

Raman spectroscopy study of compositional inhomogeneity in lithium tantalate crystals

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Abstract Raman spectra of LiTaO_3 single crystals with various stoichiometries were measured to investigate the compositional uniformity of these crystals. Raman spectra mapping demonstrates a spatial variation of the widths of the phonon bands for stoichiometric, congruent, and quasi-congruent samples. A significant radial compositional inhomogeneity is found to be a common feature of commercially available wafers having a near-congruent crystal composition (i.e., $x_c = \{[\text{Li}_2\text{O}]/([\text{Li}_2\text{O}] + [\text{Ta}_2\text{O}_5])\} \times 100\% = 47.85\text{--}48.50\%$) grown by the single-crucible Czochralski method. A maximum value of the composition gradient ∇x_c for a radial inhomogeneity of 0.163 and 0.036%/cm is measured for thin wafers diced from so-called congruent (vendors' value of $x_c = 48.50\%$) and quasi-congruent ($x_c = 47.88\%$) crystals, respectively. In crystals grown from highly Li-rich melts (starting composition 54.5 mol% Li_2O), a drastic spatial dependence of Raman bandwidths, indicating a significant gradual compositional inhomogeneity throughout the crystal, is found, which is due to a change of the melt composition during crystal growth. In contrast, the Raman bandwidths of near-stoichiometric crystals fabri-

cated by a vapor transport equilibrium (VTE) technique are found to be constant, i.e. these crystals are practically compositionally uniform. This conclusion has been confirmed by mapping the photoluminescence intensity, evidencing $\nabla x_c \leq 0.006\%/cm$ in near-stoichiometric VTE-treated crystals.

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1 Introduction

Lithium tantalate (LiTaO_3 , LT) is an advanced ferroelectric material for, e.g., surface acoustic wave (SAW), electro-optic (EO) and nonlinear optical devices. On the other hand, waveguide technology in LT crystals has attracted considerable interest for new applications such as integrated optical devices [1]. Because the refractive index of LT crystals was found to depend strongly on crystal composition [2, 3], growth of LT crystals with compositional uniformity is important, as even a relatively small crystal compositional inhomogeneity has dramatic influences on the performance of various integrated optical devices [4]. However, the difference in compositional uniformity of crystals fabricated by different methods, which are in common use today, has not been clarified yet.

Since the specific Raman bandwidths in a LT crystal generally depend on the Li deficiency (i.e., on stoichiometry) [5, 6], it is possible to determine the composition by accurate measurement of the full width at half maximum (FWHM) of certain phonon bands. In this work, mapping of Raman spectra is used to investigate the compositional uniformity of LT crystals having stoichiometric, congruent, and

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quasi-congruent composition. The presence of heterogeneity in a Raman spectra map may be regarded as the evaluation criterion to check the uniformity of stoichiometric composition.

2 Experimental

Nominally pure LT crystals with different values of their average stoichiometric compositions were characterized by confocal Raman scattering spectroscopy, as the bandwidth of some Raman bands drastically depends on the composition of the respective sample, i.e., on the concentration $[\text{Li}_2\text{O}]$, or more generally, on the composition parameter defined by $x_c = \{[\text{Li}_2\text{O}]/([\text{Li}_2\text{O}] + [\text{Ta}_2\text{O}_5])\} \times 100\%$ [6]. Since the photoluminescence (PL) intensity depends on x_c [7], the homogeneity of some LT crystals has been checked additionally by PL intensity mapping.

A LabRAM Jobin–Yvon spectrometer has been used for Raman and PL spectra measurements. Radiation of a He–Ne laser (wavelength 632.8 nm) is focused by microscopic objectives (objective used is $50\times$ (NA = 0.75) or $100\times$ (NA = 0.90)) on the crystal surface. A back scattering scheme is used to detect the Raman signal through a confocal aperture, allowing one to extract the light scattered from an extremely small region (the specific size is of the order of a few μm) of the crystal.

