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Electrical and mechanical properties of ferroelectric lead zirconate titanate/tungsten oxide ceramics

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Abstract

Ferroelectric PZT/xWO$_3$ ceramics (when $x = 0$, 0.5, 1, 3 and 5 vol%) were fabricated from PZT and nano-sized WO$_3$ powders by a solid-state mixed-oxide method. Phase characterization suggested that the reaction between PZT and WO$_3$ occurred during the sintering. This reaction seemed more pronounced with increasing the content of WO$_3$. The maximum density at approximately 97% of the theoretical value was achieved at 1 vol% of WO$_3$ addition. The grain size was reduced with an addition of WO$_3$ particles from ~7.8 μm for PZT to ~1.8 μm for 0.5 vol% WO$_3$ and ~0.8 μm for 1–5 vol% WO$_3$. Mechanical properties of PZT could be improved with an addition of WO$_3$ nano-particulates. The addition of 0.5 vol% WO$_3$ could maintain good electrical properties while increasing WO$_3$ significantly reduced dielectric and piezoelectric constants of the PZT.

Keywords: C. Electrical properties; C. Mechanical properties; D. PZT

1. Introduction

Ferroelectric lead zirconate titanate (Pb(Zr$_x$Ti$_{1-x}$)O$_3$, PZT) with perovskite-like structure has been extensively studied and are of technological interest in many sensor, transducer and actuator applications [1]. Requirements for longer lifetime and larger displacements under continuous operations in these applications imply that an improvement in mechanical properties of PZT ceramics is needed. Since 1989, the 'nanocomposite' concept [2] was introduced and has been applied to several PZT-based nanocomposite systems such as PZT/Al$_2$O$_3$, PZT/MgO, PZT/ZrO$_2$ [3], PZT/NiO [4], PZT/Ag [5] and PZT/Pt [6,7]. These nanocomposite ceramics were found to possess superior mechanical properties compared to monolithic PZT ceramic.

Most of the above studies involved additives containing acceptor ions while oxide additives containing ions with large valence (e.g. Nb^{5+}, W^{6+}) has not been much investigated even though it was found that PZT-based ceramics containing these ions possessed enhanced field-induced strain magnitude and reduced hysteresis, which are required characteristics for positioning actuator applications [8]. Compared to other donor-type B-site dopants, W-ions seemed to give higher electric field-induced strain [8]. In addition, the presence of small amount (<1 wt%) of WO$_3$ in some complex systems such as PZN–PZT and PZT–PFW–PMN was found to provide enhanced dielectric and piezoelectric properties [9,10]. Despite these available studies, addition of WO$_3$ in PZT beyond solubility limit has not been investigated. Based on ionic radii of W^{6+} ion ($r_{W^{6+}} = 0.60$ Å) and Ti^{4+} ($r_{Ti^{4+}} = 0.61$ Å), it is also expected that W^{6+} would preferentially substitute Ti^{4+} rather than Zr^{4+} ($r_{Zr^{4+}} = 0.72$ Å). This study is therefore attempted to fabricate PZT-based ceramics in which nano-sized WO$_3$ particles were chosen as the added component. The effects of WO$_3$ concentration on phase formation, densification, microstructure, mechanical and electrical properties were investigated and discussed.

2. Experimental procedure

PZT-based powders were prepared from the mixtures of in-house prepared PZT powder and nano-sized WO$_3$ powder (30–70 nm, >99%, Nanoamor). The PZT powder was prepared by ball milling reagent-grade PbO, ZrO$_2$ and TiO$_2$ powders with the chemical purity of each >99%, using distilled water as a medium. The slurry was dried using a freeze-drier. The powder was calcined at 800 °C for 2 h for a stoichiometric Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ powder. For the preparation of the PZT/

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WO_3 powders, different percentages by volume (0.5, 1, 3 and 5) of WO_3 were ultrasonically dispersed in distilled water for 30 min before mixing with PZT powder. Each batch of the mixture was prepared using the same procedure mentioned earlier to form PZT/WO_3 powders. The powders were then uniaxial pressed and sintered at 1150 °C for 2 h in a presence of $PbZrO_3$ powder.

