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PZT Nanocomposites Reinforced by Small Amount of Oxides

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Abstract

$Pb(Zr,Ti)O_3$ (PZT) nanocomposites were prepared from high purity PZT powder and small amount (0·1–1·0 vol%) of oxides, i.e. Al_2O_3, MgO and ZrO_2. Effects of the additives on mechanical and piezoelectric properties of the nanocomposites were investigated. The fracture strength and hardness of PZT nanocomposites with 0·5 vol% Al_2O_3 or 0·1 vol% MgO additives were significantly improved. The reduced grain size of the nanocomposites is considered to be responsible for the excellent mechanical properties. Though the dielectric constants of the composites were decreased with an addition of Al_2O_3 or MgO, the planar electromechanical coupling factor, K_p, of MgO-added composites was higher than that of Al_2O_3-added. As a consequence, the PZT/0·1 vol% MgO nanocomposite showed good mechanical and suitable piezoelectric properties. Addition of ZrO_2 had little effect on mechanical and electrical properties of the composites.

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1 Introduction

Lead zirconate titanate (PZT) and related materials are widely used as actuators, resonators and so on, because of their excellent piezoelectric properties. However, piezoelectric ceramics based on PZT suffer from low reliability and poor mechanical properties such as fracture strength and toughness. Improvement of the mechanical properties of PZT ceramics is strongly required.

Recently, a novel method to improve the mechanical properties of structural ceramics has been developed, namely reinforcement by nano-scale particles. Such materials are termed 'nanocomposites'.[1,2] Although the improvement of fracture strength was achieved in $BaTiO_3/SiC$,[3] PZT/Ag[4] and PZT/ZrO_2[5] systems, it is extremely difficult to maintain the electrical properties, in particular, planar electromechanical coupling factor (K_p) which is one of the most important properties in an actuator application. The cause of the reduction of K_p are generally assumed to be the reaction between PZT matrix and second phase, the small grain size and the quantity of a second phase. Therefore, PZT nanocomposites reinforced by a small amount of oxide can be expected to have a higher fracture strength and suitable K_p as required for highly reliable ceramic actuators. Furthermore the decrease in sinterability usually encountered during preparation of nanocomposites, due to the large amount of second phase added, is avoided. It is well known that the electrical and mechanical properties and microstructure of perovskite-type ferroelectric ceramics like PZT change very easily when other compounds are added.

The purpose of this study is to fabricate by the conventional process, PZT nanocomposite reinforced by a small amount of oxides and to investigate the effect of the second phase, i.e. kinds and quantity, on the mechanical and electrical properties and microstructure of the composites.

2 Experimental Procedure

The starting PZT powder used (Sakai Chemical Industry Co. Ltd, PZT5248) was prepared by hydrothermal synthesis and had a composition of $Pb(Zr_{0·52}Ti_{0·48})O_3$, which is known to show the highest piezoelectric properties in the $PbZrO_3$–$PbTiO_3$

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*To whom correspondence should be addressed. Fax: +81-52-916-4481; e-mail: ktajima@nirin.go.jp solid-solution system. The average particle size was 300 nm. For the second phase, Al_2O_3 (Taimei Chemical Co. Ltd, TMDA-R), MgO (Ube Chemical Industries Ltd, 100A) and m-ZrO_2 (Tosoh Co. Ltd., TZ0Y), with average particle sizes of 100, 15 and 50 nm, respectively, were used in this study. PZT and second phase (0·1, 0·5, 1·0 vol%) powders were wet-milled for 24 h in a polyethylene pot using isopropyl alcohol and ZrO_2 balls. Mixed slurries were dried using a rotary evaporator. Green pellets were formed by uniaxial pressing at 5 MPa followed by cold isostatic pressing (CIP) at 196 MPa. The dimensions of the green pellets were 17 mm in diameter and 2·5 mm in thickness.

Sintering was carried out using a conventional electric furnace. Green pellets were placed on platinum sheet in a 99·5% high purity alumina crucible. The sintering profile was 120 min holding time at 1200°C with a heating rate of $5°C\,min^{-1}$ in PbO atmosphere. For electrical measurements, Ag-paste was printed on both sides of the disc, and then fired at 600°C for 10 min. Poling treatment was carried out in silicon oil at 120°C for 30 min with an electric field of $2\,kV\,mm^{-1}$.

