Materials Science and Engineering B 132 (2006) 292–299

MATERIALS SCIENCE & ENGINEERING B

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# Effects of magnesium niobate precursor and calcination condition on phase formation and morphology of lead magnesium niobate powders

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Received 1 March 2006; received in revised form 26 April 2006; accepted 28 April 2006

## Abstract

A perovskite phase of lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ or PMN, powders has been synthesized by a rapid vibro-milling technique. Both columbite $MgNb_2O_6$ and corundum $Mg_4Nb_2O_9$ have been employed as magnesium niobate precursors, with the formation of the PMN phase investigated as a function of calcination conditions by thermal gravimetric and differential thermal analysis (TG–DTA) and X-ray diffraction (XRD). The particle size distribution of the calcined powders was determined by laser diffraction technique. Morphology, crystal structure and phase composition have been determined via a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) techniques. The magnesium niobate precursor and calcination condition have been found to have a pronounced effect on the phase and morphology evolution of the calcined PMN powders. It is seen that optimisation of calcination conditions can lead to a single-phase PMN in both methods. However, the formation temperature and dwell time for single-phase PMN powders were lower for the synthetic method employing a columbite $MgNb_2O_6$ precursor.

*Keywords:* Lead magnesium niobate; Magnesium niobate; Perovskite; Powder synthesis; Calcination

## 1. Introduction

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ or PMN, is one of the most widely investigated relaxor ferroelectric materials with a perovskite structure. The excellent dielectric broadening and electrostrictive properties make it a promising electroceramic material for capacitor, electrostrictive actuator, electromechanical transducer and electro-optic applications [1–3]. There has been a great deal of interest in the preparation of single-phase PMN powders as well as in the sintering and dielectric properties of PMN-based ceramics [4–6]. However, it is well documented that the formation of PMN perovskite via the solid-state reaction is often accompanied by the occurrence of unwanted pyrochlore-type phases because of the volatilisation of PbO, the low dispersion of MgO and the differences of the reactive temperature between Pb–Nb and Pb–Mg [7–9]. Hence, several innovation techniques [10–12] have been utilized to minimize the amount of pyrochlore phase formed.

The initial work of Lejeune and Boilot [10] considered the many parameters which influence the synthesis of PMN from PbO, MgO and $Nb_2O_5$ precursors, concluding that the formation of a pyrochlore phase could not be completely eliminated. Moreover, it was proposed that the reactivity of magnesium oxide with lead and niobium oxides was the definitive factor governing products of the reaction. These authors later proposed the use of $MgCO_3$ in place of MgO to increase the yield of perovskite PMN. Swartz and Shrout [7] developed an effective way of producing PMN powder in high yield by the introduction of a two-step process (the B-site precursor approach). In the method, an intermediate step to give columbite-type $MgNb_2O_6$ precursor is used to bypass the formation of the pyrochlore phases. Alternatively, Joy and Sreedhar [11] proposed the use of $Mg_4Nb_2O_9$ precursor in place of $MgNb_2O_6$ for the fabrication of pyrochlore-free PMN. More recently, Lu and Yang [12] adopted a two-stage synthesis method by precalcining the mixture of MgO and $Nb_2O_5$ at 1000 °C to form $Mg_4Nb_2O_9$. This compound was then quenched at 850–900 °C with PbO to form PMN without further soaking. This approach yielded perovskite PMN as the dominant phase, with pyrochlore impurities of less than 5% and some residual MgO. It was also claimed that the pyrochlore

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doi:10.1016/j.mseb.2006.04.034

phases and the residual MgO could be eliminated completely with the introduction of excess PbO and nitric acid, respectively. However, the preparation of PMN using $Mg_4Nb_2O_9$ precursor, to date, has not been extensive as that of PMN using $MgNb_2O_6$ precursor. Moreover, its effect on the formation of perovskite PMN phase under various calcination conditions (especially the effects of applied dwell time and heating/cooling rates) has not been adequately characterized.

