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Current Applied Physics 9 (2009) 268–273
Current Applied Physics
An official journal of the KPS
www.elsevier.com/locate/cap
www.kps.or.kr

Synthesis and electrical properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ ceramics

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Received 24 December 2006; received in revised form 15 February 2008; accepted 20 February 2008
Available online 29 February 2008

Abstract

Ceramic compositions of a combination between lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$, and lead titanate, $PbTiO_3$, were fabricated by using $Mg_4Nb_2O_9$ precursor technique. Their electrical properties with respect to temperature and frequency were examined and the effect of sintering conditions on phase formation, densification, microstructure and electrical properties of the ceramics were examined. It has been found that optimisation of sintering condition can lead to a highly dense and pyrochlore-free PMN–PT ceramics. The gradual decreasing of the physical properties of the sintered ceramics was related to the gradual decrease of density and inhomogeneous microstructure. The results also revealed that for the lower concentration of lead titanate a relaxor behavior is noticed with a high electrostrictive effect, which was almost hysteretic free. However, higher amount of lead titanate led to a normal ferroelectric behavior.

PACS: 77.22.Ch; 77.84.Dy; 77.80.–e; 77.80.Fm

Keywords: Dielectric properties; Ferroelectric properties; Lead magnesium niobate titanate

1. Introduction

The complex perovskite lead magnesium niobate–lead titanate, $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–PT), are extensively used as multilayer capacitors, electrostrictive actuators, sensors and many other electronic and microelectromechanical devices [1,2]. This is due to their excellent electrical and electromechanical properties including high relative permittivity, a broad maximum in the dielectric constant, large electrostrictivity, associated with a low thermal expansion and excellent voltage stability [1–3]. However, these importance properties are depend strongly on the purity of the raw materials and method of preparation, since they can be limited by the formation of the unwanted pyrochlore phases with poor electrical properties upon processing [4–6]. Throughout the years, considerable efforts with various preparation techniques have been proposed and used to fabricate pyrochlore-free PMN–PT ceramics [7–9]. Among these, the columbite method [6], in which prefabricated $MgNb_2O_6$ is reacted with an appropriate proportion of PbO, has been widely used in the synthesized of phase-pure perovskite PMN-based ceramics. Numerous studies [10–13] have been reported in the literature in which the columbite method was modified by using different set of reactants as precursor materials. To our knowledge there are no reports so far on the preparation of PMN–PT ceramics by using a corundum $Mg_4Nb_2O_9$ precursor. In our previous work, pure-perovskite PMN could be prepared by using $Mg_4Nb_2O_9$ precursor. This suggested that the same process would be adaptable for the formation of PMN–PT solid solutions and also would be easier than conventional methods, because the PMN structure can be stabilized by the presence of PT.

In the present study, ceramics in the $(1-x)$PMN–xPT system were fabricated by using the solid-state reaction technique with $Mg_4Nb_2O_9$ as a key B-site precursor. Their

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doi:10.1016/j.cap.2008.02.009

electrical properties with respect to temperature and frequency were examined, compared and explained on the basis of their final composition, densification, and structural development.

2. Experimental

The system under investigation was $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ or $(1-x)$PMN–xPT, where x changed from 0.1 to 0.5 at regular interval of 0.1. The starting materials were commercially available oxide powders of PbO, MgO, Nb_2O_5 and TiO_2 (Aldrich, 99.9% purity) with an average particle size of 3–5 μm. PMN powders were first synthesised from these oxides using a modified mixed oxide synthetic route described in our earlier work [14]. In this method, MgO and Nb_2O_5 are reacted at 950 °C for 2 h to form the corundum precursor $Mg_4Nb_2O_9$ [15]. The following reaction was employed for the formation of PMN [14]:

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

The resulting PMN was then reacted with PbO and TiO_2 at 800 °C for 2 h with heating/cooling rates of 30 °C/min to obtain PMN–PT. The mixing process was carried out by vibro-milling the mixture of raw materials for 2 h with corundum media in isopropyl alcohol (IPA). After wet-milling, the slurry was dried, sieved and calcined in closed alumina crucibles.

