Composition dependence of the second-harmonic phase-matching temperature in $LiNbO_3$

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Phase-matching temperatures for 90° phase matching of Nd:YAG laser light have been measured in $LiNbO_3$ crystals with different Li/Nb ratios. Their melt and solid composition had been determined chemically with an accuracy of about 0.2%. Our results contrast to earlier work, no linear dependence of the phase-matching temperature versus the Li/Nb ratio was found. The measured dependence shows that the phase-matching temperature can be used as an excellent probe for the composition of $LiNbO_3$.

Among the few ferroelectric materials suitable for applications, lithium niobate plays an important role. Because of its interesting electro-optical, nonlinear optical and piezoelectrical properties it is widely used for integrated optics, nonlinear optics, electro-optics, and surface acoustic wave devices. $LiNbO_3$ can be grown in a comparably wide composition range,[1] a large variety of dopants may be added.[2,3] Both dopants and composition influence the crystal properties in a more or less expressed way. To check the crystal composition, several physical methods have been developed. All of them use one of the crystal properties which are strongly composition dependent. Easily measurable properties include the Curie temperature,[4] the birefringence,[5,6] and the optical absorption edge.[7] A newly presented method makes use of anisotropic holographic scattering.[8] The method of measuring the phase-matching temperature for optical second-harmonic generation (SHG) depends on the fact that the extraordinary index of refraction strongly varies with both composition[9] and temperature,[10] whereas the ordinary stays rather constant.

While the other methods often are easier to apply, the SHG method may be preferred when a spatially resolved composition check of the crystal is desired. Two-dimensional[11,12] as well as three-dimensional[13] topographies of the SHG properties and thus of the crystal composition can be achieved. Here we present new results for the SHG method concerning the accurate dependence of the phase-matching temperature on the crystal composition.

The crystals used for our measurements were grown by the Czochralski technique using computer control to generate identical conditions and sizes.[14] The Li/Nb melt composition was varied in the region $45{:}55 < \text{Li:Nb} < 52{:}48$. The homogeneity of the crystals was checked by spatially resolved second-harmonic generation (SRSHG).[11,12] A typical result of these measurements is shown in Fig. 1. The SHG intensity is plotted in a contour plot as a function of temperature and crystal position. Here the dependence on the growth direction of the crystal (c axis) is given. The peak temperature shows only slight variations, indicating that the crystal exhibits excellent homogeneity.

The experimental setup for measuring the temperature for noncritical phase matching of optical second-harmonic generation used a pulsed Nd:YAG laser ($\lambda = 1064$ nm) as a light source. The expanded beam was directed to the crystal in a geometry with the c axis of the crystal perpendicular to the k direction of the light beam. The crystal temperature could be controlled by Peltier cooling, liquid-nitrogen, cooling, or oven heating within a range of -180 to 200 °C with an accuracy of about 0.3°. The generated second-harmonic intensity was detected spatially resolved by means of an optical multichannel analyzer.

The chemical composition of the crystals was determined by analyzing the Li_2O content by an ion chromatographic method after acidic decomposition.[14] The accuracy of the analysis was about 0.2%.

The dependence of the phase-matching temperatures on the melt and the solid composition of $LiNbO_3$ for different crystals is depicted in Fig. 2. For samples with a Li content below 45.5% in melt ($<46.1\%$ in the crystal), no phase matching could be achieved even down to liquid-helium temperature. Also shown in Fig. 2 are results given by other authors.[15-17] Good agreement is found for the

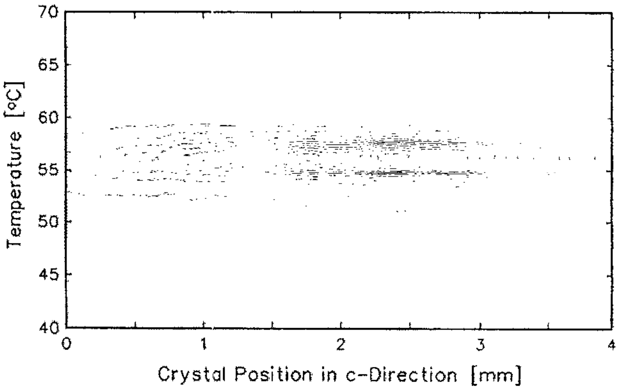

FIG. 1. SRSHG contour plot of one of the used $LiNbO_3$ crystals. Contours of equal SHG intensity are plotted as a function of temperature and crystal position in growth direction. A measure for the homogeneity of the crystal is the spatial temperature variation of the peak position.

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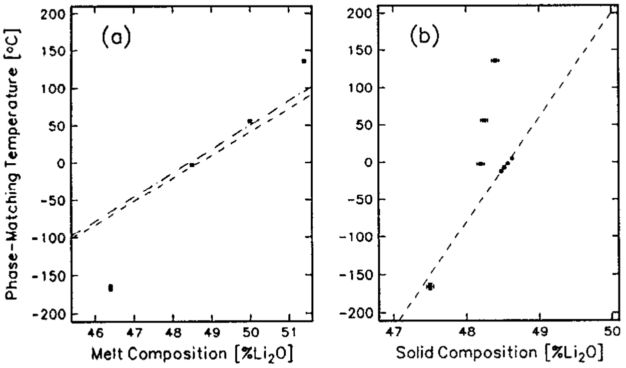

FIG. 2. Dependence of the temperature for noncritically phase-matched SHG in $LiNbO_3$ vs (a) melt and (b) solid composition. Squares: our results; circles: Chow *et al.* (taken from Ref. 16); dashed line: Noda *et al.* (Ref. 17); dash-dotted line: Fay *et al.* (Ref. 15).

medium range of the melt values and for the low concentration range of the solid values but also expressed deviations in the other ranges. Our measurements indicate that linear extrapolations (as given, e.g., by Noda *et al.*[17]) do not hold over a wider composition range. The dependence versus the solid composition shows up a more or less expressed threshold behavior as found for other properties.[18]

The sensitivity of the SHG method for homogeneity checks is approximately given by the first derivative of the measured function phase-matching temperature versus composition: dT_{PM}/dx (x: Li_2O percentage in the crystal). From our results we can derive a sensitivity which ranges from 150 K/% at low Li concentrations to 400 K/% at high Li concentrations. That means that with a relative accuracy of the measured temperatures of about 0.3 K, with the SHG method inhomogeneities down to 0.001% can be detected.

In conclusion, the SHG method for measuring the composition of $LiNbO_3$ has been applied to well-characterized samples. No simple (linear) functional dependence between phase-matching temperature and Li content—as suggested in earlier publications—can be derived. The sensitivity of the method has been shown to be extremely high, therefore it is especially suitable for homogeneity checks.

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