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Microstructure, electrical and mechanical properties of MgO nanoparticles-reinforced porous PZT 95/5 ferroelectric ceramics

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Abstract

Porous Pb $(Zr_{0.95}Ti_{0.05})$ O_3/xMgO (PZT/MgO, $x=0$, 0.1, 0.2, 0.5 and 1.0 wt%) ferroelectric ceramics were prepared with MgO nanoparticles as reinforcing phase. The effects of MgO nanoparticles on the phase, microstructure, electrical and mechanical properties of as-prepared ceramics were investigated. The results show that the grain size is reduced obviously when increasing the amount of MgO. Compared with pure porous PZT, T_C of MgO-added PZT ceramics shifts to higher temperature. Moreover, dielectric, ferroelectric and piezoelectric properties show no much degradation. Further, PZT/MgO ceramics possess enhanced mechanical properties compared to pure porous PZT ceramics, the largest increment of the fracture toughness and hardness being 31.3% and 19.8%, respectively. The optimal electrical and mechanical properties are obtained with the addition of less than 0.5 wt% MgO nanoparticles.

Keywords: PZT/MgO; Microstructure; Electrical properties; Mechanical properties

1. Introduction

Perovskite-type lead zirconate titanate with Zr:Ti ratio of 95:5 (Pb $(Zr_{0.95}Ti_{0.05})$ O_3, PZT 95/5) is an important ferroelectric material, which can undergo a phase transition from ferroelectric (FE) phase to antiferroelectric (AFE) phase under a relatively low shock stress to produce a large pulse of current or voltage. This phase transition may lead to many interesting applications, such as shock-wave power supplies and neutron generator power supplies. It has been reported that porous PZT 95/5 ferroelectric ceramics are superior to dense PZT 95/5 at low temperature during explosive shock wave loading [1]. Since then, much attention has been paid on the porosity-controlled PZT 95/5 ceramics [2,3]. However, it should be worth noting that the mechanical properties of porous ceramics are worse than those of dense ceramics, which may lead to the mechanical damage resulting in dielectric breakdown and low reliability. Researchers had verified that materials with higher fracture toughness exhibited fewer high-voltage breakdowns during explosive tests [4]. Thus, it is very important that effective measures should be taken to prepare porous PZT 95/5 ceramics with good electrical properties and improved mechanical properties.

In past decades, most researches have been focused on the improvement of mechanical properties of PZT 53/47 ceramics. Introduction of nanoparticles, fibres or polymers in ceramic matrix as a second phase to form composites are commonly adopted, such as PZT/Pt, PZT/ZrO_2, PZT/ZnO whiskers [5–8]. It is found that the appropriate second phase can improve the mechanical properties at the slight expense of some electrical properties. However, similar studies have not been reported in porous PZT 95/5 ceramics. Additionally, there are multiple structure

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phases in PZT 95/5 ceramics, including low temperature rhombohedral ($F_{R(LT)}$), high temperature rhombohedral ($F_{R(HT)}$) FE phase, cubic paraelectric (Pc) phase and orthorhombic antiferroelectric (A_O) phase. Moreover, porous PZT 95/5 ceramics possess complex pore microstructure. These characteristics make the effect of a second phase on ceramic properties more complicated. Then, research on the effect of second phase on the electrical and mechanical properties of porous PZT 95/5 ceramics is very necessary. In this paper, the porous PZT 95/5-based composites are prepared by solid state sintering method, and small amount of MgO nanoparticles is introduced to improve the mechanical performance of porous PZT 95/5 ceramics. The effects of MgO addition on the crystalline phase, microstructure, electrical and mechanical properties of PZT/MgO ceramics are investigated and discussed systematically.