Green pellets were pressed into disks and sintered at various temperatures between 900 and 1250 °C (no organic binders or any other additives were used). Each pellet to be sintered was supported by $PbZrO_3$ setters and enclosed in double alumina crucibles together with the atmosphere powder of identical composition (to minimize the possibility of PbO volatilization). Densities of the sintered pellets were determined by using the Archimedes principles. Room temperature X-ray diffraction (XRD; Philips PW 1729 diffractometer) using Ni filtered Cu K_α radiation, was used to identified the phases formed and optimum sintering condition for the manufacture of each PMN–PT composition, with the microstructural development examined by scanning electron microscopy (SEM; JEOL JSM-840A), operating at 20 kV and equipped with an energy-dispersive X-ray (EDX) analyser. For the electrical measurements the ceramics were polished using 1 μm alumina, cleaned with ultrasonic, dried and sputtered with gold. The dielectric measurement were made using an automated measurement system i.e. an LCR meter (HP-4174A), a nitrogen-fed furnace (9023 Delta design) and a desktop computer (HP-200 series). Hysteresis measurements were made using a modified Sawyer–Tower circuit controlled by a PC. This system is also capable of simultaneous measurement of strain using an LVDT and lock-in amplifier (SR830 DSP, Stanford Research).

3. Results and discussion

The X-ray diffraction patterns from sintered PMN–PT ceramics with maximum perovskite and bulk density are given in Fig. 1, where complete crystalline solutions of perovskite structure were formed throughout the whole composition ranges. Optimum sintering conditions for all ceramics were established by identifying the conditions for maximizing both the bulk density and the yield of perovskite. In general, only a pseudo-cubic symmetry was observed at low values of PT concentration, in good agreement with other workers [12,13,16]. By the influence of PT, however, several peaks split for $x \geqslant 0.4$, indicating the development of tetragonal symmetry, which continued with a further increase in PT concentration. For example, (002)/(200) peaks splitting the diffraction line around 2θ of 44–46° confirming their tetragonal symmetry, consistent with literature [12,17].

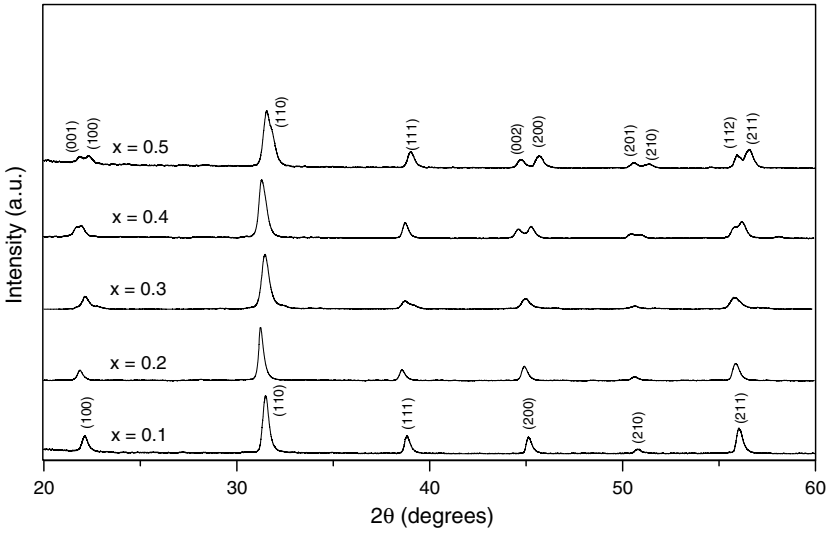

Fig. 1. XRD patterns of the $(1-x)$PMN–xPT ceramics sintered at their optimum conditions.