO in crystals with near-stoichiometric composition.⁵ These notable changes in material properties are strongly related to the elimination of Nb antisite defects (Nb_{Li}) by the substitution of Mg on Li sites.

In this letter, we investigate the influence of MgO doping on the GRIIRA properties in LiNbO₃, and demonstrate that LiNbO₃ crystals doped with MgO show remarkably lower GRIIRA than undoped LiNbO₃ crystals.

LiNbO₃ single crystals grown by two different methods were used in this study. They are denoted CLN when their stoichiometry, expressed as the ratio $c_{\text{Li}} = [\text{Li}] / ([\text{Li}] + [\text{Nb}])$, has a congruent-composition value of 48.4% and SLN when it deviates from this value in the direction of the stoichiometric composition of 50%. Crystals denoted as SLN and Mg:SLN were grown as described in earlier reports⁶ by use of a top-seeded solution growth technique from a sto-

ichiometric melt with the addition of 11 mol % of K₂O as flux and of MgO as dopant. Crystals denoted as CLN and Mg:CLN were grown by the conventional Czochralski method from congruent melt compositions. Chemical composition, Curie temperature, OH absorption wave number, and photorefractive damage threshold of the LiNbO₃ single crystals used in this study are summarized in Table I.⁷ The corresponding chemical formulas were characterized by chemical analysis as follows: The crushed samples were dissolved with HNO₃-HF solution in a closed Teflon vessel at 150 °C for one night. After being filtered for the separation of precipitated MgF₂, the yielded solution was passed through as SA-a anion exchanger for further separation of Li and Nb ions. The Li and Mg content were analyzed by an inductively coupled plasma atomic emission spectrometry (ICP-AES). The Nb ions eliminated from the resin by HCl-HF solution were precipitated by cuperon, and the precipitate was dried and incinerated. The weight of the yielded Nb₂O₅ gave the Nb content. The accuracy for [Li]/[Nb] cation ratios in Mg:SLN and Mg:CLN was 0.6% while that for MgO content amounted to 0.8%. As shown in Table I, it is clear that the SLN crystals contain lower intrinsic defect densities than conventional CLN crystals, but they still contain Nb_{Li} at levels of thousands of ppm. On the other hand, extrinsic defects such as Fe were determined by ICP analysis to be in the ppm levels. In Table I, optical damage threshold refers to the onset of optical damage. The high MgO concentration samples, according to the data presented, displayed no optical damage, therefore the optical damage threshold was never reached. The high MgO concentration samples showed a shift in the OH absorption band from 3466 to 3485 to 3552 cm⁻¹ which suggests that at those doping levels, the excess Nb⁵⁺ on Li sites has been completely replaced by Mg²⁺.⁵

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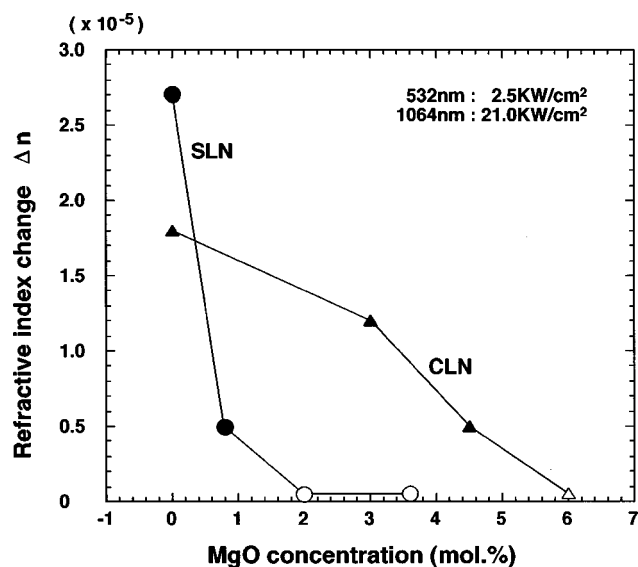


FIG. 3. Photorefractive index change vs MgO concentration in SLN and CLN crystals. Chemical formula and other material properties of these samples are listed in Table I.

[Nb] and MgO concentrations. The refractive index changes were measured along with the GRIIRA measurements shown in Fig. 2. The photorefractive index in both SLN and CLN crystals decreased monotonically with increase of MgO concentration. SLN crystals with high [Li]/[Nb] ratios show faster decreases of photorefractive index than congruent crystals. The feature similar to the GRIIRA behavior is the threshold doping level over which photorefractive index disappears along with the disappearance of GRIIRA.

The reasons for the threshold behavior of both photorefractive index and GRIIRA are probably related. Moreover, in Table I, the optical damage disappearance and the shift in the OH absorption band from 3466 to 3485 to 3532 cm^{-1} both correspond to the same threshold MgO concentrations. The comparison with the chemical formulas strongly suggests that at these doping levels the excess Nb^{5+} on Li sites has been completely replaced by Mg^{2+} .⁵

We think that GRIIRA is associated with small polaron absorption band that is centered in the near IR, much like it occurs in reduced crystals though the absorption is several orders of magnitude less for crystals measured in this work. The small polaron is believed to be formed by electron trapped by antisite Nb .^{9,10} The results of an early work¹¹ suggest that at room temperature that this trap is unstable, the decay time being in the range of milliseconds. This explains the rapid response of induced absorption on the green light power observed in Fig. 1. The significant decrease in GRIIRA over a threshold concentration can be attributed to the complete elimination of intrinsic defects of Nb_{Li} following the incorporation of Mg on Li sites.

The increase of GRIIRA with doping in the region under

threshold needs some comments. Both the rate of excitation of electrons to the conduction band and small polaron lifetime will contribute to the IR absorption along with Nb_{Li} concentration. As to the concentration, it is clear that undoped SLN crystals contain lower intrinsic defect densities than conventional CLN crystals, but they still contain Nb_{Li} at a level of thousands of ppm. Since SLN crystals show stronger GRIIRA than CLN crystals the other factors should play a very important role.

As for the excitation rate, it should be proportional to the concentration of the corresponding defects responsible for the green absorption. Fe impurity is known to contribute to excitation of electrons to the conduction band. The concentration of Fe was determined by chemical (ICP) analysis to be in the ppm levels both in SLN and CLN. This number is well below the concentration of Nb_{Li} shallow traps, even in SLN, so that it is likely that most excited electrons will be trapped by Nb_{Li} . This is why the dominant factor in GRIIRA, for the same excitation rate, is probably small polaron lifetime. In this way it is possible that small polaron lifetime increases dramatically near the threshold. This assumption has to be checked experimentally.

In summary, we have investigated green-induced infrared absorption and photorefractive index by means of the photo-thermal common-path interferometry technique. We observed that MgO doping had similar results for reducing GRIIRA in LiNbO_3 , namely that less MgO was necessary to eliminate GRIIRA in stoichiometric LiNbO_3 than in congruent LiNbO_3 . LiNbO_3 crystals doped with MgO at levels exceeding threshold concentrations of 1 mol. % for SLN and 5 mol. % for CLN exhibit no measurable GRIIRA with an irradiation up to 3.5 kW/cm^2 of green light. This remarkable decrease of GRIIRA in $\text{Mg}:\text{LiNbO}_3$ is attributed to the elimination of antisite intrinsic defects of Nb_{Li} .

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