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Effects of ZnO on the piezoelectric properties of $Pb(Mn_{1/3}Sb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ ceramics

**M.-S. Yoon · Y.-M. Kim · S.-Y. Kweon · T.-W. Hong ·
Y.-G. Lee · S.-L. Ryu · I.-H. Kim · H.-J. Kim · S.-C. Ur**

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Abstract Perovskite-type 0.05 $Pb(Mn_{1/3}Sb_{2/3})O_3$-0.95 $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PMS-PZT) was synthesized by conventional bulk ceramic processing technique. ZnO as a dopant up to 0.5 mol% was incorporated into the PMS-PZT system, and the effects on piezoelectric properties were investigated. Pyrochlore phase was not detected to form during the synthesis of the PMS-PZT system with 0~0.5 mol% ZnO addition. The highest density of 7.92 g/cm^3 was obtained when sintered at 1200°C for 2 hrs. Piezoelectric properties as a function of ZnO content were evaluated using a gain phase analyzer. Piezoelectric charge constant (d_{31}) and piezoelectric voltage output coefficient (g_{31}) increased up to −130 pC/N and -24.9×10^3Vm/N, respectively, with increasing ZnO content. Mechanical quality factor (Q_m) was shown to reduce considerably with increasing ZnO content. When 0.3 mol% of ZnO was added into the system, electromechanical coupling factor (k_p) and relative dielectric constant ($\varepsilon_{33}^T/\varepsilon_0$) reached to the maximum of 56% and 1,727, respectively.

Keywords PMS-PZT · Piezoelectric · ZnO doping

M.-S. Yoon · S.-Y. Kweon · T.-W. Hong · Y.-G. Lee ·
S.-L. Ryu · I.-H. Kim · S.-C. Ur (✉)
Department of Materials Science and Engineering,
Research Center for Sustainable Eco-Materials (ReSEM),
Chungju National University, Chungbuk 380-702, South Korea
e-mail: scur@chungju.ac.kr

Y.-M. Kim
Department of Materials Department,
Corea Electronics Corporation (CEC),
Chungbuk 380-250, South Korea

H.-J. Kim
Division of General Education, Chungju National University,
Chungbuk 380-702, South Korea

1 Introduction

Many researchers have considered modified PZT compositions to improve their electrical and mechanical property of piezoelectric materials in recent years. It is well known that Rochelle salt like crystalloid and polled $BaTiO_3$ were widely used in various electronic device applications such as piezo-transducer, actuator filter, sensor, piezo-transformers and so forth [1]. It is found that ternary compositions, $Pb(Mg_{1/3}Nb_{2/3})O_3$-PZT, $Pb(Ni_{1/3}Nb_{2/3})O_3$-PZT, $Pb(Mn_{1/3}Sb_{2/3})O_3$-PZT, $Pb(Fe_{1/2}Nb_{1/2})O_3$-PZT, $Pb(Zn_{1/3}Nb_{2/3})O_3$-PZT systems, were reported to be very attractive groups for sensors and actuators, due to their superior properties [2, 3]. Since it is commonly desired to have a low mechanical quality factor (Q_m) with low coercive field (Ec) as well as high dielectric constant for practical applications in sensor [4], PMS-PZT was considered for sensor application in this study. The aim of this work is to understand the effects of ZnO addition in the PMS-PZT system. In this work, we focused on the effect of ZnO content as a sintering aid, and investigated related sinterability, microstructure, and piezoelectric/dielectric properties.

2 Experimental procedure

Perovskite 0.05 PMS-0.95 $Pb(Zr_{0.5}Ti_{0.5})O_3+\times$(mol%)ZnO (PMS-PZT: $0\leq\times\leq0.5$) ceramics were fabricated by conventional ceramic technique. Raw materials of PbO, ZrO_2, TiO_2, MnO_2, Sb_2O_3 and ZnO were weighed and ball milled with ZrO_2 balls in distilled water for 24 hrs. Here, excess 0.01 mol% PbO was added to compensate the possible lead loss during the calcination and sintering. Dried powder mixtures were sieved under 100 mesh and then calcined at 850°C for 2 h followed by re-milling. After mixing with

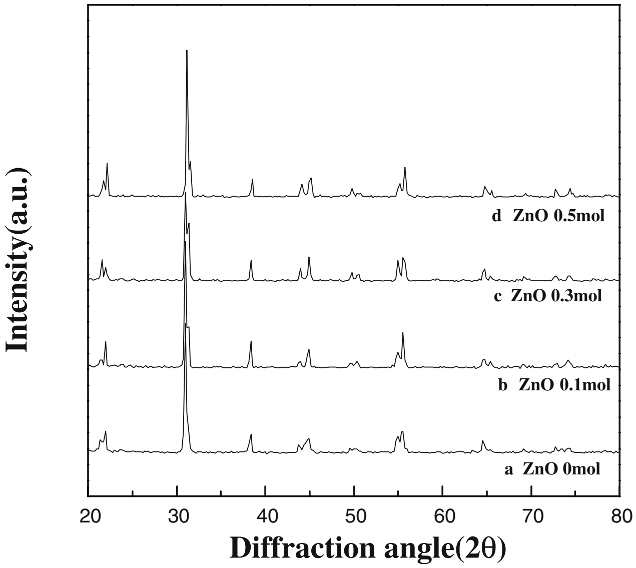


Fig. 1 XRD patterns of PMS-PZT with ZnO sintered at 1,200°C for 2 h; **a** 0.0 mol% ZnO, **b** 0.1 mol% ZnO, **c** 0.3 mol% ZnO, **d** 0.5 mol% ZnO

