Determination of homogeneity of pure and doped lithium niobate by second harmonic generation temperature phase matching

Chr. a. d. Horst, K.-U. Kasemir, and K. Betzler
Fachbereich Physik, Universität Osnabrück, Barbarastrasse 7, D-49069 Osnabrück, Germany
(Received 13 July 1998; accepted for publication 10 August 1998)

Employing a comprehensive Sellmeier equation for the refractive indices, we derive calibration curves to be used for the homogeneity characterization of lithium niobate. Applying the calculated results, quantitative homogeneity parameters can be derived from temperature tuning curves for noncritical second harmonic generation, which are usually measured to state the composition of the material. The calibration method is of interest and presently is being used for pure as well as Mg-, Zn-, and In-doped crystals in the whole concentration regime. © 1998 American Institute of Physics. [S0021-8979(98)08321-2]

I. INTRODUCTION

For many electro-optic and nonlinear optical applications, lithium niobate (LiNbO$_3$) is one of the most interesting materials currently available; for a recent review see Ref. 1. Its physical properties can be tuned by varying the composition and adding dopants. Postgrowth vapor transport equilibration (VTE) can be used to modify the lithium-to-niobium ratio of homogeneous samples, which are grown most conveniently from congruent melts. To check the homogeneity, which is a crucial parameter for most applications, means of characterization become increasingly important for the professional development of LiNbO$_3$ devices.

A thorough analysis of methods for the characterization of LiNbO$_3$ has shown that optical methods offer excellent accuracy and are also most convenient to use. Procedures based on second harmonic generation (SHG) offer superior relative and absolute sensitivities. While these techniques can be extended to provide spatially resolved two- or even three-dimensional composition scans, it is known that simply measuring the tuning curve for noncritical phase matching as a function of temperature or wavelength is often sufficient to rank similar crystals according to their relative homogeneity.

Based on numerical calculations, we will extend this method to allow absolute quantitative measurements of crystal homogeneity.

II. PRINCIPLES OF THE METHOD

The SHG intensity $I_{SHG}$ can be written as

$$I_{SHG} \sim I_0 L \left( \frac{\sin(\Delta k L/2)}{\Delta k L/2} \right)^2$$

(1)

for fundamental wavelength $\lambda$ with intensity $I_0$, phase mismatch $\Delta k = 4 \pi (n_{\lambda} - n_{\lambda/2})/\lambda$, and crystal length $L$.

The refractive indices $n_{\lambda}$ and hence $\Delta k$ depend on temperature, wavelength, and crystal composition. Early approaches tried to fit polynomial expressions to measured indices of refraction. Schlarb and Betzler proposed a generalized Sellmeier equation permitting calculation of refractive indices for LiNbO$_3$ as a function of wavelength, temperature, and lithium content. It was soon extended to describe LiNbO$_3$ doped with Mg, Zn, and In. In homogeneous materials oscillations of $I_{SHG}$ can be observed for $T \neq T_{pm}$, particularly a periodic reduction to 0 $\pm$1 pm, the observed full width at half maximum (FWHM) of the harmonic power near $T_{pm}$, is often used as an easily obtainable criterion for crystal homogeneity. Harmonic power drops to 50% for $\Delta k L/2 \approx 1.392$, thus

$$\Delta T_{pm} \simeq \frac{1.392\lambda}{\pi L} \left| \frac{\partial(n_{\lambda} - n_{\lambda/2})}{\partial T} \right|_{T=T_{pm}}^{-1}$$

(2)

assuming a linear dependence of $\Delta k$ on $T$. Any deviations from linearity will perturb the results, mainly those obtained for small $L$, where the central peak of $I_{SHG}$ extends over a wide temperature range.

