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Effect of ZnO nano-particulate modification on properties of PZT–BLT ceramics

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Abstract

This research was conducted to study the effect of ZnO nano-particulate modification on properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT)–$(Bi_{3.25}La_{0.75})Ti_3O_{12}$ (BLT) ceramics prepared by a mixed-oxide solid-state sintering method. ZnO nano-particulate was added into PZT–BLT ceramics to obtain PZT–BLT/xZnO ($x = 0$, 0.1, 0.5 and 1.0 wt%). The PZT–BLT/xZnO ceramics were investigated in terms of phase, microstructure, physical, electrical, and mechanical properties. Tetragonality of PZT–BLT crystal structure tended to increase with increasing ZnO content. ZnO addition obviously increased the density of PZT–BLT ceramics while the grain size slightly decreased. Intergranular fracture mode was observed for pure PZT–BLT ceramic while the samples contained ZnO nano-particles showed a mixed-mode inter-/trans-granular fracture. Addition of ZnO also affected hardness and fracture toughness values. Addition of ZnO nano-particulate into PZT–BLT ceramics was found to improve room temperature dielectric constant but did not have a significant effect on ferroelectric properties. These observed results were expected to be caused by the behaviors similar to a donor-doped system.

Keywords: D. Perovskite; Nano-particulates; Dielectric; Ferroelectric

1. Introduction

Ferroelectric materials have attracted considerable attention because of their possible uses in device applications such as nonvolatile random access memories, sensors, actuators, etc. [1]. $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) is certainly one of the most important ferroelectric materials that has been widely investigated. Under actual application, however, PZT still have problems related to severe polarization fatigue after bipolar switching pulses. $(Bi_{3.25}La_{0.75})Ti_3O_{12}$ (BLT) an Aurivillius structured ferroelectric material is known to possess large spontaneous polarization and high fatigue endurance but it also has high leakage current and small remnant polarization [2]. Recently, Thongmee et al. reported that improved ferroelectric properties could be obtained by addition of 10 wt% BLT in PZT matrix [3]. Moreover, the investigation on modification of PZT ceramic using metal oxide nano-particles such as Al_2O_3, MgO, ZrO_2 [4], NiO [5], WO_3 [6] and ZnO [7] have been reported to produce materials having superior mechanical properties over the monolithic PZT.

In this study, ZnO was selected as an additive for PZT–BLT matrix because of its known ability to enhance densification and improved sensitivity in materials used for sensing devices [7]. Phase, microstructure, physical, electrical and mechanical properties of these new PZT–BLT/ZnO ceramics were investigated and discussed in details.

2. Experimental

$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) and $Bi_{3.25}La_{0.75}TiO_3$ (BLT) powders were separately prepared by a conventional mixed-oxide method. These powders were mixed and calcined to produce 0.9PZT–0.1BLT composition [3]. The nano-sized ZnO powder was added to this PZT–BLT powder to form PZT–BLT/xZnO ($x = 0.1$, 0.5 and 1.0 wt%) nanocomposite powders. The powders were then uniaxially pressed into pellets and sintered at 1000 °C for 4 h. The loss of volatile components was prevented by covering them with PZT–BLT powders in a closed alumina crucible. Phase composition of the PZT–BLT/ZnO

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ceramics was characterized using X-ray diffraction method (XRD, Phillip Model X-pert). Bulk density of the ceramics was determined using Archimedes's method. Microstructure of the PZT–BLT/ZnO ceramics was observed using a scanning electron microscope (SEM, JEOL JSM-6335F). Average grain size was determined using a mean linear interception method from the SEM image. In this method, a number of straight lines were drawn on each SEM micrograph and intercepted lengths of grains were obtained and averaged. The well-polished ceramics were subjected to Vickers (Galileo Microscan) indentation for hardness (H_V) determination. Fracture toughness (K_{IC}) was determined following the method described by Antis et al. [8]. Dielectric constant and loss tangent were measured using an LCR meter (Hioki Hitester 3532-50). Ferroelectric hysteresis (P–E) loops were characterized using a computer-controlled modified Sawyer-Tower circuit.

