Influence of Zn/In codoping on the optical properties of lithium niobate

K. Kasemir, K. Betzler,[a)] B. Matzas, B. Tiegel, T. Wahlbrink, and M. Wöhlecke
Fachbereich Physik der Universität Osnabrück, Barbarastrasse 7, D-49069 Osnabrück, Germany

B. Gather
Institut für Chemie der Universität Osnabrück, Barbarastrasse 7, D-49069 Osnabrück, Germany

N. Rubinina
Moscow State University, Moscow 117234, Russia

T. Volk
Institute of Crystallography Russian Academy Science Moscow 117333, Russia

The influence of a combined doping with Zn and In on the optical properties of lithium niobate is studied. While each of these dopants is known to improve the material's nonlinear optical properties, it is an open question whether further improvements, especially of the nonlinear optical features, can be achieved by a suitable combination of dopants. Our measurements show that lithium niobate imposes certain limits which cannot be overcome. This can be described by a simple model which is based on the defect structure of lithium niobate. © *1998 American Institute of Physics.* [S0021-8979(98)08421-7]

I. INTRODUCTION

Lithium niobate is presently one of the most important crystalline materials for both linear and nonlinear optical applications. Growth properties allow the fabrication of crystals with large dimensions and excellent homogeneity. Unfortunately the material suffers from two limitations: the relatively small birefringence and the photorefractive effect — also known as optical damage.[1] Both especially restrict nonlinear optical applications of lithium niobate mainly to the near infrared region. Besides techniques which influence the Li/Nb ratio directly[2–4] the addition of dopants like Mg,[1] Zn,[5] In,[6] or Sc[7] is known to improve the material.

It is well known that with single dopants a certain limit (corresponding to a so called ''threshold'' concentration) cannot be exceeded, and preliminary studies have shown that doping with two damage resistant impurities can increase the effect of both partners.[6] It is important to study in more detail whether further improvements, especially of the nonlinear optical properties, are possible by a suitable combination of two dopants. For our investigations we selected Zn and In as typical group-II and group-III dopants, respectively. Crystals with various doping concentrations were characterized by measuring the OH^- infrared absorption, refractive indices and nonlinear optical properties (e.g., phase-matching temperature).

II. EXPERIMENTAL RESULTS AND DISCUSSION

The crystals were grown by the Czochralsky technique from a congruent melt (48.5 mol % Li_2O and 51.5 mol % Nb_2O_5) to which ZnO and In_2O_3 were added. Crystals with a Zn concentration between 0 and 4.2 mol % and In concentrations in the range 0–3 mol % were investigated. The composition of the crystals was measured using electron microprobe techniques. From these measurements the distribution coefficients of the dopants between solid and melt were determined to be about 1.2 for low concentrations of both Zn and In. For higher concentrations a slight decrease to approximately 0.8 was found. A typical dependence, the solid concentration as a function of the melt content for purely In-doped samples is depicted in Fig. 1.

A. OH^- absorption

About 30 years ago Smith *et al.*[8] described an optical absorption at about 3480 cm^{-1} in $LiNbO_3$. While they already pointed out the use of this absorption to determine the hydrogen content in the sample, its origin as OH stretch mode was established by Herrington *et al.*[9] The spectral line shape depends on the Li/Nb ratio.[10–12] Besides intensive research on undoped $LiNbO_3$, single and double doped samples have been studied for various reasons. Dopants of the transition metal or rare earth element group are used to have laser action, while the elements Mg,[1] Zn,[13,5] In,[14] and Sc[7] are chosen to reduce the optical damage. Dopants of the latter kind are responsible for a new OH vibrational transition at about 3530 cm^{-1} when exceeding a certain threshold concentration. This feature is often used to check whether doping resulted in an impurity concentration in the sample below or above threshold.

We adopted this procedure to characterize our samples. In Fig. 2 the influence of increasing In doping on the OH stretch mode spectra in undoped and Zn-doped $LiNbO_3$ is shown. Two groups of bands were observed: one with a maxima at about 3480 cm^{-1} linked by a dotted line and a second at about 3530 cm^{-1} linked by a dashed line. For single In-doped samples the frequency shift takes place between 1.05 and 1.63 mol % as already reported by Volk

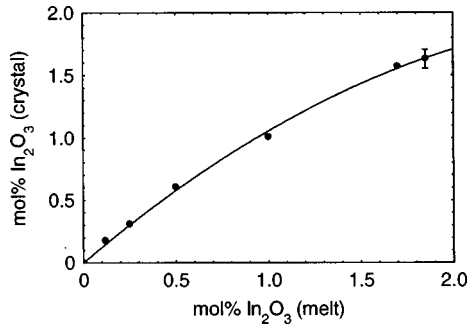[a)]Electronic mail: Klaus.Betzler@Uni-Osnabrueck.DE

FIG. 1. In concentration in the crystal as a function of the melt content for purely In doped lithium niobate.