Phase composition of the PZT/WO_3 ceramics was characterized using X-ray diffraction method (XRD, Phillip Model X-pert). Bulk density was determined using Archimedes's method. The theoretical densities of the ceramics were calculated based on theoretical densities of PZT (8.006 g cm^{-3}) 3) and WO_3 (7.16 g cm^{-3}). Surfaces of the samples were observed using a scanning electron microscope (SEM, JEOL JSM-6335F). Average grain size was determined using a mean linear intercept method. The well-polished ceramics were subjected to Knoop (Matsuzawa MXT-α) and Vickers (Galileo Microscan 2) indentations for hardness (i.e. H_V and H_K) determinations. Young's modulus (E) and fracture toughness (K_{IC}) were determined following methods described by Antis et al. [11] and Marshall et al. [12]. For electrical measurements, silver paste was fired on both sides of the polished ceramics at 700 °C for 15 min as electrodes. The dielectric properties were measured using a HP4284A LCR meter in connection with a Delta Design 9023 temperature chamber and a sample holder (Norwegian Electroceramics) capable of high temperature measurement. The ceramics were poled at a field strength of 3 kV/mm in silicone oil at 80 °C for 30 min prior to piezoelectric constant measurement using a d_{33} meter (Technologies Model S5865).

3. Results and discussion

X-ray diffraction patterns of PZT/$x$$WO_3$ (where x = 0, 0.5, 1, 3 and 5 vol%) ceramics are shown in Fig. 1. The relative amount of PZT phases could be identified from the XRD peaks in the range of $2\theta \approx 42$–47° (Fig. 1(b)), which corresponded to $(2\,0\,0)_R$ reflection of rhombohedral (R) phase and $(2\,0\,0)_T$–$(0\,0\,2)_T$ peaks of tetragonal (T) phase. For the ceramics with x = 0 and 0.5, the tetragonal splitting was clearly observed and matched with JCPDS no. 33-0784. With further increasing the content of WO_3, the co-existence of tetragonal and rhombohedral phases occurred. From Fig. 1(b), only small lattice distortion was observed which was probably due to the introduction of similar size ions W^{6+} into Ti^{4+} site of PZT lattice. X-ray diffraction results also indicated that the samples with high WO_3 concentration contained some other phases such as $Pb_2(WO)_5$ (JCPDS no. 35-0001), $PbWO_4$ (JCPDS no. 08-0476), Ti_9O_{17} (JCPDS no. 85-1061) and Ti_8O_{15} (JCPDS no. 85-1060) as shown in Fig. 1(a). These observations seemed to support the hypothesis that W^{6+} ions preferentially substituted for Ti^{4+}, resulting in cation vacancies as previously reported in other donor-doped PZT systems [13]. The cations such as Pb^{2+}, Ti^{4+} and W^{6+} which were outside the PZT lattice could then react to form the observed compounds.

As-sintered surfaces of PZT and PZT/1 vol% WO_3 ceramics are illustrated in Fig. 2 and relative densities of the ceramics are given in Table 1. At low WO_3 concentrations ($x \leq 1$ vol%), the density increased with increasing WO_3 content. Above 1 vol%, the density values became independent of the WO_3 content. The grain size was found to decrease from ~7.8 μm for the PZT to ~1.8 for 0.5 vol% WO_3 and ~0.8 μm for 1–5 vol% WO_3 ceramics. This result suggested that the use of WO_3 nanoparticles could effectively limit grain growth in PZT ceramic. This observed behavior is believed to be partially caused by the reaction products between PZT and WO_3 where they could act as inclusions that slowed grain boundary movement [14]. However, at low WO_3 concentration, no other second phases were observed but the effect of grain size reduction was more pronounced than in the case of high WO_3 concentration where second phases were present. It seemed therefore that the solute drag effect [14] was more important in this system than the second phase inclusion for the impediment of grain boundary migration.

