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Rapid Research Note

Composition dependence of the OH-stretch-mode spectrum in lithium tantalate

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The infrared absorption spectrum of the OH-stretch-mode in lithium tantalate is measured for crystals of different compositions. The spectrum exhibits two prominent lines which are representative for ideal and for Li-deficient sites in the crystal, respectively. Position, shape, and intensity of the two lines thus depend on crystal composition in a characteristic way. A comprehensive quantitative description is given which shows that the technique can be used as a sensitive non-destructive tool to rate the composition of lithium niobate.

1 Introduction Due to its excellent pyroelectric, piezoelectric, electro-optic, and nonlinear optical properties, lithium tantalate ($LiTaO_3$) is a material of growing importance for applications including detectors [1], surface acoustic wave filters [2], integrated-optical devices [3], and quasi-phase-matched wavelength converters [4]. Like lithium niobate, $LiTaO_3$ usually is grown in a congruently melting composition which differs from the stoichiometric one by a Li-deficit in the percent range. Various material properties, however, are remarkably improved in stoichiometric crystals, including, e.g., the drastically lowered electric field necessary for periodic poling [5]. Therefore growth and post-growth techniques have been developed to fabricate crystals of stoichiometric composition [6, 7]. To monitor these techniques it is necessary to rate the composition in a convenient and non-destructive way especially near the point of stoichiometry. Various methods measuring composition dependent material properties of crystals belonging to the lithium niobate family have been proposed and tested for this purpose as e. g. the determination of Curie temperature [6, 8, 9], Raman shift [10], UV absorption edge [11], refractive index [9], dielectric constant [12], or zero-birefringence temperature [13]. Common to all these techniques is a restricted absolute accuracy – even near the stoichiometric composition as the point of stoichiometry is not particularly accentuated in all these methods. As a new optical tool especially sensitive near the stoichiometric composition we introduce here the measurement of the IR absorption of the OH-stretch-mode spectrum. Distinct differences in the spectra for the congruent and for the stoichiometric compositions of lithium niobate and lithium tantalate had already been noticed earlier [14, 15]. To get a comprehensive quantitative description of the OH-spectrum we investigated this behavior in detail for $LiTaO_3$ crystals of different compositions. Our results reveal that the intensity ratio between the two characteristic lines in the spectra can be used as a very sensitive measure for the composition in the whole range between congruent

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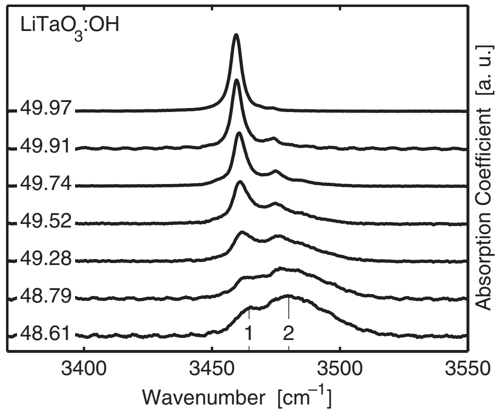

Fig. 1 Infrared absorption spectra of the OH-stretch mode in LiTaO$_3$ of various compositions. The Li$_2$O-content (in mol%) is denoted at the left. The labels '1' and '2' specifity the indices of the two lines regarded in the fit.

and stoichiometric composition. We can further show that – using such spectra – the stoichiometric composition can be accurately defined due to the peculiarity that the intensity of one of the lines approaches zero when approaching this composition.

2 Experimental For our investigations, crystals of various compositions between the congruently melting one (48.5 mol% Li$_2$O) and the stoichiometric one (50%) were prepared by vapor-transport equilibration (VTE) as described in detail recently [11]. To achieve a uniform hydrogen doping, all samples were treated in wet air for 10 hours at 800 °C. The polarized absorption spectra were measured on x-cut samples of approximately 0.3 mm thickness at room temperature with a Fourier transform spectrometer (Bruker IFS 120 HR) using a spectral resolution of 0.5 cm^{-1}. The OH absorption lines showed 95% ordinary and only 5% extraordinary polarization, therefore all evaluations were restricted to ordinary polarization. The spectra develop from broad weakly structured bands in congruent crystals to sharp lines in stoichiometric ones, as shown in Fig. 1. The *stoichiometric* shape is also revealed for samples prepared with higher amounts of Li$_2$O in the VTE treatment (up to 52%). This indicates a sharp limitation for the lithium content in the crystal at 50%, which corroborates strongly the results of other measurements [11, 13].

3 Results and discussion The shape of the spectra in Fig. 1 can be characterized by two well separated lines with composition-dependent positions, halfwidths, and intensities. One narrow line at approximately 3460 cm^{-1}, further-on denoted with index $i = 1$, dominates the spectra of near-stoichiometric crystals, the second, broader one ($i = 2$), at about 3480 cm^{-1} is characteristic for the deviation from the stoichiometric composition. Both shift with composition.

