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Mechanical and electrical properties of small amount of oxides reinforced PZT ceramics

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Abstract

Piezoelectric PZT ceramics with small amount (0.1–1.0 wt.%) of oxides (Y_2O_3, MoO_3, WO_3) were prepared by conventional sintering method. Small amount of second phase doped PZT ceramic with high fracture strength showed suitable piezoelectric properties for high power and high reliable actuator applications. Especially, the fracture strength of PZT/0.1 wt.% Y_2O_3 composite was 1.5 times higher than that of monolithic PZT and the piezoelectric properties were also increased. When the second phase addition was up to 1.0 wt.%, the electrical properties were deteriorated due to the refinement of the microstructure of PZT ceramics.

Keywords: B. Composites; C. Electrical properties; C. Mechanical properties; D. PZT; E. Actuators

1. Introduction

Ferroelectric lead zirconate titanate (PZT) ceramics, close to the morphotropic phase boundary, exhibit excellent dielectric and piezoelectric properties suitable for actuators, transducers and pressure sensors. Nevertheless, the relative low mechanical properties and reliability are still a great disadvantage for these applications [1,2]. Therefore, it is necessary to design the microstructure possessing excellent mechanical characters.

Niihara had reported that small amount of submicro- or nano-scale second phases could largely improve the mechanical properties of ceramic matrix [3]. In the past few years, the novel design idea has been applied in the field of functional ceramics. In $BaTiO_3$/SiC [4], PZT/ZrO_2 [5] and PZT/Ag [6] systems, the second phases have obviously improved the fracture strength and fracture toughness of ceramic matrix. However, the problem of property trade-off, i.e. a deterioration of electrical properties, in particular, electromechanical coupling factor, still remains unsolved. It is well known that electromechanical coupling factor is one of the most important properties in actuator applications. Therefore, the suitable k_p and/or k_t is required for highly reliable ceramic actuators as well as higher fracture strength.

In this study, small amount oxides doped PZT-based composites are fabricated by conventional sintering method. The effects of the second phases on the mechanical and electrical properties have been investigated.

2. Experimental

High purity commercial Pb_3O_4, ZrO_2 and TiO_2 were mixed to form the compositions of Pb $(Zr_{0.52}Ti_{0.48})O_3$. The mixture was wet ball milled for 6h using distilled water and iron balls as the grinding medium. The oven-dried powder was crushed and calcined at 850 °C for 2h. Different amounts (0.1–1.0 wt.%) of oxides (Y_2O_3, MoO_3, WO_3) were added to the calcined powder, which once again wet ball milled for 24 h. After drying, the powders were pressed into discs (Φ17×2 mm) and rectangle bodies (42×42×8 mm). The materials were sintered at 1260 °C for 1.5 h in an atmosphere controlled by the sintered $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramic powder. For electrical measurements, Ag-paste was pasted on both sides of the discs and then fired at 600 °C for 30 min. For mechanical measurements, the slender beam speci-

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mens (36×4×3 mm) were cut from the sintered bodies and one of the major faces (dimensions of 36×4 mm) was polished with diamond paste to obtain mirror surface.

The phase analysis of the samples was based on X-ray diffraction data from a Guinier-Hägg camera with use of Cu$K_{\alpha 1}$ radiation and Si as internal standard. The obtained photographs were evaluated with a computerized scanner system. The bulk density was determined by using the Archimedes method in water. Fracture strength was measured on the slender bars by three-point bending method. The span was 30 mm and the rate of loading was 0.5 mm/min. Fracture toughness was measured by the indentation fracture (IF) technique using a micro-Vickers diamond indenter. The indentation load of 49 N was applied for 15 s. The microstructure of the sintered composites was analyzed by field emission scanning electron microscope (FESEM) (JSM-6700F, Jeol, Japan). The average of PZT grain size was determined by the linear intercept method from the SEM image of the surfaces of thermally etched samples. For piezoelectric properties, the specimen were poled in silicon oil at 120 °C for 20 min by applying electric field of 2.5 kV/mm. The dielectric constants at 1 KHz and electromechanical coupling factors were measured by resonance and antiresonance method using an impedance analyzer (HP4294A).