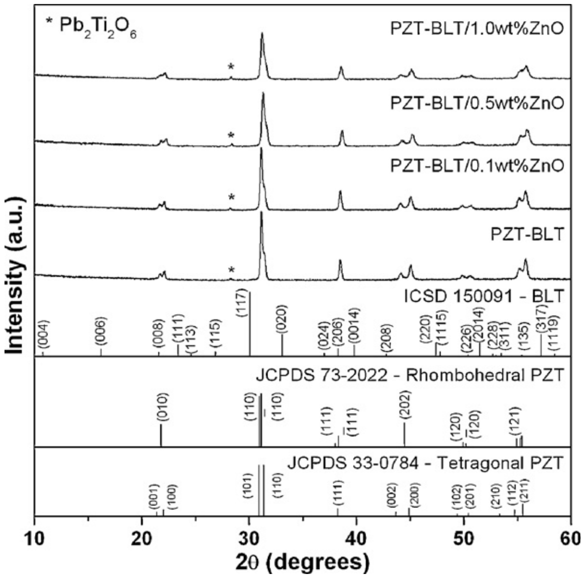

Fig. 1. XRD patterns of PZT–BLT/ZnO ceramics.

3. Results and discussion

XRD patterns of 0.9PZT–0.1BLT ceramics are shown in Fig. 1. The patterns indicated mainly tetragonal phase of PZT without BLT peaks. This result indicated complete dissolution of BLT in PZT lattice. The addition of ZnO (0.1–1.0 wt%) into PZT–BLT slightly shifted all peaks to the right while the tetragonal structure was maintained. It showed that addition of ZnO into PZT–BLT resulted in a small contraction of unit cell. A low-intensity peak at $2\theta \approx 28^\circ$ in all XRD patterns was observed regardless of ceramic composition. It was found that this impurity peak most likely belonged to the pyrochlore phase $Pb_2Ti_2O_6$ (JCPDS file No. 26-0142). This pyrochlore phase was also reported to be often observed in PZT thin film [9]. From XRD integrated peak intensity, the amount of this pyrochlore phase slightly increased with increasing ZnO concentration. It can be seen from XRD patterns that increasing the content of ZnO caused a slight change in lattice parameters and degree of tetragonality (c/a) as listed in Table 1. The values for measured bulk density of the ceramics tended to increase with increasing ZnO content. It was expected that Zn^{2+} ions were considered entering the B sites of the ceramics and induced oxygen vacancies which helped expedite lattice diffusion, leading to the enhancement of the density of the ceramic [10]. In addition, cation vacancies (i.e. from Pb^{2+} and Ti^{4+} sites) could also play a role in improving densification process.

SEM micrographs of fractured PZT–BLT/ZnO surfaces are shown in Fig. 2 and the values of measured grain size are listed in Table 1. Microstructure of pure PZT–BLT revealed mainly inter-granular fracture. The samples with incorporation of ZnO nano-particles showed a mixed-mode of inter-/trans-granular fracture. The ceramic samples in this study possessed nearly the same grain size. However, it had a slowly decreasing trend and for 1 wt% ZnO-doped ceramic, the grain size was found to be smallest.

Mechanical properties of the ceramics in terms of Vickers hardness (H_V) and fracture toughness (K_{IC}) were investigated and the results are shown in Fig. 3. At low ZnO concentrations (x = 0–0.5 wt%), the hardness values were more or less stable at ~2.3 GPa. An increase of ZnO content to 1.0 wt% rapidly increased the hardness value to ~5.1 GPa. The changes in hardness were believed to be contributed by both grain size and density values. Grain boundaries are known as stress concentration sites, which acted as effective obstacles to dislocation pile-up in the adjacent grains, leading to harder material [11]. This was a reason that a ceramic with smaller grain size showed higher hardness value compared to those with larger grains. Fracture toughness result showed that an addition of 0.1–0.5 wt% ZnO into PZT–BLT ceramic increased fracture toughness values from 0.81 to 1.15 MPa $m^{1/2}$. Further increasing ZnO content to 1.0 wt% sharply dropped the fracture toughness value to 0.51 MPa $m^{1/2}$. This was believed to be caused by a driving force for crack extension which was reduced in the ceramics containing smaller grains.

Table 1
Crystal structure and physical properties of PZT–BLT/ZnO ceramics.

