

## COMMUNICATIONS

**Composition dependence of the ultraviolet absorption edge in lithium tantalate**

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(Received 11 September 2002; accepted 3 December 2002)

Comprehensive preparations of lithium tantalate crystals with compositions ranging from the congruent to stoichiometric ones have been carried out. Vapor transport equilibration treatments were used to determine the composition of the samples with an absolute accuracy of 0.05 mol %. This absolute determination of the composition can serve as the basis for convenient relative methods where an easily measurable physical property allows a simple determination of the composition. As an example, we present a study of the fundamental absorption edge in the near-ultraviolet region. © 2003 American Institute of Physics. [DOI: 10.1063/1.1542689]

LiTaO<sub>3</sub> (LT), the second member of the lithium-niobate family, has been in the shadow of the famous compound LiNbO<sub>3</sub> (LN), although most of its properties are as favorable as those of LN. Both compounds have a congruently melting composition which does not coincide with the stoichiometric one, but shows a Li deficiency. The more perfect lattice of stoichiometric samples minimizes the line broadening in many spectral features and, from an application point of view even more importantly makes the material less susceptible to optical damage. Furthermore, a reduction of the coercive field is obtained, which is a significant parameter for the production of periodically poled nonlinear optical devices.<sup>1</sup> Two methods are known to grow stoichiometric material, the high temperature top seeded solution growth from potassium containing flux used for LN (Ref. 2) and the double crucible Czochralski method used for both LN and LT.<sup>1,3</sup> A third method, the vapor transport equilibration (VTE) process, is a postgrowth annealing procedure.<sup>4</sup> The availability of such LT crystals has stimulated several studies of physical properties as a function of composition (usually the Li<sub>2</sub>O content  $c_{Li}$ ), like the Curie temperature,<sup>3,5,6</sup> lattice parameters,<sup>3,7</sup> the UV absorption edge,<sup>3,6</sup> the index of refraction,<sup>6</sup> and holographic grating properties.<sup>8</sup> Only two reports deal with more than the congruent and stoichiometric compositions.<sup>5,6</sup> A general drawback is their very limited compositional resolution, a lack of information which prevents conclusive comparisons of nearly stoichiometric samples often showing a nonlinear behavior of physical properties on the composition as will be shown later.

Using the VTE treatment,<sup>4,5</sup> we prepared several samples of different compositions in the range from 48.2 to 50.0 mol % Li<sub>2</sub>O. Starting crystals for VTE processing were fabricated from Czochralski-grown boules of congruently melting composition. A furnace with resistance heating and

air atmosphere was used to grow  $y$ - and  $z$ -oriented crystals of optical quality. These were cut into plates of 0.3–0.5 mm thickness. In order to prepare powder charges with specified  $c_{Li}$  for a VTE treatment, starting chemicals Li<sub>2</sub>CO<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub> with a purity of 99.99% were used. To eliminate moisture, the Li<sub>2</sub>CO<sub>3</sub> was dried at 180 °C for 24 h. For 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<sub>2</sub>O<sub>3</sub> plate were used to cap the crucible. To perform a slow drive out of CO<sub>2</sub> 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<sup>-1</sup> was used to obtain 800 °C. After 10 h, the temperature was raised to 900 °C with 10 °C/h<sup>-1</sup> and held for 24 h. In 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.

After that pretreatment, the powder was milled, remixed, and loaded into the crucible again. LiTaO<sub>3</sub> crystals were arranged on a platinum graticule just above the powder surface and the crucible was closed. The temperature was increased to 1200 ± 5 °C quickly and held for 140 h. Then, the furnace was cooled down in about 15 h. The processing time of 140 h was derived from several experiments. Shorter times (<100 h) resulted in samples with cracks, which can be ascribed to Li inhomogeneities. To check whether the equilibration was complete for the used conditions, VTE treatments at 1200 °C and 1380 °C for 140 h with equal powder compositions and crystals of the same dimensions were performed. Both experiments yielded to identical absorption spectra of the crystals. From this, one can conclude a complete Li equilibration with the powder for the described conditions. In order to determine the Li content of the powder

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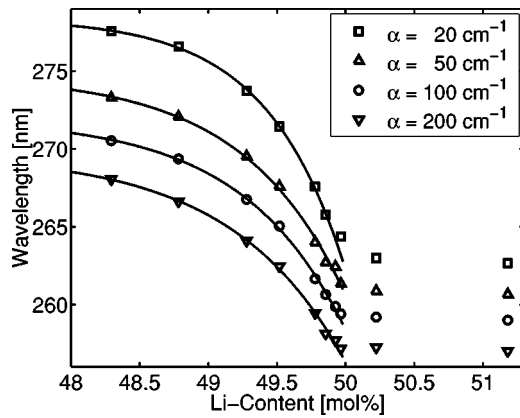


FIG. 1. Composition dependence of the wavelengths for various fixed absorption coefficients (extraordinary polarization). The Li content (mol %) denotes the Li<sub>2</sub>O molar concentration in the powder used. Below 50.0 mol %, this concentration is identical to that in the treated crystals. Markers indicate experimental data, the lines are fits according to Eq. (1).

and the crystals, an accurate weight control of the platinum components and the powder was carried out during all experiments. Thus, it was possible to calculate the evaporation losses of Li<sub>2</sub>O. To avoid the effect of impurity losses from Ta<sub>2</sub>O<sub>5</sub>, a 120 g powder charge of Ta<sub>2</sub>O<sub>5</sub> was annealed at 1200 °C for 140 h. Taking these results into account, all additional losses of the powder during the VTE treatments could be attributed to Li<sub>2</sub>O. Applying all of these steps, an absolute accuracy for the composition of ±0.05 mol % was achieved.