TABLE I. Parameters for Sellmeier equation (1).

	n_o	n_e
λ_0	223.219	218.203
μ_0	1.1082×10^{-6}	6.4047×10^{-6}
A_{IR}	3.6340×10^{-8}	3.0998×10^{-8}
A_0	4.5312×10^{-5}	3.9466×10^{-5}
$A_{Nb_{Li}}$	-7.2320×10^{-8}	11.8635×10^{-7}
A_{Mg}	-7.3548×10^{-8}	7.6243×10^{-8}
A_{Zn}	6.7963×10^{-8}	1.9221×10^{-7}
A_{In}	-2.4×10^{-7}	4.7×10^{-7}

et al.,[14] while in crystals with 1.8 mol % ZnO already less than 0.9 mol % causes the same shift. At a Zn rate of 4.2 an addition of less than 0.6 mol % is able to produce this shift. This clearly demonstrates that first Zn and In add up and second that In is more powerful than Zn. In the last series of spectra with a varying In content but a fixed Zn content of 4.2 mol %, it is seen that an increase from about 1 to 2 mol % In broadens the band considerably. This suggests that one cannot simply improve the optical properties by simply raising the doping of In and Zn. This point of view will be discussed in more detail on the basis of refractive index measurements in Sec. II B.

B. Refractive indices

With an interferometric method[15] we measured the refractive indices of 19 samples co-doped with up to 3 mol % In_2O_3 at fixed ZnO concentrations of 0, 1.8, and 4.2 mol %, respectively.

In order to fit the experimental data we extended the generalized Sellmeier equation which so far succesfully described the refractive indices of pure[16] as well as Mg,[17] Zn,[18] and In single-doped[19] crystals (for a detailed explanation of the Sellmeier fit used please refer to Schlarb and Betzler[20]). We assume that in codoped crystals all dopants contribute in a cumulative way linearly to the dielectric function — at least up to a certain dopant-specific limit. The extended generalized Sellmeier equation is defined as
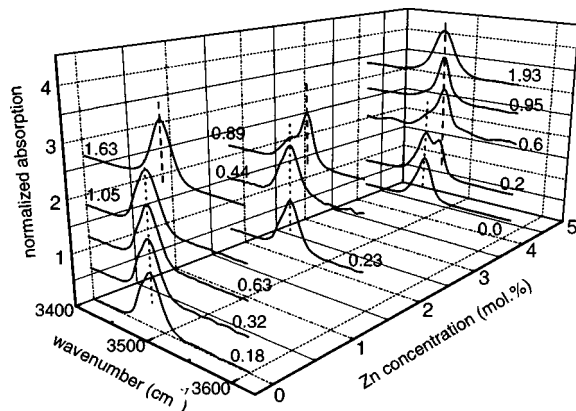
$$n^2 = \frac{A_0 + A_{Nb_{Li}}c_{Nb_{Li}} + A_{Mg}c_{Mg} + A_{Zn}c_{Zn} + A_{In}c_{In}}{\{\lambda_0 + \mu_0[f(T) - f(T_0)]\}^{-2} - \lambda^{-2}}$$
$$+ A_{UV} - A_{IR}\lambda^2, \tag{1}$$

with

$$f(T) = T^2 + 4.0238 \times 10^5 \left[\coth\left(\frac{261.6}{T}\right) - 1\right],$$

$$c_{Nb_{Li}}$$

$$= \begin{cases} \frac{2}{3}(50 - c_{Li}) - c_{Mg}/\alpha_{Mg} - c_{Zn}/\alpha_{Zn} - c_{In}/\alpha_{In} & \text{if} > 0, \\ 0 & \text{otherwise;} \end{cases}$$

$$\tag{2}$$

$$T_0 = 297.5; \quad A_{UV} = 2.6613; \quad \alpha_{Mg} = 5.0;$$
$$\alpha_{Zn} = 6.5; \quad \alpha_{In} = 1.5,$$

where the wavelength λ is in nm, the temperature T is in K, and the concentrations of the dopants Mg, Zn, In are percentages in the crystal. The Li content c_{Li} has to be extrapolated to undoped $LiNbO_3$ according to $c_{Li} = [Li_2O]/([Li_2O] + [Nb_2O_5])$. The ordinary or extraordinary index of refraction is chosen by selecting the corresponding values for λ_0, μ_0 and the A parameters from Table I.