ZnO content (wt%)	Lattice parameters (Å)		Tetragonality, c/a	Density (g/cm^3)	Relative density (%)	Grain size (μm)
	a	c				
0	4.0183	4.0968	1.0195	7.63 ± 0.09	95.71	1.05 ± 0.11
0.1	4.0166	4.1012	1.0211	7.65 ± 0.03	96.23	0.97 ± 0.12
0.5	4.0048	4.0898	1.0212	7.71 ± 0.05	98.12	0.84 ± 0.09
1.0	4.0132	4.0968	1.0208	7.73 ± 0.04	99.84	0.71 ± 0.09

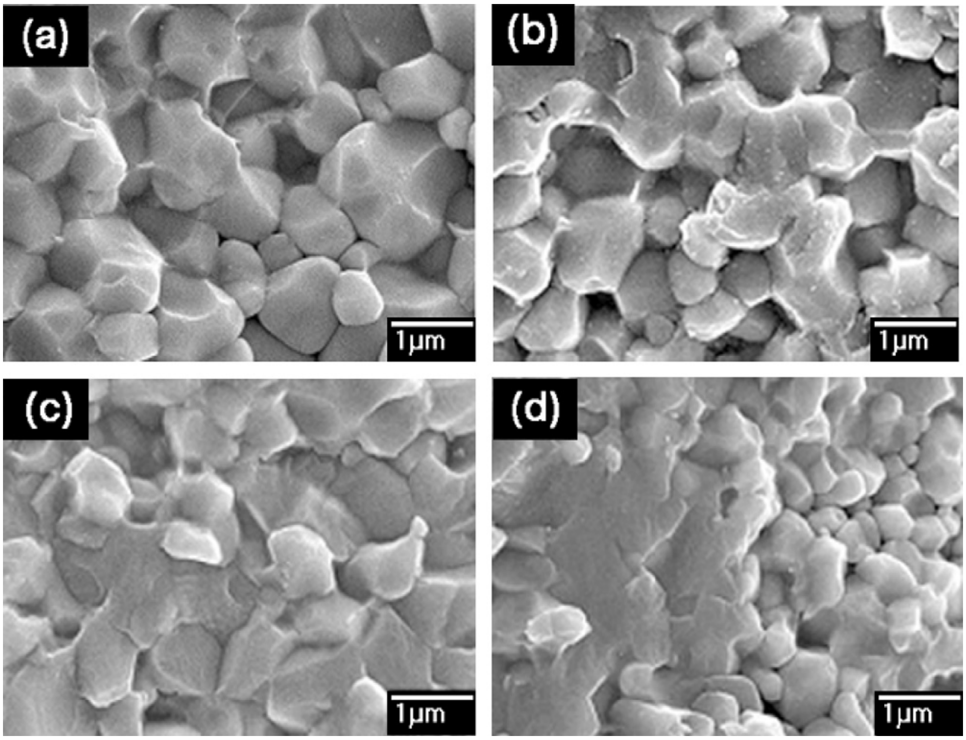

Fig. 2. SEM images of fracture surfaces of PZT–BLT/ZnO ceramics, where (a)–(d) represent $x = 0$, 0.1, 0.5 and 1 wt%, respectively.

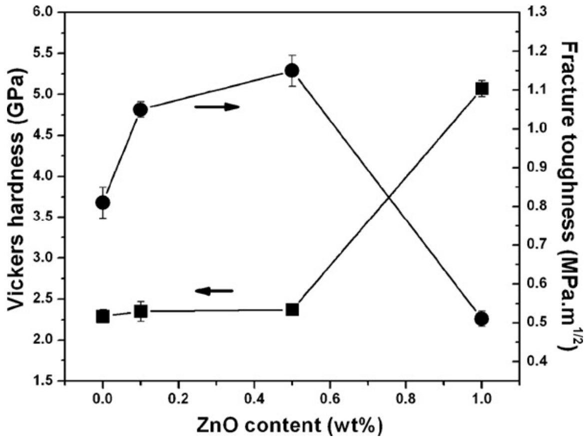

Fig. 3. Vickers hardness and fracture toughness of PZT–BLT/ZnO ceramics.