Bulk density was determined by the Archimedes method in water, and the relative density calculated using the theoretical density. Fracture strength was measured by the piston-on-ring biaxial flexure test[6,7]. It has been reported for alumina and silicon nitride that the value of strength measured by this method is almost the same as that of the four points bending test.[8] Hardness and fracture toughness were measured by the indentation fracture method and calculated using the equation proposed by Niihara *et al.*[9] Fracture surface and microstructure were observed with a scanning electron microscope (SEM). The average grain size of each composites was measured and calculated by an intercept method using SEM photograph. The dielectric constant at 1 kHz and the frequency characteristics were measured by an impedance analyzer (HP4194A). The planar electromechanical coupling factor K_p was calculated according to Ref. 10.

3 Results and Discussion

Relative densities of the PZT composites sintered at 1200°C in air are shown in Table 1. All of the composites showed a relative density higher than 97%. No remarkable change was observed on addition of a second phase, and the small quantity added had little effect on the sinterability in the conventional process.

Fracture strength, hardness and fracture toughness of the composites are also shown in Table 1. MgO- and Al_2O_3-dispersed PZT composites had higher fracture strength than monolithic PZT. The fracture strengths of PZT/0·1 vol% MgO and PZT/0·5 vol% Al_2O_3 composites were 119 and 115 MPa, respectively, which is about 1·7 times higher than that of monolithic PZT (69 MPa). The hardness of the composites was significantly improved by addition of 0·1 vol% second phase, in particular, MgO addition. However, the fracture toughness of these composites was slightly decreased. In contrast, there was little improvement in the mechanical properties of ZrO_2-dispersed composites.

In order to analyze these results, the microstructure of sintered bodies was observed by SEM. SEM images of the typical fracture surfaces of monolithic PZT and composites are shown in Figs 1–4. The average grain sizes of the composites calculated by an intercept method using SEM photographs are plotted in Fig. 5. In monolithic PZT, the fracture mode was completely intergranular (Fig. 1). In the composites that show high strength and hardness, viz. 0·5 vol% Al_2O_3- and 0·1 vol% MgO-dispersed composites, the fracture mode changed from intergranular to intragranular. Moreover, though the monolithic PZT had a grain size of about 8 μm, addition of 0·1 vol% MgO and 0·5 vol% Al_2O_3 reduced the grain size significantly to less than 1 μm. In the ZrO_2-added composites, intragranular fracture was partly observed and the grain size was essentially the same as in monolithic PZT, as shown in Fig. 4. It is likely that the small quantity of second phase particles acts to both reduce the grain size and reinforce the grain boundaries. The improvement of fracture strength and hardness can be explained by the grain size reduction and the matrix grain boundary reinforcement.[11] The small degradation in fracture toughness of the MgO- and Al_2O_3-added composites is considered to result from the decrease in crack deflection on changing to an intragranular fracture mode.

The observed difference in microstructure and fracture mode between MgO- and Al_2O_3-added composites and the ZrO_2-added composite may be associated with diffusion of Al^{3+} or Mg^{2+} onto lattice sites in the PZT crystal structure, thereby altering surface and/or grain boundary energies of the matrix. Growth of the matrix grains in the PZT/Al_2O_3 and PZT/MgO composites is thought to be inhibited by reaction between the matrix and second phases. The small grain size results in high mechanical properties. In contrast, because of the relatively low reactivity between PZT and ZrO_2,[5] ZrO_2 has little effect on microstructure development and therefore also the mechanical properties. Observation of the microstructure by SEM showed that the second phases were homogeneously dispersed in the PZT matrix. The particle size of the

