ELSEVIER

Ceramics International 30 (2004) 1353–1356

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Investigation on the microstructure and ferroelectric properties of porous PZT ceramics

Zeming He*, J. Ma, Ruifang Zhang

School of Materials Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

Received 26 November 2003; received in revised form 16 December 2003; accepted 22 December 2003

Available online 7 May 2004

Abstract

In the present work, porous lead zirconate titanate (PZT) ceramics were fabricated by introducing pore-forming agent polymethyl methacrylate (PMMA) and sintering green compacts at low temperature. The phase, the microstructure, and the ferroelectric properties of the prepared ceramics were characterized. The correlation of microstructure with ferroelectric properties was discussed. The porosity increased with increase in the added PMMA content at a given sintering temperature or decreasing the sintering temperature at a fixed added PMMA content. The dielectric constant and the dielectric loss of the investigated samples decreased with increase in the frequency. The dielectric constant decreased and the dielectric loss increased with the increase in the addition content of PMMA at fixed frequency and sintering temperature. At same porosity, the sample with macropores showed lower dielectric constant and dielectric loss, compared to the sample with micropores.

Keywords: D. PZT; Porous ceramics

1. Introduction

Lead zirconate titanate (PZT) is an important ferroelectric material, which plays a remarkable role in modern electroceramic industry. The application of the PZT component is wide, including nonvolatile memory elements, pyroelectric detectors, piezoelectric transducers, and photoelectric devices [1,2]. Recently, porous PZT ceramics have been paid huge attentions due to their possibility of enhancing some parameters with respect to dense materials. Moreover, air inclusions in the materials could reduce the effective acoustical impedance and hence improve the acoustic matching between the component and the media through which signals can be transmitted or received [3–5].

In the present work, porous PZT ceramics were fabricated from two approaches. One method used sintering of PZT powders at low temperature, and another sintering of powder mixtures of PZT and polymethyl methacrylate (PMMA). As the pore-forming agent, PMMA would burn off during sintering and leave macropores in the ceramic matrix. For the prepared ceramics, the phase and the microstructure were characterized, and the dielectric constant and the dielectric loss were measured. The correlation of porosity and pore size with ferroelectric properties are discussed.

2. Experimental procedure

The designed composition was $Pb(Zr_{0.525}Ti_{0.475})O_3 + 0.005Y_2O_3 + 0.005Nb_2O_5 + x$PMMA, where $x = 0$, 12, 24, and 36 vol.%, respectively. PZT-based powders were synthesized from commercially available PbO, ZrO_2, TiO_2, Y_2O_3, and Nb_2O_5 powders (Coors Ceramics, USA). The weighted powders for the designated PZT composition were mixed for 6 h with zirconia balls as the grinding media and ethanol as the solvent in a planetary ball miller (Restch, USA). After milling, the resultant slurry was dried in an oven and then the powders were calcined in a high-temperature furnace (Carbolite, UK) at 850 °C for 120 min. After drying and sieving, the calcined powders were mixed with PMMA powders (Struers, Denmark) and the mixtures were ball-milled again. The mixed powder was fed in a 10 mm stainless steel die and subjected to uniaxial pressure of 150 MPa. The formed green compacts with different added PMMA contents were sintered at different temperatures of 1000, 1050, 1100, and 1150 °C, isothermally

* Corresponding author. Tel.: +65-67904590; fax: +65-67909081.
E-mail address: zmhe@ntu.edu.sg (Z. He).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.108

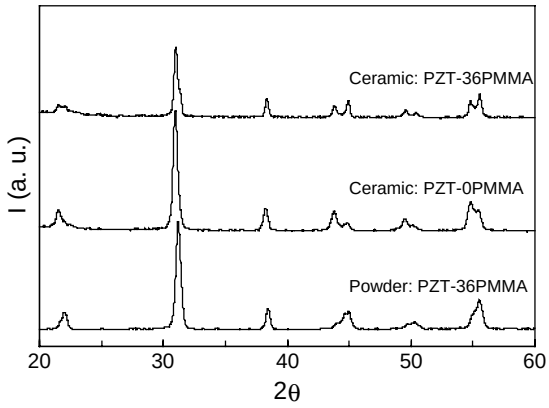

Fig. 1. XRD patterns of the prepared powder and the ceramics sintered at 1150 °C.

