TITLE: Thermal Fixing of Holographic Gratings in Nearly Stoichiometric LiNbO3 Crystals

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Thermal fixing of holographic gratings in nearly stoichiometric $LiNbO_3$ crystals

Gábor Mandula[a], Krisztián Lengyel[a], László Kovács[a*], Mostafa A. Ellabban[b], Romano A. Rupp[b], and Martin Fally[b]

[a] Crystal Physics Laboratory, Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, H-1121 Budapest, Konkoly-Thege M. út 29-33, Hungary
[b] Institute of Experimental Physics, Vienna University, A-1090 Vienna, Strudlhofgasse 4, Austria

ABSTRACT

The thermal decay of holographic gratings recorded using the conventional two-wave mixing technique has been studied in congruent and nearly stoichiometric $LiNbO_3$ crystals doped with Mn. The activation energies of this process have been determined in the 70-130 °C range for congruent and 20-80 °C range for nearly stoichiometric crystals, the obtained values being 1.06 ± 0.03 and 1.10 ± 0.03 eV, respectively. The kinetics of the OH^- absorption spectrum has also been studied in undoped nearly stoichiometric $LiNbO_3$ between 40-120 °C. The time dependence of the band intensities can be characterized by exponential time constants obeying the Arrhenius-law. The average activation energy, $E_a \approx 1.1 \pm 0.1$ eV is in good agreement with those obtained from the thermal decay indicating that the hologram fixing process in nearly stoichiometric $LiNbO_3$ is governed by proton migration.

Keywords: hologram fixing, thermal decay, activation energy, proton migration, OH^- absorption.

1. INTRODUCTION

The light-induced refractive index change, the so called photorefractive effect has been discovered in $LiNbO_3$ [1]. This effect can be used for recording volume phase holograms in the crystal. A thermal fixing procedure has also been developed to reduce the degradation of recorded holograms during read-out[2]. It is assumed that in the annealing step thermally activated ionic movement compensates for the electronic space-charge field, while a subsequent homogeneous illumination at room temperature develops the stable refractive index pattern. It has been shown that hydrogen ions are responsible for the fixing in $LiNbO_3$:Fe[3] and in crystals having high OH^- concentrations[4]. In both cases congruent crystals were studied. It is known, however, that a number of physical properties including the photorefractive effect and OH^- absorption depends on the crystal composition. In the present work the relation between the thermal fixing process and the hydroxyl ion absorption will be studied in nearly stoichiometric $LiNbO_3$ crystals.

2. EXPERIMENTAL

Congruent (Li/Nb=0.945) and nearly stoichiometric $LiNbO_3$ crystals were grown by the Czochralski and the top-seeded solution growth methods, respectively, in the Crystal Physics Laboratory, Budapest. The crystals used for holographic recording were doped with 10^{-3} mol/mol Mn. Before each recording phase the samples were heated to 140 °C and illuminated by intense homogeneous white light for 40 minutes to erase the possible gratings remaining from the previous experiment. Then a typical two-wave mixing experiment was applied to record a grating ($\Lambda \approx 2$ μm) in the crystal at room temperature using the 488 nm radiation of an Ar-ion laser. The diffraction efficiency of the grating was read out by a low intensity 633 nm He-Ne laser. After the recording process the sample was heated to fixed temperatures and the thermal decay of the diffraction efficiency was measured. The temperature ranges were chosen to obtain time constants between 1 minute and 100 hours. Accordingly, the temperature ranges used for these measurements were 70-130 °C for the congruent and 20-80 °C for the nearly stoichiometric crystals.

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[*] Further author information
L.K. (correspondence): Email: lkovacs@szfki.hu

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An undoped nearly stoichiometric $LiNbO_3$ crystal was used for detailed IR absorption measurements performed using a Jasco FT/IR-300E spectrometer. The composition of the undoped sample was determined to be Li/Nb ≈ 0.988 [5] by UV absorption edge measurement. The composition of the nearly stoichiometric Mn-doped crystal was estimated to be the same as that of the undoped crystal, since the shape of the OH^- absorption bands, which strongly depends on the composition[6], is practically identical in both crystals. A z-cut sample was placed in a Specac heated transmission cell, the temperature of which could be controlled between room temperature and 250 °C with a precision of about 1 °C. Following a standard one-hour annealing procedure at 250 °C, the evolution of the OH^- absorption spectra was measured at selected temperatures between 40-120 °C. About 50-100 scans were collected and averaged in about 5 minutes for each spectrum recorded with a resolution of 1 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Thermal fixing

