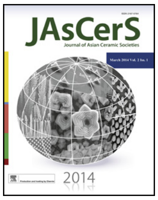
Journal of Asian Ceramic Societies 4 (2016) 46–54

HOSTED BY

Contents lists available at ScienceDirect

Journal of Asian Ceramic Societies

journal homepage: www.elsevier.com/locate/jascer



Dielectric and electrical properties of $LiNbO_3$ ceramics

A. El Bachiri*, F. Bennani, M. Bousselamti

Laboratory of Condensed Matter Physics, Department of Physics, Faculty of Science, Ibn Tofail University, BP 133, 14 000 Kenitra, Morocco

ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form
18 September 2015
Accepted 10 November 2015
Available online 17 December 2015

Keywords:
Conductivity
Impedance spectroscopy
Polaron
Ceramics

ABSTRACT

$Li_{1-x}Nb_{1+x/5}O_3$ (where $x = 0$, 0.025, 0.045, 0.075) ferroelectric ceramics were prepared by the solid-state reaction method; X-ray diffraction patterns indicate that single phase was formed for pure LN ceramics. The electrical behavior of the ceramics was studied by impedance spectroscopy technique in the 300–1000 °C temperature range. Impedance analysis was performed revealing a conductivity data which fitted in the modified power, $\sigma_{ac}(\omega) = A \cdot \omega^{n_1} + B \cdot \omega^{n_2}$ and evidence of two types of conduction process. The low-frequency conductivity is due to long-range ordering (near frequency-independent) and high-frequency conduction due to the localized orientation hopping mechanism. The static conductivity is determined for all compositions from Cole–Cole diagrams, and the evolution vs temperature is studied as a function of the Li/Nb ratio.

1. Introduction

Lithium niobate has been the subject of extensive studies. Due to its excellent piezoelectric pyro-electric, electro-optic and photorefractive properties, lithium niobate $LiNbO_3$ (LN) has become one of the most important crystal materials for research because of its several device applications, such as in photorefractive devices, holographic memories, electro-optic modulators, waveguide structures, etc. [1–4]. The structure of ferroelectric $LiNbO_3$(LN) belongs to space group R3C and can be considered as a superstructure of the α-Al_2O_3 corundum structure with Li^+ and Nb^{5+} cations along the c axis [5]. LN is well known to be narrow-range non-stoichiometric compounds; the solid solubility range extends from about 50 to 52% mol Nb_2O_5 for LN [4].

LN is usually grown with congruent non-stoichiometric composition and exhibits a certain amount of deficit of lithium (Li) showing specific intrinsic defects in its crystals which considerably change its acoustical, optical and other properties because the excess Nb^{5+} ions in congruent position of LN occupy only the regular Li-sites. So its required local charge neutrality can be guaranteed by oxygen vacancies, by Li vacancy at Li-site or by Nb vacancy at Nb-sites [6–10]. Different defect models were proposed to account for the non-stoichiometry [11], the oxygen vacancy model was eliminated [7,12] and among see the cation site vacancy models, the Li-site vacancy model [7,13,14] seems more probable than the Nb-site vacancy model [8,15,16]. Therefore, the Li-deficient crystal may be formally regarded as one with an Nb surplus, or in other words, a decreasing Li content is accompanied by an increasing content of the heavier Nb. The existence of such a stacking defect, Nb on a Li-site (Nb antisite), was repeatedly proved by structure studies [8,17]. According to precise data of X-ray and neutron diffraction, only 1% of the Li-site is occupied by Nb (Nb antisite), whereas about 4% of the Li-sites are empty (Li vacancy) [5]. This existence of a high concentration of Li vacancies in congruent LN was confirmed by other structure reports [17,18] and NMR (Nuclear Magnetic Resonance) spectroscopy studies [19].

However, polycrystalline lithium niobate due to its dielectric and piezoelectric properties, etc. also has important technological applications. Otherwise, those properties are strongly dependent on the method of preparation. Dielectric and electrical properties of $LiNbO_3$ ceramics have been investigated in the past several years. To ensure practical device applications, it is necessary to improve the ferroelectric and electrical properties [20–22].

