Journal of Alloys and Compounds 584 (2014) 93–100

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Molten salts activated by high-energy milling: A useful, low-temperature route for the synthesis of multiferroic compounds

Anayantzin Hernández-Ramírez [a], Antonia Martínez-Luévanos [a], Antonio F. Fuentes [b,c], Anna-Gay D. Nelson [c], Rodney C. Ewing [c], Sagrario M. Montemayor [a,c,*]

[a] Facultad de Ciencias Químicas, Universidad Autónoma de Coahuila, V. Carranza s/n, Saltillo, Coahuila 25280, Mexico
[b] CINVESTAV Unidad Saltillo, Apdo. Postal 663, Saltillo, Coahuila 25000, Mexico
[c] Earth and Environmental Science, University of Michigan, 3514 C.C. Little Building, 1100 N. University Avenue, Ann Arbor, MI 48109-1005, United States

ARTICLE INFO

Article history:
Received 15 May 2013
Received in revised form 23 August 2013
Accepted 2 September 2013
Available online 15 September 2013

Keywords:
Ceramics
Ferroelectrics
Oxide materials
Mechanochemical processing
Sintering
Magnetic measurements

ABSTRACT

There are only a few multiferroic compounds, among which $BiFeO_3$ is the most important. Research the synthesis of bismuth ferrite, with novel and improved magnetic and electrical properties, has been mainly based on the use of hydrothermal or sol gel methods. However, these methods require either rather extreme conditions or several steps for synthesis. We demonstrate that the use of molten salts, activated by high energy milling, results in pure nanometric $BiFeO_3$, $LaFeO_3$ and intermediate phases in the $Bi_{1-x}La_xFeO_3$ system. The chemical reagents used are $Bi(NO_3)_3{\cdot}5H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and NaOH. A brief milling process of the reagents creates an amorphous precursor and crystalline $NaNO_3$. The thermal treatment of the precursors, at 500 °C for two hours, produces a crystalline mixture of $Bi_{1-x}La_xFeO_3$ and $NaNO_3$. Simple washing eliminates the $NaNO_3$. The characterization of intermediates and final products, through thermal analysis, X-ray diffraction and scanning electronic microscopy, allows the inference of possible mechanism. In addition, vibrating sample magnetometry (VSM) and ferroelectric tests show the typical magnetic and electric polarization loops characteristic of these materials even when formed at the nano-scale.

1. Introduction

A wide variety of synthesis methods has been used successfully in obtaining perovskite type oxides [1–5]. Among all of them, the solid-state method has been primarily used to synthesize multiferroic perovskites [6–10]. However, recently, scientists have focused their efforts on developing several alternative synthesis routes, which may be of use in the synthesis of multiferroic materials [11–15]. An important aspect to emphasize while one proposes a new synthetic route is environmental responsibility. Accordingly, there are two attractive synthetic routes, which show different levels of success for the synthesis of bismuth ferrite (a room temperature multiferroic material): ball milling and molten salts [16,17]. Ball milling has an enormous advantage with respect to other chemical routes, which involve several steps of synthesis and/or purification of products, due to its simplicity. Unfortunately, in most of the cases, subproducts are obtained with the $BiFeO_3$ [18], and, as well, high annealing temperatures are required to obtain crystalline material [18,19]. Moreover, the molten salts method has the possibility of "manipulating" the shape of the crystals obtained by a simple change of the chemical conditions, which depend of the chemical nature of the molten salt, such as solubility, ionic strength, pH and temperature (melting point). However, it is still difficult to obtain pure $BiFeO_3$ and high temperatures of ~1000 °C are required [20,17]. Perhaps, the most important advantage of the synthesis route proposed in this work, with respect to wet methods, is that in this case is not necessary the use of any kind of solvents. As an example of this, is possible to mention that in the co-precipitation method, a lot of high pH residues are generated.

This paper demonstrates that a combination of ball milling followed by the use of molten salts results in the formation of $BiFeO_3$, $LaFeO_3$, as well as $Bi_{1-x}La_xFeO_3$ intermediate compositions, at only 500 °C. In addition to this achievement, the attained magnetic and ferroelectric properties were similar to those reported for $BiFeO_3$ synthesized using high temperatures or complex routes with several long steps, such as by solid-state method or sol–gel routes.