2. Experimental procedure

The porous PZT/MgO ceramics were prepared by solid state sintering method, in which polymethyl methacrylate (PMMA, diameter size of 15 μm) was used as pore formers and MgO nanoparticles (99.9% purity, 50 nm spheres, Aladdin) as reinforcing phase. The designed composition was $Pb_{0.99}(Zr_{0.95}Ti_{0.05})_{0.98}Nb_{0.02}O_3$ powders + 1 wt% PMMA + x wt% MgO, where $x=0$, 0.1, 0.2, 0.5 and 1.0 wt%, respectively. First, PZT 95/5 powders were synthesized from appropriate quantities of high-purity oxide powders using solid-state processing route. Second, PMMA and MgO nanoparticles were ball-mill mixed for 6 h with the synthesized PZT 95/5 powders with zirconia balls as the grinding media and alcohol as the solvent. After drying, the powders were mixed with 6 wt% polyvinyl alcohol (PVA) binder. Then, the mixed powders were pressed under 200 MPa to form ∅16 mm disks. After the binder burnout, the pressed samples were then sintered in a sealed alumina crucible at 1330 °C for 90 min in PbO-rich atmosphere to minimize the lead loss during sintering. For testing their electrical properties, the as-prepared porous PZT 95/5 ceramics were processed into disks with a diameter of 12.5 mm and a thickness of 1 mm, and coated with silver paste to form electrodes. Next, the ceramic samples were polarized under a direct current field of 3 kV/mm at 100 °C in a silicon oil bath for 10 min.

X-Ray diffraction (XRD, D/max2550V, Rigaku, Japan) analysis was conducted using Cu K_α radiation with a scanning step of 0.02° from 10° to 80°. The microstructure of the as-prepared ceramics was observed by scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan) with backscattered electron (BSE) mode. The bulk density was determined using Archimedes' method. The theoretical densities of the ceramics were calculated based on theoretical densities of PZT 95/5 (8.08 g/cm^3) and MgO (3.58 g/cm^3). The fracture toughness (K_{IC}) and hardness (H_V) of sintered and polished specimens were evaluated by the indentation fracture technique described by Chad S. Watson and Pin Yang using a Vickers diamond indenter (TUKON-2100B, Instron Co., USA) with a peak load of 19.6 N for 15 s [9]. The dielectric properties were obtained by measuring the capacitance and dielectric loss at 1 kHz in the temperature range from room temperature to 400 °C using a LCR meter (HP4284A, USA). The piezoelectric constant (d_{33}) was measured using a quasi-static piezoelectric d_{33} meter (Model ZJ-3d, Institute of Acoustics, Academia Sinica, China). The polarization-electric field hysteresis loops at room temperature were characterized with aix ACCT TF Analyzer 2000 (aixACCT Co., Germany), combined with a high voltage power supply (Model 604 system, Trek, USA).

3. Results and discussion

3.1. Crystal phase and morphology analyses of ceramics

Fig. 1 shows the XRD patterns of porous PZT 95/5 ceramics with different MgO addition. There are only the diffraction peaks of perovskite-type PZT phase within the adopted range of MgO amount, indicating no new reaction phases formed between PZT and MgO phases.

The BSE images of porous PZT 95/5 ceramics with different MgO addition are presented in Fig. 2. For pure porous PZT 95/5 ceramics, the grain size is about 6 μm (Fig. 2(a)). With increasing the amount of MgO nanoparticles, its grain size decreases from ~6 μm to ~2 μm (Fig. 2(b)–(e)), which is consistent with the previous report [10]. This grain refinement mainly resulted from the pinning effect of MgO nanoparticles as the second phase (identified by circle in Fig. 2(f)) situating at the grain boundary, which slowed down migration of grain boundary and then inhibited grain growth. With increasing MgO addition, more MgO nanoparticles may locate at the grain boundaries. Therefore, the grain growth is inhibited and the grain size becomes smaller. Nevertheless, the effect becomes weaker when the addition of MgO nanoparticles is above 0.2 wt%.

