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XPS study of Li/Nb ratio in $LiNbO_3$ crystals. Effect of polarity and mechanical processing on $LiNbO_3$ surface chemical composition

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ABSTRACT

Different sections of congruent lithium niobate (CLN) crystals have been studied using X-ray photoelectron spectroscopy (XPS). We have developed a method for measuring the lithium-to-niobium atomic ratio Li/Nb from the ratio of the Li1s and Nb4s spectral integral intensities with an overall error of within 8 %. Polarity and mechanical processing affect the Li/Nb ratio on CLN crystal surfaces. The Li/Nb ratio is within the tolerance (0.946 ± 0.074) on the negative cleave surface Z, and there is excess lithium ($Li/Nb = 1.25 \pm 0.10$) on the positive surface. The positive surfaces of the 128° *Y* cut plates after long exposure to air exhibit LiOH formation indications (obvious lithium excess, higher Li1s spectral binding energy and a wide additional peak in the O1s spectrum produced by nonstructural oxygen). XPS and glow discharge optical electron spectroscopy showed that mechanical processing of differently oriented crystals (*X*, *Z* and 128° *Y*) and different polarities dramatically reduces the Li/Nb ratio. *In situ* fluorine adsorption experiments revealed the following regularities: fluorine adsorption only occurred on crystal cleaves and was not observed for mechanically processed specimens. Positive cleave surfaces have substantially higher fluorine adsorption capacity compared to negative ones.

1. Introduction

Ferroelectric lithium niobate crystals $LiNbO_3$ (LN) are widely used in functional devices of acoustic and optical electronics (modulators, gates, surface acoustic wave filters, piezoelectric ultrasonic emitters, piezoelectric actuators, various components of integral optics devices etc.) due to their unique electrooptical, piezoelectric and nonlinear properties.

It is well known that $LiNbO_3$ exists in a wide range of solid solutions, i.e. from 44.5 to 50.5 mol % Li_2O. Most of commercially grown crystals have chemical compositions near the congruent melting point, i.e. 48.3–48.6 mol % Li_2O [1]. Congruent crystals may have spatial composition inhomogeneity expressed as fluctuations of cations atomic ratio, Li/Nb.

Even greater Li/Nb ratio deviations are typical of $LiNbO_3$ coatings used as electrooptical and ferroelectric layers in various devices. Lithium deficiency in these films is detected by X-ray diffraction as the presence of the $LiNb_3O_8$ phase [2,3]. Synthesis of layers with the optimum composition requires Li/Nb ratio control.

Li/Nb ratio is of special importance for surface chemical composition analysis of $LiNbO_3$ coatings and crystals. Polar and nonpolar LiNbO3 cut surfaces have become independent objects of analysis in theoretical works [4–8]. The calculations for the cut surfaces using a first-principles density functional theory demonstrated that the surface stoichiometry differs from that for a bulk-terminated face. For the LN Z-cut, a strong influence of the spontaneous polarization of the material on the surface structure was found. The stoichiometry of the positive and negative surfaces under the same experimental conditions should be quite different: the –Nb-O3-Li2 and the O-Li- terminations for the positive and negative faces respectively [4,7]. For the nonpolar LN X-cut, the dominant –Li12 termination was predicted by density functional theory and atomic force microscopy supported [7,8].

Analysis of the structural models of the most stable LN surface terminations [4,7,8] was made in the assumption of the absence of foreign adsorbates. The effect of adsorbed molecules on the LN Z-cut surface under ambient conditions is investigated elsewhere

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[6]. The adsorption of the main air components at the LN surface was simulated from first-principles, and striking differences in the adsorption behavior at oppositely polarized surfaces were found. A theoretical study of surface reconstruction and surface charge at different temperatures [5] has shown that all the thermodynamically stable surfaces formed at different temperatures reduce their surface charge, suggesting that the compensation of polarization charge is a driving force for the observed structural modifications.

Various analytical tools are used for $LiNbO_3$ crystal surface investigation [8–11], e.g. atomic force microscopy, coaxial-impact collision ion scattering spectroscopy (CAICISS), ion scattering spectroscopy (ISS), temperature programmed desorption (TPD), reflection high energy electron diffraction (RHEED), low energy electron diffraction (LEED), X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS). However, those works do not provide Li/Nb ratio data although XPS offered that possibility because fundamentals of quantitative analysis were set forth long ago by P. Steiner and H. Hochst [12]. It seems that the absence of Li/Nb ratio data is caused by the very low intensity of the Li1s photoelectron line. The ISS method does not detect lithium because of its low atomic weight.

Raman spectroscopy is often used for assessing $LiNbO_3$ stoichiometry. It was shown [13] that the widths of the E(TO) mode of the 150 cm^{-1} line and the A_1 mode of the 872 cm^{-1} line depend on stoichiometry. Transition from stoichiometric to congruent composition leads to an increase in the width of the E(TO) line from 6.75 cm^{-1} to 10.97 cm^{-1} and the an increase in the width of the A_1 mode from 20.1 cm^{-1} to 30.35 cm^{-1}. Taking into account the error of the measurements, the sensitivity of the methods could be assessed to be 0.06 mol% Li_2O. However, this is only an indirect estimate as the shape and position of the lines also depend on structural defects that are not always avoidable.

