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A study of microstructure and electrical properties of lead zirconate titanate doped with Pr_6O_{11}

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Lead zirconate titanate (PZT) doped with praseodymium, $Pb_{1-x}Pr_x(Zr_{0.54}Ti_{0.46})O_3$, x=0.01, 0.03 and 0.05 ceramics were prepared by the conventional mixed oxide method and were sintered at 1200 °C for 1 hour. The perovskite rhombohedral and tetragonal phases were identified by XRD spectra. From the SEM micrographic investigation, the grain size was observed to decrease as more Pr_6O_{11} was added to the PZT ceramics, while the sintered density increased from 7.3 to 7.8 g/cm^3. A dependence of dielectric constant on grain size was observed. The ferroelectric and piezoelectric properties were enhanced with increased Pr dopant.

Key words: PZT, Pr_6O_{11}, microstructure, piezoelectric properties.

Introduction

The perovskite lead zirconate titanate Pb(Zr, Ti)O_3 (PZT) system are piezoelectric materials which are employed in various types of actuators and transducers. Impurities doped into perovskite PZT [1-3] play an important role in many physical applications, particularly lanthanum doped in the PZT system [4-6] is responsible for a change of dielectric properties under illumination which is used in the optical memories. The aim of this research is to study the influence of Pr-doping on the microstructure and electrical properties of $Pb(Zr_{0.54}, Ti_{0.46})O_3$ ceramics.

Methodology

Three nominal compositions of $Pb_{1-x}Pr_x(Zr_{0.54}Ti_{0.46})O_3$, x=0.01, 0.03 and 0.05, (PPZT) ceramics were prepared via a conventional mixed oxide method. The commercial-grade oxide powders of PbO, ZrO_2, TiO_2 (all high purity, 99.9%, Fluka chemika) were used, and praseodymium oxide (Pr_6O_{11}) powder (99.95%, Aldrich) was used as a 1, 3 and 5 mol% dopant. The powders were carefully weighed and mixed by zirconia wet ball milling for 24 h using acetone as a media. Then the powder mixture was dried on a hot plate for 12 h at 100 °C. After drying the powder mixture was calcined in a closed alumina cup at 800 °C for 4 h at a constant heating rate of 300 °C h^{-1}, and then cooled down in the furnace at the same rate. The calcined powder was ball-milled again to crush agglomerates, and was pressed at a pressure of 150 MPa in a 13 mm die into pellets. The pellets were placed in a sealed alumina crucible and were sintered for 1 h at 1200 °C in a $Pb(Zr_{0.54}Ti_{0.46})O_3$ +10%PbO atmosphere in order to suppress lead loss from the pellets at elevated temperatures. The pellet ceramics were characterized for weight loss, sintered density using a density determination (AG 204, Metter Toledo). Powder x-ray diffraction (XRD) analysis was carried out to determine the phase structure. For the scanning electron microscopic (SEM) investigation, the pellets were hot etched at 100 °C lower than the sintering temperature, and were thinned to about 1 μm using ion-beam etching. The dielectric properties of the ceramics were determined using an HP 4194A impedance/gain phase analyzer at a frequency of 1 kHz. The ferroelectric polarization versus electric field (P-E) measurements were performed using an RT66A standard ferroelectric test system. The piezoelectric coefficient d_{33} was measured using a piezoelectric d_{33} meter. The electromechanical coupling factor k_p was derived from the equation:

$$k_p=\left(\frac{f_a-f_r}{0.395f_r-0.574(f_a-f_r)}\right)^{1/2},$$

where f_r (the resonant frequency) and f_a (the anti-resonant frequency) were determined by a resonant and anti-resonant technique.