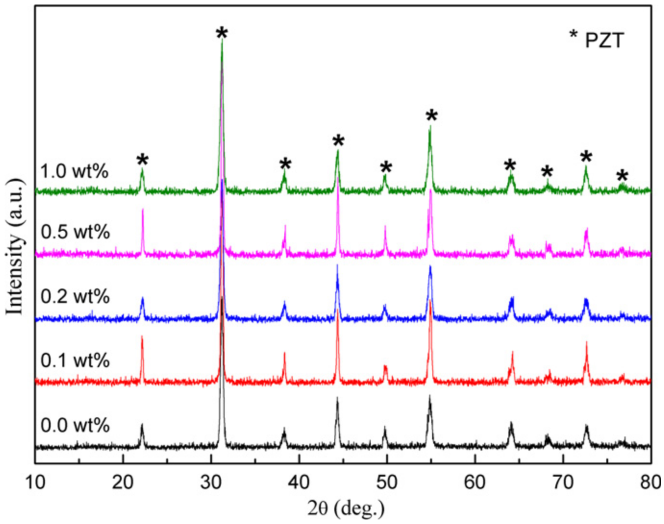

Fig. 1. XRD patterns of porous PZT 95/5 ceramics with different MgO addition.

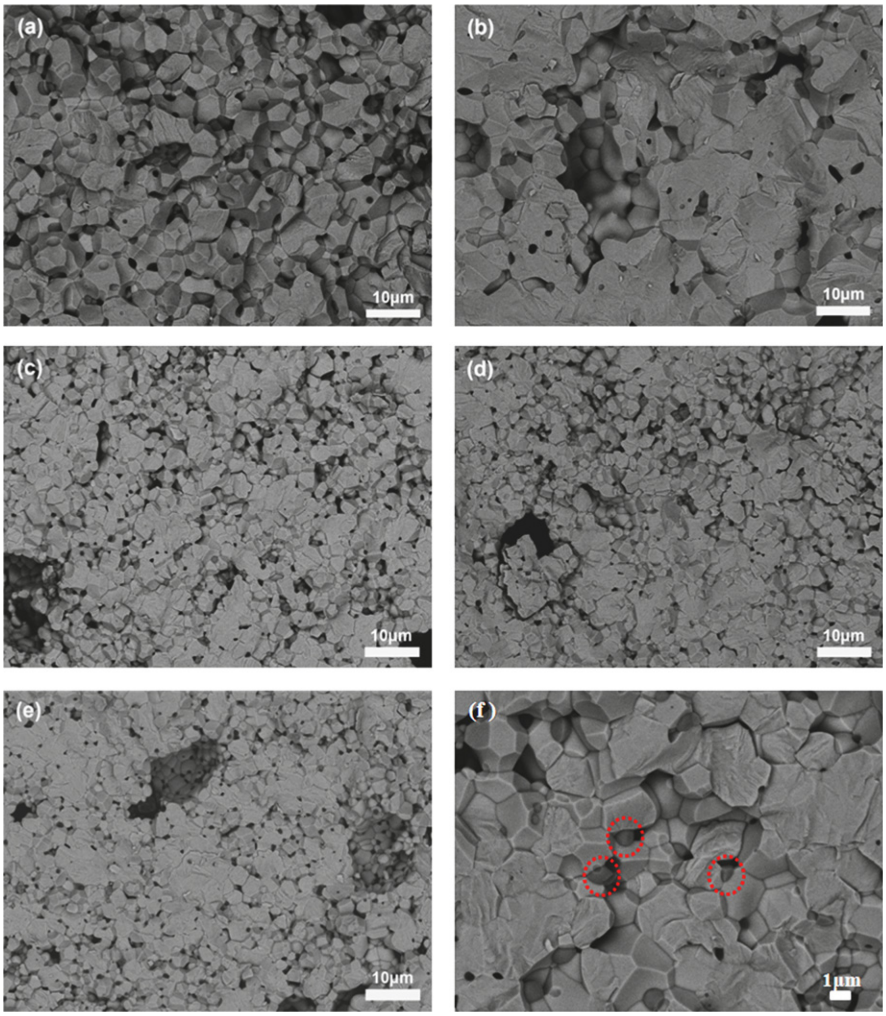

Fig. 2. SEM photographs of fracture surface of porous PZT/MgO ceramics. (a) 0.0 wt%, (b) 0.1 wt%, (c) 0.2 wt%, (d) 0.5 wt%, (e) 1.0 wt% and (f) magnified microstructure of MgO grain in ceramics.