Abbreviations: A, agate; YZO, yttria partially stabilized zirconia.

* Corresponding author. Present address: The University of Michigan, Department of Earth & Environmental Science, 3514 C.C. Little Building, 1100 North University Avenue, Ann Arbor, MI 48109-1005, United States. Tel.: +52 7347573375; fax: +52 8444155752.

E-mail addresses: smmontemayor@gmail.com, msagrari@umich.edu, sagrario.martinez.montemayor@uadec.edu.mx (S.M. Montemayor).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.09.003

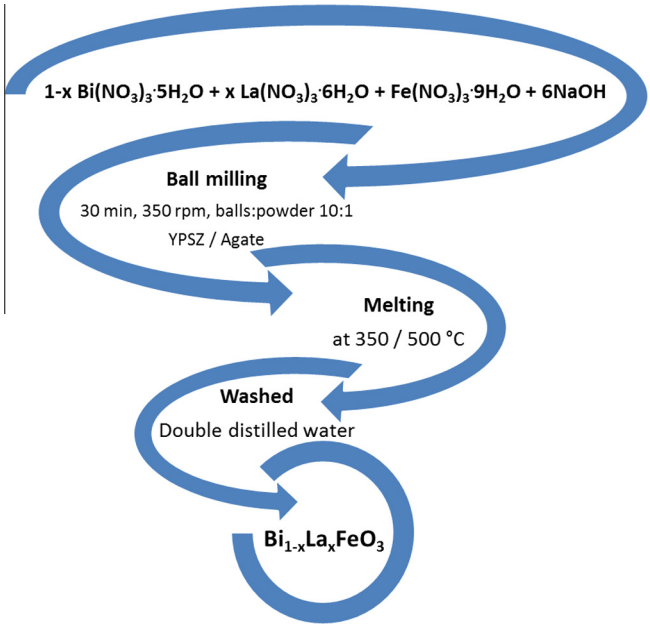

Fig. 1. Flowchart of the general procedure to synthesize $Bi_{1-x}La_xFeO_3$.

2. Experimental

2.1. Synthesis

The chemical reagents used were $Bi(NO_3)_3{\cdot}5H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and NaOH purchased from Aldrich. Stoichiometric amounts of Bi^{3+}, La^{3+} and Fe^{3+} nitrates, to obtain $Bi_{1-x}La_xFeO_3$, were mixed with the stoichiometric amount of NaOH. Then, the mixture was collocated in a container with 20 mm diameter balls (grinding media) and it was milled for 30 min in a planetary ball mill using a rotating disk speed of 350 rpm and a balls-to-powder mass ratio of 10 to 1. The effect of two different milling materials, on the reagents, was evaluated by the use of agate (A) and yttria partially stabilized zirconia (YZO). After the milling, the samples were transferred to an YZO crucible and heated to 350 or 500 °C for three hours. After their cooling, the precursors were washed with double-distilled water to dissolve the yielded $NaNO_3$. Fig. 1 shows a flowchart of the experimental procedure.

2.2. Characterization

In order to identify the crystalline phases present in different steps of the reaction, X-ray diffraction was used, the equipment employed was a Phillips X'Pert (PANalytical) and a Ni-filtered Cu Kα radiation in a range from 10 to 80° (2θ) and using steps of 0.025° (2θ)/s. Crystallite average size was deduced from XRD patterns (h k l planes: 0 1 2) using the maximum Bragg angle and the line integral breadth in Scherreŕs equation [21]. The thermal stability of the precursors was determined through thermal analysis (both differential and gravimetric DTA-TG measurements). A typical experiment used 15 mg of sample, a heating rate of 5 °C/min and a static air atmosphere to record the curves in a Perkin–Elmer Pyris Diamond TG/DTA analyzer. Microstructural characteristics and a semi-quantitative analysis of the element content were determined by scanning electron microscopy using a TOPCON SM-510, for which the chosen samples were ultrasonically dispersed in ethanol and casted on a lacey carbon–copper grid. Magnetic properties of all