PVA (1 wt.%) and drying, powders were pressed into discs (ϕ 25 mm) with a stress of 100 MPa. Specimens were sintered at 1,200°C with a heating rate of 1°C/min. PbO-rich atmosphere was maintained to minimize the lead loss during sintering. Phase analyses for the sintered bodies were carried out using an X-ray diffractometer and microstructures were investigated using a scanning electron microscope(SEM). In order to measure the electrical properties, silver paste was coated to form electrodes on both sides of the sample, then subsequently fired at 650°C for 20 min. The dielectric and piezoelectric properties were measured using an impedance/gain phase analyzer (HP-4194 A) after poling under 2 kV/cm at 120°C in a silicone oil bath for 20 min. Piezoelectric properties were calculated based on the resonance measurement method [5].

3 Results and discussion

Figure 1 shows X-ray diffraction (XRD) patterns of the sintered PMS-PZT ceramics with ZnO addition. All patterns appeared to be perovskite type of solid solution, and pyrochlore phase was not observed in all samples. It can be noted that the peak splitting appeared at (002) and (200) plane position, which means they consist of tetragonal phases and rhombohedral phases of perovskite at peaks of 2θ=42~46° range. It is also shown that tetragonality(degree of tetragonal peak separation) increases with increasing ZnO content, indicating that Zn^{+2} ions(0.88°C) are substituted for the smaller B site ions rather than into Sb^{+5} sites. Thus, it can be deduced that the PMS-PZT specimens are of the morphotropic phase boundary (MPB) composition coexisting tetragonal and rhombohedral phases [6, 7].

Figure 2 shows the SEM micrographs of the thermally etched surface of specimens sintered at 1,200°C for 2 h. Average grain size increased from 4 to 20 μm with increasing ZnO content, and the abrupt grain coarsening could be considered to occur possibly due to the liquid phase formation by the eutectic reaction between PbO and ZnO [7].

Figure 3a shows piezoelectric voltage coefficient (g_{31}) and piezoelectric charge constant (d_{31}) as a function of ZnO content in PMS-PZT composition. Piezoelectric voltage coefficient (g_{31}) increased up to -24.9×10^3 Vm/N (at 0.4 mol% ZnO) and piezoelectric charge constant (d_{31}) increased up to −130 pC/N (at 0.3 mol% ZnO), respectively. Figure 3b shows electromechanical coupling factor (k_p) and mechanical quality factor (Q_m) as a function of ZnO content in PMS-PZT composition. The density (ρ) and dielectric constant ($\varepsilon_{33}^T/\varepsilon_0$) were measured as a function of ZnO content in PMS-PZT composition, as shown in Fig. 3c.

Mechanical quality factor (Q_m) was shown to reduce considerably with increasing ZnO content. Piezoelectric charge constants tend to increase possibly due to the ease of dipole movement as a consequence of the decrease in coercive field and internal stress with grain coarsening. However, excessive grain coarsening over the critical limit might result in decreasing overall number of domains. Moreover, piezoelectric charge constants could be decreased by introducing oxygen vacancies, which could move to the oxygen sublattice, and they formed reorientable dipoles with dopant cations. These dipoles aligned in the direction of the polarization vector in the domain and created internal fields that stabilized the domain configuration and reduced the mobility of domain walls [8]. Piezoelectric voltage constant shows the maximum at 0.4 mol% of ZnO, at which the ratio of piezoelectric constant to dielectric constant ($g_{31} = d_{31}/\varepsilon_{33}^T$) becomes maximum. When 0.3 mol% of ZnO is