Mechanical properties of the ceramics in terms of Vickers hardness (H_V), Young's modulus (E) and fracture toughness (K_{IC}) were investigated and their values are listed in Table 1. It

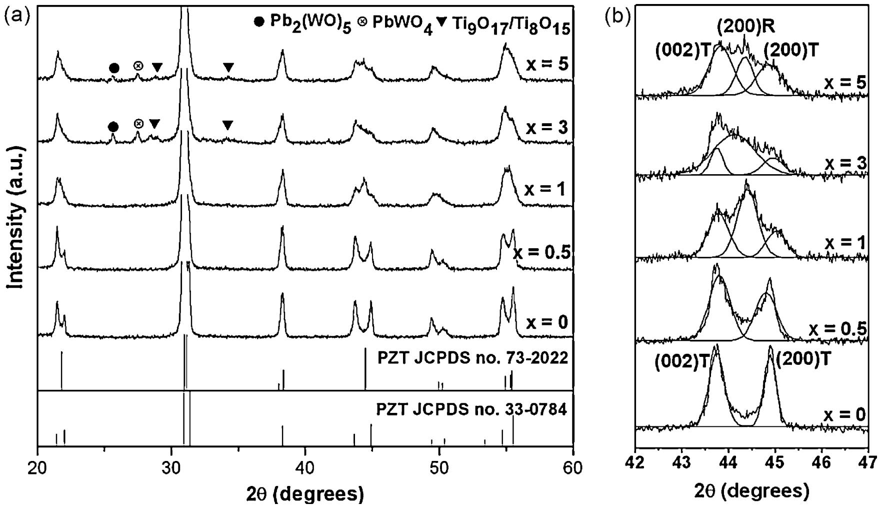

Fig. 1. XRD patterns of PZT/$x$$WO_3$ ceramics, where x = 0, 0.5, 1, 3 and 5 vol%.

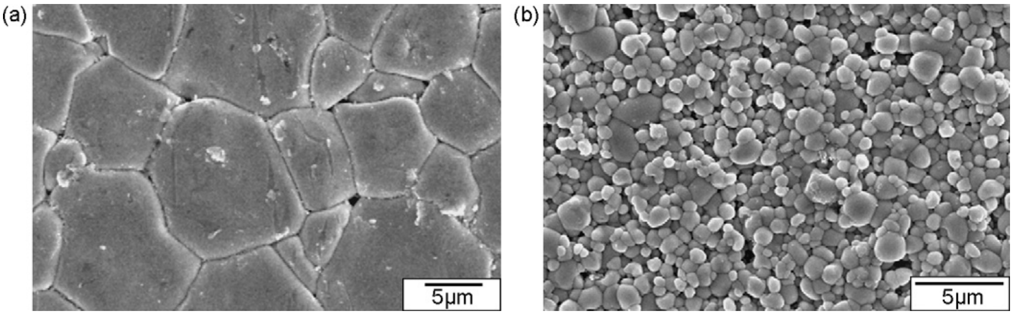

Fig. 2. SEM micrographs of (a) monolithic PZT and (b) PZT/1 vol% WO_3 ceramics.

Table 1
Physical and mechanical properties of PZT/WO_3 ceramics

WO_3 content (vol%)	Relative density (%)	Grain size (μm)	Mechanical properties		
			H_V (GPa)	E (GPa)	K_{IC} (MPa m$^{1/2}$)
0	91.3	7.87	2.1	76	2.2
0.5	95.5	1.84	2.8	93	3.0
1	96.7	0.80	3.8	108	4.0
3	94.7	0.88	3.0	78	3.8
5	96.7	0.84	3.4	102	3.9