3.2. Physical performance analyses

The relative density of PZT ceramics with different MgO addition is presented in Table 1. It is found that the relative density slightly decreases with increasing amount of MgO, indicating that MgO addition deteriorates the densification to some degree. And, the more MgO added, the worse densification of PZT ceramics, which similar phenomenon had been reported on Al_2O_3 compacts containing inclusions [11]. It could be explained that the migration rate of grain boundary was slowed down by the second phase of MgO nanoparticles locating in grain boundaries during the densification process, showing decreased density.

As expected, the fracture toughness (K_{IC}) and hardness (H_v) of all PZT/MgO ceramics are greater than that of pure porous PZT ceramics (seen in Table 1). The hardness increases 31.3% when 0.2 wt% MgO added, and the fracture toughness increases 19.8% with 0.5 wt% MgO inclusion. These results indicated that MgO nanoparticles could enhance the mechanical properties of porous PZT ceramics. It is well known that the hardness and fracture toughness are mainly dependent on the grain size and porosity of the material. According to the Hall–Petch relationship, the smaller grain size can exhibit better hardness and fracture toughness because fine grains cause higher density of grain boundaries to retard crack propagation [10]. As shown in Fig. 2, comparing with pure porous PZT ceramics, the grain size of porous PZT/MgO ceramics was gradually reduced with increasing MgO content, thus the mechanical properties accordingly increased. Moreover, examinations of the fracture surfaces via SEM (seen in Fig. 2) have also revealed that the transgranular fracture of the ceramics obviously occurs with addition of MgO nanoparticles, which indicates that the grain boundary is strengthened by the MgO nanoparticles [12]. A possible toughening mechanism associated with porous PZT/MgO ceramics may account for the fine grains and grain boundary enhancement [13,14].

3.3. Dielectric, ferroelectric and piezoelectric properties

The dielectric constants (ε_r) of porous PZT/MgO ceramics with different amount of MgO nanoparticles as a function of temperature are shown in Fig. 3(a). The obvious dielectric

Table 1
Mechanical and electrical properties of porous PZT/xMgO (wt%) ceramics.

Properties	$x=0.0$	$x=0.1$	$x=0.2$	$x=0.5$	$x=1.0$
Relative density (%)	89.4 (0.3)	89.5 (0.3)	88.6 (0.4)	87.2 (0.4)	87.2 (0.4)
H_v (GPa)	1.97 (0.06)	1.97 (0.06)	2.36 (0.06)	2.18 (0.06)	2.32 (0.06)
K_{IC} (MPa/m$^{1/2}$)	0.88 (0.02)	1.02 (0.02)	1.11 (0.02)	1.16 (0.04)	1.09 (0.04)
P_r (μC/cm^2)	34	33	31	31	25
E_c (v/mm)	1221	1271	1412	1391	1389
d_{33} (pC/N)	65	62	58	56	55

Note: The number in Parentheses is error number.