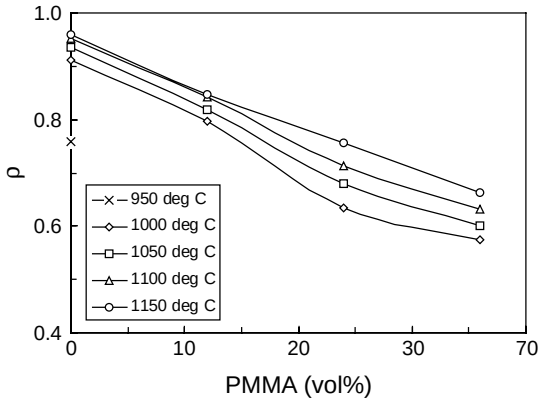

Fig. 2. Variations of relative density with PMMA content of the samples sintered at different temperatures.

held for 120 min in the high-temperature furnace. The PZT green compact without PMMA added was also sintered at 950 °C for 30 min to achieve low density. During sintering, all the compacts were placed in a covered alumina crucible that contained $PbZrO_3$ disks to produce a PbO-excess atmosphere.

The density of the sintered component was measured from its mass and dimensions. The relative density was obtained from the ratio of the measured density to the theoretical density of PZT, which was taken as 8 g cm^{-3} [6]. An X-ray diffractometer (Shimadzu, Japan) with Cu Kα radiation was used to reveal the phases of the mixed powders and the sintered samples. The microstructure of the sintered component was examined by a JSM-5410 scanning electron microscopy (JEOL, Japan). For the measurement of ferroelectric properties, the thickness of the sample was ground to 0.8 mm and silver paste (Agar, UK) was applied on both surfaces. The dielectric constant and the dielectric loss were measured