3. Results and discussion

X-ray diffraction analysis for PZT composites indicated that PZT matrix was a tetragonal ferroelectric phase, regardless of the kinds and quantities of oxide additions. All the peaks were identified as tetragonal PZT, indicating no unwanted reaction phases between second phases and PZT matrix. The influence of oxide additions on the relative density of PZT composites is shown in Fig. 1. The relative densities decreased slightly with increasing the content of the second phases and the values of PZT composites with 0.1 wt.% additives was almost the same of monolithic PZT. It indicates that the small quantity second addition has little effect on the sinterability of PZT ceramics, while more second phases would inhibit the densification of the ceramic matrix.

Fig. 2 shows fracture strength and fracture toughness of PZT composites as a function of oxide additions. Fracture strength of PZT composites with 0.1 wt.% second phases were higher than that of monolithic PZT. In particular, the value of PZT/0.1 wt.% Y_2O_3 was 120 MPa, which was almost 1.5 times higher than that of monolithic PZT (81 MPa). Generally, fracture strength is determined by critical flaw size, which strongly depends on average grain size and fracture toughness [7]. As shown in Fig. 2, the fracture tough-

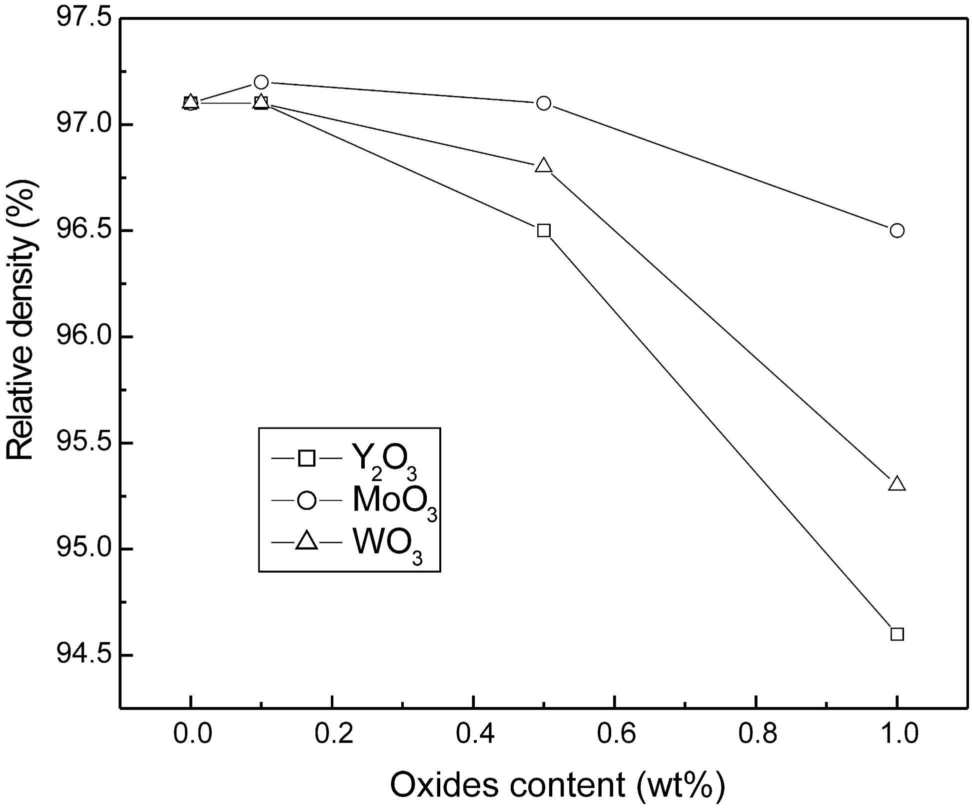

Fig. 1. Relative density changes of PZT with the oxide content.