Undoped $LiNbO_3$ crystals show only weak light-induced refractive index change. The photorefractive effect can be enhanced by transition metal dopants; for this purpose a scarcely studied dopant, manganese, has been selected both for the congruent and the nearly stoichiometric crystal. After having created a periodic space charge field in these Mn-doped crystals, the relaxation of the diffraction efficiency was monitored at the chosen annealing temperatures. During this fixing process mobile ions compensate for the electronic space charge field, resulting in the decay of the diffraction efficiency. A typical time decay curve is shown in Figure 1 for the nearly stoichiometric crystal at 50 °C. The refractive index change, Δn has been calculated from the diffraction efficiency, η by using the formula

$$\eta = \sin^2 (\pi \, d \, \Delta n / \lambda \cos \theta) \tag{1}$$

where λ is the wavelength of the reading beam, θ is the angle of incidence within the crystal, and d is the thickness of the crystal. The time dependence of the refractive index change was fitted by the following equation:

$$\Delta n (t) = \Delta n_s \exp (-t / \tau) \tag{2}$$

where Δn_s is the saturation value of the refractive index change, and τ is the time constant of the relaxation process. In a thermally activated process τ follows the Arrhenius-law, i.e. the logarithm of the time constant yields a straight line as a function of reciprocal temperature. Figure 2 shows these lines both for congruent and nearly stoichiometric crystals. From the slope of the lines the activation energy of the process has been evaluated. The calculations lead to $E_a = 1.06 \pm 0.03$ eV, and $E_a = 1.10 \pm 0.03$ eV for the congruent, and the nearly stoichiometric crystals, respectively. So the activation energies of the thermal fixing process were found to be the same within experimental error for Mn-doped $LiNbO_3$ crystals having rather different compositions. These values agree perfectly with those obtained for congruent $LiNbO_3$ crystals in an early paper of Staebler and Amodei[7]. It has to be mentioned, however, that later a wide range of activation energies from 0.9 to 1.4 eV has been found both for hologram decay and ionic conductivity in $LiNbO_3$ depending on the hydroxyl impurity concentration, the range of temperature used in the experiments, the oxidation state and the dopant concentration as pointed out in Ref. 8 and references therein.

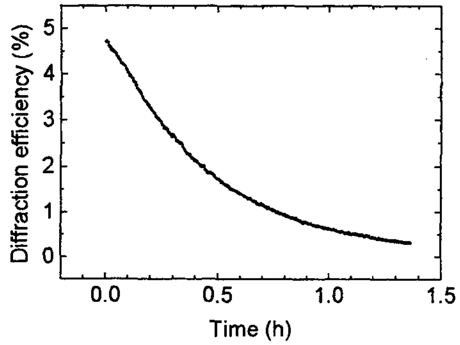

Figure 1. Evolution of the diffraction efficiency at 50 °C in a nearly stoichiometric Mn-doped $LiNbO_3$ crystal after recording of the grating at 20 °C.

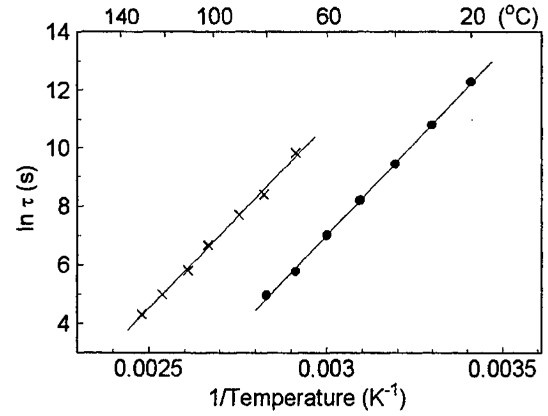

Figure 2. The Arrhenius-plot of the decay time constants for congruent (crosses) and nearly stoichiometric (dots) $LiNbO_3$ crystals.

The similar activation energy values obtained for hologram decay and ionic conductivity, the latter being linearly proportional to the hydrogen content of the crystal [9,10,11], suggested that hydroxyl ions or protons are the thermally activated ions responsible for the fixing process. Direct evidence for the proton mobility during fixing was only given in congruent $LiNbO_3$:Fe[3] and in crystals having high OH^- concentrations[4]. In the next section we will show that the proton mobility can be demonstrated in the nearly stoichiometric crystal by a new method, i.e. by monitoring the temperature dependence of the OH^- band shape.

3.2. OH^- absorption

The absorption spectrum of the hydroxyl stretch mode in congruent $LiNbO_3$ is broad and complex. In the nearly stoichiometric crystal, however, the band components corresponding to different defect sites are narrower than in congruent $LiNbO_3$ [6], which makes the decomposition much more reliable. It has already been reported that the spectrum can be satisfactorily described by the assumption of four components[12]. Figure 3 shows the decomposition of the OH^- band of an undoped nearly stoichiometric $LiNbO_3$ crystal into four Lorentzian components having wavenumbers 3465, 3472, 3479, and 3488 cm^{-1}. By careful analysis of the OH^- spectra we have observed that the intensity of the absorption band components at a given temperature changes with time, conserving the total area under the band constant. The intensities are assumed to be proportional to the proton concentrations in the corresponding defect sites. Therefore we may conclude that the protons migrate among the different sites until they reach a thermodynamic equilibrium, and they do not diffuse out of the crystal.

