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Journal of the European Ceramic Society 26 (2006) 111–115

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Reaction sintering of lead zinc niobate–lead zirconate titanate ceramics

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Received 13 June 2004; received in revised form 5 October 2004; accepted 16 October 2004
Available online 8 December 2004

Abstract

Lead zinc niobate (PZN)–lead zirconate titanate (PZT) ceramics were produced by the reaction-sintering process. The specimens were prepared directly from a mixture of their constituent oxides without any calcination step. When 50% PZN was added to tetragonal $Pb(Zr_{0.47}Ti_{0.53})O_3$ ceramics, the densities and electrical properties were found to be optimal ($\rho = 7.91\ g/cm^3$, $K = 1947$ at 1 kHz and room temperature, $d_{33} = 530\ pC/N$, $k_p = 0.61$). However, the specimen containing more than 50% PZN showed reduced density and decreased electrical properties, due to the formation of pyrochlore phases. The improved densification behavior of the reaction-sintering process was attributed to the enhanced diffusion of lattice defects, which were created by differences in the ionic valence of the B-sites ions of the perovskite structure.

Keywords: PZT; PZN; Reaction sintering, Piezoelectric properties

1. Introduction

Lead zirconate titanate ($Pb(Zr,Ti)O_3$; PZT) ceramics have been regarded as one of the most important ferroelectrics due to their excellent dielectric, piezoelectric and electro-optic properties.[1–3] PZT-based solid solution systems have been investigated by incorporating them with other ABO_3-type perovskites, especially relaxor-type materials, for the purpose of improving their sinterability, and their dielectric and piezoelectric properties.[4–7]

Among the numerous relaxor-type perovskites with an $A(B'B'')O_3$ structure, lead zinc niobate ($Pb(Zn_{1/3}Nb_{2/3})O_3$; PZN) is a typical relaxor ferroelectric material with a broad phase transition region and large dielectric constants.[8–11] However, single phase PZN is difficult to sinter in the perovskite structure by the conventional ceramic process, due to the formation of the pyrochlore phase.[12] The addition of other perovskite materials, such as barium titanate ($BaTiO_3$),[13] lead titanate ($PbTiO_3$)[14] or PZT,[5] has been found to be effective in stabilizing PZN in the perovskite structure. Especially, when tetragonal PZT ($Pb(Zr_{0.47}Ti_{0.53})O_3$) was incorporated with PZN by a conventional solid-state reaction method, a stable perovskite phase with excellent piezoelectric properties was obtained.[5] However, all of these processes employed a calcination step for the purpose of phase formation, as well as a sintering step for densification.

Recently, there have been reports that relaxor-based ceramics were prepared by reaction sintering, where the oxide mixtures were directly sintered at high temperature without undergoing the calcination step.[15–17] Reaction sintering is a simple and economical processing technique, in which the reactions between the constituents take place during sintering at high temperatures. However, PZT-based ceramics were difficult to prepare by reaction sintering, because large amounts of excess PbO were needed to induce the liquid phase sintering.[18,19]

The purpose of this study is to investigate the sintering behavior and electrical properties of PZN–PZT ceramics prepared by the reaction-sintering process. Different amounts

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doi:10.1016/j.jeurceramsoc.2004.10.005

of PZN were added to tetragonal $Pb(Zr_{0.47}Ti_{0.53})O_3$ ceramics and then the densification behavior and microstructure evolution of the PZN–PZT ceramics were systematically observed. The phase evolution, dielectric properties and piezoelectric properties were measured and correlated with the composition and densification behavior of the system.

2. Experimental procedure

PZN–PZT ceramics with the nominal composition $Pb[(Zn_{1/3}Nb_{2/3})_x(Zr_{0.47}Ti_{0.53})_{1-x}]O_3$ ($0.2 \leq x \leq 0.8$) were prepared by conventional solid state reactions. Commercial oxide powders of PbO, ZnO, Nb_2O_5, TiO_2 (99.9% purity, Aldrich Chemicals, USA) and ZrO_2 (99% purity, Aldrich Chemicals, USA) were used as the starting materials. Appropriate amounts of PbO, ZnO, Nb_2O_5, ZrO_2 and TiO_2 for the stoichiometric PZN–PZT were milled in alcohol with ZrO_2 balls for 4 h, following which the slurry was dried. The milled powders were directly pressed into 10 or 15 mm diameter pellets without calcination, and then isostatically pressed at 200 MPa.