Table 1. Mechanical and electrical properties of composites

Sample	*R.D (%)*	*Strength (MPa)*	*Hv (GPa)*	K_{IC} *(M Pam$^{0.5}$)*	ε_r^{a} *(unpoled)*	$\varepsilon_{33}^{T}\varepsilon_0^{a}$ *(poled)*	k_p*(%)*
PZT	97·9	69	2·7	1·5	1128	1379	41·4
0·1 vol% Al_2O_3	98·3	103	3·5	1·3	1093	1078	20·0
0·5 vol% Al_2O_3	98·4	115	3·9	1·4	1093	1045	12·2
1·.0 vol% Al_2O_3	97·7	115	4·1	1·4	1029	1028	10·1
0·1 vol% MgO	97·0	119	4·2	1·3	995	983	38·1
0·5 vol% MgO	97·3	88	4·0	1·5	949	915	20·0
1·0 vol% MgO	97·3	92	3·8	1·5	991	927	20·9
0·1 vol% ZrO_2	98·6	70	3·0	1·2	1158	1396	44·6
0·5 vol% ZrO_2	97·7	65	2·9	1·4	1205	1248	32·7
1·0 vol% ZrO_2	97·5	70	2·7	1·4	1193	1205	35·8

[a] Measurement at 1 kHz.

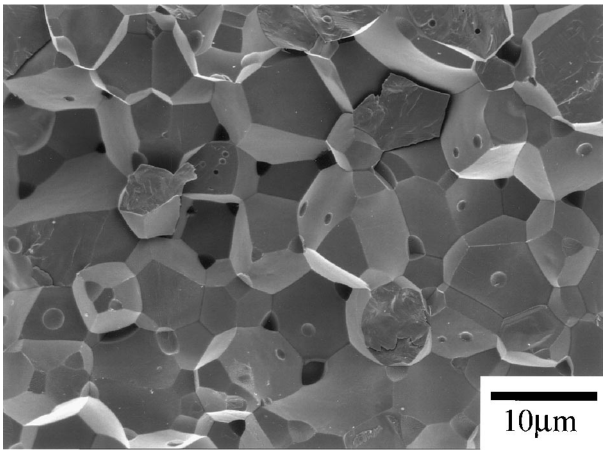

Fig. 1. SEM photograph of monolithic PZT.

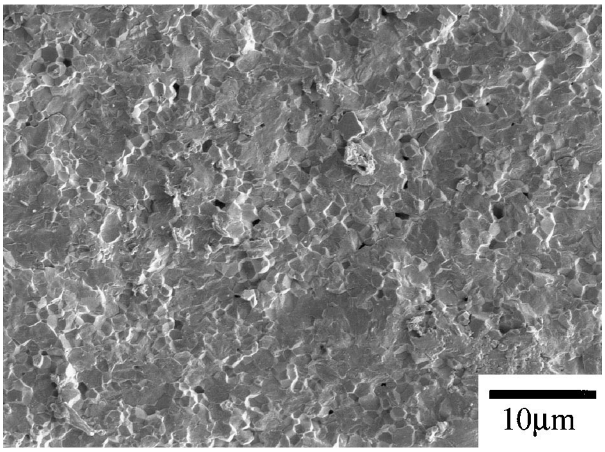

Fig. 2. SEM photograph of PZT/0·5 vol% Al_2O_3 composite.

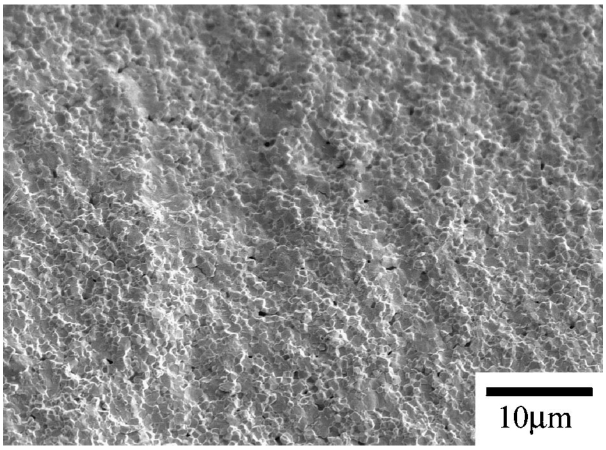

Fig. 3. SEM photograph of PZT/0·1 vol% MgO composite.

