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Short communication

Effects of excess ZnO addition on La-doped PZN–PZT ceramics prepared by hot pressing

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Abstract

Effects of excess ZnO addition on phase structure, dielectric and piezoelectric properties in La-doped Lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN)–PZT systems have been investigated. Addition of excess ZnO helps to suppress the formation of the pyrochlore phase. Microstructure revealed the grains size to decrease with excess ZnO addition. Enhanced T_{max} and d_{33}, and reduced ε_{max} and Tan δ were observed. Adding proper excess ZnO in La-like doped PZN-based systems seems an effective approach to suppress the formation of the pyrochlore phase, enhance piezoelectric constant d_{33} and reduce dielectric loss.

Keywords: A. Hot pressing; B. Additions; C. Electrical properties; D. Perovskite

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1. Introduction

Lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), is a relaxor ferroelectric exhibiting a broad maximum of its dielectric constant characterized by a strong frequency dispersion, strong piezoelectric and electrostrictive behavior[1]. PZN–PZT relaxor ferroelectrics are promising materials for use in high performance electromechanical actuators and transducers where sensitivity control is required [2].

However, single phase PZN is difficult to sinter in the perovskite structure by the conventional ceramic process, due to the formation of the pyrochlore phase [3]. It has been concluded that at elevated temperature, the perovskite decomposes into ZnO, volatile PbO and the cubic pyrochlore phase [4]. The addition of excess MgO in PMN-based ceramics has been shown to have a beneficial effect to reduce and even eliminate formation of the pyrochlore phase [5–7]. In PZN–PT single crystal growth, proper excess ZnO helped attain high-quality large single crystals [8]. Nevertheless, there are few studies on excess ZnO addition in PZN-based ceramics. The study described here is devoted to the detailed investigations of excess ZnO addition in La-doped PZN–PZT systems.

2. Experimental procedure

The base composition was $0.7[Pb_{1-x}La_x(Zr_{0.55}Ti_{0.45})_{1-x/4}O_3]–0.3Pb(Zn_{1/3}Nb_{2/3})O_3$, in which x equals to 7 mol%, designated as La-doped PZN–PZT. Excess of 1 mol%, 3 mol% and 5 mol% nonstoichiometric ZnO were added to the base compositions, designated as base + xZnO. The raw materials were PbO (>98%), TiO_2 (>98%), ZrO_2 (>98%), La_2O_3 (>99.9%), ZnO (>97%) and Nb_2O_5 (>99%). The mixtures in stoichiometric ratios were ball-milled for 36 h, sieved and pressed to pellets of 20 mm diameter. Specimens were prepared by hot pressing. The processes of calcining and sintering were 900 °C for 2 h and 1150 °C for 6 h with a pressure of 90 MPa. An excess of 3 wt.% PbO was added to compensate for PbO volatility during sintering.

X-ray diffraction (XRD) pattern was obtained using an automated diffractometer (RAX-10, Rigaku, Tokyo, Japan) with Cu Kα radiation with a scanning speed of 1 min^{-1} and a step size of 0.02°. The perovskite phase contents of specimens were estimated quantitatively by comparing the major peak intensities of the (1 1 0) and (2 2 2) reflections of the perovskite and the pyrochlore structures, i.e., $I_{peroc(110)}/$

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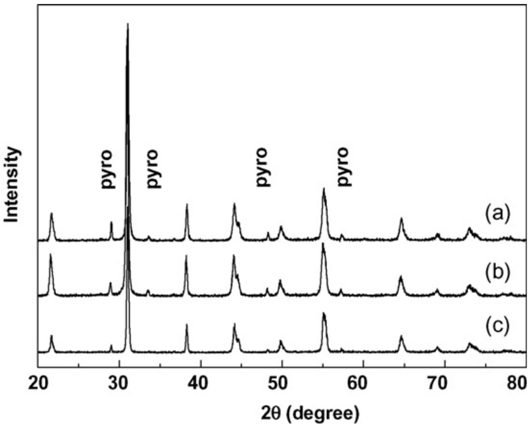

Fig. 1. XRD patterns of La-doped PZN–PZT ceramics with various excess ZnO addition: (a) 0 mol% ZnO; (b) 2 mol% ZnO and (c) 5 mol% ZnO.

($I_{perov(110)} + I_{pyro(222)}$). Dielectric measurements were carried out using an HP 4192 impedance analyzer. The piezoelectric coefficient (d_{33}) was investigated using a quasi-static piezoelectric d_{33}-meter (ZJ-3A, Institute of Acoustics Academic Sinica, Beijing, China). The microstructures were observed on the fracture surfaces using an LEO 1350 VP.

3. Results and discussion

For PZN-based ceramics, the perovskite phase was unstable and the pyrochlore phase was very likely to form, which was detrimental to electrical properties [9]. XRD patterns of La-doped PZN–PZT ceramics with various excess ZnO additions are showed in Fig. 1. Pyrochlore phase could be observed in base composition. However, the ratios of the pyrochlore phase in specimens decreased with increasing excess ZnO addition in La-doped PZN–PZT systems. The perovskite phase contents are 91%, 92% and 94%, respectively, for 0 mol%, 2 mol% and 5 mol% ZnO excess addition. Shrout and Halliyal [9] state that pure PZN is indeed a thermodynamically unstable compound. It was concluded that heating above 850 °C inevitably leads to the decomposition of the perovskite into the cubic pyrochlore, ZnO, and volatile PbO [4], as shown in the reaction below. When excess ZnO was added, according to reaction dynamics, the reaction proceeded to the left, i.e. excess ZnO promoted the perovskite phase against the pyrochlore phase. Hence, the pyrochlore phase was suppressed.

$$6\mathrm{Pb}(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3 \rightarrow \mathrm{Pb}_3\mathrm{Nb}_4\mathrm{O}_{13} + 2\mathrm{ZnO} + 3\mathrm{PbO} \qquad (1)$$

Fig. 2 shows SEM photographs of the fractured surfaces of La-doped PZN–PZT specimens. It can be seen that grains prepared by hot pressing sintering are dense and uniform with clear grain boundaries. The grain size decreased with increasing excess ZnO addition.

