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M. FALK✉
K. BUSE

Thermo-electric method for nearly complete oxidization of highly iron-doped lithium niobate crystals

Institute of Physics, University of Bonn, Wegelerstraße 8, 53115 Bonn, Germany

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ABSTRACT A new method is presented, allowing the nearly complete oxidization of lithium niobate crystals ($LiNbO_3$), doped with large amounts of iron oxide (0.05–3 wt. % Fe_2O_3) utilizing annealing at 700 °C in the presence of externally applied electric fields. The treatment results in a concentration ratio of Fe^{2+} and Fe^{3+} ions of less than 2×10^{-3}. Strong oxidization of iron in $LiNbO_3$ reduces the photorefractive effect and is therefore of particular interest for nonlinear-optical applications.

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1 Introduction

Lithium niobate crystals enable holographic recording and nonlinear optical frequency conversion [1, 2]. Important material properties like sensitivity and dynamic range for holographic recording, as well as resistance against the photorefractive effect in nonlinear optical applications are crucially determined by doping. The most studied dopant in $LiNbO_3$ is iron. It occurs in $LiNbO_3$ in two valence states, 2+ and 3+ [3]. Exposure with visible light excites electrons from Fe^{2+} to the conduction band. Inhomogeneous illumination, e.g., with a holographic interference pattern yields a charge transport in the conduction band because of the bulk photovoltaic effect [4], diffusion and drift. The electrons are finally trapped by Fe^{3+} sites, preferentially in the darker areas. Space charge fields build up and modulate the refractive index through the electro-optic effect. This allows storage of volume phase holograms all together. However, in nonlinear-optical experiments these refractive index changes, that are also present in nominally undoped crystals, are unwanted because they disturb the phase matching conditions and the beam profile. Thermal annealing changes the concentration ratio $c_{Fe^{2+}}/c_{Fe^{3+}}$ of Fe^{2+} and Fe^{3+} ions [5, 6]. This is a method to control and tailor the strength of the photorefractive effect. Usually nominally iron-free crystals still contain some ppm of Fe because of the universal presence of this element in crystal growth apparatus, and iron contamination of the source materials. For photorefractive applications doping levels of 0.02–0.2 wt. % Fe_2O_3 are optimum [7]. Crystals with high doping levels (> 0.5 wt. % Fe_2O_3) are also studied [8, 9]. They show an anomalously high dark conductivity that is attributed to tunnelling of electrons between neighboring Fe sites [10, 11]. The absorption of $LiNbO_3$:Fe crystals is determined by the overall iron concentration as well as by the $c_{Fe^{2+}}/c_{Fe^{3+}}$ concentration ratio: Fe^{2+} absorbs in the visible and near infrared, but Fe^{3+} has only a weak absorption at 483 nm that results from a spin forbidden transition [12].

In this article a method is introduced that allows nearly perfect oxidization of iron especially in highly doped $LiNbO_3$ crystals, i.e., almost all Fe^{2+} ions are oxidized to Fe^{3+}. The experiments may lead to a better general understanding of the processes occurring during thermal annealing. The method may also enlarge the $c_{Fe^{2+}}/c_{Fe^{3+}}$ range that can be adjusted for tailored photorefraction as well as for improved optical damage resistance of nominally iron-free crystals.

2 Experimental methods

The measurements are performed with congruently melting lithium niobate samples doped with 0.05, 0.5, 1, 2, and 3 wt. % iron oxide (Fe_2O_3), that are grown by Crystal Technology. The size of the crystals are $4 \times 5 \times 6\ mm^3$ (0.05 wt. %), $1 \times 10 \times 8\ mm^3$ (0.5 wt. %), $9 \times 7 \times 1\ mm^3$ (1 wt. %) and $1 \times 8 \times 6\ mm^3$ (2 wt. % and 3 wt. %). Gold paste electrodes are added to two opposing surfaces. The crystals are heated to 700 °C with a ramp of 3 °C/min, kept for 6 hours at this temperature and afterwards cooled with −3 °C/min back to room temperature. The procedure is performed in air. During the entire process a voltage of 1000 V is applied with a current limitation of 0.1 mA, i.e., for higher conductivities at elevated temperatures the voltage is automatically reduced to avoid currents larger than 0.1 mA. After the cooling process the voltage is turned off. For comparison a crystal, that is doped with 2 wt. % Fe_2O_3, is oxidized conventionally (12 h at 1000 °C in O_2 atmosphere without any external electrical field).