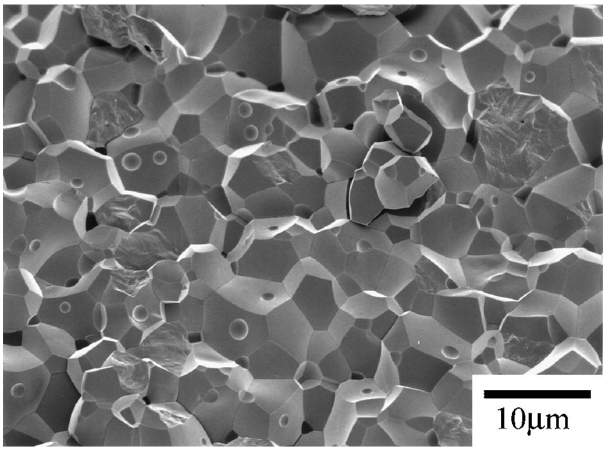

Fig. 4. SEM photograph of PZT/0·5 vol% ZrO_2 composite.

dispersed second phase is estimated to be approximately 'nano-sized' 100–500 nm. As mentioned previously, a small quantity of dispersed particles is enough to control the grain growth and as a consequence to effectively reinforce the PZT matrix.

Dielectric and piezoelectric properties are also shown in Table 1. The dielectric constant of the unpoled PZT/Al_2O_3 composites slightly decreased with increasing second phase content. In the case of unpoled PZT/MgO and PZT/ZrO_2 composites, the dielectric constant was changed little an addition of the second phase. However, the dielectric constant of the poled PZT and PZT/ZrO_2 composites increased after poling, whereas, that of PZT/Al_2O_3 and PZT/MgO composites showed little change after poling. This means that domain switching caused by the poling is prevented by those second phase particles which are incorporated within the matrix grains. Moreover, domain clamping due to the reduced grain size[12] is

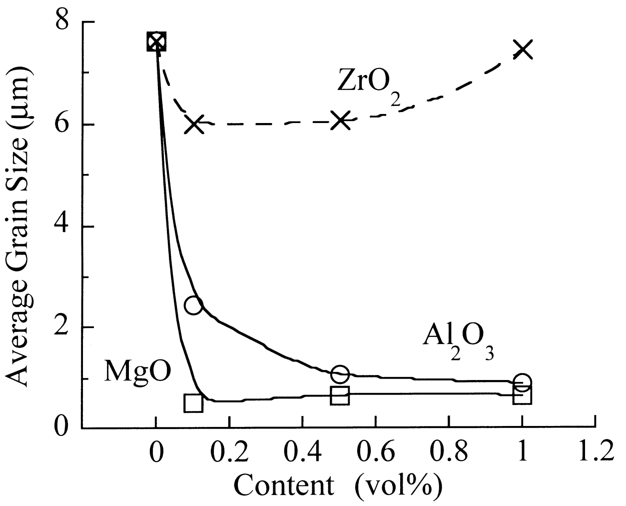

Fig. 5. Average grain size change of PZT composites.

considered to be another reason responsible for the low dielectric constant of Al_2O_3- and MgO-dispersed composites. K_p of the composites was also decreased by Al_2O_3 or MgO addition. The K_p of the Al_2O_3-added composite was less than that of the MgO-added composites. In particular, the PZT/0·1 vol% MgO composite, which showed excellent mechanical properties, possessed the same high value of K_p as that of monolithic PZT. It seems that the explanation for the degradation of K_p lies in the grain size reduction. However, the difference in K_p between Al_2O_3- and MgO-added composites could not be explained by the grain size effect. From the result of solubility of aluminum in PZT,[13] we consider this difference to be responsible for the crystal or domain structure change, due to the reaction or solid solution of oxides with PZT.

4 Conclusion

High strength PZT-based composites with 0·1∼1·0 vol% Al_2O_3 and MgO were successfully prepared by conventional sintering method. Fracture strength of 0·1 vol% MgO or 0·5 vol% Al_2O_3 added PZT composites was 1·7 times higher than that of commercially available PZT. Al_2O_3 and MgO which react or solid solute with PZT more easily had strong influence on the microstructure development of PZT ceramics. This novel nanocomposites featuring reinforcement of small amount of second phase with reaction or solid solution would be proposed in the present study. The K_p of MgO-added composites was higher than that of Al_2O_3-added that. This difference can be considered to be responsible for the crystal or domain structure change, due to the reaction or solid solution of oxides with PZT. As a consequence, the PZT/0·1 vol% MgO nanocomposite showed good mechanical and suitable piezoelectric properties for high reliable ceramic actuators.

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