In our study we investigated crystals with different compositions x_c ranging from 47.2 to 49.97 %, according to specifications provided by the crystal suppliers. It should be noted that we have taken into account the findings reported in [2], where the congruent composition of LT was determined to be less than or equal to 47.7 mol% Li_2O . On the other hand, many researchers reported values ranging from 48.3 to 48.5 mol% Li_2O as the true congruent composition (e.g., see [3, 8–11]), which are called congruent throughout these works. Thus it has been established [2] that the use of the Czochralski (CZ) growth process and a melt composition of 48.39 mol% Li_2O yield crystals with a practically uniform solid composition between 47.85 and 47.88 mol% Li_2O , which is explained by the lithium rejection from the growth interface, which is exactly balancing the Li loss at the melt surface. We call these crystals quasi-congruent [6].

To examine this growth issue, LT wafers were obtained from five different suppliers. The suppliers were Crystal Technology Inc., Ltd., Deltronic Crystal Industries Inc. Ltd., Yamaju Ceramics Co. (YCC), Shin-Etsu Chemical Co., and North Crystals Co. Besides these commercially available LT wafers, several experimental samples have been also investigated: (1) Z- and X-cut plates of nominally pure congruently melting crystals grown from a melt with composition of 48.50 ± 0.04 mol% Li_2O ; (2) Z- and X-cut plates of

nearly stoichiometric (49.97 ± 0.01 mol% Li_2O) LT single crystals fabricated by the crystal growth team of Osnabrück University, using the vapor transport equilibration (VTE) technique [8, 9]; and (3) bulk samples of a crystal grown from a highly Li-rich melt (initial melt composition 54.5 mol% of Li_2O). All samples were optical-grade polished with surfaces perpendicular to the corresponding crystallographic axes.

3 Experimental results

The dependence of the Raman spectra on x_c was investigated in the various LT crystals. Figure 1 shows the Raman bandwidth of the phonon band at 600 cm^{-1} as a function of x_c , according to our previous study of the experimentally grown crystals with known compositions [6]. The Raman spectra changes are caused by an increase of the intrinsic defect concentration, such as $[\text{Ta}_{\text{Li}}]$ and $[\text{V}_{\text{Li}}]$ with $[\text{Li}_2\text{O}]$ reduction. The substitution of Li by Ta reduces the translational symmetry of the lattice and changes ionic masses and force constants. Each of these effects contributes to the line widths of the lattice modes. As the compensation by Ta ions is proportional to the amount of missing Li ions, the Li deficit should show up linearly in the variation of the mode line widths, similar to LiNbO_3 crystals [12]. As a result, if the Raman bandwidth of any crystal area is evaluated experimentally, a local value of x_c for this crystal area can be estimated. However, the Raman spectra measurement, which is basically performed on a local point, must be recorded at many positions to inspect the wafer surface's uniformity. At the same time, as our micro-Raman spectrometer has an automatic mapping function, Raman spectroscopy represents a fast and easy way to check the distribution of defects in an entire crystal. Therefore, a more efficient way to evaluate compositional uniformity may be based solely on Raman measurements.

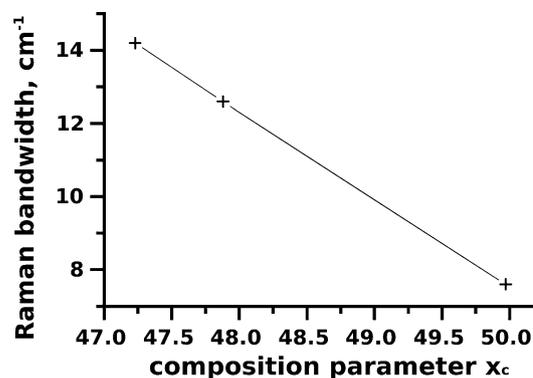


Fig. 1 Bandwidth γ of phonon band A_1 (600 cm^{-1}) as a function of x_c for LT crystals with different composition. From the linear fit to the measured data a local composition value of x_c can be estimated by $x_c[\%] = 53.1468 - 0.4180\gamma$ [cm^{-1}]

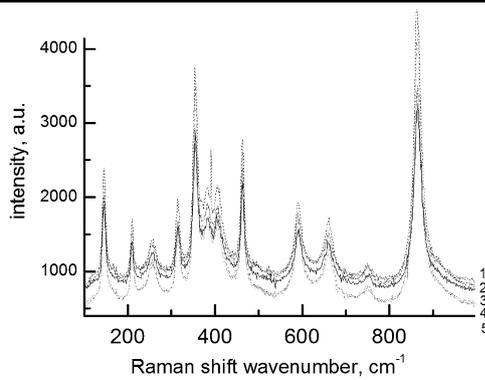


Fig. 2 Variation of Raman spectra along the growth direction in so-called congruent LT crystal grown from melt with 48.5 mol% Li_2O . (1) to (5) denote the different areas along the crystal boule: (1) is near the boule bottom, and the corresponding axial position is $X = 0$; (2) is 4 mm above the boule bottom, i.e. $X = 4$ mm; (3) is for $X = 20$ mm; (4) for $X = 54$ mm; (5) for $X = 58$ mm, i.e. the top area near the “boule shoulder” (the name of this area is taken from [10])