For a quantitative measure of the composition dependence we describe the measured spectra by an appropriate fit in which we use the weighted sum $S = A_1L_1 + A_2L_2$ of two Lorentzians L_1 and L_2 defined as

$$L_i = \frac{1}{\pi} \cdot \frac{\sigma_i}{(\nu_i - \nu)^2 + \sigma_i^2}, \qquad i = 1, 2. \tag{1}$$

As shown in Fig. 2 (left) the line positions ν_i show a strictly linear dependence on the crystal composition. This conforms with the dependence of the lattice parameters on composition [6] if we assume a dependence of ν_i on the O–O distance as e. g. proposed by Libowitzky [16]. From his formula we derive a slope of about 2.7 which is close to the experimental finding of 3.5 for the unperturbed mode ν_1 (see below). For the line width (Fig. 2 right), however, the dependencies differ remarkably. Whereas for line 1 the halfwidth is practically constant, for line 2 a strong increase with the deviation from the stoichiometric composition is found, which approaches a saturation value at larger deviations. This is a clear indication that line 1 reflects the ideal, stoichiometric lattice, line 2 the distorted, non-ideal one.

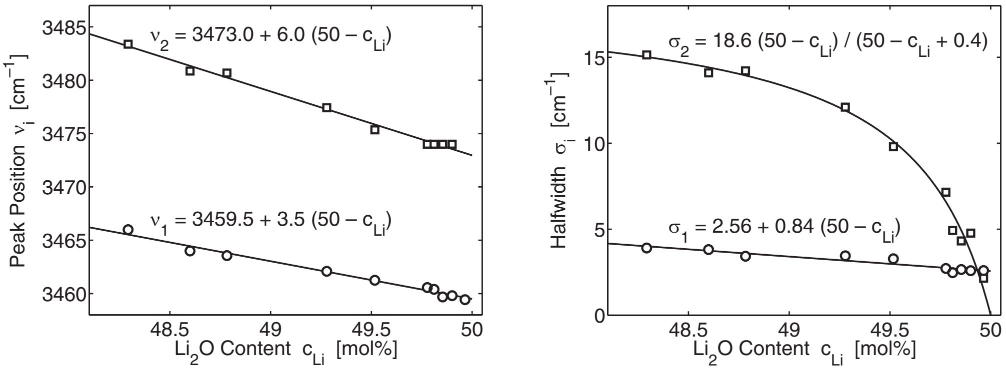

Fig. 2 Peak positions (left) and halfwidths (right) of the OH lines in lithium tantalate, values for the single spectra are denoted by dots, experimental errors are in the order of the dot size. Fits according to the formulas given are indicated by solid lines.

Even more interesting is the intensity ratio $A_2/A_1$of the two lines, plotted in Fig. 3 as function of the composition. This dependence can be excellently fitted by a quadratic behavior

$$A_2/A_1 = 6.85\,(50 - c_{\mathrm{Li}})^2 \tag{2}$$

as shown by the full line in Fig. 3. The quadratic dependence indicates that line 2 is due to OH positions which are influenced by two disordered Ta ions (probably so-called antisite defects [17]). This can also explain the remarkable broadening of this line.

The functional dependence of the intensity ratio between the two lines in the spectra depicted in Fig. 3 can be used as a sensitive measure for the composition of lithium tantalate

$$c_{\mathrm{Li}} = 50 - 0.38\,(A_2/A_1)^{0.5}. \tag{3}$$

The experimental data as well as the fit show that line 2 vanishes exactly at the stoichiometric composition, i.e. when an ideal lattice is approached. This makes the technique especially sensitive in this region, even concerning the absolute error. To rate this error, we calculated the RMS deviation of the measured points from the fit curve. The value of 0.049 found for the points near the stoichiometric composition corresponds to an accuracy in the Li_2O-content of 0.02 mol%. Far away from the stoichiometric point, however, the fit gets worse, the RMS deviation grows to a value of 0.26 – corresponding to a reduced accuracy of 0.1 mol%. The large difference is due to the fact that near the stoichiometric composition we deal with two well separated narrow spectral lines whereas far from it we have to rate a weak line on top of a dominating broad one. For spectra with broad lines, therefore, in addition to the intensity ratio also the line positions should be concerned (for the appropriate equations see Fig. 2) which will improve the accuracy to approximately 0.05 mol%.

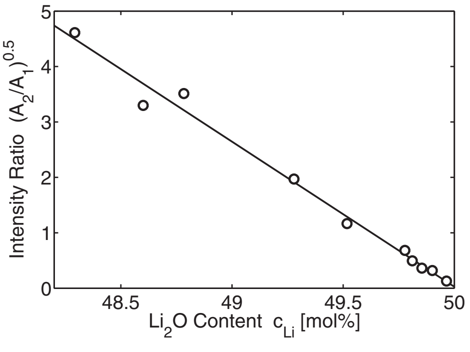

Fig. 3 Ratio of the OH-line intensities in lithium tantalate as a function of the composition. Plotted is the square root of the intensity ratio versus the Li_2O content to show the quadratic behavior. Dots indicate values for the separate spectra, the solid line represents the quadratic fit described in the text.

4 Conclusion The infrared stretch-mode spectrum of OH in lithium tantalate shows an expressed dependence on the crystal composition. Two lines dominate the spectrum, representing stoichiometry and deviation from it. Utilizing the fits given here, the intensity ratio of these two lines can be used as a sensitive measure to monitor the composition in a convenient and non-destructive way. Near the stoichiometric composition, the technique proposed yields an accuracy (0.02 mol%) which is unmatched by other techniques (at most 0.05 mol%). At compositions far from the stoichiometric one the accuracy is still comparable to that of the best other techniques.

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