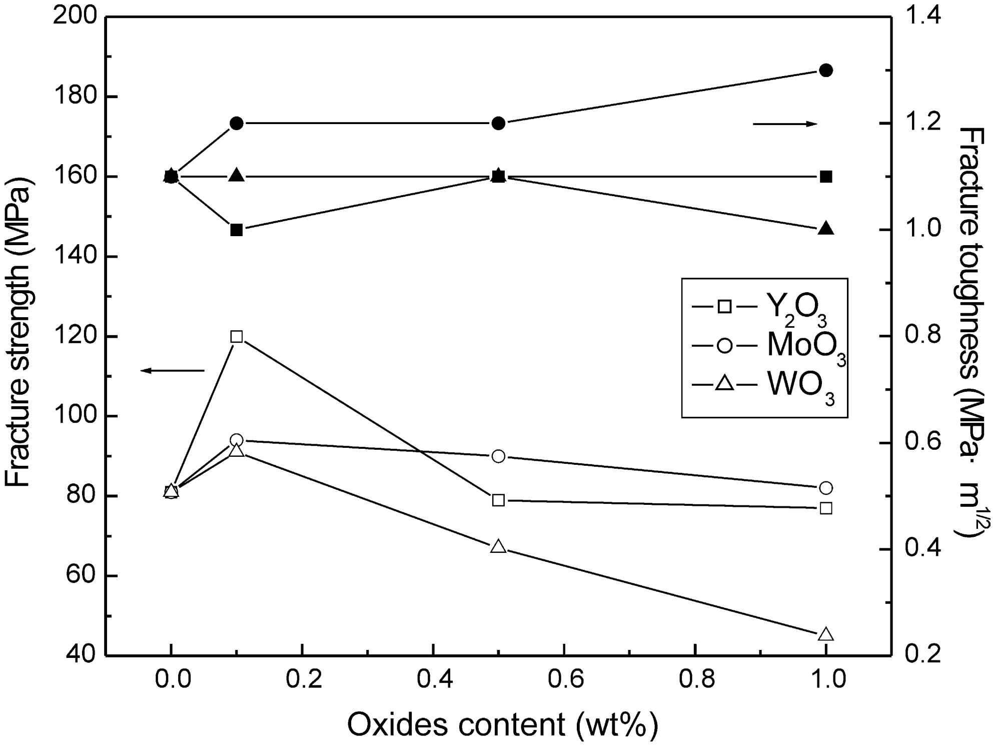

Fig. 2. Fracture strength (open symbols) and fracture toughness (closed symbols) change with the oxide content.

ness changes little with the content of the second phases. Therefore, the contribution to the strengthening owning to fracture toughness is small. SEM images of the typical fracture surface for monolithic and composites are shown in Fig. 3. It is obvious that the fracture mode of composites is predominantly intergranular as well as that of monolithic PZT. The average grain sizes of PZT/0.1 wt.% MoO_3 and PZT/0.1 wt.% WO_3 composites were about 3 μm and similar to that of monolithic PZT, whereas, that of 0.1 wt.% Y_2O_3 doped composite was significantly reduced to about 1.5 μm. Therefore, the remarkable improvement of fracture strength of PZT/0.1 wt.% Y_2O_3 composites may be associated with the reduction of the average grain size of ceramic matrix, which results in high mechanical properties. A small quantity of Y_2O_3 particles is enough to inhibit the growth of matrix grain and refines the microstructure of PZT matrix. As a result, small amount of Y_2O_3 additions can effectively reinforce the ceramic matrix. When increasing the content of second phases, the reduction of fracture strength can be explained by the decreases of the densification of the PZT matrix.

Dielectric and piezoelectric properties are shown in Table 1. Except for the 1.0 wt.% MoO_3 doped composite, the dielectric constant of PZT composites showed a little increase in comparison to that of monolithic PZT. These observations can be associated with the donor doping effect on the dielectric constant. The Y^{3+}, Mo^{6+} and W^{6+} can substituted the cations in the A- or B-side of the perovskite of PZT ceramic, and serve as donor ions. The donor substitutions in PZT crystal structure can effectively improve the dielectric constant of PZT [8]. However, the dielectric constant slightly decreased with increasing the content of oxide additions. The dielectric constant of PZT composites showed a slight reduction after poling, whereas, that of monolithic PZT increased a little after poling. It is likely that the doped second phases had prevented the domain switching and resulted in the reduction of dielectric constant after poling. The electromechanical planar and thickness coupling factors, k_p and k_t of PZT composites showed little change with dopants. When the additions increased to 1.0 wt.%, the values of k_p and k_t decreased

Table 1

Sample	ϵ_{33}(unpoled)	ϵ_{33}^{T}(poled)	k_p	k_t
PZT	911	938	0.48	0.43
0.1 wt.%Y_2O_3	1006	992	0.50	0.40
0.5 wt.%Y_2O_3	985	954	0.30	0.27
1.0 wt.%Y_2O_3	913	878	0.23	0.14
0.1 wt.%MoO_3	977	964	0.43	0.47
0.5 wt.%MoO_3	961	937	0.42	0.40
1.0 wt.%MoO_3	792	724	0.29	0.30
0.1 wt.%WO_3	933	858	0.47	0.43
0.5 wt.%WO_3	1038	979	0.42	0.39
1.0 wt.%WO_3	1281	1170	0.38	0.29