The purpose of this study was to compare the two B-site precursor synthetic routes of PMN 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 procedure

$Pb(Mg_{1/3}Nb_{2/3})O_3$ was synthesised by a similar methodology of B-site precursor mixed oxide synthetic route, as reported earlier [4]. Starting precursors were as follows: PbO (JCPDS file number 77-1971), MgO (periclase: JCPDS file number 71-1176) and $Nb_2O_5$ (JCPDS file number 80-2493) (Aldrich, 99% purity). These three oxide powders exhibited an average particle size in the range of 3.0–5.0 μm. First, two intermediate phases of magnesium niobate: $MgNb_2O_6$ and $Mg_4Nb_2O_9$ were separately prepared by the solid-state reaction method previously reported [13,14], employing an optimised calcination conditions of 1000 °C for 4 h with heating/cooling rates of 30 °C/min and 950 °C for 2 h with heating/cooling rates of 25 °C/min, respectively. The following reaction sequences were then proposed for the formation of PMN:

1. The columbite route:

$$3PbO(s) + MgNb_2O_6(s) \rightarrow 3Pb(Mg_{1/3}Nb_{2/3})O_3(s) \quad (1)$$

2. The corundum route:

$$12PbO(s) + Mg_4Nb_2O_9(s) + 3Nb_2O_5(s) \rightarrow 12Pb(Mg_{1/3}Nb_{2/3})O_3(s) \quad (2)$$

Instead of employing a ball-milling procedure ($ZrO_2$ media under acetone for 24 h [7]), a McCrone vibro-milling was used. In order to improve the reactivity of the constituents, the milling process was carried for 2 h (instead of 30 min [4]) with corundum media in isoproponal. After drying at 120 °C for 2 h, various calcination conditions were applied in order to investigate the formation of PMN phase in each calcined powders.

The reactions of the uncalcined powders taking place during heat treatment were investigated by thermal gravimetric and differential thermal analysis (TG–DTA, Shimadzu) using a heating rate of 10 °C/min in air from room temperature up to 900 °C. Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Philips PW 1729 diffractometer) using Ni-filtered Cu Kα radiation, to identify the phases formed and optimum calcination conditions for the manufacture of PMN powders. The mean crystallite size was determined using the diffraction peak (1 1 0) of the perovskite pattern by using Scherrer equation [15]. Particle size distributions of powders were determined by laser diffraction technique (DIAS 1640 laser diffraction spectrometer), with the grain size and morphologies of powders observed by scanning electron microscopy (SEM; JEOL JSM-840A). The chemical composition and structure of the phases formed were elucidated by transmission electron microscopy (CM 20 TEM/STEM) operated at 200 keV and fitted with 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. Powder samples were dispersed in solvent and deposited by pipette on to 3 mm holey copper grids for observation by TEM. In addition, attempt was made to evaluate the crystal structures of the observed compositions/phases by correcting the XRD and TEM diffraction data.

## 3. Results and discussion

TGA and DTA results for the mixtures synthesized by both B-site precursor methods are shown in Figs. 1 and 2, respectively. In general, similar trend of thermal characteristics is observed in both precursors. As shown in Fig. 1, the powders prepared via both B-site precursor mixed oxide methods demonstrate three distinct weight losses. The first weight loss occurs below 200 °C, the second one between 200–300 °C and the final one after 750 °C. In the temperature range from room temperature to ∼150 °C, both samples show small thermal peaks in the DTA curves, Fig. 2, 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 [13,16]. In comparison between the two B-site precursor routes, after the first weight loss, the columbite route shows a slightly higher weight loss over the temperature range of ∼50–220 °C, followed by a much sharper fall in specimen weight with increasing temperature from ∼250 to 350 °C. This columbite-precursor method also exhibits larger overall weight loss (∼1.25%) than that of the corundum route (∼1.00%).

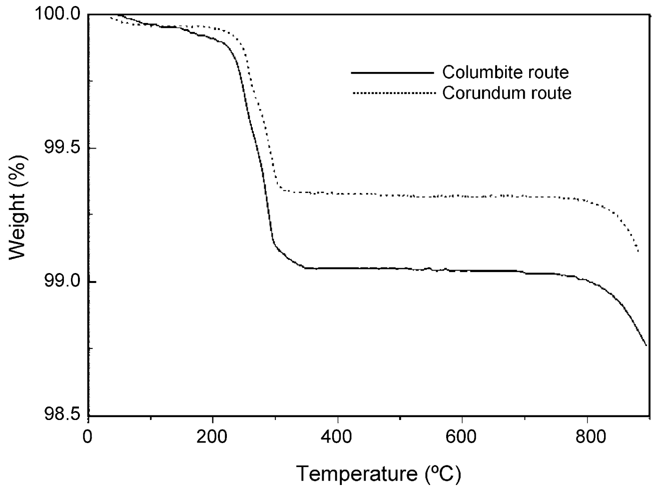

Fig. 1. TGA curves of the mixtures derived from columbite- and corundum-route.