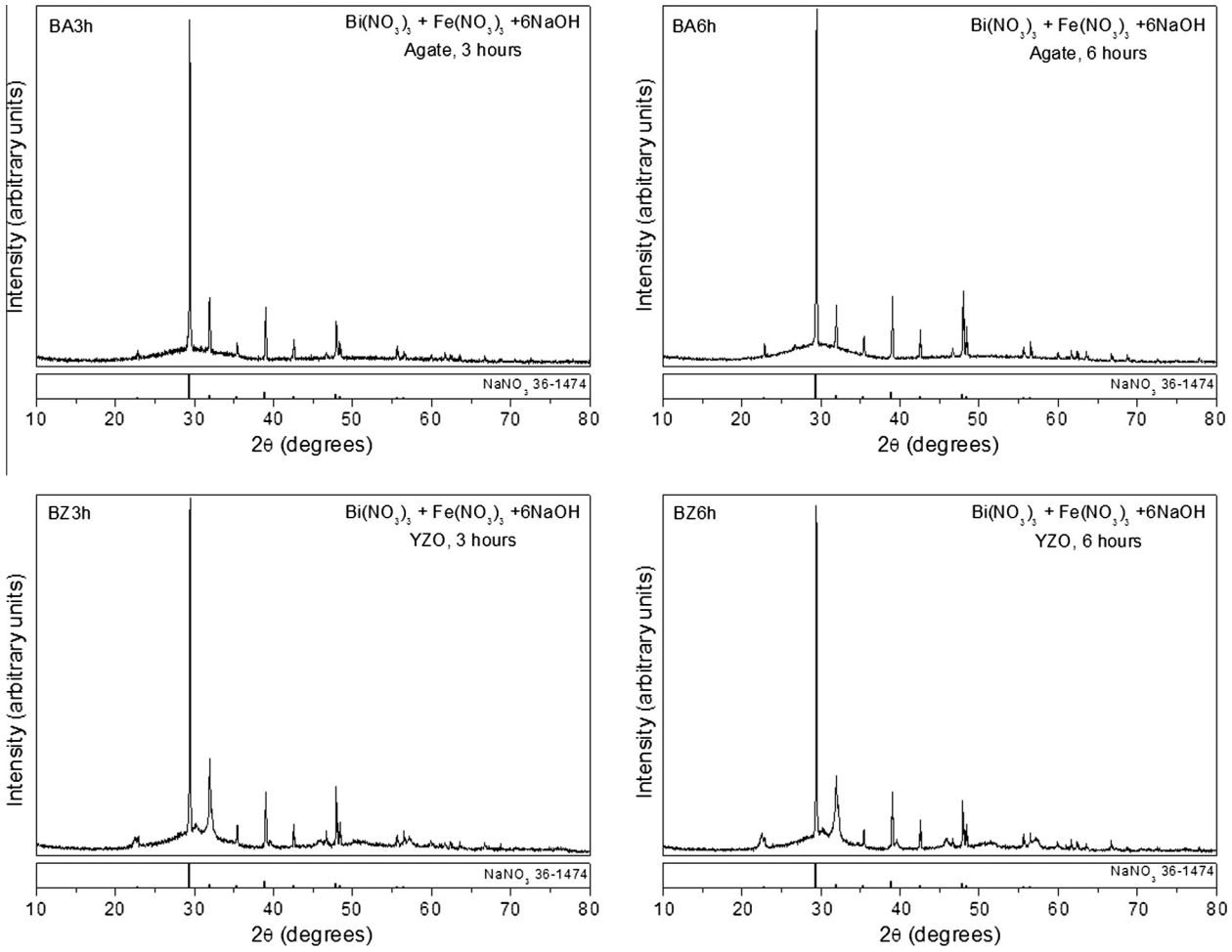

Fig. 2. XRD patterns of the powders obtained from the ball milling of the stoichiometric mixture to synthesize $BiFeO_3$. Agate (upper) and YZO (lower). Reaction times 3 h (left) and 6 h (right).