can be seen that these mechanical characteristics of the PZT/WO_3 ceramics were superior to those of PZT ceramic. The hardening of the PZT/WO_3 ceramics over the PZT ceramic was mainly associated with the grain size reduction due to the additive as well as the incorporation of some W^{6+} ions into the perovskite structure of PZT, and the reaction products between PZT and WO_3 in the composition with high WO_3 concentration. The maximum H_V of 3.8 GPa was achieved in the PZT/1 vol% WO_3. Table 1 also shows that values of E depended critically on density, regardless of the WO_3 content. Trend of K_{IC} values was found to be similar with that of H_V. The high K_{IC} value of 4 MPa m$^{1/2}$ was achieved in the sample contained 1 vol% WO_3 where the maximum density and smallest grain size were achieved. Enhancement of K_{IC} in this study was most likely due to the effect of reduced grain size. Based on the multi-domain grain model and investigation of PLZT (9/65/35) ceramics, the small grain with size in order of less than ~2 μm contained single domain whose residual compressive stress after sintering process could not be released [8]. Therefore, in this study, it seemed that such residual stress might inhibit crack propagation and caused an increase in K_{IC}. From Table 1, addition of WO_3 more than 1 vol% produced PZT/WO_3 ceramics with comparable grain size and K_{IC}, further supporting the above hypothesis.

The results from dielectric measurement are summarized in Table 2. Curie temperature (T_C) of the PZT ceramic in this study was 396 °C, in agreement with the value (~400 °C) reported by others [15]. Increasing the content of WO_3 shifted the T_C to lower temperatures. A further increase of additive >1 vol%, however, shifted the T_C values back to higher temperature region. The variations in T_C values can be explained by changes in internal stress due to porosity which was modified by the addition of WO_3 [16]. At T_C, the small reduction in ε_r from 26,289 for the PZT to 24,411 for the PZT/0.5 vol% WO_3 was observed. Further increasing WO_3 content beyond 0.5 vol% caused a sharp decrease in ε_r with increase in tan δ values. At room temperature, the maximum ε_r of 1294 was achieved for the sample contained 0.5 vol% of WO_3 and gradually reduced when the content of WO_3 was further increased. This maximum ε_r value was ~200 higher than the ε_r of PZT. Piezoelectric constant (d_{33}) values also showed similar trend to the room temperature dielectric constant. The highest d_{33} value of 369 pC/N was achieved with 0.5 vol% WO_3 added sample, which was higher than that of PZT. Room temperature electrical measurement results indicated that a small content of WO_3 (≤0.5 vol%) provided optimum electrical characteristics for the PZT ceramic, suggesting a practical limit of WO_3 concentration in the PZT. Increasing the additive beyond this

Table 2
Dielectric and piezoelectric properties of PZT/WO_3 ceramics measured at 10 kHz

WO_3 content (vol%)	T_C (°C)	Dielectric properties (at T_{Max})		Dielectric properties (at RT)		Piezoelectric properties
		ε_r	tan δ	ε_r	tan δ	d_{33} (pC/N)
0	396	26289	0.3730	1106	0.0066	203
0.5	381	24411	0.0372	1294	0.0194	369
1	367	7173	0.0594	1092	0.0285	130
3	399	3885	0.0615	877	0.0230	45
5	413	3002	0.0842	719	0.0176	44

limit, however, degraded the electrical properties. This was thought to be affected by the domain clamping caused by significant reduction of grain size [4]. Apart from this, presence of non-ferroelectric/non-piezoelectric phases in the PZT matrix could also inhibit the domain switching process in PZT grain which decreased the values of dielectric and piezoelectric constants.

4. Conclusions

The PZT/WO_3 ceramics were successfully fabricated by a simple solid-state mixed-oxide method. Addition of WO_3 nanoparticulates in the range of 0–5 vol% to PZT matrix could improve densification but inhibit grain growth. The WO_3 additive provided materials with superior mechanical properties compared to the PZT. The optimum mechanical properties could be achieved with an addition of 1 vol% WO_3. Under this investigation, electrical properties tended to reduce with increasing the content of WO_3. Nevertheless, the optimum room temperature dielectric and piezoelectric constants was achieved with the sample contained 0.5 vol% WO_3. This study suggested new PZT-based ceramic system with excellent mechanical properties and acceptable electrical properties for alternative use as electronic materials.

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