ELSEVIER

Journal of Alloys and Compounds 465 (2008) 522–526

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Effect of niobate B-site precursors on phase formation and particle size of lead nickel niobate powders

O. Khamman, R. Yimnirun, S. Ananta*

Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Received 26 May 2007; accepted 1 November 2007

Abstract

A perovskite phase of $Pb(Ni_{1/3}Nb_{2/3})O_3$ or PNN powders has been synthesized by a rapid vibro-milling technique. Both $NiNb_2O_6$ and $Ni_4Nb_2O_9$ have been employed as nickel niobate precursors, with the formation of the PNN phase investigated as a function of calcination conditions by DTA and XRD techniques. Morphology and phase composition have been determined via a combination of SEM and EDX techniques. The nickel niobate precursor and calcination condition have been found to have a pronounced effect on the phase and morphology evolution of the calcined PNN powders. It is seen that optimization of calcination conditions can lead to a single-phase PNN in both methods. However, the formation temperature for single-phase PNN powders was lower for the synthetic method employing a $NiNb_2O_6$ precursor.

Keywords: Lead nickel niobate; Nickel niobate; Perovskite; Relaxor ferroelectrics

1. Introduction

The excellent dielectric broadening and electrostrictive properties make lead nickel niobate, $Pb(Ni_{1/3}Nb_{2/3})O_3$ or PNN, a promising material for capacitor, electrostrictive actuator, and electromechanical transducer devices [1–3]. Because of these important technological applications, there has been a great deal of interest in preparation of single-phase PNN powders as well as in the sintering and dielectric properties of PNN-based ceramics [3–7].

However, it is well-documented that the formation of PNN perovskite via the solid-state reaction is often accompanied by the occurrence of unwanted pyrochlore-type phases because of the volatilization of PbO and the low dispersion of NiO [4–6]. Hence, several material processing techniques, for example, combustion [7], co-precipitation [8] and hydrothermal [9], have been introduced as alternative to the solid-state reaction of mixed oxides to minimize the amount of pyrochlore phase formed. All of these techniques are aimed at reducing the temperature of preparation of the compound even though they are more involved and complicated than the mixed oxide route.

The columbite-precursor method which was first developed by Swart and Shrout [10] is probably one of the most fundamental, practical routine method which has been used, and it has been modified intensively for the preparation of PNN powder in the last decade [4–6]. In this method, an intermediate step to give columbite-type $NiNb_2O_6$ precursor is used to bypass the formation of the pyrochlore phases. Alternatively, the use of $Ni_4Nb_2O_9$ precursor in place of $NiNb_2O_6$ has been proposed for the fabrication of pyrochlore-free PNN [11]. However, the preparation of PNN using $Ni_4Nb_2O_9$ precursor, to date, has not been extensive as that of PNN using $NiNb_2O_6$ precursor. The potential of this alternative route was evaluated in comparison with conventional columbite route to produce PNN materials.

The purpose of this work was to compare the two B-site precursor synthetic routes of PNN formation and the characteristics of the resulting powders. The phase formation and morphology of the powders calcined at various conditions will be studied and discussed.

2. Experimental

$Pb(Ni_{1/3}Nb_{2/3})O_3$ was synthesized by a similar methodology of B-site precursor mixed oxide synthetic route (Fig. 1), as reported earlier [6,7,12]. Starting precursors were as follows: PbO (JCPDS file number 77-1971), NiO (JCPDS file number 73-1519) and Nb_2O_5 (JCPDS file number 30-0873) (Aldrich, 99% purity). These three oxide powders exhibited an average particle size in the range

---

* Corresponding author.
E-mail address: suponananta@yahoo.com (S. Ananta).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.11.002

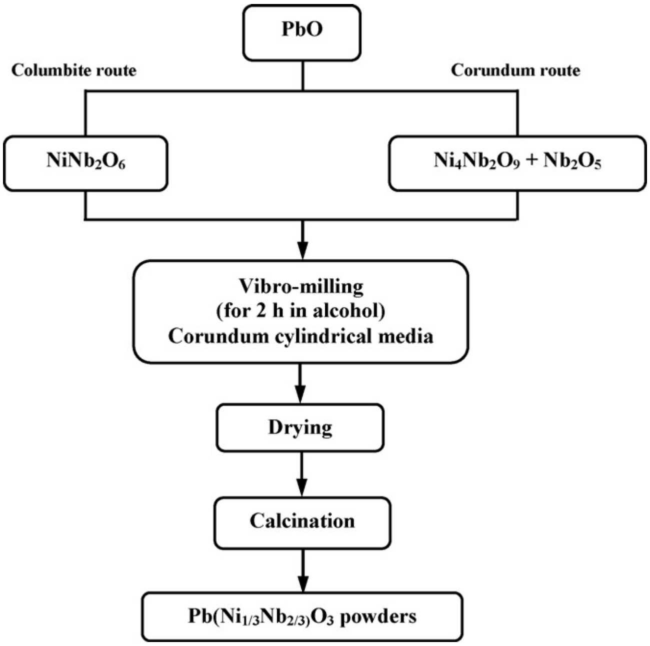

Fig. 1. A two-stage solid-state reaction routes for PNN powders.