Dielectric permittivity and dielectric loss at 1 kHz versus temperature curves of La-doped PZN–PZT system are shown in Fig. 3. The maximum dielectric constant of La-doped PZN–PZT at 1 kHz is decreased from 23960 for 0 mol% ZnO, to 17421 for 5 mol% ZnO. Furthermore, excess ZnO addition decreased ε_r, accompanied by increased T_{max}. The data are shown in Table 1. Specially, excess ZnO addition increased the piezoelectric constant of d_{33} and decreased the dielectric loss, Tan δ, as shown in Table 1. Enhanced piezoelectric constant

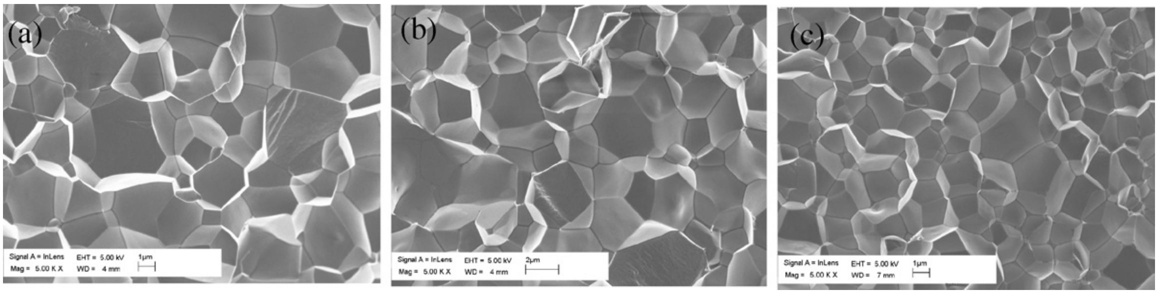

Fig. 2. SEM microstructures of the fractured surfaces of the specimens: (a) 0 mol% ZnO; (b) 2 mol% ZnO and (c) 5 mol% ZnO.

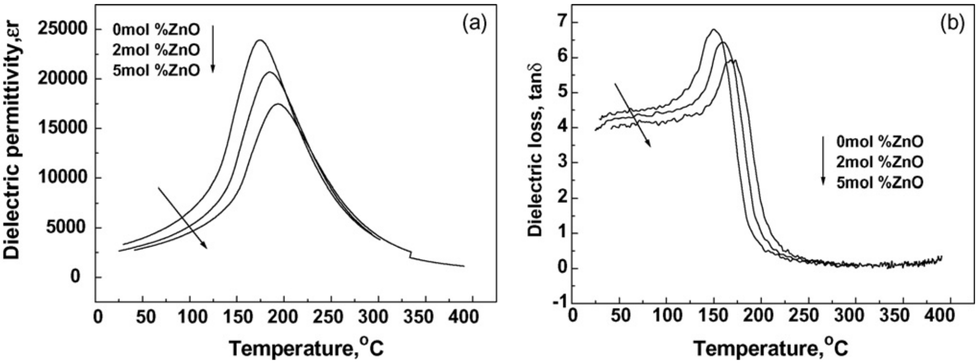

Fig. 3. Dielectric permittivity (a) and dielectric loss (b) at 1 kHz as a function of temperature for La-doped PZN–PZT ceramics with different excess ZnO addition.

Table 1
The phase transition temperature T_{max}, dielectric permittivity ε_r, dielectric loss Tan δ and piezoelectric constant d_{33} of La-doped PZN–PZT specimens with excess ZnO addition

Compositions	T_{max} (°C)	ε_r (10 kHz)	Tan δ (%)	d_{33} (10^{-12} C/N)
La-doped PZN–PZT	174	3420	4.11	607 ± 10
La-doped PZN–PZT + 2% ZnO	184	2834	3.96	656 ± 10
La-doped PZN–PZT + 5% ZnO	194	2660	3.85	680 ± 10

might be ascribed to the suppression of the detrimental pyrochlore phase. According to ionic radius, additions of ZnO mostly enter the B-site of the perovskite structure. These excess ions formed a tighter structure, resulting in smaller grain, decreased ε_r and Tan δ. However, piezoelectric constant of d_{33} did not reduce but enhanced due to formula (1) above.

4. Conclusions

Effects of excess ZnO addition in La-doped PZN–PZT systems prepared by hot pressing sintering were investigated. The addition of excess ZnO was proved helpful to suppress the detrimental pyrochlore phase. Grains size decreased duo to tighter structure resulting from excess ZnO addition. Furthermore, enhanced T_{max} and d_{33}, and reduced ε_{max} and Tan δ were observed. Suppressed pyrochlore phase achieved enhanced d_{33}. Adding proper excess ZnO addition in La-doped PZN-based ceramics is a novel approach to improve properties of ceramics with enhanced d_{33} and decreased Tan δ.

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