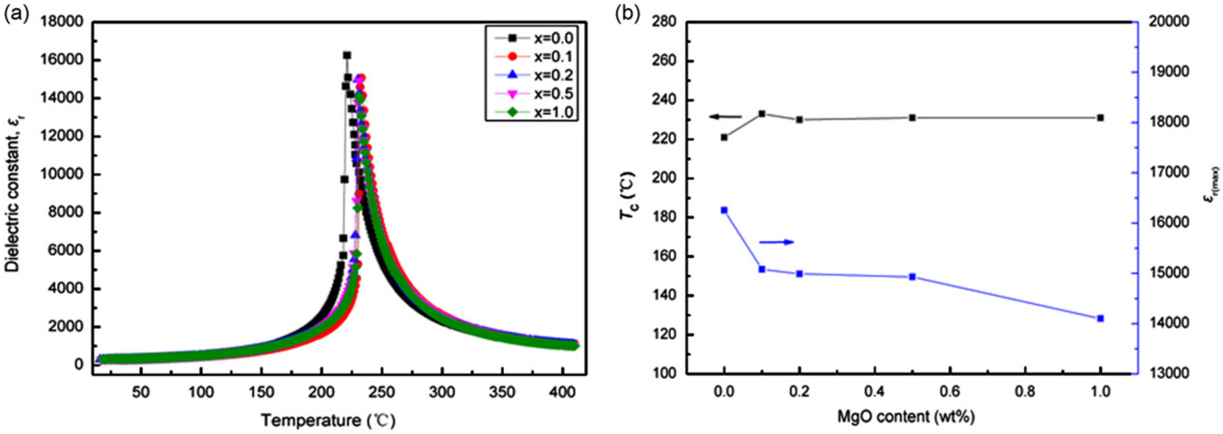

Fig. 3. (a) Dielectric constant of porous PZT 95/5 ceramics with different MgO addition as a function of temperature at 1 kHz; (b) T_C and $\varepsilon_{r\ (max)}$ as a function of MgO content.

peak can be seen from Fig. 3(a), associating with FE-P$_C$ phase transition. Fig. 3(b) shows the Curie temperature (T_C) and dielectric constant maximum ($\varepsilon_{r\ (max)}$) as a function of MgO content. It can be found that T_C of pure porous PZT 95/5 ceramics (221 °C) shifts to higher temperature (230–233 °C) with MgO addition, which indicates that MgO additive can enhance and stabilize the FE phase. Considering that pores did not change phase transition temperature, it could be deduced that this behavior was mainly because of the B-sites replacement caused by MgO. Since Mg^{2+} ion (0.72 Å) was similar in size to Ti^{4+} ion (0.61 Å) and Zr^{4+} ion (0.72 Å), a few of Mg^{2+} ions could still diffuse into B-sites of perovskite structure to play the role of "harden" doping though most Mg^{2+} ions locating at grain boundaries, which had been confirmed by previous reports [15,16]. Based on T_C value and grain size of porous PZT/MgO ceramics with different MgO content, it could be inferred that MgO addition mainly played the role of "harden" doping when its amount was within 0.1 wt%. And when 0.2–1.0 wt% MgO was added, some MgO (less than 0.1 wt%) entered into perovskite structure as dopant, while the other MgO nanoparticles located at grain boundaries as the second phase. Besides, the dielectric constant maximum gradually reduces with increasing MgO amount, which may be related to the following points. First, as a result of substitution of Ti^{4+} or Zr^{4+} ion by Mg^{2+} ion, oxygen vacancies were created in the system to compensate charge neutrality and led to the collapse of BO$_6$ octohedra, which pinned the movement of the domain walls. Second, smaller grain size implies more grain boundaries, which might "pin" the domain walls and directly restricts the switching of domain and polarization under electric field. Thus, these factors brought about low dielectric constant [17].