Results and Discussion

Weight loss and sintered density

Evaporation of PbO during sintering the three nominal ceramic compositions, $Pb_{1-x}Pr_x(Zr_{0.54}Ti_{0.46})O_3$, x=0.01, 0.03 and 0.05 (PPZT), was detected by the weight loss as shown in Fig. 1, where it can be seen that the weight loss of the $Pb_{0.95}Pr_{0.05}(Zr_{0.54}Ti_{0.46})O_3$ ceramics occurred

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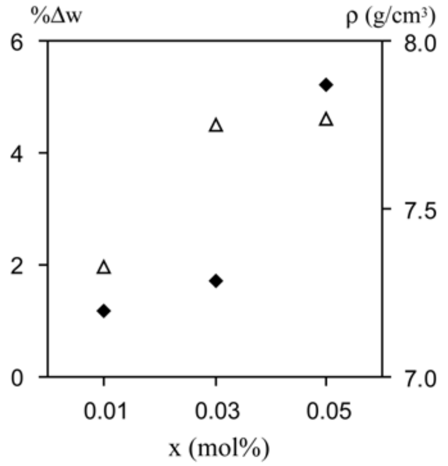

Fig. 1. Weight loss (%Δw: ◆) and sintered density (ρ: △) as a function of Pr content (x) for PPZT ceramics.

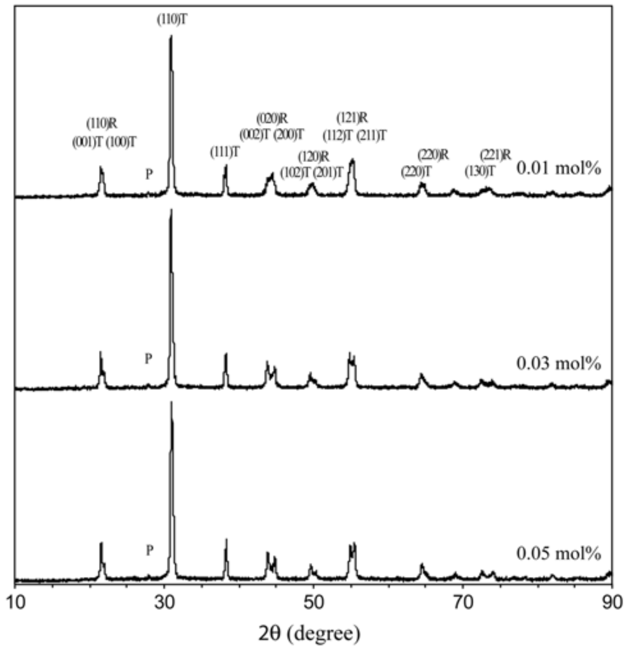

Fig. 2. XRD patterns of PPZT ceramics.

dramatically (5.1%). The sintered densities are also plotted as a function of praseodymium content in Fig. 1, which increased from 7.3 to 7.8 g/cm^3 as the Pr dopant increased.

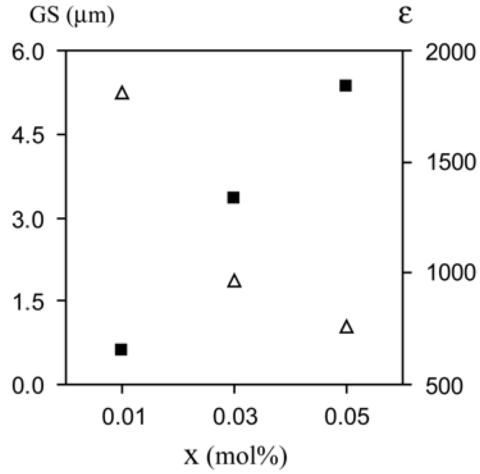

Fig. 4. Average grain size (GS: △) and dielectric constant (ε: ■) as a function of Pr composition of PPZT ceramics.

Phase formation and microstructure

Powder XRD patterns of the PPZT ceramics as a function of Pr composition are shown in Fig. 2. The XRD results show small amount of the pyrochlore phase (P) in each composition. Perovskite phase formation for the rhombohedral (R) and tetragonal (T) symmetries were identified using JCPDS No. 33-784 and 73-2022, respectively. The grain size changes by dopant content are confirmed by SEM micrographs in Fig. 3, which was decreased as the Pr content increased. The average grain sizes (GS) determined from a line intercept method of PPZT ceramics are presented in Fig. 4.

