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Magnesium-doped near-stoichiometric lithium tantalate crystals for nonlinear optics

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We investigate optical damage effects and coercive fields of $LiTaO_3$ crystals and show that these properties may be tailored for applications in nonlinear optics by Mg doping and vapour transport equilibration treatments.

1 Introduction

Lithium tantalate ($LiTaO_3$) crystals are favoured materials for nonlinear optical applications, especially for second harmonic generation via quasi phase-matching [1–3]. In this case light-induced refractive index changes (optical damage) which even occur in pure crystals because of internal defects, are highly detrimental. It is well known that in $LiTaO_3$ crystals of the congruently melting composition (about 48.5 mol% Li_2O) Ta_{Li} antisite defects (Ta on Li site) are responsible for the optical damage effects [4].

A considerable reduction of this undesired optical damage in $LiTaO_3$ crystals has been achieved by vapour transport equilibration (VTE) treatments [5–7]. By this technique the Li_2O concentration was increased approximately to that of the stoichiometric composition (50.0 mol% Li_2O). Light-induced birefringence changes $\delta\Delta n = \Delta n_e - \Delta n_o$ (e and o denote extraordinary and ordinary polarization) were investigated at light intensities up to 2×10^7 Wm^{-2}. At a wavelength $\lambda = 488$ nm the changes $\delta\Delta n$ decreased from values of about 2×10^{-3} for the congruent crystals to values smaller 5×10^{-5} for the near-stoichiometric samples. However, this improvement is accompanied by a strong decrease of the coercive field which considerably reduces the stability of periodically poled domain structures necessarily required for quasi phase-matching.

In the present contribution we determine the coercive field of $LiTaO_3$ crystals quantitatively as a function of the Li_2O concentration. To work against the strong decrease of the coercive field we suggest $LiTaO_3$ crystals doped with MgO and report on investigations of coercive field and optical damage. The influence of VTE treatments is studied, too.

2 Experimental

$LiTaO_3$ crystals of the congruently melting composition are grown by the Czochralski technique. One crystal is doped by adding 2.0 mol% MgO to the melt. By VTE treatments we prepared several samples of different compositions in the range from 48.5 to 50.0 mol% Li_2O [8]. In order to prepare powder charges with a specified Li_2O content c_{Li} for a VTE treatment, starting chemicals Li_2CO_3 and Ta_2O_5 with a purity of 99.99% were used. To eliminate moisture, the Li_2CO_3 was dried at 180 °C for 24 h. For

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the preparation of a 120 g powder charge, the starting materials were milled, mixed, and loaded into a cylindrical platinum crucible of 50 mm height and 50 mm in diameter. A platinum lid film and an Al_2O_3 plate were used to cap the crucible. After that pretreatment, the powder was milled, remixed, and loaded into the crucible again. The $LiTaO_3$ crystals of 1.0 mm thickness were arranged on a platinum graticule just above the powder surface and the crucible was closed. The temperature was increased to (1380 ± 10) °C quickly and held for 286 h. Then, the furnace was cooled down in about 24 h. To perform a slow drive out of CO_2 and a good prereaction, the following procedures were applied. In all experiments, the processing temperature was determined using a thermocouple near the powder surface. First, the arrangement was heated up quickly to 600 °C. Then, an increase of 4 °C/h was used to obtain 800 °C. After 10 h, the temperature was raised to 900 °C with 10 °C/h and held for 24 h. At the end, the furnace was cooled down in about 12 h. We tested various modifications of the experimental steps to prove that these conditions are best suited to minimize losses and to maximize homogeneity.

For the coercive field measurements an electrical field is applied increasing with a constant ramp. It is known [9–11] that the electrical field E_f necessary for domain switching with forward poling is higher than the necessary field E_b with the following backward poling. With forward poling the electrical field is applied against the direction of the original polarization present in the crystal, whereas with backward poling the field is applied in the direction of the original polarization. This asymmetry can be explained by an internal field E_{int} [9]:

$$E_c = (E_f + E_b)/2\,, \qquad E_{int} = (E_f - E_b)/2\,. \tag{1}$$

As an example, Fig. 1 shows the poling behaviour of a VTE-treated $LiTaO_3$ crystal containing (49.3 ± 0.1) mol% Li_2O. The current density is plotted as a function of the applied electric field during poling. The fields E_f for forward poling and E_b for backward poling yield the coercive field E_c and the internal field E_{int} according to Eq. (1).