As shown in Fig. 4, hysteresis loops of PZT 95/5 ceramics regularly change with the amount of MgO additive. The remnant polarization (P_r) and coercive electric field (E_c) are listed in Table 1. The remnant polarization gradually decreases with increasing MgO content. However, the coercive electric field firstly increases (≤ 0.2 wt% MgO addition), then almost remains stable. Moreover, the piezoelectric constants d_{33} of porous PZT/MgO ceramics decreases with the increase of MgO content, which is also shown in Table 1. These behaviors were mainly attributed to the occupation of Mg^{2+} ion on the B-site of perovskite structure, which led to domain wall difficult to switch under electric field. Thus, it resulted in decrease of P_r and d_{33}, meanwhile increase of E_c. Besides, as mentioned above, the decreased grain size causes the reduction of domain switch ability and polarizability. Then, the ferroelectric and piezoelectric properties of PZT/MgO ceramics also worsen with increasing MgO content because of the decreasing grain size. But, it is luckily that P_r and d_{33} only slightly decrease when MgO addition is less than 0.5 wt%. Considering that the amount of doping MgO and the grain size would not almost

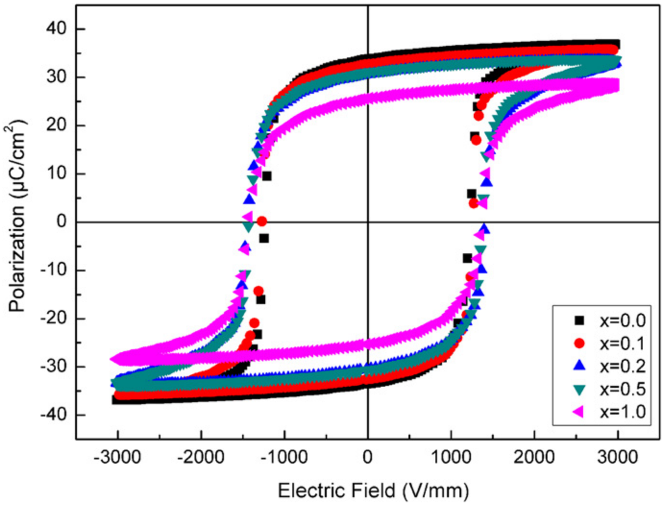

Fig. 4. Ferroelectric hysteresis loops of porous PZT 95/5 ceramics with different MgO addition.

vary with the MgO addition (> 0.2 wt%), the influence of MgO addition on E_c was not so apparent. Therefore, E_c becomes stable when MgO content is more than 0.2 wt%.

4. Conclusions

The porous PZT/MgO ceramics were prepared with MgO nanoparticles as reinforcing phase by solid state sintering method. The effects of MgO nanoparticles on the microstructure, electrical and mechanical properties of porous PZT/MgO ceramics were investigated. MgO addition restricts the grain growth and slightly reduces the densification because of MgO as a second phase locating in grain boundary. Further, MgO nanoparticles have important influence on dielectric, piezoelectric and ferroelectric properties. With the increase of MgO addition, ε_r, d_{33} and Pr gradually decrease, while Ec increases. Compared with pure porous PZT 95/5 ceramics, Tc of porous PZT/MgO ceramics shifts to higher temperature. The phenomena were mainly attributed to the B-sites replacement of Mg^{2+} ion in the perovskite structure and the "pinning effect" of domain wall caused by reduction of grain size. Moreover, MgO nanoparticles obviously improve K_{IC} and H_v of porous PZT 95/5 ceramics. The superior electrical and mechanical properties are achieved in the porous PZT/MgO ceramics with the addition of less than 0.5 wt% MgO nanoparticles.