Electrical properties

Dielectric measurement on PPZT pellets are reported in Table 1. When more Pr dopant was added into the PZT ceramics, the dielectric constant (ε) was enhanced

Table 1. Dielectric, ferroelectric and piezoelectric properties of PPZT ceramics

Composition (mol%)	ε	tanδ	P_r ($\mu C/cm^2$)	E_c (kV/cm)	k_p	d_{33} (pC/N)
0.01	652	0.0330	180.3	0.826	0.41	204.2
0.03	1337	0.0321	180.5	1.329	0.60	469.6
0.05	1842	0.0367	200.3	1.592	0.60	513.5

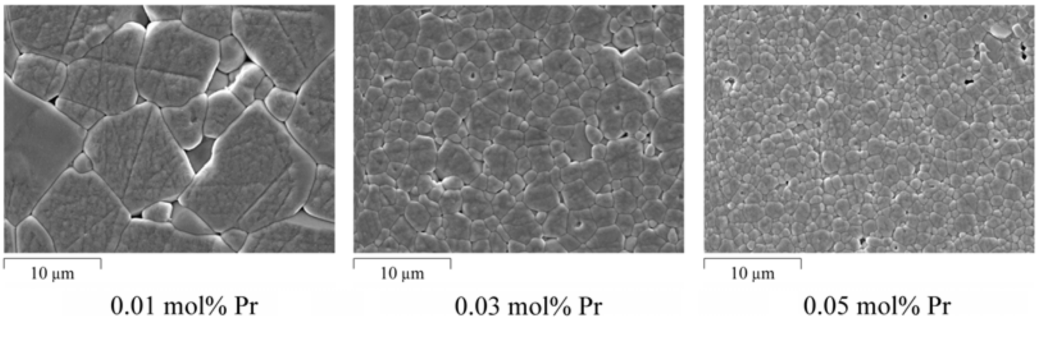

Fig. 3. SEM micrographs of PPZT ceramics revealing the microstructural dependence on Pr content.

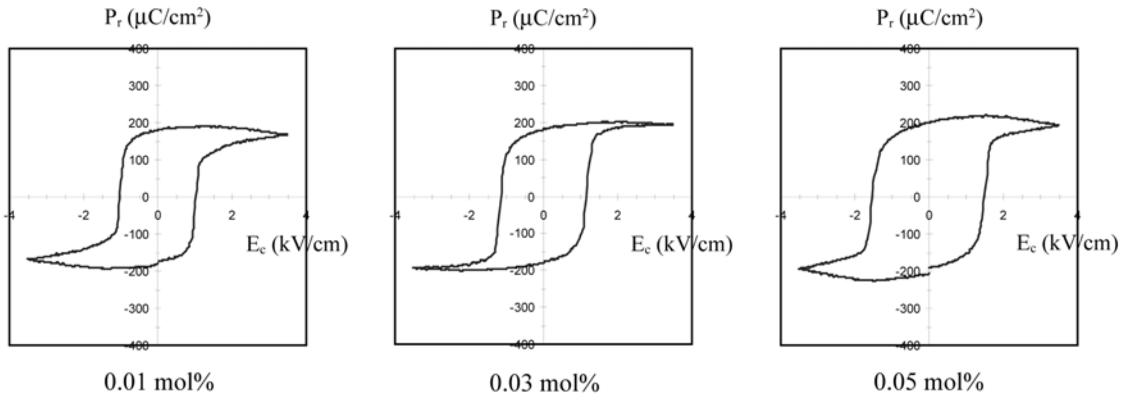

Fig. 5. Effect of composition (x) on the P-E hysteresis loops for PPZT ceramics.

which may be due to the smaller grain size of the pellet as shown in Fig. 4. The polarization-electric field (P-E) measurements for the specimens are summarized in Fig. 5, where rectangular hysteresis loops are observed.

The remanent polarization P_r and coercive field E_c were observed to increase significantly with increased Pr content. This is probably due to more (PbO) weight loss of the higher Pr content ceramics. The piezoelectric properties of PPZT ceramics are also listed in Table 1. The electromechanical coupling factor of PPZT ceramics with x=0.03 and 0.05 was found to be equal to 0.60, while the piezoelectric coefficient increased with increased Pr content.

Conclusions

Lead zirconate titanate doped with praseodymium oxide, $Pb_{1-x}Pr_x(Zr_{0.54}Ti_{0.46})O_3$ with x=0.01, 0.03 and 0.05, ceramics were studied. It was found that the average grain size was reduced with more Pr dopant, while the sintered density was increased. The dielectric, ferroelectric and piezoelectric properties were observed to depend on the Pr dopant content. Excellent dielectric, ferro-electric and piezoelectric properties belong to the 0.05 mol% Pr dopant ceramics.

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