Recently, Mg-doped $LiNbO_3$ ceramics has been prepared by polymeric precursor method [23], the Simoes et al. analysis indicated that the pure LN and doped with 1 mol% Mg have good potentials for evaluation of their piezoelectric applications.

Nitta [24] prepared the sodium-lithium niobate ceramic by the solid-state method.

The Nitta analysis indicated that the presence of small amounts of $LiNbO_3$ dissolved in $NaNbO_3$ modifies its dielectric characteristics.

---

* Corresponding author. Tel.: +212 666445886.
E-mail address: bachiri3abdo@yahoo.fr (A. El Bachiri).

Peer review under responsibility of The Ceramic Society of Japan and the Korean Ceramic Society.

http://dx.doi.org/10.1016/j.jascer.2015.11.006

Solid solution with $LiNbO_3$ can exhibit piezoelectric, ferroelectric and electro-optic behaviors [25]; sol–gel processing [25,26] has become popular for producing ceramic materials.

$LiNbO_3$ (LN) is isomorphous with $LiTaO_3$ (LT). Several studies have reported on the changes in electrical conductivity of the lithium tantalite ceramics [27,28]. By complex impedance spectroscopy, Huanosta et al. [27] studied the variation of the conductivity as a function of the stoichiometry in $Li_{1-5x}Ta_{1+x}O_3$. F. Bennani et al. [28] studied the modification of the electrical properties of pure and Ni-doped lithium tantalate.

The electrical properties of polycrystalline $LiNbO_3$ have been less studied, although some related works are found in the literature [20,29]. This study presents the contribution of the complex impedance spectroscopy to the investigation of the properties of polycrystalline $LiNbO_3$ in the 300–1000 °C temperature range.

In the present paper, we study the modification of the electric properties of LN ceramics with different stoichiometries; the electrical properties were investigated by impedance spectroscopy. We have tried to improve our understanding by analyzing the electrical response of the grain and grain boundary effects, making an interpretation of the microscopic process that allows discerning the role of grain and grain boundary.

2. Experimental

Pure $LiNbO_3$ samples, with a general formula $Li_{1-x}Nb_{1+x/5}O_3$ (where $x=0$, 0.025, 0.045, 0.075), from Li_2CO_3 and Nb_2O_5 powders, were used. The starting materials were high-purity $LiCO_3$ (>99.9%) and Nb_2O_5 (>99.9%). Lithium carbonate and niobium oxide are mixed by attrition with ZrO_2 balls in isopropanol in the 1/3 balls, 1/3 isopropanol and 1/3 solid phase ratio and shaken for 12 h. After the sedimentation, the mixture was dried in a rot-vapor. The samples were fired in three steps of 10 h, with 400 °C, 600 °C and 800 °C. Powders were then isostatically pressed at 2500 bars to give pellets of 13 mm in diameter and 1 mm in thickness and were sintered at 1000 °C for 4 h with a heating rate of 100 °C/h. To clarify the exact composition of the materials studied, an analysis of cations was made using ICP-AES (inductively coupled plasma-atomic emission spectroscopy), in the central analysis unit of the CNRS in Vernaison (France).

For a few compositions, we analyzed three or four samples of the same composition, to check the reliability of the analyses. The concentrations of elements for each sample are S_1 (Li: 0.4158, Nb: 0.4128), S_2 (Li: 0.4033, Nb: 0.4153), S_3 (Li: 0.3954, Nb: 0.4169), and S_4 (Li: 0.3822, Nb: 0.4194) using the following equations ($x*1+y*5=6$ neutrality electric and $\frac{x}{y}=\frac{\mathrm{Li}}{\mathrm{Nb}}=R$ ratio of concentration of elements with R is ratio prepared) with $Li_xNb_yO_3$ formulae of sample. The number of vacancies was calculated by subtraction of the amount of cation sites. The errors in the formulae obtained were estimated to be about 0.8% for Li, 0.1% for Nb. The formulae obtained are reported in Table 1.

Ceramics were characterized by X-ray diffraction with a Philips PW 1729 diffractometer using the Cu K_α wavelength.