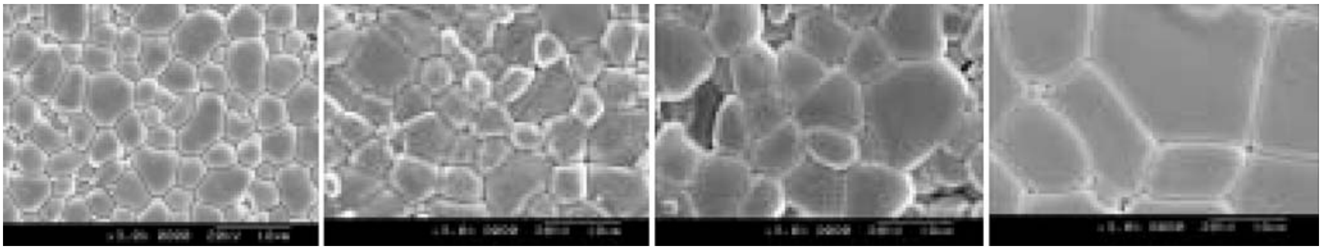
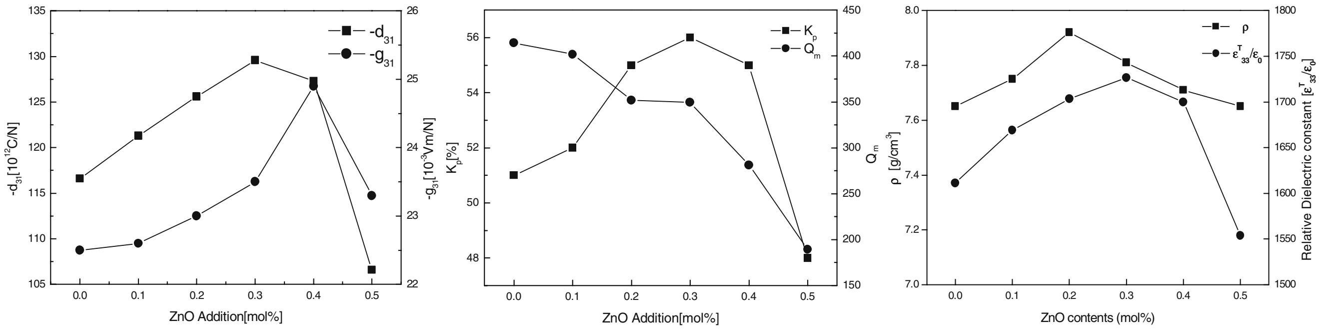


Fig. 2 SEM micrographs 0.05 Pb(Mn$_{1/3}$Sb$_{2/3}$)O$_3$-0.95 Pb(Zr$_{0.5}$Ti$_{0.5}$)O$_3$with ZnO addition (sintered at 1,200°C for 2 h); **a** 0.0 mol% ZnO, **b** 0.1 mol% ZnO, **c** 0.3 mol% ZnO, **d** 0.5 mol% ZnO



a **b** **c**

Fig. 3 **a** Piezoelectric voltage output coefficient ($-g_{31}$) and piezoelectric charge constant ($-d_{31}$), **b** Electromechanical coupling factor (k_P) and mechanical quality factor (Q_m), **c** Density (ρ) and dielectric constant ($\varepsilon_{33}^{T}/\varepsilon_0$) as a function of ZnO contents in 0.05 Pb($Mn_{1/3}Sb_{2/3}$)O_3-0.95 Pb($Zr_{0.5}$,$Ti_{0.5}$)O_3 system

added into the system, electromechanical coupling factor (k_p) showed maximum values of 56%. As can be noticed from XRD analysis in Fig. 1 phase transition from rhombo-rich to tetra-rich region appeared to proceed as ZnO content increased, and MPB formed at 0.3 mol% of ZnO content. As a consequence, the numbers of effective polarization directions were believed to increase whilst Q_m gradually decreased with increasing ZnO content. Here, even though an increase in Q_m was expected above 0.3 mol% of ZnO owing to the increased oxygen vacancies, gradual decrease in Q_m was shown. This might be presumably due to the increase in resonance impedance induced by voids formation inside grains and/or introduction of impurities at grain boundaries during abrupt grain coarsening. As shown in Fig. 3c, densities all over the composition range were shown to be over 95% of theoretical, and the highest density of 7.92 g/cm^3 was obtained at 0.2 mol% of ZnO. Meanwhile, the highest dielectric constant ($\varepsilon_{33}^{T}/\varepsilon_0$) obtained was 1,727 at 0.3 mol% of ZnO. Sintered density tends to increase with increasing grain size, but it is shown to decrease in case of ZnO content higher than 0.2 mol%. This could be attributed to the abrupt grain coarsening induced by liquid phase formation as a result of the eutectic reaction between PbO and ZnO. It is well known that relative dielectric constants generally depend upon grain size, porosity and vacancy. Relative dielectric constant might be increased with increasing grain size and density while it can be decreased with increasing oxygen vacancies induced by substitution of Zn^{+2} ions and tetragonality [9].

4 Conclusions

PMS-PZT modified with ZnO was successfully synthesized to form peroveskite structure by solid state reaction. It was observed that grain size increased with increasing ZnO content. When 0.3 mol % of ZnO added, dielectric constant (d_{31}) reached to the maximum (-132 pC/N). Mechanical quality factor (Q_m) abruptly decreased with increasing ZnO content. When 0.3 mol % of ZnO was added, electromechanical coupling factor (k_p) and relative dielectric constant ($\varepsilon_{33}^{T}/\varepsilon_0$) were reached to the maximum with 56% and 1,727, respectively. Since piezoelectric voltage constant increased with decreasing relative dielectric constant, it can be noticed to be the maximum at 0.4 mol%, at which the ratio of piezoelectric constant to dielectric constant becomes maximum. With these results, it can be deduced that PMS-PZT system with 0.3 mol% ZnO addition could be a candidate for sensor application.

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