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# LiZnNb<sub>4</sub>O<sub>11.5</sub>: A novel oxygen deficient compound in the Nb-rich part of the Li<sub>2</sub>O–ZnO–Nb<sub>2</sub>O<sub>5</sub> system

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#### ABSTRACT

A novel lithium zinc niobium oxide LiZnNb<sub>4</sub>O<sub>11.5</sub> (LZNO) has been found in the Nb-rich part of Li<sub>2</sub>O–ZnO–Nb<sub>2</sub>O<sub>5</sub> system. LZNO, with an original  $\alpha$ -PbO<sub>2</sub> related structure, has been synthesized by the routine ceramic technique and characterized by X-ray diffraction and transmission electron microscopy (TEM). Reflections belonging to the LZNO phase, observed in X-ray powder diffraction (XRPD) and electron diffraction, have been indexed as monoclinic with unit cell parameters *a*=17.8358(9)Å, *b*=15.2924(7)Å, *c*=5.0363(3)Å and  $\gamma$ =96.607(5)° or as  $\alpha$ -PbO<sub>2</sub>-like with lattice constants *a*=4.72420(3)Å, *b*=5.72780(3)Å, *c*=5.03320(3)Å,  $\gamma$ =90.048(16)° and modulation vector **q**=0.3*a*\*+1.1*b*\* indicating a commensurately modulated  $\alpha$ -PbO<sub>2</sub> related structure. The monoclinic cell is a supercell related to the latter. Using synchrotron powder diffraction data, the structure has been solved and refined as a commensurate modulation (superspace group P112<sub>1</sub>/n( $\alpha\beta$ 0)00) as well as a supercell (space group P2<sub>1</sub>/b). The superspace description allows us to consider the LZNO structure as a member of the proposed  $\alpha$ -PbO<sub>2</sub>-Z (3+1)D structure type, which unifies both incommensurately and commensurately modulated structures. HRTEM reveals several types of defects in LZNO and structural models for these defects are proposed. Two new phases in Li<sub>2</sub>O–ZnO–Nb<sub>2</sub>O<sub>5</sub> system are predicted on the basis of this detailed HRTEM analysis.

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#### 1. Introduction

Lithium niobate (LN: LiNbO<sub>3</sub>) is an important material in the optical industry and it is of great interest for many applications, such as optical waveguides, surface acoustic wave devices, electro-optic modulators, second harmonic generators, holographic storage and others [1]. Li-deficiency in LN crystals introduces intrinsic defects [2] which significantly increase the photorefractive effect and thus reduce the optical damage resistance. These defects can be reduced by increasing the stoichiometry or adding some dopants [3]. Usually, commercial LN crystals for laser applications are doped with MgO for increasing the damage threshold [4]. However, a different type of optical damage (the so-call dark trace) induced by a high-power laser beam still remained in the MgO-doped crystals. This limits their performance in high-power applications. Volk et al.

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[5] reported that the dark trace could be removed by using ZnO-doping. An optimization of the photorefractive and optical properties of ZnO-doped LN crystals requires a detailed knowledge of the phase formation in the  $Li_2O$ -ZnO-Nb<sub>2</sub>O<sub>5</sub> system especially in the Nb-rich part.

Two lithium zinc niobium oxides LiZnNbO<sub>4</sub> [6] and Li<sub>2.98</sub> Zn<sub>0.51</sub>Nb<sub>2</sub>O<sub>7</sub> [7] are known in the Li<sub>2</sub>O–ZnO–Nb<sub>2</sub>O<sub>5</sub> system. The first one crystallizes in the spinel-type structure while the structure of the second compound is unknown. The phase formation in the ZnO–Nb<sub>2</sub>O<sub>5</sub> system however is better studied in the Zn-rich part; the ZnO–Nb<sub>2</sub>O<sub>5</sub> phase diagram shows two congruent compounds having compositions Zn<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub> (3ZnO:Nb<sub>2</sub>O<sub>5</sub>) and ZnNb<sub>2</sub>O<sub>6</sub> (ZnO:Nb<sub>2</sub>O<sub>5</sub>) [8]. Later Ballman and Brown showed that ZnNb<sub>2</sub>O<sub>6</sub> is not congruently melting [9]. ZnNb<sub>2</sub>O<sub>6</sub> forms in a columbite-type (or α-PbO<sub>2</sub>-type) structure [10] in direct equilibrium with β-Nb<sub>2</sub>O<sub>5</sub> and not as a low temperature transformation from the rutile structure [9,11]. Zn<sub>7</sub>Nb<sub>2</sub>O<sub>12</sub> (7ZnO:Nb<sub>2</sub>O<sub>5</sub>) with a cubic spinel structure is formed in the presence of ZnO vapour [12]. The Zn<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub> (4ZnO:Nb<sub>2</sub>O<sub>5</sub>) phase with a corundum-related structure has been prepared at