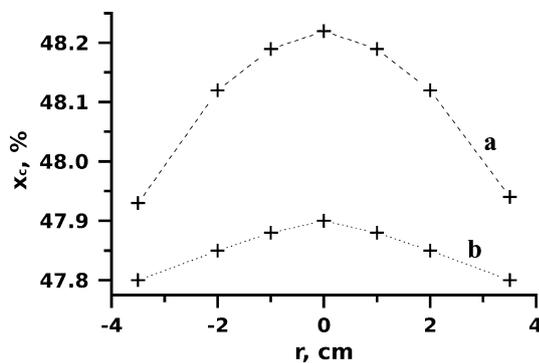


Fig. 3 Spatial distribution of the composition parameter x_c along the lateral direction showing radial inhomogeneity of a standard congruent LT wafer (a) and quasi-congruent LT wafer (b)

In Fig. 2 this spatial dependence along the growth direction of the crystals is shown. In the so-called congruent LT crystals, the Raman bandwidth gradually increases with increase of the distance from the top of the crystal. This indicates that the composition gradually changes as it grows. In addition, the variation of the Raman bandwidth along the lateral direction was measured, and a significant level of radial compositional inhomogeneity has been found in all non-stoichiometric experimental crystals.

Raman mapping demonstrates a pronounced variation of phonon bandwidths for wafers of both congruent and quasi-congruent composition, pointing to a significant compositional inhomogeneity in wafers diced from standard crystals produced by the single-crucible CZ growth method; see Fig. 3. The composition gradient ∇x_c (relative composition change per unit length) depends on the orientation and position of the wafer relative to an as-grown crystal boule used for wafer fabrication. The maximum value of ∇x_c for radial inhomogeneity is found to be 0.163 and 0.036%/cm

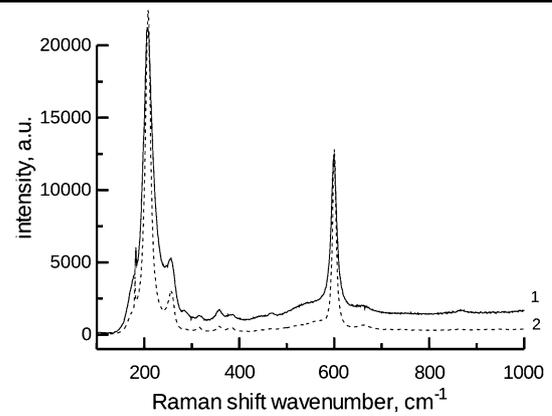


Fig. 4 Raman spectra of off-congruent (“stoichiometric”) LT crystal grown from (1) Li-rich melt (with 54.5 mol% Li_2O) and (2) near-stoichiometric LT crystal fabricated by a VTE method. Broadening of the four most intensive Raman bands, weak (but evident) extra bands and marked PL intensity (background intensity in the spectral range from 300 to 1000 cm^{-1}) in the spectrum of off-congruent LT point to a significant concentration of intrinsic defects in contrast to VTE-LT crystals

in wafers cut from congruent and quasi-congruent crystals, respectively. Thus, the vendors’ value of x_c should be regarded either as a starting composition parameter of the melt used, or as a value averaged over different parts of many wafers. According to the specifications of the so-called quasi-congruent LT crystals supplied by Crystal Technology Inc. [13] and Deltronics Crystal Industries Inc. [14], these crystals should have an average composition of $x_c = 47.88 \pm 0.015\%$, a small compositional inhomogeneity within thin crystal wafers and a small dispersion of composition among various wafers. However, the minimum value of the radial inhomogeneity, $\nabla x_c \approx 0.015\%/cm$, was observed only for a 2-cm-radius central part of some best quasi-congruent wafers. At the same time, even such a small level of compositional inhomogeneity was found to be not acceptable for fabrication of integrated optical devices [4]. On the other hand, for LT wafers grown from melts with ~ 48.5 mol% Li_2O , having compositions of $x_c = 48.22$ – 48.40% in the center, radial dispersions in the range $0.05 \leq \nabla x_c \leq 0.163\%/cm$ are obtained.