of 3.0–5.0 μm. First, two intermediate phases of nickel niobate: $NiNb_2O_6$ and $Ni_4Nb_2O_9$ were separately prepared by the solid-state reaction method previously reported [13,14], employing an optimized calcination conditions of 900 °C for 4 h with heating/cooling rates of 30 °C/min and 1050 °C for 2 h, with heating/cooling rates of 30 °C/min, respectively. The following reaction sequences were then proposed for the formation of PNN:

1. The columbite route:

$$3PbO(s) + NiNb_2O_6(s) \rightarrow 3Pb(Ni_{1/3}Nb_{2/3})O_3(s) \tag{1}$$

2. The corundum route:

$$12PbO(s) + Ni_4Nb_2O_9(s) + 3Nb_2O_5(s) \rightarrow 12Pb(Ni_{1/3}Nb_{2/3})O_3(s) \tag{2}$$

Instead of employing a ball-milling procedure (ZrO_2 media under acetone for 48 h [6]), a McCrone vibro-milling was used. In order to reduce the processing time, the milling process was carried for only 2 h (instead of 12 h [12]) with corundum media in isopropanol. After drying at 120 °C for 2 h, various calcination conditions were applied in order to investigate the formation of PNN phase in each calcined powders.

The reactions of the uncalcined powders taking place during heat treatment were investigated by differential thermal analysis (DTA, Shimadzu) using a heating rate of 10 °C/min in air from room temperature up to 1200 °C. Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Philips PW 1729 diffractometer) using Ni-filtered CuKα radiation, to identify the phases formed and optimum calcination conditions for the manufacture of PNN powders. The mean crystallite size was determined using the diffraction peak (1 1 0) of the perovskite pattern by using Scherrer equation [15]. The grain size and morphologies of calcined PNN powders were observed by scanning electron microscopy (SEM; JEOL JSM-840A). The chemical composition of the phases formed was also elucidated by an energy-dispersive X-ray (EDX) analyser with an ultra-thin window. EDX spectra were quantified with the virtual standard peaks supplied with the Oxford Instruments eXL software.

3. Results and discussion

DTA result for the mixtures synthesized by both B-site precursor methods is shown in Fig. 2. In general, similar trend of thermal characteristics is observed in both precursors. In the temperature range from room temperature to ~150 °C, both samples show small thermal peaks in the DTA curves, which are related to the first weight loss. These DTA peaks can be attributed to the decomposition of the organic species such as rubber lining from the milling process similar to our earlier reports [11–14]. By increasing the temperature up to ~700 °C, the solid-state reaction occurs between oxide precursors. The broad exothermic characteristic in both DTA curves represents that reaction, which has a maximum at ~450 and 600 °C for columbite- and corundum-routes, respectively. However, it is to be noted that there is no obvious interpretation of these peaks, although it is likely to correspond to a phase transition reported by a number of workers [4,6,12]. The different temperature, intensities and shapes of the thermal peaks for the two precursors here probably are related to the different starting materials especially nickel niobate and consequently, caused by the removal of species differently bonded in the network, reactivity of different species (difference in type and dispersion of NiO) in the powders. These data were used to define the range of temperatures for XRD investigation between 500 and 1150 °C. It is to be noted that a significant thermal change in DTA curves observed at temperatures above 800 °C may be attributed to the PbO volatilization typically found in lead-based ferroelectrics, consistent with other investigators [8,16,17].

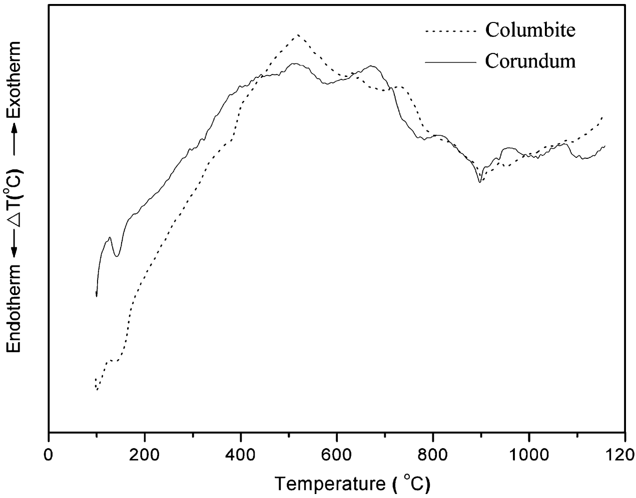

Fig. 2. DTA curves of the mixtures derived from columbite- and corundum-routes.

To study the phase development with increasing calcination temperature in each synthetic route, they were calcined at various temperatures for 2 h in air with constant heating/cooling rates of 10 °C/min, followed by phase analysis using XRD technique. As shown in Fig. 3 (columbite route), for the uncalcined powder and the powder calcined at 500 °C, only X-ray peaks of PbO and $NiNb_2O_6$ precursors are present. Similarly, it is seen that unreacted precursors of PbO, Nb_2O_5 and $NiNb_2O_6$ are detected from the original mixture up to 550 °C for the corundum route (Fig. 4). These observations indicate that no reaction was yet triggered during the vibro-milling or low firing processes, in agreement with literature [11,18,19]. It is seen that PNN crystallites were developed in the powders at a calcination temperature