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1973 K, using a pressure of P=9 GPa [13]. Zn<sub>0.67</sub>Nb<sub>11.33</sub>O<sub>29</sub> (2ZnO:17Nb<sub>2</sub>O<sub>5</sub>) crystallizes in monoclinic and orthorhombic modifications and is found in the Nb-rich part of the ZnO-Nb<sub>2</sub>O<sub>5</sub> phase diagram [14]. In addition to LN (Li<sub>2</sub>O:Nb<sub>2</sub>O<sub>5</sub>) only the LiNb<sub>3</sub>O<sub>8</sub> (Li<sub>2</sub>O:3Nb<sub>2</sub>O<sub>5</sub>) phase is known in the Nb-rich part of the Li<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub> system [15,16].

In this paper, we study a novel compound, LiZnNb<sub>4</sub>O<sub>11.5</sub>, in the Nb-rich part of the Li<sub>2</sub>O–ZnO–Nb<sub>2</sub>O<sub>5</sub> system and discuss the relation of the LiZnNb<sub>4</sub>O<sub>11.5</sub> structure with the structure of  $\alpha$ -PbO<sub>2</sub> [17].

#### 2. Experimental

Lithium zinc niobium oxide LiZnNb<sub>4</sub>O<sub>11.5</sub> (LZNO) is synthesized from a (1:2:4) stoichiometric mixture of Li<sub>2</sub>CO<sub>3</sub> (99.99%), ZnO (99.99%) and Nb<sub>2</sub>O<sub>5</sub> (99.99%) by the routine ceramic technique at 1323 K for 100 h in air followed by quickly quenching from 1323 K to liquid nitrogen. XRD pattern of LiZnNb<sub>4</sub>O<sub>11.5</sub> has been checked using the JCPDS PDF-2 Data Base and does not contain reflections of initial phases and previously known LiNb<sub>3</sub>O<sub>8</sub> or ZnNb<sub>2</sub>O<sub>6</sub> phases (Cards 36-0307 and 37–1371).

Lithium, zinc and niobium contents were determined by inductively coupled plasma (ICP) emission spectrometry performed on a JY-38P (Jobin Yvon, France) equipped with a monochromator with linear dispersion 0.56 nm mm<sup>-1</sup>, RF plasma generator with power output of 1.5 kW at 27.12 MHz and photoelectric registration of the spectrum radiation intensity. For ICP measurements the LZNO sample has been fused with  $K_2S_2O_7$  (99.99%) at 1023 K for 100 h in a quartz crucible. After cooling, the melt was immersed in a pyrex beaker containing a 2 M H<sub>2</sub>SO<sub>4</sub> (concentrated) and 5% H<sub>2</sub>O<sub>2</sub> (70% solution) mixture and heated on a hot plate at 353 K for 2 h till complete sample dissolving. For determination of Li, Zn and Nb the prepared initial solution has been diluted by distilled water to 5 times, 20 times and 200 times, respectively.

Second-harmonic generation (SHG) responses of the powder samples were measured in reflection mode. A Q-switch pulsed Nd:YAG laser operated at a wavelength of  $\lambda_{co}$  = 1064 nm was used as a radiation source with a repetition rate of 4 pulses per second and a pulse duration of about 12 ns. The laser beam was split into two beams to excite the radiation at the halve wavelength,  $\lambda_{2co}$ =532 nm, simultaneously on samples to be measured and on a reference sample: polycrystalline  $\alpha$ -SiO<sub>2</sub>. The incident-beam peak power was about 0.1 MW on a spot of 3 mm in diameter on the surface of the sample. The absence of a noticeable SHG signal confirms the choice of a centrosymmetric space group.

Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements for LZNO were performed on a NETZSCH STA 409 thermoanalyzer in the temperature range from 300 to 1323 K with heating/cooling rates of 10 K/min. Sintered kaolin was used as reference material. Weigh loss or the absence of some thermal effects were not observed on heating/cooling TG and DSC curves, respectively. TG and DSC measurements show that LZNO is stable in the temperature range from 300 to 1323 K without any first order phase transition in the structure.

X-ray powder diffraction (XRPD) data were collected at room temperature on a SIEMENS D500 diffractometer equipped with a primary SiO<sub>2</sub> monochromator (CuK $\alpha_1$  radiation,  $\lambda$ =1.5406 Å, Bregg–Brentano geometry) and a position sensitive detector (BRAUN). The data were collected over the range of 5°–100° in  $2\theta^{\circ}$  with steps of 0.02 °2 $\theta$ .

