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Determination of the Ta and Nb ratio in $LiNb_{1-x}Ta_xO_3$ by total reflection X-ray fluorescence spectrometry

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Abstract

A procedure for evaluation of the mass ratio between Ta and Nb in $LiNb_{1-x}Ta_xO_3$ single crystals by total reflection X-ray fluorescence spectrometry (TXRF) is described. The developed procedure does not require chemical preparation of the samples and it proves to be fast (30 min for sample preparation and 10 min for analysis), precise (down 1% RSD) and easy to perform. To check the methodology, the lattice parameter of each $LiNb_{1-x}Ta_xO_3$ sample was determined by powder X-ray diffraction. While the *a* hexagonal lattice parameter remains constant, a strong and linear dependence of the *c* hexagonal lattice parameter with Ta content in molar percentage has been observed for the first time.

Keywords: TXRF; Lithium niobate tantalate; XRD; Lattice parameter

1. Introduction

The technological importance of lithium niobate (LN) and lithium tantalate (LT) is in the combination of a large array of diverse and useful dielectric, elastic and electro-optical properties [1]. The possibility of growing high-quality large single crystals from a melt increases their importance. Furthermore, both materials are nowadays considered key materials for the development of integrated photonic devices, such as modulators or optical amplifiers. The crystalline solid solution $LiNb_{1-x}Ta_xO_3$ (LNT) is actually being investigated and it is theoretically a very useful material because its refractive index and its electro-optical properties can be modified from those of LN to LT, by changing the Ta/Nb or LT/LN ratio (it is the same to speak of Ta/Nb or LT/LN molar ratio because the molar relation is one to one) in the crystal from 0% molar content of LT to 100% molar content of LT. Thus, it is very important to obtain the desired structural (such us lattice parameter) and ferroelectric properties of the crystals.

For this study we take advantage of the wide separation between the solid–liquid lines from the LN-LT system phase diagrams (Fig. 1) [2]. The difficulties found in growing LNT bulk crystals with a homogeneous composition [3–5] provide us the opportunity to obtain several layers with different LT/LN ratio from a few growth experiments.

The difficulties involved in digestion processes of such compounds [6] suggest the use of a technique where a previous digestion of the sample in not needed. Total reflection X-ray fluorescence spectrometry (TXRF) was elected because it is a well-known technique that offers fast operation and acceptable precision. Its main features and potential applications can be found in the paper of Prange [7] or Tölg et al. [8]. Procedures described by of Fernández-Ruiz et al. [9–11] can be used for TXRF analysis of LNT samples to determine the LT/LN ratio.

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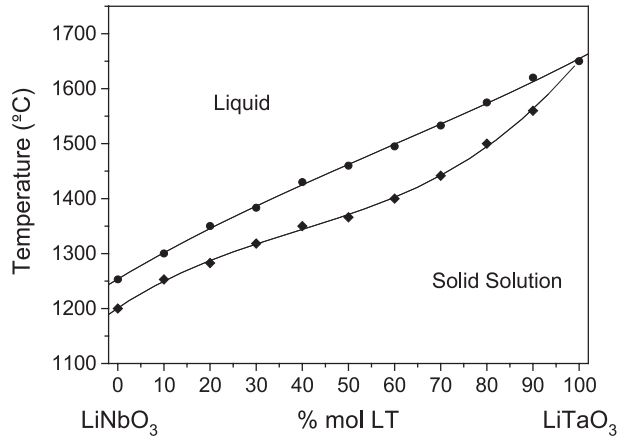

Fig. 1. High-temperature $LiNbO_3$–$LiTaO_3$ phase diagram.

It is known that Ta and Nb atoms occupy the lattice octahedral sites in $LiNb_{1-x}Ta_xO_3$. By using TXRF analysis to obtain the mass proportion of Nb and Ta present in a certain crystal, we can derive a simple and general expression as shown in Eq. (1).

$$\frac{100}{C_{\mathrm{Ta}}} = \frac{A_{\mathrm{Nb}}(1-x)}{A_{\mathrm{Ta}}x}, \tag{1}$$

where C_{Ta} is the mass of Ta relative to 100 mass units of Nb; A_{Nb} and A_{Ta} are the atomic weights of Nb and Ta, respectively, and x is the Ta stoichiometric substitution coefficient.