3 Experimental results

The temporal evolution of current and voltage is shown in Fig. 1. During the heating ramp the electrical resistance of the crystal decreases, i.e., the current increases until

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✉ Fax: +49-228-734038, E-mail: falk@physik.uni-bonn.de

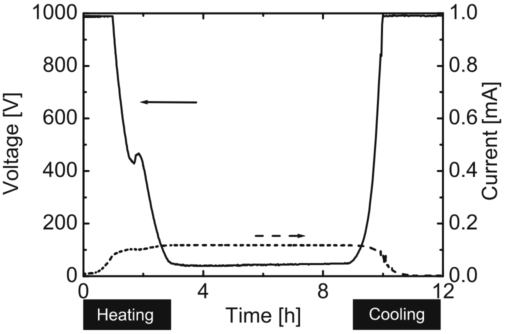

FIGURE 1 Time dependence of the voltage and the current during the annealing procedure

the limitation of 0.1 mA is reached. After this the current stays constant, but the voltage decreases. Once the temperature of 700 °C is reached, current and voltage remain constant until the cooling ramp starts. Then the electrical resistivity of the crystal increases. A reproducible anomaly of the resistivity can be seen during the heating ramp: the resistivity increases temporarily while the temperature rises.

A photo of a crystal, that is doped with 2 wt. % Fe_2O_3, before and after annealing is shown in Fig. 2. After the treatment the entire crystal is nearly homogeneously transparent. The edge between the dark and the transparent region is noticeably sharp. A fully transparent region starts to appear near the cathode and gets larger during the thermo-electric annealing.

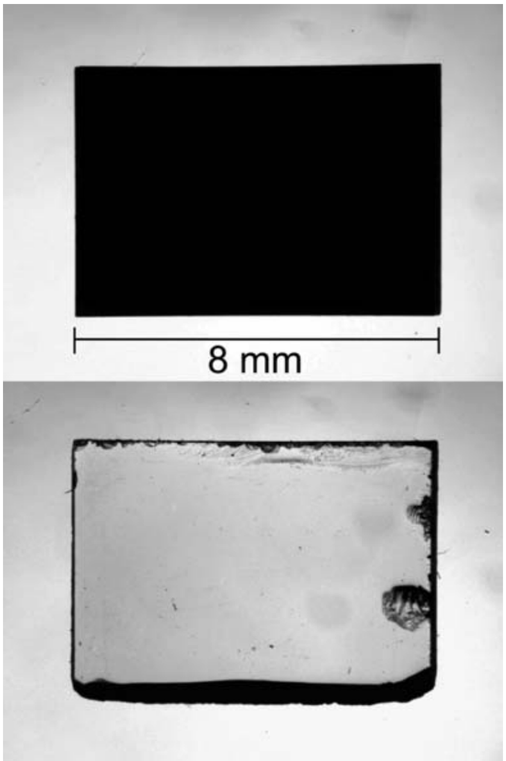

FIGURE 2 These photographs show a $LiNbO_3$ crystal, that is doped with 2 wt. % Fe_2O_3, before and after the thermo-electric treatment. The cathode was at the top, the anode at the bottom of the crystal. The absorption decreases drastically. The damage at the right side of the transparent crystal happened during polishing after the annealing

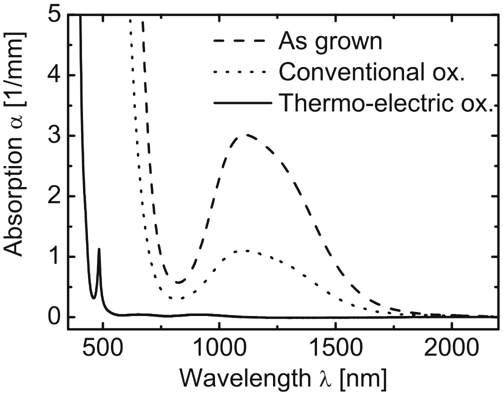

FIGURE 3 Absorption coefficient α for ordinarily polarized light versus the wavelength λ for a crystal that is doped with 2 wt. % Fe_2O_3 before and after the thermo-electric annealing. For comparison the spectrum of a conventionally oxidized crystal is added

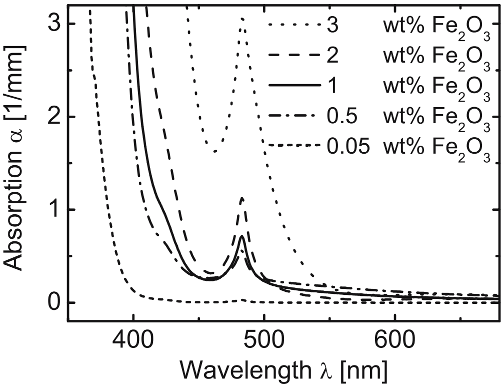

FIGURE 4 Absorption coefficient α for ordinarily polarized light versus the wavelength λ for all crystals after annealing.