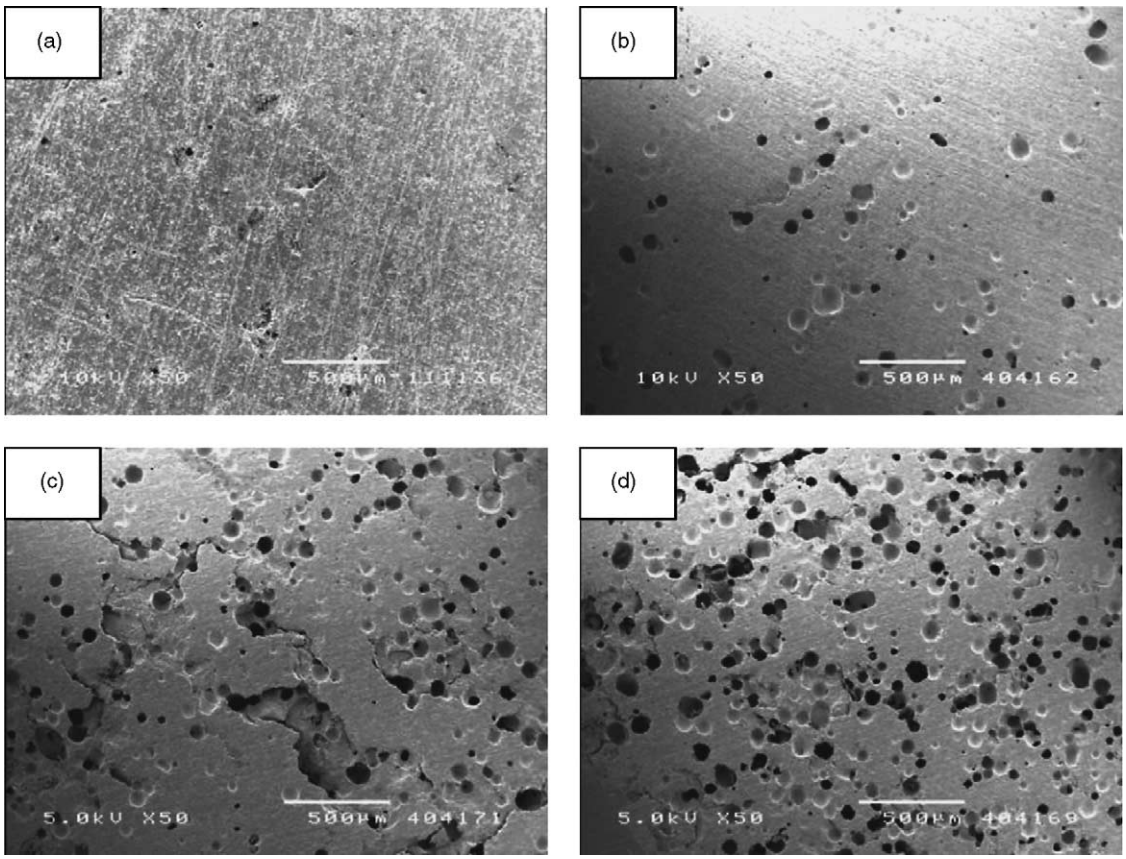

Fig. 3. SEM images of the samples sintered at 1150 °C. (a) PZT-0PMMA, (b) PZT-12PMMA, (c) PZT-24PMMA, and (d) PZT-36PMMA.

using a HP4194A impedance/gain-phase analyzer (HP, USA).

3. Results and discussion

Fig. 1 shows the XRD patterns of the mixed powder PZT-36PMMA and the ceramics PZT-0PMMA and PZT-36PMMA sintered at 1150 °C. It is noted that PZT materials with perovskite structure were exhibited for both the calcined powder and the sintered ceramic. No other phase was detected. The XRD results indicate that the processes of synthesis and sintering of PZT employed in the present work are appropriate.

The variations of relative density, with PMMA addition content, of the samples sintered at different temperatures are shown in Fig. 2. The relative density decreases, or the porosity increases with increase in the added PMMA content at a fixed temperature, and at a given PMMA content, the relative density increases with the increase of the sintering temperature. The density changes with PMMA content and sintering temperature are easy to understand. During sintering, PMMA burnt off leaving pores in the PZT matrix. The more the added PMMA, the more the porous in the material microstructure. On the other hand, low-sintering temperature led to low density. In Fig. 2, the relative density of PZT-0PMMA sintered at 950 °C is also shown, which is nearly the same as that of PZT-24PMMA sintered at 1150 °C.

Fig. 3 shows the SEM images of the samples with different PMMA contents sintered at 1150 °C. It can be seen that for PMMA-containing green compacts, macropores (100 to 250 μm) were formed in the ceramics after sintering. As the content of the added PMMA increases, the porosity increases, which is consistent with the density of results shown in Fig. 2.

The dielectric constants and the dielectric losses measured at different frequencies of the sintered samples are shown in Figs. 4 and 5, respectively. As the frequency increases,

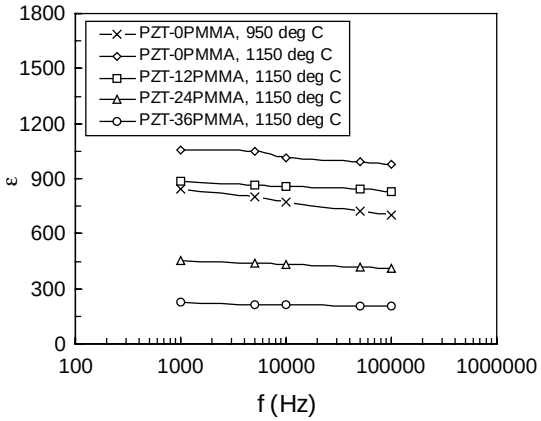

Fig. 4. Variations of dielectric constant with frequency of the samples sintered at 950 and 1150 °C.

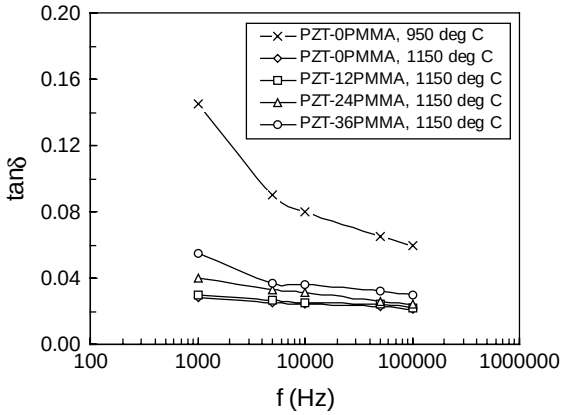

Fig. 5. Variations of dielectric loss with frequency of the samples sintered at 950 and 1150 °C.