As Nash et al. deduced from calculations for undoped LiNbO$_3$, the broadening of $\Delta T_{pm}$ in inhomogeneous crystals is influenced by the way in which the constituents vary as a

Electronic mail: Klaus.Betzler@Uni-Osnabrueck.DE
function of crystal position, e.g., step-like, linear, Gaussian etc. An effective width, defined via the total area under the SHG tuning curve as

\[ \Delta T_{pm}^* = \frac{\int I_{SHG}(T) dT}{I_{SHG}(T_{pm})} \]  

proved to be independent of the model used and should be preferred at least for strongly inhomogeneous samples.

For pure LiNbO₃, both \( \Delta T_{pm} \) and \( \Delta T_{pm}^* \) can be approximated by curves based on “stretched exponentials”

\[ (\Delta T_{pm}L)(c_L) = A + Be^{-(c_L-c_L^0)^{\beta}} \]  

with only four adjustable parameters for \( c_L \) \in [48.4⋅50.0] mol % Li₂O and \( L \in [0.1\cdot10.0] \) mm.

A. Observed width

The derivative of the SHG birefringence versus temperature in Eq. (2) can be evaluated by means of the generalized Sellmeier equation for lithium niobate.\(^5\) Equation (2) can then be approximated by Eq. (4) with reasonable accuracy using the fit parameters listed in Table I. Maximal relative deviations from \( \Delta T_{pm} \) are smaller than 10⁻³ for \( L \geq 0.33 \) mm and still below 10⁻² for \( L \geq 0.11 \) mm. As an effect observable only at low \( c_L \) (corresponding to low \( T_{pm} \)), the product \( \Delta T_{pm}L \) tends to grow slightly for decreasing \( L \) instead of remaining constant. The reason for this is the nonlinear temperature dependence of \( \Delta k \) which shows up more remarkably for larger \( \Delta T_{pm} \).

B. Effective width

From a mathematical point of view, the integral in Eq. (3) should be calculated from \(-\infty\) to \(\infty\). Using the Sellmeier equation we could extend our numerical simulations from \( T=0 \) K up to temperatures \( T \) where \( I_{SHG}(T) \) falls below machine precision. The experimentally accessible temperature interval, however, is usually further limited, yielding smaller integrals in Eq. (3).

Moreover, the disappearing first derivative of \( \Delta k(T) \) for low temperatures leads to a constant \( I_{SHG}(T) \) for a large temperature interval as shown in Fig. 2. Most pronounced in the case of thin crystals or for small \( c_L \), \( \Delta T_{pm}^*(c_L)L \) tends to oscillate with \( c_L \) and \( L \). Depending on whether the integration at low \( T \) extends over a broadened minimum or side maximum of \( I_{SHG} \), the error in \( \Delta T_{pm}^*L \) might be up to 3% for the example given in Fig. 2.

Nash et al. did not observe this problem because of their linear assumption for \( \Delta k(T) \). By choosing \( T= -200 \) °C as a lower integration limit, we tried to minimize these oscillations while still matching common experimental temperature ranges.

Consequently, the fit accuracy of Eq. (4) decreases for very small crystals. Relative deviations, which are well below 10⁻³ for \( L \geq 2 \) mm, approach 10⁻² for \( L \geq 0.5 \) mm.

III. RESULTS

When comparing nominally equivalent crystals, the most homogeneous specimen can easily be detected as the one

---

### TABLE I. Fit parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \Delta T_{pm} )</th>
<th>( \Delta T_{pm}^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.8080</td>
<td>2.6550</td>
</tr>
<tr>
<td>B</td>
<td>11.625</td>
<td>14.530</td>
</tr>
<tr>
<td>C</td>
<td>48.103</td>
<td>48.098</td>
</tr>
<tr>
<td>D</td>
<td>0.3694</td>
<td>0.3345</td>
</tr>
</tbody>
</table>
yielding the smallest $\Delta T_{\text{pm}}^*$ or $\Delta T_{\text{pm}}$. For ranking samples of different length $L$, the widths $\Delta T$ must be normalized by multiplying with the length according to

\[
(\Delta T_{\text{pm}}^* L)_i \Rightarrow (\Delta T_{\text{pm}}^* L)_k,
\]

where indices $i$ and $k$ denote the respective sample. Of course one has to bear in mind the precision limitations discussed in previous sections, i.e., slight deviations for small samples.

