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ScienceDirect

Ceramics International 41 (2015) 7847–7852

CERAMICS INTERNATIONAL

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Characterization of magnesium doped lanthanum orthoniobate synthesized by molten salt route

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Received 15 January 2015; received in revised form 20 February 2015; accepted 22 February 2015
Available online 2 March 2015

Abstract

Molten salt synthesis method has been used to prepare the single phase magnesium doped lanthanum orthoniobate. The phase composition has been checked by X-ray diffraction method and the microstructure studies have been performed by scanning electron microscopy. The high temperature properties of the material have been investigated by thermogravimetry and electrochemical impedance spectroscopy. A dependence between sample total conductivity and temperature has been found supporting the thesis that there is strong correlation between apparent activation energy of conductivity and structural phase transition at ~500 °C. It has been also shown that the conductivity of magnesium doped lanthanum orthoniobate synthesized by the molten salt route reaches values of ~1 mS/cm at 720 °C in wet hydrogen.

Keywords: Proton conductors; X-ray diffraction; Electrochemical impedance spectroscopy; Thermogravimetry

1. Introduction

Lanthanum niobates are a group of compounds with interesting properties, from both scientific and technical points of view. The research in the field of these ceramic materials' properties can be dated from 70's when the fluorescent properties of rare-earth niobates have been investigated [1–11]. In following years the interest in optical properties of this group of materials continued [12–16]. Moreover, interesting structural properties of these ceramics have been studied. Lanthanum niobate undergoes the structural phase transition from the monoclinic Fergusonite structure to the tetragonal Scheelite structure at the temperature approximately 500 °C [17,18]. It has been shown that in the case of dopants introduced into the structure on the lanthanum sublattice the temperature of transition varies only by a small extent [19–21], whereas in the case of niobium-site substitution it changes noticeably (down to room temperature in the case of high doping by antimony or vanadium) [22,23]. While it does not influence the phase transition temperature, lanthanum site doping influences both optical and electrical properties of rare-earth niobates. Introducing the smaller rare-earth lanthanide atom into lanthanum niobate leads to an enhancement of the luminescence properties [13]. On the other hand electrical properties of lanthanum niobate may be modified if the material is doped by non-lanthanide M^{2+} ions. The choice of ion which is suitable for doping is determined mainly by the ionic radii of candidates and their interactions with the lattice of lanthanum niobate [24]. Therefore elements like e.g. calcium, strontium or magnesium are used as acceptor dopants and for which the proton conductivity rise is observed [25–30]. For example, proton conductivity of $La_{0.99}Ca_{0.01}NbO_{4-\delta}$ in wet hydrogen reported by Hausgrud and Norby is about 10^{-3} S/cm at 900 °C while in the case of the undoped material the conductivity is two orders of magnitude lower [27].

In this work the properties of magnesium doped lanthanum niobate synthesized by molten salt route are presented. Molten salt synthesis is a method occasionally used in ceramic materials processing. It is one of the methods of preparing ceramic powders and involves the usage of a molten salt (e.g. NaCl, KCl) as a medium for the reaction between the substrates (oxides and/or

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http://dx.doi.org/10.1016/j.ceramint.2015.02.121
0272-8842/

carbonates). The main advantages of this method are relatively low calcination temperature and uniform grain size of result powders. Our previous research dedicated to the molten salt synthesis of rare-earth niobates has shown that this method is suitable to synthesize single phase powders of these compounds [19,20,25,31].

2. Experimental

Magnesium doped lanthanum niobate, $La_{0.98}Mg_{0.02}NbO_{4-\delta}$ powder, was synthesized by the molten salt route. Stoichiometric amounts of MgO (Sigma Aldrich 99,99%), Nb_2O_5 (Merck 99.99%) and La_2O_3 (Sigma Aldrich 99.99%, preheated at 900 °C for 3 h) were ground, mixed with the KCl salt (POH 99.9%) and then heated at 1000 °C for 4 h. Since the temperature of synthesis was above melting point of KCl (704 °C [32]) the synthesis occurred in a liquid environment. After cooling, the salt residues were washed by deionised water and the powder was dried at 70 °C for 24 h. Afterwards, the powder was uniaxially pressed into pellets and sintered at 1500 °C for 12 h. X-ray diffraction patterns (XRD) were recorded using an X'Pert Pro diffractometer with CuK_α radiation. The scans were collected in the 2θ range of 20–124°. Phase identification was performed with X'Pert High Score Plus software using the JCPDS database. A scanning electron microscope (SEM) FEI Quanta FEG 250 with an Everhart-Thornley detector was used to determine the microstructure of sintered gold coated samples. EDS analysis was performed on carbon coated samples with an EDAX Apollo X-SDD energy-dispersive X-ray spectroscopy detector (EDS). The thermogravimetric studies correlated with mass spectrometry were carried out using a Netzsch STA 449F3 and a Netzsch QMS 403 in the temperature range from 35 °C to 1000 °C with heating rate of 5 °C/min for ground samples of approximate weight of 40 mg. Density measurements were conducted by the standard Archimedes method in isopropanol.

