Journal of Alloys and Compounds 584 (2014) 402–405

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

A two step molten method for low temperature synthesis of $La_{0.9}Bi_{0.1}AlO_3$ relaxor nanocrystalline

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ARTICLE INFO

Article history:
Received 25 July 2013
Received in revised form 9 September 2013
Accepted 11 September 2013
Available online 20 September 2013

Keywords:
Molten salt synthesis
$La_{0.9}Bi_{0.1}AlO_3$
Nanocrystalline
Microstructure
Dielectric

ABSTRACT

The perovskite-type $La_{0.9}Bi_{0.1}AlO_3$ (LBAO) relaxor nanocrystalline have been prepared by a novel two-step molten method consisting of a mechanically milling induced metathesis reaction followed by calcining at temperature above nitrates melting point. The results show that the pure LBAO phase has been obtained at about 550 °C, which is lowered by about 500 °C comparing to a conventional solid-state reaction. The present particles were characterized by rhombohedral perovskite structure in space group *R-3C*, consisting of plate-like nanostructures with an average size of ~50 nm. Moreover, LBAO ceramics densified from nanocrystalline show the improved dielectric properties compared to parent $LaAlO_3$, which is promising for development of new lead-free ceramic devices.

1. Introduction

In recent years, there has been significant interest in developing lead-free oxides for dielectric devices applications. It is well known that the thermal and chemical stabilities of the oxides are very important for applying them as dielectric materials or as buffer layers in memory devices [1–3]. In the lead-free oxides, lanthanum aluminate, $LaAlO_3$, has received tremendous interest because it has a large band gap energy of 5.6 eV, a relatively high dielectric constant of 20–27, and is thermally stable up to 2100 °C [4–7]. Recently, Ye et al. have found that the introduction of bismuth ions to $LaAlO_3$ favors to improve the dielectric properties, which can be attributed to the high polarizability of Bi^{3+} ion with a lone electron pair [8]. Later, Si et al. synthesized a $LaAlO_3$-$BiAlO_3$ ceramic system through the conventional solid-state reaction and reported that $La_{0.9}Bi_{0.1}AlO_3$ (LBAO) composition enjoys excellent dielectric relaxor properties compared to pure $LaAlO_3$ paraelectric ceramics [9]. However, in order to obtain pure LBAO perovskite phase, the high calcining temperature of 1100 °C is necessary so that the mixtures of raw oxides have sufficient thermal energy to overcome the atomic/ionic diffusion barriers for the conventional solid-state reaction. It should be noted that the needed high-temperature heating in this method not only is energy consuming, but also causes unfavorable phenomenon such as high agglomeration and the large particle sizes of product powders. In comparison, nanocrystalline powder has a higher inherent surface area, which provides a significantly higher stored energy for solid-state densification, and ultimately results in a higher bulk density and improved electric properties.

The molten salt synthesis (MSS) method is one of the simplest, highly cost-effective techniques to prepare crystalline, chemically pure, single-phase nanoscale multicomponent metal oxides [10]. Compared to the conventional solid-state reactions, the molten salt in liquid form can accelerate the diffusion rate of the raw species, leading to a reduction of the reaction time and temperature. In the current report, a modified two step molten salt method, i.e. LBAO precursor was firstly prefabricated by a mechanically milling induced metathesis reaction, and then calcined in the molten nitrates medium, has been proposed to prepare LBAO nanocrystalline. At low temperature of 550 °C, we were able to generate gram quantities of LBAO nanostructures that were not only reasonably pure and single-crystalline but also possessed smooth and well-defined edges. For the merit of super sintering ability of nanostructures, the LBAO ceramics with high density have been prepared and the related dielectric properties have been investigated.