According to the phase diagram of the Li_2O – Ta_2O_5 pseudo-binary system, the $\text{Li}_{1-x}\text{Ta}_{1+x}\text{O}_3$ solid solution with a stoichiometric composition ($\text{Li}:\text{Ta} = 50:50$) was found to coexist in equilibrium with a Li-rich liquid phase near the eutectic point [15]. Using this phase relationship, Li-rich melts were used for crystal growth by the CZ method and the initial composition of the melt was set at 54.5 mol% Li_2O , which should theoretically allow [15] for the growth of a stoichiometric LT (SLT) crystal. Compositional uniformity of this LT crystal was measured by Raman spectra that we have recorded in different areas of the crystal boule, resulting in maximum values $\nabla x_c = 0.215\%/cm$. Furthermore, the Raman spectra analysis demonstrates (Fig. 4) that

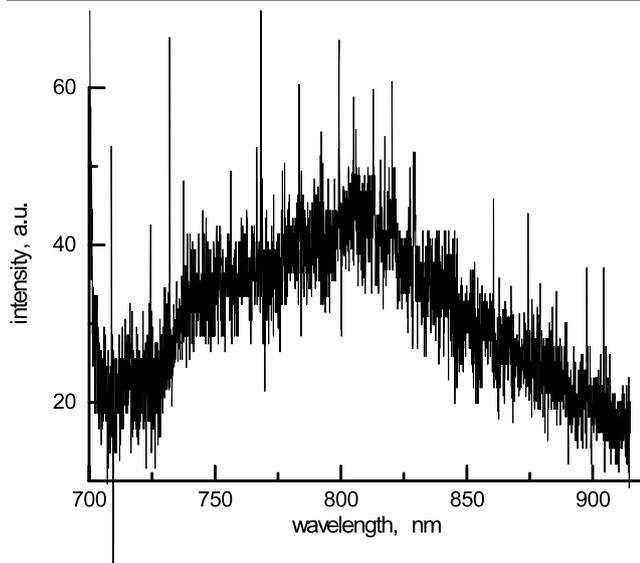


Fig. 5 PL spectrum of X -cut wafer of near-stoichiometric VTE-LT crystal ($x_c = 49.97\%$) at high-intensity excitation via focused beam (microscope objective $50\times$ ($NA = 0.75$)) of a 5-mW He–Ne laser. Polarization geometry is $X(YZ)X$

any area of the crystal grown from a Li-rich melt has a significant inherent Li deficiency.

In contrast to the former results, Raman spectroscopy measurements show that near-stoichiometric crystals ($x_c = 49.97\%$) produced by the VTE technique [8, 9] are practically compositionally uniform. In such VTE-LT crystals, except for the region near the crystal surface, the Raman bandwidth is found to be constant along the lateral direction. These results confirm the recent finding [16], that the CZ method combined with the VTE technique enables both homogeneity and near-stoichiometry of the crystal composition. It should be noted that a rather high degree of compositional uniformity was recently also reported for near-stoichiometric LT crystals grown by the double-crucible CZ growth technique [10].

The uniformity of VTE-LT crystals has been further confirmed by mapping of the photoluminescence (PL) intensity with the aid of a confocal Raman spectrometer. Figure 5 shows an example of a PL spectrum excited by a strongly focused beam of a He–Ne laser in a near-stoichiometric VTE-LT crystal ($x_c = 49.97\%$). A broad luminescence band is centered at a wavelength of 820 nm (this band has a larger intensity in the both congruent and quasi-congruent crystals). Although measured PL intensities cannot be used directly as an absolute measure of the stoichiometric composition, in-plane PL intensity mapping may be effectively used for tomography of composition inhomogeneities of LT wafers. Such a PL intensity map obtained with a LabRAM Jobin–Yvon spectrometer in automatic (XY) scan mode for high-intensity excitations at a wavelength of 632.8 nm is shown in Fig. 6 for the VTE-LT crystal. Although the PL

intensity is quite uniform, for a quantitative analysis of the residual inhomogeneity it is necessary to study the dependence of the PL intensity on x_c .