For the investigation of light-induced refractive index changes at light intensities up to 10^7 Wm^{-2} a single-beam setup is used (Sénarmont compensator) [6]. The extraordinarily polarized beam of an Ar^+ ion laser at a wavelength $\lambda = 488$ nm is focused by a lens to a $(1/e^2)$ diameter of approximately 80 μm and collimated to the sample. The intensity of this pump beam can be controlled by a combination of $\lambda/2$-plate and polarizer. The light-induced changes of the birefringence are determined by a weak He–Ne laser beam ($\lambda = 633$ nm) which is focused roughly to half of the diameter of the pump beam. In order to bring the pump beam and the test beam into the same direction, both beams are superimposed by the use of a non-polarizing beam splitter. The polarization of the test beam is oriented at an angle of 45° towards the optical axis of the sample (*c*-axis) which is situated in the plane perpendicular to the wave vectors of the test and pump beam. Inside the crystal the incident wave is split into an ordinary (with n_o) and an extraordinary wave (with n_e) due to birefringence. These two waves possess different phase velocities, i.e., the superposition results in an elliptically polarized beam. Behind the crystal a $\lambda/4$-plate is introduced at an angle of 45° with respect to the *c*-axis to get linearly polarized light. Depending on the natural birefringence of the crystal the polarization of the incident light is rotated and a second polarizer is

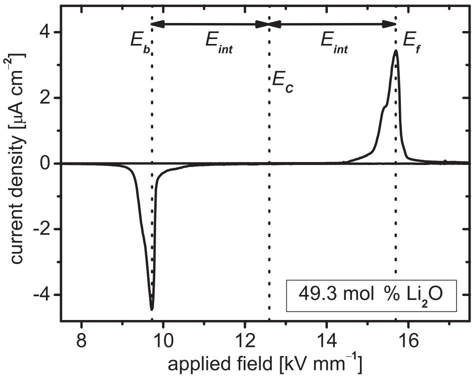

Fig. 1 Current density as a function of the applied electric field during poling of a VTE-treated $LiTaO_3$ crystal containing (49.3 ± 0.1) mol% Li_2O. The field E_f indicating poling with the forward process by the right hand current peak and the field E_b indicating poling with the backward process by the left hand current peak yield the coercive field and the internal field E_{int} according to Eq. (1).

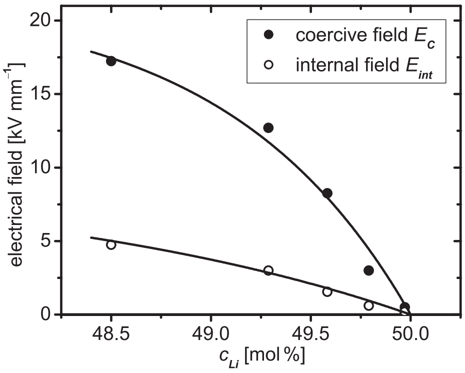

Fig. 2 Coercive field E_c and internal field E_{int} (symbols) for $LiTaO_3$ crystals of various Li_2O concentrations c_{Li}. The solid lines are fits according to Eqs. (3) and (4), respectively.

adjusted to block this probe light completely. A light-induced change of the birefringence $\delta\Delta n$ leads to an additional rotation of the polarization of the probe light. The intensity I_T behind the second polarizer is given by

$$I_T = I_0 \sin^2 (\pi\, d\delta\Delta n/\lambda)\,, \tag{2}$$

where I_0 is the incident light intensity and d is the thickness of the crystal. After each measurement the samples are heated to 300 °C for half an hour to erase the generated refractive index changes completely.

3 Results and discussion

In Fig. 2 the results for the coercive and the internal field of undoped crystals as a function of the Li_2O concentration are summarized. The coercive field E_c of (17.5 ± 1.0) kV mm^{-1} for congruent $LiTaO_3$ decreases with increasing Li_2O concentration c_{Li}. The behaviour can be described by an exponential relation (for LiO_2 concentrations smaller 50%):

$$E_c = 21.6\ \text{kV mm}^{-1}(1 - \exp\,[(c_{Li} - 50.0\ \text{mol\%})\ 1.1\ \text{mol\%}^{-1}])\,. \tag{3}$$

A similar relation holds for the internal field E_{int}:

$$E_{int} = 9.5\ \text{kV mm}^{-1}(1 - \exp\,[(c_{Li} - 50.0\ \text{mol\%})\ 0.5\ \text{mol\%}^{-1}])\,. \tag{4}$$

The decrease of E_c and E_{int} is in principle of advantage because the external electric field necessary for poling also decreases. For the stoichiometric sample exhibiting small light-induced refractive index changes, however, the coercive field is smaller than 0.5 kVmm^{-1}. This may be a problem for the stability of periodically poled domains.

For this reason we investigate the $LiTaO_3$ crystal doped with 2 mol% MgO in the melt. We find for the as grown sample a coercive field of (9.1 ± 0.5) kV mm^{-1} and light-induced birefringence changes $\delta\Delta n$ between 10^{-5} and 10^{-4} at intensities of 10^7 Wm^{-2}. The birefringence values seem to be sufficiently small, but for poling now very large external electric fields have to be applied.

Further improvements can be achieved by VTE treatments of the Mg-doped crystal using a pure powder with more than 50.0 mol% Li_2O. In the near-stoichiometric Mg-doped crystal the light induced birefringence changes $\delta\Delta n$ are additionally reduced by a factor of 2 and a coercive field of (1.7 ± 0.5) kV mm^{-1} is found. This value seems to be a good compromise. On the one hand, the periodically poled domains should show sufficient stability, on the other, the fields necessary for poling are moderate.

4 Conclusions

Near-stoichiometric Mg-doped $LiTaO_3$ crystals prepared by vapour transport equilibration are attractive materials for nonlinear optics. Optical damage effects are sufficiently small and coercive fields may be tailored by VTE treatments.

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