In this work we used X-ray photoelectron spectroscopy (XPS) as the main analytical tool in spite of the difficulties caused by the very low intensity of the Li1s line. Glow discharge optical electron spectroscopy (GDOES) was used as an additional tool for it is widely used for rapid product control in metallurgy and can be adapted to the analysis of oxide crystals and coatings [14].

The initial aim of this work was to develop an XPS Li/Nb ratio assessment method and to estimate the potential error. Congruent lithium niobate (CLN) crystals were used as reference specimens. Test specimens were cut and cleaved out of differently shaped crystals with various crystallographic orientations; in addition, commercial treated plates were analyzed. The Li/Nb ratio fluctuations proved to be high for different surfaces. Lithium and niobium peak intensity ratios were reproducible and close to the theoretical ones [12,15,16] for non-polar cleave specimens, and we therefore used these specimens for testing our Li/Nb ratio measurement technique.

The new quantitative analytical tool was used for controlling Li/Nb ratio deviations observed on the surfaces of polar cleaves and for analyzing the dependence of these deviations on charge sign and mechanical processing, and this became the final aim of this work.

2. Material and methods

2.1. CLN single crystals

Single crystal specimens were made from commercially available congruent $Li_{0,946}NbO_{2,973}$ single crystals (ELAN Ltd, Saint-Petersburg, Bogoroditsk Plant of Technochemical Products) that were Cz-grown from the melt containing 48.6 mol% Li_2O and 51.4 mol% Nb_2O_5 and polarized along the [0001] crystallographic direction, the Z axis. Polar *Z*- and *Y* 128°-cut and *X*-cut crystals were used. The crystals differed in shapes, sizes and surface treatment, see Table 1.

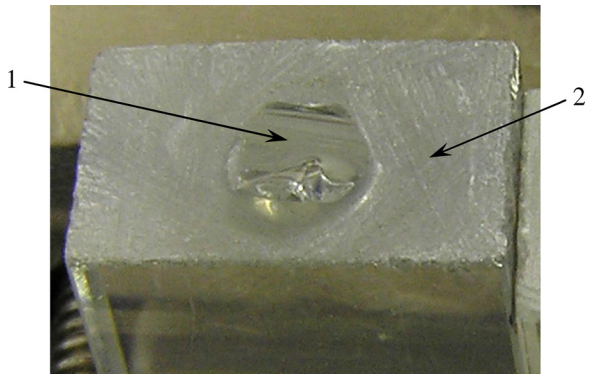

Fig. 1. Photo of the specimen obtained from rectangular batch *C* crystal by cutting with a diamond ring in the peripheral area and subsequent breaking in the central part ex-situ before loading into the spectrometer: (1) central part – *Z* cleave and (2) peripheral area – *Z* cut.

Cleaved specimens were fractured *ex-situ* before loading into the spectrometer. The cleave surfaces were not smooth but had small sections that were either parallel to the *Z* axis, or perpendicular to the *Z* axis or perpendicular to the *X* axis with a satisfactory accuracy.

The rectangular batch *C* and batch *D* crystals were first notched with a diamond ring in the peripheral areas so a 2–3 mm diam. central part remained intact, and before loading into the spectrometer the specimens were broken. As a result two samples of different polarity were obtained and each individual specimen had two sections: the central one with a cleaved surface and the peripheral one with a cut surface (Fig. 1).

2.2. Polarity control

Crystal surface polarity was controlled using a rapid method for detecting the sign of the charge induced on the crystal edges during its straining in the direction perpendicular to the surface; a storage oscilloscope was used. A slight impact of the oscilloscope probe on the test surface produced elastic compression strain in the crystal, and excess charge accumulated on the crystal edges located perpendicularly to the strain direction. A negative charge was induced on the surface located at the end of the dipole moment vector, and a positive charge was induced on the surface located at the beginning of the dipole moment vector. The surface electric potential was measured with the oscilloscope which displayed a wave-shaped extinction signal. If the first half-wave had a negative sign, then a negative charge was induced on the respective surface and the respective surface had the "+" sign, and on the contrary, if the first half-wave had a positive sign, then that surface had the "–" sign. The other half-waves of the signal are associated with crystal restoration to the initial unstrained state and are therefore of no interest for polar surface sign determination.

2.3. XPS

XPS studies were carried out on two instruments, PHI 5500 ESCA and PHI 5000 VersaProbe II. In the PHI 5500 ESCA, photoemission was excited by standard MgKα radiation ($h\nu$ = 1253.6 eV) with a power of 250 W. The analysis area diameter was 1100 μm. In the VersaProbe II spectrometer we used monochromatic Al kα radiation with a power of 25 or 50 W and analysis area diameter of 100 or 200 μm, respectively. The residual gas pressure in the chamber was within 1×10^{-7} Pa.

The full elemental composition was determined from the survey spectra in the 0–1100 eV range recorded at the analyzer pass energy