both the dielectric constant and the dielectric loss decreases for all the investigated samples, which is a normal behavior in general ferroelectrics [7,8]. For the samples sintered at 1150 °C, the dielectric constant decreases and the dielectric loss increases with the increase of the PMMA content at a fixed frequency. This is mainly attributed to the macropores, which introduces low dielectric constant and high dielectric loss in PZT ceramic matrix [4]. To compare the difference between micropore and macropore on the ferroelectric properties, the dielectric parameters of PZT-0PMMA sintered at 950 °C are also included in Figs. 4 and 5. As stated, the porosity of PZT-0PMMA sintered at 950 °C is nearly the same as that of PZT-24PMMA sintered at 1150 °C. Their dielectric parameters at a fixed frequency, however, are different. Compared with the conventional sintered microporous ceramic, the material with macropores exhibits lower dielectric constant and dielectric loss. The observed pore-size effect on dielectric constant is consistent with that reported by Roncari et al. [4]. In general, the material with micropores has more total pore surface, which results in larger grain–pore contact area for unit grain, and more stress caused by the motion of the domain wall could be relaxed. In a sense, compared with the macroporous structure, the material with microporous structure could enhance the mobility of the domain wall. As a result, higher dielectric constant and dielectric loss are exhibited in PZT-0PMMA sintered at 950 °C, while lower dielectric constant and dielectric loss are exhibited in PZT-24PMMA sintered at 1150 °C [9].

4. Conclusions

In the present work, porous PZT ceramics were achieved using the processes of adding the pore-forming agent PMMA and low-sintering temperature. At a given sintering temperature, the porosity increased with increase in the added PMMA content, and at a fixed PMMA content, the density increased with increase in the sintering temperature. For the

investigated samples, the dielectric constant and the dielectric loss decreased with increase in the frequency. The dielectric constant decreased and the dielectric loss increased with the addition of PMMA content, at fixed frequency and sintering temperature. Compared with the sample with micropores, the sample with macropores possessed lower dielectric constant and dielectric loss, though their porosities were almost the same.

References

[1] R.E. Newnham, G.R. Ruschau, Smart electroceramics, J. Am. Ceram. Soc. 74 (3) (1991) 463–480.
[2] G.H. Haertling, Ferroelectric ceramics: history and technology, J. Am. Ceram. Soc. 82 (4) (1999) 797–818.
[3] S. Kumamoto, K. Mizumura, Y. Kurihara, H. Ohhashi, K. Okuno, Experimental evaluation cylindrical ceramic tubes composed of porous $Pb(ZrTi)O_3$ ceramics, Jpn. J. Appl. Phys. 30 (9B) (1991) 2292–2294.
[4] E. Roncari, C. Galassi, F. Craciun, C. Capiani, A. Piancastelli, A microstructural study of porous piezoelectric ceramics obtained by different methods, J. Eur. Ceram. Soc. 21 (2001) 409–417.
[5] J.-F. Li, K. Takagi, M. Ono, W. Pan, R. Watanabe, A. Almajid, M. Taya, Fabrication and evaluation of porous piezoelectric ceramics and porosity-graded piezoelectric actuators, J. Am. Ceram. Soc. 86 (7) (2003) 1094–1098.
[6] A.I. Kingon, J.B. Clark, Sintering of PZT ceramics: II. Effect of PbO content on densification kinetics, J. Am. Ceram. Soc. 66 (4) (1983) 256–260.
[7] K. Kar, J. Mal, R.N.P. Choudhary, Structural and dielectric properties of complex PLZT ceramics, J. Mater. Sci. Lett. 16 (1997) 328–331.
[8] Z. He, J. Ma, R. Zhang, T. Li, PZT-based materials with bilayered structure: preparation and ferroelectric properties, J. Eur. Ceram. Soc. 23 (2003) 1943–1947.
[9] S.-J. Yoon, A. Joshi, K. Uchino, Effect of additives on the electromechanical properties of $Pb(Zr,Ti)O_3$–$Pb(Y_{2/3}W_{1/3})O_3$ ceramics, J. Am. Ceram. Soc. 80 (4) (1997) 1035–1039.