The electrical measurements are carried out as function of temperature in an atmosphere of normal lab air. Platinum electrodes were deposited on the pellet surface by painting. The painted pellets were placed in the oven at 700 °C for 2 h, to ensure the adhesion of the electrodes on the ceramic. The evolution of the conductivity was by complex impedance spectroscopy. Isothermal measurements were carried out between 300 and 1000 °C with temperature steps of 50 °C or 100 °C. The instrumentation comprised a solatron-1260 Impedance Gain phase analyzer controlled by a PC computer. The range of measuring frequencies was 1 Hz to 10 MHz. Applied voltage was always 0.5 V.

Table 1
Chemical formulae obtained by analysis and proposed formulae in good agreement with the model of Iyi ($[Li_{1-x}Nb_{x/5}(V_{Li})_{4x/5}]NbO_3$) [13], with different stoichiometries of LN (where □ denotes the empty Li-site).

Samples	Li/Nb	Experimental formulae	Proposed formulae
S_1	1.007	$Li_{1.0064}Nb_{0.999}O_3$	$[Li_{0.0064}Li][Nb]O_3$
S_2	0.971	$Li_{0.976}Nb_{1.005}O_3$	$[Li_{0.976}Nb_{0.005}\square_{0.019}][Nb]O_3$
S_3	0.948	$Li_{0.957}Nb_{1.009}O_3$	$[Li_{0.957}Nb_{0.009}\square_{0.034}][Nb]O_3$
S_4	0.911	$Li_{0.925}Nb_{1.015}O_3$	$[Li_{0.925}Nb_{0.015}\square_{0.06}][Nb]O_3$

Table 2
Values of cell parameters a, c, ratio c/a and cell volume of samples S_1, S_2, S_3 and S_4.

Li/Nb		a (Å)	c (Å)	c/a	Cell volume (Å^3)
S_1	1.007	5.1402	13.8577	2.6959	317.06
S_2	0.971	5.1425	13.8696	2.6970	318.89
S_3	0.948	5.1531	13.8734	2.6922	319.04
S_4	0.911	5.1517	13.8705	2.6924	318.80

3. Results and discussion

Ceramics were characterized by X-ray diffraction and scanning electron microscopy. Fig. 1 shows the X-ray patterns of samples S_2 and S_3, and they exhibit the structure of pure $LiNbO_3$ [30], and uniform grain size of about 3 μm.

3.1. Cell parameters

The cell parameters were determined from X-ray patterns recorded at scanning speed of ¼°2θ/min and were refined by least square method calculations. They are reported in Table 2. When the Li/Nb ratio decreases, cell parameters and volume increase because the content of substitution of Li^+ ions by Nb^{5+} increases. If we know that the ionic radius of Nb^{5+} (64 pm) is slightly smaller than that of Li^+ (76 pm), we should then observe a decrease in these parameters and not an increase. But as the substitution of Li^+ by Nb^{5+} is accompanied by creation of vacancy to keep electrical neutrality of the product, the oxygen molecules forming the octahedron containing this vacancy have the tendency to repel because they are not any more attracted by the cation Li^+. Therefore, the mesh increases in volume; these observations are in good agreement with the results obtained by Fan et al. [31].

The densities obtained after sintering stage average 4.1 g/cm^3, or 89% of theoretical density (4.625 g/cm^3), this value is similar to that obtained by Simoes [23], and also the SEM micrograph of sample S_2 (inset Fig. 1) shows that the material is dense, and that its grains are homogeneous and almost spherical, fairly regular shape, with the presence of a low porosity, with an average grain size lying between 2 μm and 3 μm.

3.2. Impedance spectroscopy

In order to analyze the grain and grain boundary effects in $LiNbO_3$, we employ the impedance [32] spectra as a function of temperature (300–1000 °C) and frequency (1–10^6 Hz). The goal of this investigation is to improve our understanding by analyzing the electrical response of the grain and grain boundary effects, making an interpretation of the microscopic process that allows discerning the role of grain and grain boundary. The impedance data were usually modeled by an ideal equivalent electrical circuit comprising of resistance (R) and capacitance (C). The equivalent circuit is based on the brick-layer model [32]. These polycrystallines show that grain and grain boundary impedance can be represented by equivalent circuit as given in Fig. 2. The circuit consists of series combination of grain and grain boundary elements. The grain circuit consists of parallel combination of grain resistance (R_g) and