In the absence of comparable reference crystals with the same composition and dopant concentration, or when a more quantitative analysis is required, it becomes necessary to calculate $\Delta T_{\text{pm}}^*$ or rather the size-independent product $\Delta T_{\text{pm}}^* \cdot L$ for an ideal sample from the refractive indices. This can be accomplished only numerically, using the Sellmeier description for the refractive indices.

A. Undoped LiNbO$_3$

Figure 3 shows calculated curves for the ideal observed and effective widths for undoped LiNbO$_3$ with a lithium content ranging from 48.3% to 50.0%. Undoped LiNbO$_3$ is usually grown with rather good homogeneity so each of the width values discussed can be used for characterization. This is verified by a comparison with the experimental data from different samples. The rankings via observed and effective width both yield the same results: The crystals grown near the congruently melting composition exhibit better homogeneity than the crystals near the stoichiometric composition. A simple direct comparison of the width values of the individual crystals would—as a mistake—have proved the opposite. This emphasizes the necessity for calculated reference curves.

B. Doped LiNbO$_3$

As doped LiNbO$_3$ crystals usually are less homogeneous than undoped ones, the effective width will be a better measure in this field. We therefore concentrate on the effective width despite the slightly higher experimental effort to measure it.

The calculated dependences as a function of dopant concentration for Mg, Zn, and In are shown in Figs. 4, 5, and 6, respectively. Doped LiNbO$_3$ is usually grown from a congruent melt. Because exact definitions of congruency vary slightly among authors, we choose a range of lithium concentrations from 48.4 to 48.6 mol % Li$_2$O for doped material. Considering this variation, previously published data for Mg doped crystals$^{11}$ do attest to rather uniform crystal composition.

For all of the considered dopants, the calculated ideal $\Delta T_{\text{pm}}^* \cdot L$ shows a decrease with rising dopant concentration up to a certain threshold$^{13}$ followed by an increase in further rising concentration.

Characterizing a set of recently grown In doped$^8$ crystals we observed a steep increase in the deviation between measured $\Delta T_{\text{pm}}^* L$ and ideal values (Fig. 6). For these samples, this must be explained as an increase of inhomogeneity with
the further addition of In$_2$O$_3$, emphasizing the well known difficulty of growing LiNbO$_3$:In of high optical quality.  

C. Quantitative homogeneity criterion

In the deviation of the measured real effective width from the calculated ideal one can only serve as a qualitative measure to rank crystals. To use it as a quantitative measure we developed calibration curves which relate this deviation to a corresponding inhomogeneity of Li content or dopant concentration.

As a means of comparison for inhomogeneous crystals we define a quality parameter $\xi$:

$$\xi = \frac{(\Delta T^*_{pm}L)_{ideal}}{(\Delta T^*_{pm}L)_{real}}.$$  \hspace{1cm} (6)

Assuming a Gaussian normal distribution for the concentration $c_X$ of X = Li, Mg, Zn, or In with standard deviation $\sigma$, we calculated the weighted superposition of the resulting SHG intensities as a function of temperature:

$$I_\sigma(c_X,T) = \frac{1}{\sqrt{2\pi}\sigma^2} \times \int \exp \left[ -\frac{1}{2} \left( \frac{c-c_X}{\sigma} \right)^2 \right] I_{SHG}(c,T) dc.$$  \hspace{1cm} (7)

FIG. 8. Calculated quality parameter $\xi$ for Mg-doped LiNbO$_3$ as a function of assumed variation $\sigma$, $c_{Li}=48.5$ mol % Li$_2$O, concentration of dopant $c_{Mg}$ in mol % MgO.

FIG. 9. Calculated quality parameter $\xi$ for LiNbO$_3$ doped with different molar concentrations $c_{Zn}$ of ZnO as a function of assumed variation $\sigma$, $c_{Li}=48.5$ mol % Li$_2$O.