After the annealing, surface decorations can be seen all over the crystal, but mainly near the cathode. Absorption spectra are shown in Fig. 3. For comparison the spectrum of the conventionally oxidized crystal is added. The absorption, that origins from Fe^{2+} [12], is strongly lowered apart from the well known Fe^{3+} absorption peak [12] at 483 nm that grows with the iron concentration as it can be seen in Fig. 4.

4 Discussion

It is reported that annealing in the presence of an externally applied electric field leads to a reduction of $KNbO_3$ crystals [13]. But the absorption spectra in the Figs. 3 and 4 show that by the proposed thermo-electric treatment $LiNbO_3$:Fe crystals get strongly oxidized. Thermal annealing of weakly-doped $LiNbO_3$ crystals in the presence of external electric fields has already been conducted many years ago [5], and also an increase of the transparency has been found, which was attributed to iron-outdiffusion. However, today it is known that in weakly doped crystals just the Fe^{2+}/Fe^{3+} concentration ratio is changed [3]. This is obviously also true for large doping levels. Because of the Fe^{3+} peak at 483 nm (Fig. 4) it can be ruled out that in the experiments presented in this article the transparency results from iron outdiffusion. The Fe^{2+} concentration can be deduced from the absorption [3] at 477 nm: $c_{Fe^{2+}} = 2.16 \times 10^{21}\ \mathrm{m}^{-2}\,\alpha_{477\ \mathrm{nm}}$, but the peak around 483 nm, that origins from Fe^{3+}[12], superimposes the absorption at 477 nm. By subtracting the peak from the absorption spectrum we get an upper limit of the absorption caused by Fe^{2+}. Assuming that the iron concentration in the melt and in the crystal are the same we can approximate the Fe^{3+} concentration $c_{Fe^{3+}}$ by the iron content c_{Fe} in the melt. It is obvious that the crystal is strongly oxidized, i.e., the assumption $c_{Fe^{3+}} = c_{Fe}$ is well justified. All together we get $c_{Fe^{2+}}/c_{Fe^{3+}} < 2 \times 10^{-3}$ for all crystals. However, the absorption at 477 nm does not necessarily result from remaining Fe^{2+} centers, it is very possible that the real $c_{Fe^{2+}}/c_{Fe^{3+}}$ ratio is orders of magnitude smaller than the upper limit stated here. Thus the crystals are extremely oxidized. The anomalous increase of the resistivity during the heating ramp (Fig. 1) can also be attributed to the oxidization that is accompanied by a decrease of mobile charge carriers.

To explain the novel thermo-electric oxidization method in $LiNbO_3$, it is reasonable to consider the drift of Li ions in the external electrical field as the crucial effect. Lithium ions are the most mobile ions in $LiNbO_3$ [14]. Probably they leave the crystal near the cathode, form compounds and build up surface decorations. For charge compensation an Fe^{2+} ion gets oxidized to Fe^{3+}:

$$\mathrm{Li}^{+}_{\mathrm{LiNbO_3}} + \mathrm{Fe}^{2+} \rightarrow \mathrm{Li}^{0}_{\mathrm{surface}} + \mathrm{Fe}^{3+} \qquad (1)$$

So the thermo-electric oxidization process can also be viewed as solid state electrolysis of the material. Hydrogen ions, that are always present in $LiNbO_3$ to some extent [15] may also migrate and leave the crystal, but they are too few to compensate for the oxidization.

Residual Fe impurities in nominally iron-free $LiNbO_3$ crystals used in nonlinear optics can cause unwanted photorefraction (“optical damage”). The thermo-electric treatment presented here may eliminate iron in the valence state 2+ and hence also reduces the photorefractive effect in such crystals. Most likely the method presented here also works for other bi-valent ions such as Cu^{+}/Cu^{2+} for example.

5 Conclusion

In this letter it is shown that highly doped $LiNbO_3$:Fe crystals can be oxidized strongly by means of a combination of annealing and an electrical field.

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