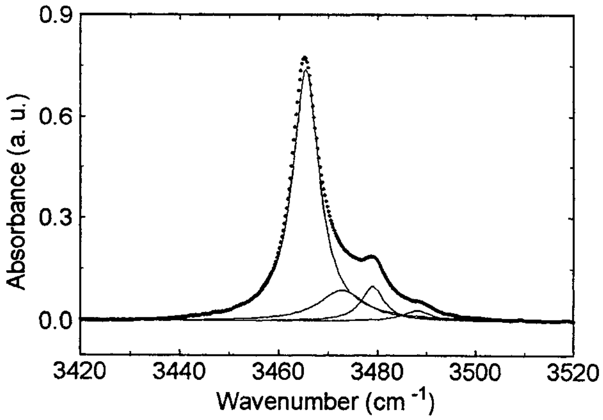

Figure 3. Decomposition of the OH^- stretching vibrational band in a nearly stoichiometric $LiNbO_3$ crystal. Dots represent the experimental spectrum, continuous lines are the fitted Lorentzian components.

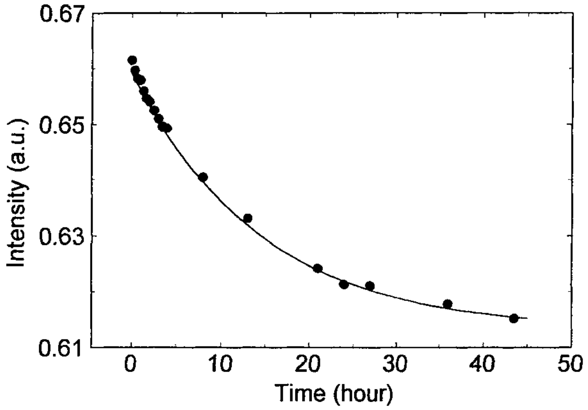

Figure 4. Intensity of the 3465 cm^{-1} OH^- band component as a function of time at 110 °C. An exponential decay curve (continuous line) was fitted to the experimental points (dots) resulting in a time constant of about 14.4 hours.

The applied initial one-hour annealings at 250 °C were sufficient to achieve a reproducible starting state for subsequent measurements. In fact, during this heat treatment no change of the OH^- absorption band shape could be observed, indicating that at this temperature the protons reach the thermodynamic equilibrium rather quickly. Following this standard procedure the temperature was set to a selected value between 40-120 °C and the measurements of spectral evolution were started by recording the spectral changes for about 25-160 hours depending on the temperature. The decomposition of the spectra is described in detail elsewhere[13]. The intensities of the four Lorentzians were plotted for each temperature as a function of time. After a relatively fast change observable mainly at lower temperatures (40-80 °C) a much slower process becomes dominant. During this slow process the intensity of the 3465 and 3479 cm^{-1} bands decreased, while that of the 3472 and 3488 cm^{-1} bands increased. The temporal dependence of the intensities can be characterized by a time constant obtained by fitting an exponential function to the data. As an example Figure 4 shows the decrease of the intensity of the 3465 cm^{-1} component as a function of time at 110 °C, yielding a time constant of about 14.4 hours. Since the change of the band intensities is also a thermally activated process one may plot the time constants versus the reciprocal temperature, and similarly to the hologram decay, an Arrhenius-type behaviour is expected. Indeed, the time constants between 80-120 °C obey the Arrhenius-law for each component. The activation energies for the four components listed above are 1.34 ± 0.08, 1.0 ± 0.2, 0.9 ± 0.1, and 1.04 ± 0.08 eV, respectively. Although the error bars are relatively large for some of the components, the average activation energy calculated to be $E_{av} \approx 1.1 \pm 0.1$ eV is in good agreement with those determined from the thermal fixing experiments. This agreement supports the assumption that the hologram fixing process is governed by protonic migration in the nearly stoichiometric crystal.

4. CONCLUSIONS

We have shown that the thermal activation energy of the dark decay of the holographic grating recorded using the two-wave mixing technique in congruent and nearly stoichiometric Mn-doped $LiNbO_3$ crystals is 1.06 ± 0.03 and 1.1 ± 0.03 eV, respectively. This agreement indicates that the crystal composition has no remarkable effect on the thermal fixing process in $LiNbO_3$:Mn. On the other hand, it has been demonstrated that the shape of the OH^- stretching vibrational band in $LiNbO_3$ changes with time until the moving protons reach a thermodynamic equilibrium at a given temperature. A careful analysis of the OH^- band shape at different temperatures allowed us to determine the activation energy of the proton migration ($E_{av} = 1.1 \pm 0.1$ eV). The agreement between the activation energy of the thermal decay and the protonic migration suggests that the protons are responsible for the thermal fixing process in nearly stoichiometric $LiNbO_3$ crystals as well.

ACKNOWLEDGEMENTS

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