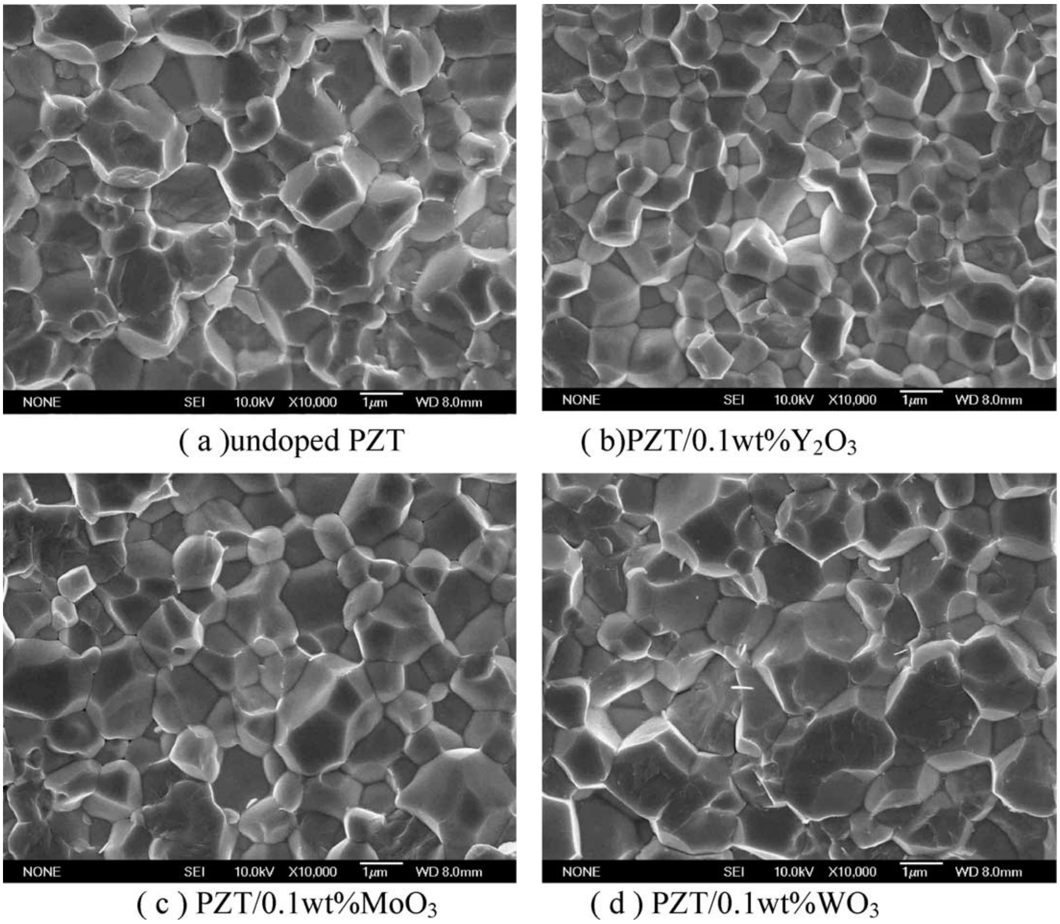

Fig. 3. SEM micrographs of the fracture surface for doped and undoped PZT.

significantly. These reductions can be explained by the prevention of domain switching caused by second phases. Moreover, the grain sizes of PZT composites with 1.0 wt.% oxide additives are reduced to less than 1 μm. Therefore the domain clamping due to the reduction of grain size [9] is considered to be another reason responsible for the low k_p and k_t of 1.0 wt.% second phases doped composites. However, 0.1 wt.% oxide additions doped PZT composites with high mechanical characters showed suitable k_p and k_t values (higher than 0.40) for high power actuator applications. Especially, the values of PZT composite with 0.1 wt.% Y_2O_3 addition were higher than those of monolithic PZT as well as fracture strength.

4. Conclusion

The mechanical and electrical characters of undoped and 0.1–1.0 wt.% oxides doped PZT composites were investigated. The mechanical and electrical properties of PZT ceramics could be improved simultaneously by doping 0.1 wt.% Y_2O_3 addition. Fracture strength of this composite was 1.5 times higher than that of Y_2O_3 free PZT and the coupling factor k_p increased to 0.5. The electrical properties deteriorated with higher dopants than 0.1 wt.%. These results might be due to the hindered domain switching processes and domain clamping due to the reduction of grain size. However, the PZT/0.1 wt.% Y_2O_3 composite showed high fracture strength and suitable piezoelectric properties for high power ceramic actuators.

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