The pressed pellets were sintered in air at 1200 °C for 2 h using sealed alumina crucibles. A lead atmosphere was employed to minimize the evaporation of PbO during sintering, by using an equimolar mixture of PbO and ZrO_2. An excess of 0.5 wt.% PbO was added to compensate for lead loss during sintering. The density of the sintered PZN–PZT pellets was measured by the water immersion method (Archimedes method). The sintered disks were lapped on their major faces and silver electrodes were made from a low-temperature silver paste by firing at 500 °C for 30 min to enable electrical measurements to be taken. The piezoelectric samples were poled in a silicone oil bath at 150 °C by applying an electric field of 2 kV/mm for 10 min and then cooling them under the influence of the electrical field. The samples were aged for 24 h prior to testing.

X-ray diffraction (XRD, MXP18A-HF, Cu Kα radiation, MAC Science, Tokyo, Japan) was used to determine the perovskite/pyrochlore phase ratio in the sintered specimens using the following equation:[20]

$$\%\,\mathrm{Pyro} = \frac{(I_{222})_{\mathrm{Pyro}}}{(I_{110})_{\mathrm{Pero}} + (I_{222})_{\mathrm{Pyro}}} \times 100 \tag{1}$$

The microstructure development was studied by means of a field-emission scanning electron microscope (FE-SEM, JSM-6330F, JEOL Technics, Tokyo, Japan). Dielectric measurements were taken at room temperature using an impedance analyzer (SI1260 Impedance/Gain-Phase Analyzer, Solartron, Berkshire, UK). The piezoelectric coefficient (d_{33}) was measured with a quasi-static piezoelectric d_{33}-meter (ZJ-3D, Institute of Acoustics Academic Sinica, Beijing, China). The electromechanical coupling factor (k_p) was measured by the resonance and anti-resonance technique using the impedance analyzer and was calculated from the following formula:

$$\frac{1}{k_p^2} = \frac{0.395 f_r}{f_a - f_r} + 0.574 \tag{2}$$

where f_r and f_a are the resonance and anti-resonance frequencies, respectively.[21] The field-induced longitudinal strain (s_{33}) was monitored by using a displacement sensor (DT/2/S, Solartron, West Sussex, UK) and a high voltage power supply source (BERTAN, Hicksville, NY, USA).

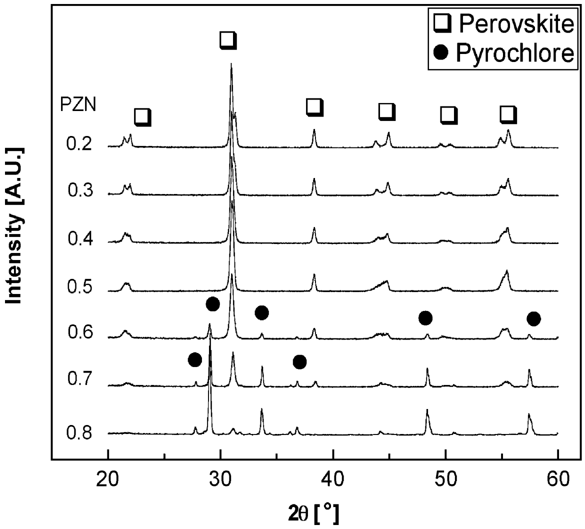

Fig. 1. X-ray diffraction patterns of xPZN − (1 − x)PZT (Zr/Ti = 47/53, x = 0.2–0.8) specimens sintered at 1200 °C.

3. Results and discussion

The formation of the perovskite and pyrochlore phases in the xPZN − (1 − x)PZT (Zr/Ti = 47/53, x = 0.2–0.8) specimens produced by the reaction-sintering process were studied and analyzed by XRD. The XRD patterns from this system are shown in Fig. 1. When 20% PZN was added, the tetragonal phase was formed in the specimen. As the PZN content increased to 30%, a weak rhombohedral peak began to appear. As the PZN content was further increased, the rhombohedral peak became stronger. Because PZN has a rhombohedral structure, the observation of increased rhombohedral peaks with increased PZN content was understandable. When the proportion of PZN added was 60%, pyrochlore phase began to form along with the perovskite phase. As the PZN content increased to 70% and 80%, the pyrochlore content was increased to 59% and 93%, respectively. These phase analyses indicated that the stable perovskite phase was formed in the PZN–PZT ceramics only when the PZN content was less than 60%.

Fig. 2A–C show the scanning electron microscopy images of the fracture surfaces of the xPZN − (1 − x)PZT