X-ray synchrotron powder diffraction data were collected at the beamline BM01A (Swiss-Norwegian Beamline) at ESRF, Grenoble. A wavelength of 0.6942 Å was selected using a Si(111) double crystal monochromator, and the synchrotron beam was focused to a size of  $0.3 \text{ mm} \times 0.3 \text{ mm}$  using a combination of curved mirrors and a sagitally bent second crystal. The sample was positioned into a borosilicate capillary of 0.5 mm diameter, and the data were collected at room temperature. A mar345 image plate detector was used to register the powder patterns. The sample-to-detector distance of 250 mm was calibrated using a LaB<sub>6</sub> reference powder. Exposure time was typically 30 s per image, and the sample was rotated during the data collection at a speed of 1 degree per second. Exposure times were chosen to avoid any pixel saturation. The integration of the 2D powder data was done using the fit2d software package [18]. The powder diffraction data cover the range  $0.0025 \le 2\theta \le 34.758$  with steps of  $0.005 \ ^{\circ}2\theta$ . Rietveld [19] refinements of LZNO structure were carried out using the JANA2006 [20] programme packages. Illustrations were produced with the JANA2006 programme packages in combination with the program DIAMOND [20].

Electron diffraction (ED) and high-resolution transmission electron-microscopy (HRTEM) investigations were made on crushed samples deposited on holey carbon grids. Energy dispersion X-ray (EDX) analysis and ED patterns were obtained using a Philips CM20 microscope with a LINK-2000 attachment. For the EDX analysis, results were based on the Nb<sub>L</sub> and Zn<sub>L</sub> lines in the spectra. HRTEM observations were performed using a JEOL 4000 EX microscope operating at 400 kV having 1.7 Å point resolution. Simulations of the HREM images were performed using the CrystalKit and MacTempas software packages.

#### 3. Results

#### 3.1. Elemental contents

The elemental analysis performed by ICP gives for the Li, Zn and Nb content 1.2+0.2, 10.7+0.5, and 59.0%+1.8 wt%, respectively. This is close to the LiZnNb<sub>4</sub>O<sub>11.5</sub> composition (calc. wt%: 1.11 (Li), 10.42 (Zn), 59.18 (Nb) and 29.30 (O)).

The Zn:Nb ratio was confirmed by local EDX analysis in the transmission electron microscope, in combination with ED for structure identification of each crystallite. The cation ratio was found to be Zn:Nb=1.0:4.00 (19.5  $\pm$  2.0 at% Zn, 80.5  $\pm$  2.0 at% Nb). This is close to the bulk LZNO composition determined by ICP and reveals a homogenous element distribution in the sample.

#### 3.2. X-ray powder diffraction

A preliminary analysis of strong reflections in the XRPD pattern revealed the new compound to have  $\alpha$ -PbO<sub>2</sub> related substructure (space group *Pbcn*) with unit cell parameters: a=4.727 Å, b=5.731 Å, c=5.0363 Å, V=136.4 Å<sup>3</sup>. However, several extra reflections were visible in the pattern (Fig. 1), which could not be assigned to any previously known LiNb<sub>3</sub>O<sub>8</sub> or ZnNb<sub>2</sub>O<sub>6</sub> phase. The reflections belonging to the LZNO phase gwere indexed on the base of a monoclinic unit cell with unique *c* axis: (1) *a*=18.5788(9)Å, *b*=15.2924(7)Å, *c*=5.0363(3)Å and  $\gamma$ =  $107.517(5)^{\circ}$  or (2) a=17.8358(9)Å, b=15.2924(7)Å, c=5.0363(3)Å and  $\gamma = 96.607(5)^{\circ}$ . According to one of the standard crystallography rules, if a crystal structure can be described in two or more different monoclinic settings (space group, unit cell parameters, etc.), the setting with the minimal deviation of the monoclinic angle from 90° should be selected. Systematic extinctions (0k0, k=2n; 00l, l=2n; hk0, k=2n) together with the SHG data result in the space group  $P2_1/b^{1}$ 

<sup>&</sup>lt;sup>1</sup> The transformation matrix from the orthorhombic  $\alpha$ -PbO<sub>2</sub> subcell to the monoclinic LZNO supercell is  $T = \begin{pmatrix} 1 & \overline{3} & 0 \\ 3 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$  in the matrix equation  $A_{\text{LZNO}} = A_{\alpha$ -PbO<sub>2</sub>T.

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