Dielectric constant and dielectric loss measured at room temperature were plotted as a function of frequency as shown in Fig. 4 and their values are tabulated in Table 2. The result indicated that the dielectric constant and loss values gradually increased with increasing ZnO content. These results were believed to be due to the fact that PZT–BLT is actually a donor-doped system, in which Bi^{3+} and La^{3+} replaced Pb^{2+} sites (considering that these ions have similar radii, i.e. $r_{Bi3+} = 1.17$ Å, $r_{La3+} = 1.16$ Å and $r_{Pb2+} = 1.19$ Å [12]). The cation vacancies were created due to electroneutrality. From X-ray diffraction data, the formation of $Pb_2Ti_2O_6$ phase indicated the presence of Pb^{2+} and Ti^{4+} vacancies. It was therefore expected that the increase in cation vacancies was greater than the increase in oxygen vacancies from ZnO dissolution, causing the PZT–BLT/ZnO ceramic to behave like a donor-doped

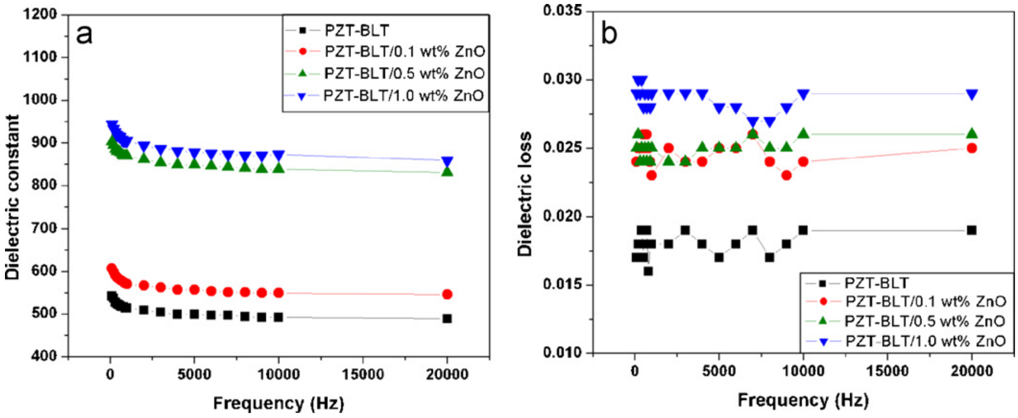

Fig. 4. Plots of frequency dependence on (a) dielectric constant and (b) dielectric loss of PZT–BLT/ZnO ceramics measured at room temperature.

Table 2
Dielectric and ferroelectric properties of PZT–BLT/ZnO ceramics.

ZnO content (wt%)	Dielectric props.		Ferroelectric props.		Loop squareness (R_{sq})
	ε_r	tan δ	P_r/P_{max}	E_c/E_{max}	
0	492	0.0190	0.70	0.50	0.89
0.1	549	0.0240	0.67	0.50	0.86
0.5	838	0.0260	0.64	0.50	0.85
1.0	873	0.0290	0.63	0.50	0.91

Note: Dielectric properties measured at frequency of 10 kHz at room temperature.

system. Therefore, in terms of dielectric constant and loss, an increase in values was therefore observed.

Ferroelectric property parameters of PZT–BLT/ZnO ceramics are illustrated in Table 2. Because of the temperature and field dependence of ferroelectric properties of ceramics, these parameters have been normalized in a form of P_r/P_{max} and E_c/E_{max} values [13]. From the data, addition of ZnO did not significantly change ferroelectric properties values. Therefore, the unbalanced concentration between cation and anion vacancies seemed to be the main factor determining its physical and electrical properties.

4. Conclusions

In this study, PZT–BLT/ZnO compounds were successfully prepared by a solid-state mixed-oxide method and the ceramics were fabricated by a conventional sintering process. Apparent changes in crystal structure and microstructure due to added ZnO were observed. An addition of ZnO improved densification, inhibited grain growth and improved hardness of PZT–BLT ceramics. An addition of 0.5 wt% ZnO gave higher value of fracture toughness than that of monolithic PZT–BLT ceramic. Dielectric constant of the ceramics increased with increasing ZnO content. Nevertheless, ferroelectric characteristics of this ceramic system were not significantly changed with ZnO content. In this system, the unbalanced cation and anion defects seemed to be the main factor that caused PZT–BLT/ZnO ceramics to behave like a donor-doped system.

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