The polarized absorption was measured with a Bruins Instruments Omega 10 spectrometer with a wavelength accuracy of 0.1 nm, using mercury emission lines for the wavelength calibration. Polished y- and z-cut samples of about 0.5 mm thickness with a density of scratches not exceeding 1% of the illuminated area were measured at 22 °C with high spectral resolution (0.1 nm). Because of small slitwidths, sample heating is negligible. Crystal orientation is not critical; deviations of less than 5° are acceptable. The absorption data have been corrected for reflection losses applying standard equations.<sup>9</sup> The index of refraction has been taken from Ref. 10. We neglected the variation of the index of refraction with composition and temperature, because its influence on the reflection is very weak.<sup>6,10</sup>

Figure 1 shows the characteristic wavelengths λ<sub>i</sub> for various fixed absorption coefficients α<sub>i</sub>=20, 50, 100, and 200 cm<sup>-1</sup> measured as a function of the lithium content c<sub>Li</sub> (in mol % Li<sub>2</sub>O). Plotted are the data for extraordinary light polarization, for ordinary polarization similar results are found.

TABLE I. Fit parameters for extraordinary polarization.

α <sub>i</sub> (cm <sup>-1</sup> )	A <sub>i</sub> <sup>e</sup> (nm)	B <sub>i</sub> <sup>e</sup> (nm)	C <sub>i</sub> <sup>e</sup>
20	278.93	15.77	1.75
50	274.78	14.14	1.36
100	272.15	13.57	1.35
200	269.89	13.43	1.22

TABLE II. Fit parameters for ordinary polarization.

α <sub>i</sub> (cm <sup>-1</sup> )	A <sub>i</sub> <sup>o</sup> (nm)	B <sub>i</sub> <sup>o</sup> (nm)	C <sub>i</sub> <sup>o</sup>
20	276.69	14.18	1.51
50	273.37	13.26	1.34
100	271.26	12.83	1.28
200	269.06	12.71	1.17

Recently, Kim *et al.*<sup>6</sup> reported absorption edge values for five different LT compositions in the range of about 45 to 50 mol %. They deduced the absorption edge from the transmission when its value becomes 1/e of the maximum. Without knowledge of the thickness of their sample, we cannot present a quantitative comparison, but a qualitative one. The general trend is not in contradiction to our findings. In the composition range 48 to 50 mol %, covered by this work, they reported only two values, while we investigated seven crystals. This, of course, allows much more detailed conclusions which will be worked out next.

As in the case of LN, the position of the absorption edge is a very sensitive measure for the composition of LT crystals. In addition, the experimental data show that the Li content is limited to 50.0 mol %, indicating that regular Li sites can be occupied by Ta ions, but no Li can substitute regular Ta ions.

For c<sub>Li</sub> below 50 mol %, the dependence can be described by an exponential fit function with three parameters A<sub>i</sub>, B<sub>i</sub>, and C<sub>i</sub>:

$$\lambda_i = A_i - B_i \exp[(c_{Li} - 50)C_i]. \quad (1)$$

The respective parameters for the various absorption coefficients are summarized in Table I for extraordinary and in Table II for ordinary polarization.

The fit parameters are derived for a temperature of 22 °C. For other temperatures T not too far from this temperature (±10 °C) a correction of -0.12 nm/°C for both light polarizations has to be applied, the negative sign indicating a redshift of the absorption edge for increasing temperatures like in LN.

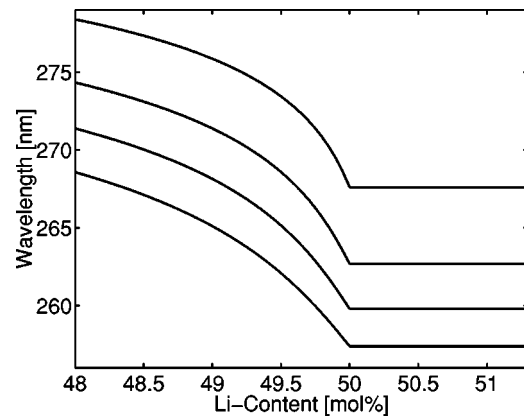


FIG. 2. Simulated composition dependence of the characteristic wavelengths for several absorption coefficients.

To get an explanation for the measured dependence of the ultraviolet absorption edge on crystal composition, we carried out a simple model calculation. Therein, an appropriate overlay of an additional near ultraviolet absorption, caused by tantalum antisite ions to the base absorption, was assumed. We presumed in the model calculation that—as found in the case of lithium niobate (Ref. 11) for niobium ions—the concentration of tantalum antisite ions increases at Li concentrations below 50%. At and above 50%, we took the concentration of the tantalum antisites to be constant at a negligible low equilibrium value. The therewith expected dependencies for several arbitrarily chosen absorption coefficients selected with similar ratios as in Fig. 1 are shown in Fig. 2. The good correspondence with the experimental results proves that the simple model chosen may well account for the measured composition dependence of the absorption edge.

The research was mainly supported by the Verbundprojekt 13N8076 of the BMBF, and to some extent by the Graduate College 695 “Nonlinearities of Optical Materials”

financed by the Deutsche Forschungsgemeinschaft (DFG) and the Federal State of Niedersachsen.

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