Rearranging these terms, we obtain Eq. (2) which yields the value of the Ta stoichiometric substitution coefficient x,

$$x = \frac{C_{\mathrm{Ta}}A_{\mathrm{Nb}}}{100A_{\mathrm{Ta}} + C_{\mathrm{Ta}}A_{\mathrm{Nb}}}. \tag{2}$$

This semi-quantitative analysis can be accomplished for any arbitrary LNT compound.

2. Experimental section

2.1. Instrumentation

The analysis by TXRF was performed by using a Seifert EXTRA-II spectrometer (Rich Seifert, Ahrensburg, Germany), equipped with a tungsten X-ray fine focus lines and a Si (Li) detector with an active area of 80 mm^2 and a resolution of 157 eV at 5.9 keV (Mn K_α). Ta–L and Nb–K were the X-ray fluorescence lines observed for the determined elements. These transition lines are detectable in the energy range 0–40 keV without overlap problems. The measurements were performed working at 50 kV and filtered with a 100-μm Ni film, adjusting the intensity so that a count rate of about 5000 cps was achieved.

Quasi-elastic light scattering spectroscopy (QELS) was used to determine the particle size distribution in suspension of the analysed samples. The QELS measurements were done on an AutoSizer IIc (Malvern Instruments, UK), equipped with a He–Ne 5-mW laser, a photo-multiplier and a data acquisition system controlled by the Malvern AutoSizer computer package.

Powder X-ray diffraction (PXRD) was used to determine the parameters a and c of the hexagonal lattice for different LNT samples. The PXRD instrument was a D-5000 (Siemens, Germany) equipped with a Cu K_α X-ray source (λ=0.15418 nm) and a scintillation detector. The spectra were acquired from 2θ=20° up to 130° in with a step size of 0.02° and an acquisition time of 2 s per step.

2.2. Detection limits

The detection limits (DL) associated with the evaluated elements, Nb and Ta, were calculated according to Prange [7] using Eq. (3)

$$DL = \frac{3M}{A}\sqrt{\frac{B}{\tau}} \tag{3}$$

where M is the evaluated element mass, A and B are the areas of the peak and background associated with each element, respectively, and τ is the acquisition time.

For the experimental determination of the detection limits, ICP single-element standard solutions of well-known concentration (Merck KGaA, Darmstadt, Germany) were used. 20 ng of each element was deposited on a sample carrier and its spectrum was acquired during 1000 s with a dead time of 30%. The detection limits measured at the K and L lines of Nb and Ta were 15 pg and 11 pg, respectively.

2.3. Relative sensitivity factors calibration

Samples were ground in particle sizes under 1 μm, in order to avoid the need for matrix correction in TXRF [9]. The response curve, i.e., relative fluorescence intensity vs. atomic number, is one of the most important and critical aspects to obtain a correct quantification by TXRF. To accomplish the relative sensitivity calibration for Nb and Ta, ICP single-element standard solutions of well-known concentration were used, with the following certified concentrations, C(Nb)=1000±2 mg L^{-1} and C(Ta)=994±2 mg L^{-1}. One milliliter of each standard was taken, to obtain concentrations of C(Nb)=500 mg L^{-1} and C(Ta)=497 mg L^{-1}. Five aliquots of 2 μL of the solution were deposited on five carriers. The solvent was evaporated on a ceramic plate at 50 °C in a class A-100 laminar flow chamber. The five preparations were analysed in the 0–40-keV energy range, with an acquisition time of 1000 s and a 30% dead time. Fig. 2 represents the obtained spectrum for the mixed standard solution of 500 mg L^{-1} Nb and Ta.

Deconvolution and integration of the observed lines were accomplished with the computer package AN-10000 (Oxford Instrument, High Wycombe, UK). Nb–K lines