2. Experimental procedure

In our experiment, the two step molten salt method, consisting of a mechanically milling induced metathesis reaction and short calcining at low temperatures, was employed to prepare $La_{0.9}Bi_{0.1}AlO_3$ (LBAO) nanoparticles. Firstly, the raw materials of $Al(NO_3)_3{\cdot}9H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$ and $La(NO_3)_3{\cdot}6H_2O$ were weighted according to the chemical formula of $La_{0.9}Bi_{0.1}AlO_3$. Then the above mixture of nitrates was combined with NaOH, transferred to the nylon container together with 10 mm diameter zirconia balls as grinding media and ground for 12 h in a planetary ball

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http://dx.doi.org/10.1016/j.jallcom.2013.09.075

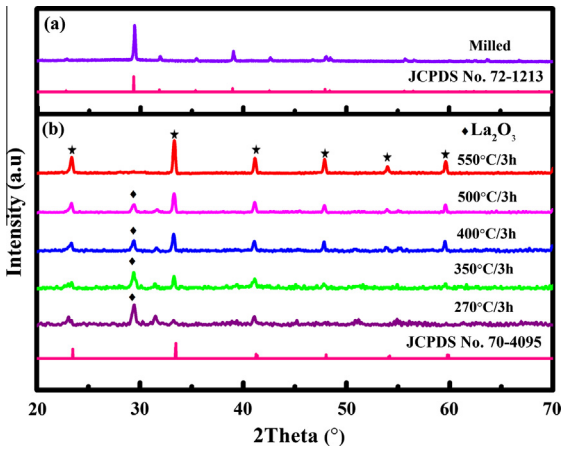

Fig. 1. (a) XRD patterns of a mixture consisting of hydrated Bi, Al and La nitrates and sodium hydroxide after milling. (b) XRD patterns of the products after calcining at different temperatures and removing the soluble $NaNO_3$ flux. Reflections marked with diamonds and stars are those characteristics of La_2O_3 and LBAO, respectively. Standard XRD patterns corresponding to $NaNO_3$ (JCPDS No. 72-1213) and $LaAlO_3$ (JCPDS No. 70-4095) are included as references.

mill with a rotating speed of 400 rpm. In order to obtain the salt-balanced condition such that there were no alkali metals or nitrates excess, the molar ratio of NaOH versus total nitrates maintains 3:1 according to the following reaction:

$$x\mathrm{Bi(NO_3)_3\cdot 5H_2O} + (1-x)\mathrm{La(NO_3)_3\cdot 6H_2O} + \mathrm{Al(NO_3)_3\cdot 9H_2O} + 6\mathrm{NaOH} \rightarrow \mathrm{Bi_xLa_{(1-x)}AlO_3} + 6\mathrm{NaNO_3} + (18-x)\mathrm{H_2O}(x=0.1) \quad (1)$$

After pretreating at 120 °C for 2 h, the dried activated precursor materials were transferred to an alumina crucible, and calcined at a heating rate of 5 °C/min up to 270–550 °C, maintained at that temperature for 3 h in air, and subsequently quenched to room temperature. The quenched solidified melts were suspended in hot distilled water to remove the soluble sodium nitrate by-product. The precipitates were centrifuged and purified with deionized distilled water several times, and dried in an oven at 120 °C for 4 h. We can easily and routinely scale up this molten salt synthesis process to produce grams of single-crystalline nanoparticles. For the measurements of electrical properties, the obtained nanoparticles were pressed into pellets without any additive, and then sintered at 1300 °C for 4 h to in a sealed alumina crucible. The densities of the specimens were determined by the Archimedes method and the average density of LBAO samples were above 97% of the theoretical density. For comparison, using the starting materials of Bi_2O_3, La_2O_3, and Al_2O_3, LBAO powders and ceramics were synthesized through the conventional solid-state reaction process and the corresponding results are reported.

The crystal structures were recorded on X-ray diffractometer (XRD; Brucker AXS, Germany) using Cu Kα radiation and analyzed by Rietveld refinement technique. The microstructural features were observed by scanning electron microscopy (SEM, Hitachi S-3500) and transmission electron microscopy (TEM; Model JEM-2000F, JEOL, Tokyo, Japan). The frequency dependences of the dielectric constant ε_r and loss tangent $\tan\delta$ were measured at room temperature using a multifrequency inductance capacitance resistance (LCR) meter (Agilent E4980A, Santa Clara, CA).