Impedance spectroscopy was performed using a Novocontrol FRA analyzer in the frequency range 1 MHz–0.01 Hz, amplitude 500 mV, on dense pellets painted with two porous Pt electrodes (previously fired at 900 °C for 30 min, ESL 5542). The temperature has been adjusted by a controller from 750 to 350 °C. The measurements were performed in wet hydrogen (5% H_2O). The impedance data were deconvoluted using a ZView software to obtain contributions associated with grain (bulk), grain boundaries and electrode phenomena. The values of grain conductivity were calculated using the relation between impedance and sample geometrical dimensions according to Eq. (1). Where the R is impedance obtained from EIS spectrum, S – the electrodes surface, and l – the distance between electrodes.

$$\sigma = \frac{1}{R}\frac{S}{l} \tag{1}$$

Activation energy of the conductivity was calculated by the standard Arrhenius equation.

$$\sigma = \frac{A}{T} e^{\frac{-E_a}{kT}} \tag{2}$$

3. Results and discussion

3.1. X-ray diffraction and scanning electron microscopy results

Fig. 1 presents the X-ray diffraction patterns of the samples synthesized by the molten salt synthesis route. Fig. 1a presents the diffractograms collected for the powders after the molten salts synthesis whereas Fig. 1b that for the dense bulk sample. All the reflections were indexed within the monoclinic structure of lanthanum niobate. This implies that the reactions occurring between the substrates in the molten salt lead to synthesis of single phase lanthanum niobate samples. Scanning electron microscopy studies with the use of energy-dispersive X-ray spectroscopy (EDS) did not reveal the presence of secondary phases. Therefore the chemical composition of the studied ceramics may be considered as uniform.

Fig. 2 presents the SEM micrographs of the sintered samples. Fig. 2a shows a relatively large fragment of the sample surface (approximately 100 μm × 100 μm) whereas Figs. 2b and c – fragments containing smaller and larger grains, respectively. Fig. 2d depicts a contact point between three adjoining grains. One can see that the grains are connected well one to another. Only a few small and closed pores are visible. This means that sintering at 1500 °C leads to the formation of dense samples. It should be noted that the measured density of the samples sintered at 1500 °C was equal to 98% of the theoretical density. The sizes of the crystal grains seen in Fig. 2 vary from 2 to 20 μm. Analysis of SEM images with the average grain intercept method allowed determining the average grain size. The average grain size is equal to 6.8 μm (from Fig. 2a) whereas the size of the majority of grains is about 4.5 μm (from Fig. 2a and b). Therefore, the grains in the ceramics obtained with the molten salt synthesis may be considered as relatively large with a large size distribution. In comparison, Bi et al., for the $La_{0.98}Ca_{0.02}NbO_{4-\delta}$ samples synthesized by the solid state synthesis at similar sintering temperature (1550 °C), reported grains of the 1–4 μm size [33]. Large, well connected grains in the ceramics

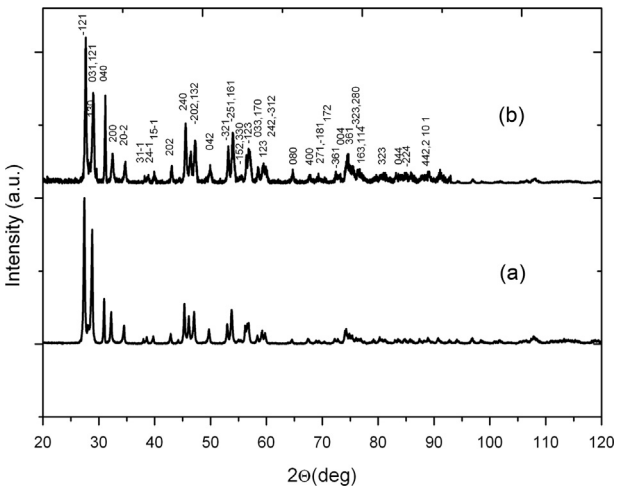

Fig. 1. Room temperature XRD spectra of $La_{0.98}Mg_{0.02}NbO_{4-\delta}$ (a) as-prepared powders and (b) sintered sample.