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References

[1] B.A. Tuttle, P. Yang, J.H. Gieske, J.A. Voigt, T.W. Scofield, D.H. Zeuch, W.R. Olson, Pressure-induced phase transformation of controlled-porosity $Pb(Zr_{0.95}Ti_{0.05})O_3$ ceramics, Journal of the American Ceramic Society 84 (6) (2001) 1260–1264.
[2] T. Zeng, X.L. Dong, C.L. Mao, Z.Y. Zhou, H. Yang, Effects of pore shape and porosity on the properties of porous PZT 95/5 ceramics, Journal of the European Ceramic Society 27 (4) (2007) 2025–2029.
[3] D.A. Hall, J.D.S. Evans, S.J. Covey-Crump, R.F. Holloway, E.C. Oliver, T. Mori, P.J. Withers, Effects of superimposed electric field and porosity on the hydrostatic pressure-induced rhombohedral to orthorhombic martensitic phase transformation in PZT 95/5 ceramics, Acta Materialia 58 (20) (2010) 6584–6591.
[4] R.H. Dungan, L.J. Storz, Relation between chemical, mechanical, and electrical properties of Nb_2O_5–modified–95Mol% $PbZrO_3$–5Mol% $PbTiO_3$, Journal of the American Ceramic Society 68 (10) (1985) 530–533.
[5] H.J. Hwang, K. Tajima, M. Sando, M. Toriyama, K. Niihara, Fatigue behavior of PZT-based nanocomposites with fine platinum particles, Journal of the American Ceramic Society 81 (12) (1998) 3325–3328.
[6] Y.G. Wu, T.C. Feng, Fabrication and mechanical reinforcement of piezoelectric nanocomposites with ZrO_2 nanoparticles embedded in situ, Journal of Alloys and Compounds 491 (1-2) (2010) 452–455.
[7] H.B. Lin, M.S. Cao, Q.L. Zhao, X.L. Shi, D.W. Wang, F.C. Wang, Mechanical reinforcement and piezoelectric properties of nanocomposites embedded with ZnO nanowhiskers, Scripta Materialia 59 (7) (2008) 780–783.
[8] H. Chen, X.L. Dong, T. Zeng, Z.Y. Zhou, H. Yang, The mechanical and electric properties of infiltrated PZT/polymer composites, Ceramics International 33 (7) (2007) 1369–1374.
[9] C.S. Watson, P. Yang, Chem-Prep PZT 95/5 for Neutron Generator Applications: Effects of Lead Stoichiometry on the Microstructure and Mechanical Properties of PZT 95/5, Sandia Report Nno. SAND2004-4402, Sandia National Laboratoris, Albuquerque, 2004.
[10] S. Jiansirisomboon, M. Promsawat, O. Namsar, A. Watcharapasorn, Fabrication-structure-properties relations of nano-sized NiO incorporated PZT ceramics, Materials Chemistry and Physics 117 (1) (2009) 80–85.
[11] W.H. Tuan, E. Gilbart, R.J. Brook, Sintering of heterogeneous ceramic compacts, Part 1 Al_2O_2–Al_2O_3, Journal of Materials Science 24 (3) (1989) 1062–1068.
[12] F.X. Li, X.X. Yi, Z.Q. Cong, D.N. Fang, PZT nanocomposites reinforced by small amount of MgO, Modern Physics Letters B 21 (24) (2007) 1605–1610.
[13] B.W. Chua, L. Lu, M.O. Lai, G.H.L. Wong, Effects of complex additives on toughness and electrical properties of PZT ceramics, Journal of Alloys and Compounds 381 (1–2) (2004) 272–277.
[14] S. Jiansirisomboon, T. Sreesattabud, A. Watcharapasorn, Electrical and mechanical properties of ferroelectric lead zirconate titanate/tungsten oxide ceramics, Ceramics International 34 (4) (2008) 719–722.
[15] K. Tajima, H.J. Hwang, M. Sando, K. Niihara, PZT nanocomposites reinforced by small amount of oxides, Journal of the European Ceramic Society 19 (6-7) (1999) 1179–1182.
[16] M. Promsawat, A. Watcharapasorn, T. Sreesattabud, S. Jiansirisomboon, Effect of ZnO nano-particulates on structure and properties of PZT/ZnO ceramics, Ferroelectrics 382 (2009) 166–172.
[17] M. Dong, Z.G. Ye, Microstructure and electrical properties of sol–gel derived $Pb(Zr_{0.53}Ti_{0.47})O_3$/MgO nanoparticles and composite ceramics, Ferroelectrics 262 (2001) 213–218.