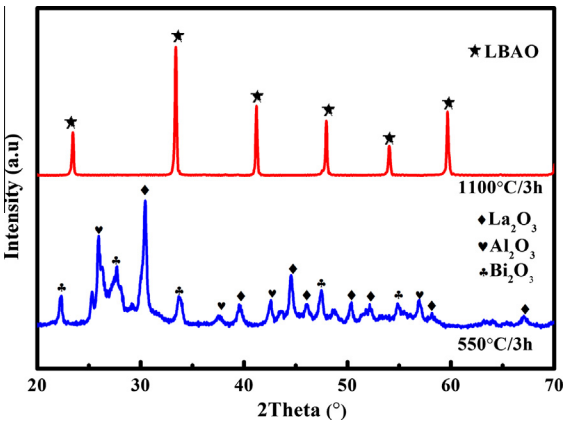

Fig. 2. XRD patterns of the products prepared by conventional solid-state reaction.

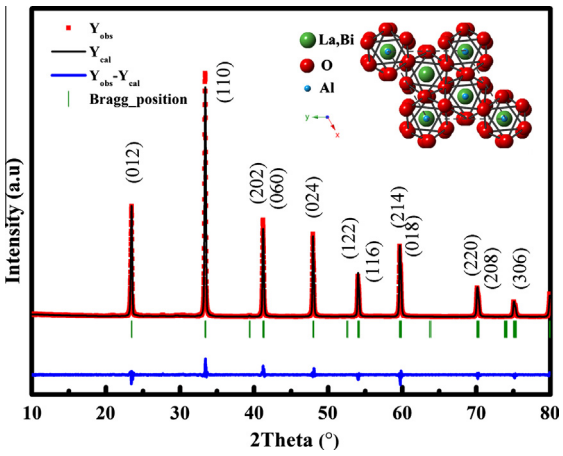

Fig. 3. XRD pattern recorded at room temperature and the Rietveld refinement profile for the LBAO powders calcined at 550 °C through the two step molten salt method. Inset: the projection along the *z* axis of LBAO crystal structure.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of a mixture consisting of hydrated Bi, Al and La nitrates and sodium hydroxide after milling, together with standard data of $NaNO_3$ (JCPDS card no. 72-1213). It is obvious that a mechanically induced metathesis reaction took place in the milling stage and $NaNO_3$ is the only crystalline product identified in the XRD pattern and La, Al and Bi species are present as amorphous phases. This phenomena is similar to the observation in the molten synthesis of $LaAlO_3$ by Mendoza-Mendoza et al. [11]. It is deduced that in mechanically induced metathesis reaction, the exchange of ionic species between reactants generates *in situ* sodium nitrate ($NaNO_3$) and at the same time produces La-, Al- and Bi-containing precursor materials. The obtained $NaNO_3$ can not only play as non-aqueous melt salt role, but also behave as Lux-Flood base providing oxide ions [11]. Moreover, though the detailed structure characterization of the La-, Al- and Bi containing precursor materials is difficult within the resolution of the XRD technique, it can be expected that the poorly crystalline precursor materials possess high reactivity, facilitating the formation of LBAO in molten nitrates. Fig. 1(b) shows the XRD patterns of the products synthesized at different temperature for 3 h. Before characterization, the water soluble $NaNO_3$ has been removed from the quenched solidified powders by washing. As there is no JCPDS-ICDD data for LBAO, the standard data of $LaAlO_3$ (JCPDS card no. 70-4095) has been used as a reference due to the similar structure [9]. As can be seen in Fig. 1(b), for the 270 °C calcined pow-

Table 1
Structure parameters determined for $LaAlO_3$ and LBAO calcined at 550 °C for 3 h from XRD data.

	$LaAlO_3$	$Bi_{0.1}La_{0.9}AlO_3$
$a = b$(Å)	5.3589(1)	5.3661(10)
c(Å)	13.0858(3)	13.1208(10)
c/a	2.4282	2.4451
V(Å^3)	325.45(9)	327.20(9)
Al–O(Å)	1.8986(2) × 6	1.9020(2) × 6
La(Bi)–O(Å)	2.5294(3) × 3	2.5328(3) × 3
	2.6781(2) × 6	2.6841(2) × 6
	2.8295(5) × 3	2.8333(5) × 3
Ave_{La-O}(Å)	2.6788	2.6847
O–O(Å)	2.6781(2) × 4	2.6920(5) × 4
	2.6841(2) × 4	2.6956(5) × 4
Ave_{O-O}(Å)	2.6851	2.6899