4 Discussion

As has been shown experimentally, the congruent and quasi-congruent crystals show a significant degree of compositional inhomogeneity. It may be concluded that the growth process for LT has not yet reached the maturity level exhibited by LiNbO₃(LN). For example, commercially available LN crystals have a compositional uniformity of ± 0.003 mol% Li₂O within large-diameter boules [17]. From this value a composition gradient $\nabla x_c \leq 6 \times 10^{-4}\%$ /cm can be obtained, which is undetectable by Raman and other modern methods. Because LT has the much higher melting point of $T_m = 1650^\circ\text{C}$ compared to LN ($T_m = 1253^\circ\text{C}$ for congruent composition), at such relatively high temperatures Li₂O out-diffusion during growth is likely to be high. This results in off-congruent (Li deficient) and compositionally non-uniform LT crystals exhibiting a large number of defect sites [2]. Because earlier grown crystal parts (top of boule) have a longer exchange time with the surrounding atmosphere, the exchange (Li deficit) is more pronounced in those regions (see Fig. 2). Such an inhomogeneity level is not acceptable for most applications of wafers diced from LT crystals.

The value of extraordinary refractive index n_e is sensitive to the stoichiometric composition x_c and tends to change during crystal growth as $\partial n_e / \partial x_c = 0.0065$ (mol%)⁻¹ [10]. However, applications on integrated optics require maximum fluctuations of x_c within a wafer to be below 0.01 %, which corresponds to 6.5×10^{-5} in terms of refractive index fluctuations. It is extremely hard to measure such a small difference using direct methods, and only indirect methods, based on the measurement of intermediate physical parameters, may be suitable. Although Raman scattering tomography is not suitable for direct determination of the refractive index itself, it may be used to evaluate the uniformity of the stoichiometry composition as well as the distribution of intrinsic strain. Therefore, from the in-plane composition x_c within the wafer surface one may conclude to the homogeneity of the (extraordinary) refractive index n_e of the respective sample [10, 11], which is a crucial property for integrated optical devices having rather large dimensions along the (main) propagation direction of guided light. Note that the effect of nonuniform intrinsic strain, manifesting itself in a spatially dependent frequency shift of Raman bands [18], has not been observed in all the studied LT crystals. Thus, Raman tomography may be employed for acceptance inspection of advanced LT wafers for integrated optical device fabrication. According to the previously published findings [6, 18, 19], Raman tomography should be applicable to wafers of all orientations.

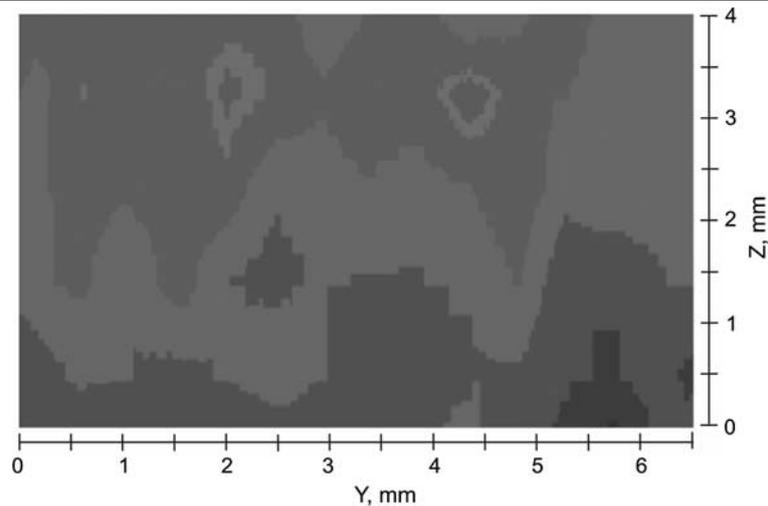


Fig. 6 In-plane tomography of photoluminescence (PL) intensity of the *X*-cut surface of a near-stoichiometric VTE-treated LT wafer. The excitation wavelength was 632.8 nm with a power of about 5 mW, corresponding to the high-intensity excitation regime (LabRam confocal microscope with objective 100 × (NA = 0.90) and 150- μ m confocal

aperture, thus photometered depth is estimated to be around 6 μ m). PL intensities are shown by a linear gray scale, where the relative difference between maximum (*bright gray*) and minimum (*black*) PL intensities is described by a factor of 1.12