While a complete and proven microscopic model is yet unavailable, Eqs. (1) and (2) do make simple assumptions for the defect structure of Li-deficient $LiNbO_3$ which are based on the structure models developed by Abrahams and Marsh[21]
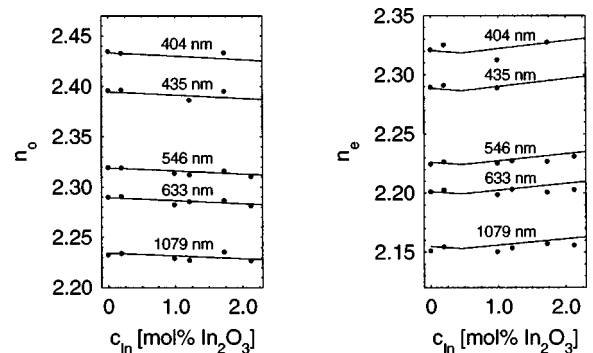

FIG. 2. Normalized OH absorption of $LiNbO_3$ doped with various amounts of In (mole percentage denoted by the numbers at the curves) and three distinct concentrations of Zn (0, 1.8 and 4.2 mol % in the sample).

FIG. 3. Variation of ordinary (n_o) and extraordinary (n_e) index of refraction as a function of In content in the crystal for codoped $LiNbO_3$ with 4.2 mol % ZnO for selected wavelengths at 296 K. Curves calculated with proposed Sellmeier equation, points are experimental data.
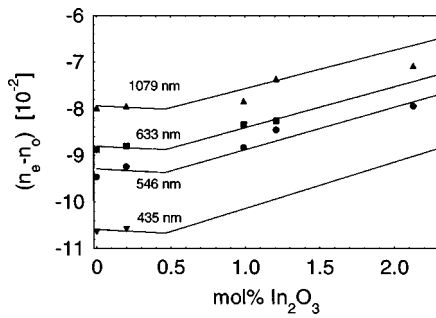
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FIG. 4. Calculated (lines) and experimental birefringence data for LiNbO$_3$:Zn:In with 4.2 mol % ZnO in comparison for selected wavelengths at 296 K.

and Iyi *et al.*,[22] respectively. The concentration of intrinsic Nb antisite defects $c_{Nb_{Li}}$ hence decreases linearly with increasing content of the dopants c_X up to a threshold α_X, which is obtained empirically. Above this threshold value, no further decrease of the Nb concentration occurs, the Nb sublattice is kept intact, and dopants are incorporated only at Li sites.

To extend the generalized Sellmeier equation to the case of codoping, all parameters were adopted from the Sellmeier fits for the respective individual dopants.[16–19] A comparison between calculated and measured refractive indices is shown in Fig. 3 for LiNbO$_3$ codoped with 4.2 % Zn and varying In content. Calculated and measured values agree well within a standard deviation of about $\Delta n = 3.2 \times 10^{-3}$ estimated for the complete range of codoping.

The excellent agreement between measured and calculated refractive indices becomes even more obvious by calculating the sensitive birefringence $(n_e - n_o)$ and comparing it to the experimental data as demonstrated in Fig. 4. The extraordinary index of refraction and consequently the birefingence show an abrupt change of slope, resulting in a minimum which — based on our assumptions — corresponds to a complete removal of Nb antisites.

C. Nonlinear optical properties

All phase-matching conditions for nonlinear effects can be derived from the refractive indices given by the Sellmeier equation. As an example the noncritical colinear phase matching temperature T_{PM} is presented in Fig. 5 for doubling
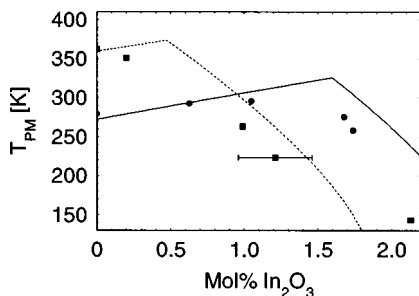

FIG. 5. Phase-matching temperature T_{PM} as a function of In content for single-doped LiNbO$_3$:In (points, solid line) and codoped (boxes, dashed line) LiNbO$_3$:In,Zn with 4.2 mol % ZnO.

the Nd:YAG radiation of 1064 nm. Please note that up to a threshold T_{PM} increases with added dopants in both single and codoped LiNbO$_3$ mostly as a result of diminishing Nb antisites. Further doping leads to a decrease of T_{PM} which, according to the premise, is caused by the dopants only. This behavior is similar to that exhibited by Mg and Zn single-doped crystals.[23]

III. CONCLUSION

Codoping with two or more dopants can be used to vary the optical properties of LiNbO$_3$ in a way similar to that using single dopants. Furthermore, the optical damage of congruent LiNbO$_3$ is greatly reduced. Yet combining Mg, Zn and In does not provide *complete* control over the refractive indices or T_{PM}, especially the high T_{PM} of stoichiometric LiNbO$_3$ ($\sim$530 K) which is not reached. Codoping can be used, however, to facilitate the fine tuning of the optical properties. The presented Sellmeier fit for the first time allows us to calculate linear and nonlinear optical properties of LiNbO$_3$ for a wide range of codoping, Li/Nb ratio, wavelength and temperature.

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