FIG. 10. Quality parameter $\xi$ for LiNbO$_3$:In ($c_{Li}=48.5$ mol % Li$_2$O) calculated as a function of assumed variation $\sigma$ for selected mol % In$_2$O$_3$ ($c_{In}$).

The $\Delta T^*_{pm}$'s of these curves were inserted for $(\Delta T^*_{pm}L)_{real}$ into Eq. (6) to obtain a simulation of imperfect crystals.

The relationship between the quality parameter $\xi$ and the size of the standard deviation $\sigma$ is shown in Figs. 7–10.

For undoped LiNbO$_3$ (Fig. 7), a single universal calibration curve is valid for the whole concentration range of interest.

In doped LiNbO$_3$, most of the physical parameters change their behavior at the so called threshold concentration of the dopant. This threshold concentration tends to be approximately 5 mol % MgO, 6.5 mol % ZnO, and 1.5 mol % In$_2$O$_3$, respectively, for congruently grown doped LiNbO$_3$. In view of this fact, for each of the regarded dopants three calibration curves—for the concentration ranges below, around and above the threshold, respectively—are obtained (Figs. 8–10).

Special care must be taken for concentrations near this peculiar threshold $c_t$. As Fig. 11 shows for LiNbO$_3$:Mg, $T_{pm}$ reaches a maximum at $c_t$. Consequently all deviations $\sigma_{Mg}>0$ result in a diminution of the measured value for $T_{pm}$. The same effect tends to tighten $I_\sigma(c_X,T)$ near $c_t$. The parameter $\xi$ is raised accordingly, pretending improved crystal quality except for the case of In, where the strong decrease of $\xi$ with $\sigma_{In}$ for concentrations $c_{In}>c_t$ seems to compensate for this effect.

FIG. 11. Phase-matching temperature $T_{pm}$ for congruent LiNbO$_3$:Mg for different $\sigma_{Mg}$, based on the proposed simple model for inhomogeneous materials.
To characterize a sample, one has to calculate the quality parameter $\xi$ using the measured real effective width and the ideal one given in Figs. 3–6. Applying the respective calibration curve, $\xi$ then can be directly related to the concentration distribution in the sample.

Applying this procedure to the above mentioned In-doped crystals with 0.3, 0.6, and 1 mol % $\text{In}_2\text{O}_3$ from the declining quality parameters $\xi=0.93$, 0.76, and 0.34 we can state variations of $c_{\text{In}}$ by $\sigma_{\text{In}}=0.05$, 0.1, and 0.3 mol % $\text{In}_2\text{O}_3$. Likewise the obtained $\xi$ could originate from Li variations $\sigma_{\text{Li}}=0.009$, 0.017, and 0.05 mol % $\text{Li}_2\text{O}$. Together, both values for each sample can be regarded as a combined upper limit for the concentration inhomogeneities.

**IV. CONCLUSION**

Measuring $\Delta T_{\text{pm}}L$ offers an easy way to rank crystals with nominally similar properties. The effective width value $\Delta T_{\text{pm}}^*$ is better suited for crystals of arbitrary homogeneity, and a fit for both $\Delta T_{\text{pm}}$ and $\Delta T_{\text{pm}}^*$ in undoped LiNbO$_3$ and for $\Delta T_{\text{pm}}^*$ in doped LiNbO$_3$ is given. To spare tedious calculations based on the more precise Sellmeier equation, the graphed quality parameters $\xi$ for pure as well as doped LiNbO$_3$ might prove useful. Deviations from exact homogeneity can be detected by measuring the effective width and relating it to the ideal one and can be quantitatively evaluated using the calibration curves given. Deconvoluting the SHG intensity as measured with nonuniform samples thus allows one to find a bracketing interval for the Li content or dopant concentrations in lithium niobate.

**ACKNOWLEDGMENT**

Financial support from the Deutsche Forschungsgemeinschaft (Grant No. SFB 225) is gratefully acknowledged.