At the same time, the PL spectra measurement may be used as a complimentary or primary method for the evaluation of compositional uniformity of nominally pure LiTaO₃ crystals. Combined solution of the previously derived equations, describing the dissociation-annihilation process [20] and the PL excitation [7], gives the following result for the dependence of the polaron PL intensity I_{lum} on the exciting cw light intensity J :

$$I_{\text{lum}} \sim AJ^{3/2}(0.5 - x_c/100\%)^{1/2} \quad (1)$$

where A is a proportionality coefficient related to the degree of small residual chemical reduction (i.e., concentration of bipolarons in nonilluminated crystal), quantum efficiency of luminescence, absorption cross section for bipolarons (B), generation and recombination rate of single polarons (P) within a photoinduced second-order reaction [20]: $B \Leftrightarrow P + P$.

Thus, the PL intensity should decrease with x_c , tending to zero at $x_c \rightarrow 50\%$. We see that relation (1) is in good agreement with the general feature of experimentally observed dependences of I_{lum} on x_c and J . Therefore, the contrast in the PL intensity map, which is related to the variation of x_c in near-stoichiometric LT crystals, can be described by

$$\partial(I_{\text{lum}})/\partial x_c \sim 0.5AJ^{3/2}/(0.5 - x_c/100\%)^{1/2} \quad (2)$$

According to the latter relation, to obtain a higher PL contrast, it is necessary to use an excitation with the highest acceptable intensity J . Using our experimental data on the PL contrast (see Fig. 6) with respect to the signal-to-noise ratio and the absolute value of $x_c = 49.97 \pm 0.01\%$ provided by

VTE-LT crystal's producer [8,9], the relative compositional resolution of confocal PL mapping is estimated by (2) to be about ≤ 0.0025 mol% [Li₂O] in this particular case. At the lower limit of the near-stoichiometric range ($x_c \approx 49.6\%$), the relative compositional resolution must be worse (about 0.012 mol% [Li₂O]). Of course, the evaluation accuracy of the absolute value of x_c with the aid of PL spectroscopy may be worse than these figures, as it is mainly limited by the accuracy of the data on x_c for standard samples used for calibration of relative variations. Another limiting factor consists of the fact that in near-congruent crystals the PL intensity depends primarily on the degree of the residual chemical reduction and secondarily on the relatively small variation of the stoichiometric composition within the specific range of the inhomogeneity of these crystals. However, there is a rather good quantitative correlation between the spatial variations of the PL intensity and Raman bandwidth in all the near-congruent crystals studied (e.g., see Fig. 2). It may be concluded that the residual chemical reduction degree is almost constant along LT crystals fabricated in standard conditions.

The PL intensity map may provide more detailed information on the composition distribution compared to that achieved with a Raman map. For example, no difference in the Raman bandwidths was observed at different regions of the near-stoichiometric LiTaO₃ crystals fabricated by the VTE technique. At the same time, the PL intensities differ by 1.12 times (Fig. 6), which allows one to highlight a lateral compositional non-uniformity of $\nabla x_c \leq 0.006\%/cm$, while the absolute average value of the composition is $x_c = 49.97 \pm 0.01\%$ in these VTE-LT crystals.

5 Summary

Raman spectroscopy was used for a non-destructive determination of the real composition of LiTaO_3 crystals with various average stoichiometric compositions. Besides, Raman spectra tomography was used for the absolute evaluation of the compositional uniformity with a rather good accuracy of about ± 0.03 mol% Li_2O . Additional photoluminescence (PL) spectroscopy was used for the mapping of small relative variations of the composition in near-stoichiometric crystals, reaching a high accuracy of $\leq \pm 0.0025$ mol% Li_2O in some particular cases.

Our Raman data point out a significant compositional inhomogeneity in commercially available LiTaO_3 wafers diced from so-called congruent and quasi-congruent crystals, which are in common use today. At the same time, Raman and PL tomography measurements show that the near-stoichiometric crystals (49.97 ± 0.01 mol% Li_2O) produced by the VTE technique are practically compositionally uniform. This confirms the prospects of the VTE technique and leads us to assume it to be a promising alternative to the direct melt growth technique for fabrication of compositionally uniform LT crystals acceptable for integrated optical applications.

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