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Toughening of PZT Piezoelectric Ceramics by In-Situ Complex Structures

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Abstract

A new approach for toughening PZT piezoelectric ceramics has been developed, where some piezoelectric secondary phase tending to form plate-like or columnar structures was incorporated into PZT matrix to generate the in-situ complex structures and therefore to enhance the fracture toughness. In $(Pb_{0\cdot92}Sr_{0\cdot08})(Zr_{0\cdot52}Ti_{0\cdot48})O_3$–$Bi_4Ti_3O_{12}$ *system, the significantly enhanced fracture toughness of* $2{\cdot}8\,MPa.m^{1/2}$ *was easily achieved, whereas a much lower value of about* $1{\cdot}0\,MPa.m^{1/2}$ *was measured for the pure PZT ceramics. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

$Pb(Zr,Ti)O_3$ (PZT) ceramics are the most widely used excellent piezoelectric materials. However, they generally indicate poor mechanical performance, i.e. low bend strength and low fracture toughness, and this shortage becomes the most serious for the compositions near to MPB (morphotropic phase boundary) where the most excellent piezoelectric properties are indicated.[1] On the other hand, high strength and high fracture toughness are strongly required in piezoelectric ceramics for high frequency and high power applications and for the situations where complex mechanical processing is required. Hence, in recent years, more and more attentions has been focused on understanding and improving mechanical properties of PZT piezoelectric ceramics.[1–6] Yamamoto *et al.* [4] reported the enhancement of strength of PZT ceramics by introducing SiC whisker into the matrix, and Malic *et al.*[5] also enhanced the strength of PZT ceramics through the effect of martensitic transformation of dispersed ZrO_2 particles. Takahashi *et al.*[1,6] showed an approach to improve the mechanical properties of PZT ceramics by creating monoclinic ZrO_2 (m-ZrO_2) fiber and tetragonal ZrO_2 (t-ZrO_2) fiber reinforced composites. They found that the fracture toughness was improved but the strength decreased in m-ZrO_2 fiber reinforced system, and the t-ZrO_2 fiber reinforced system could enhance the fracture toughness significantly without strength decrease. However, there is a common problem in all the cases described above in that the serious consequent damage on piezoelectric properties can never be avoided.

The authors[7] have proposed a new concept of materials design for achieving enhanced mechanical properties combined with superior piezoelectric performance in PZT based ceramics, in which a secondary piezoelectric phase tending to form plate-like or columnar structures was incorporated into PZT matrix to generate the in-situ complex structures and therefore to enhance the mechanical properties of PZT ceramics. In this paper, the toughening of PZT piezoelectric ceramics by incorporating $Bi_4Ti_3O_{12}$ (hereafter referred to as BIT) secondary phase was determined and discussed with emphasizing the effects of in-situ complex structures, and the dielectric and piezoelectric properties of such composite ceramics were also discussed.

2 Experimental Details

A typical commercial composition $Pb_{0\cdot92}Sr_{0\cdot08}(Zr_{0\cdot52}Ti_{0\cdot48})O_3$ was adopted to prepare the $(1-x)$PZT-$x$$Bi_4Ti_3O_{12}$ (hereafter referred to as $(1-x)$PZT/xBIT) composite ceramics ($x = 3$, 6, 9, 12 and 15mol%). First, the end-member powders of PZT and BIT were respectively synthesized by the conventional solid state reaction processes, from high purity $SrCO_3$, PbO, Bi_2O_3, TiO_2 and ZrO_2 powders. Then PZT and $Bi_4Ti_3O_{12}$ powders were pressed at 98MPa into cylindrical compacts with dimensions of 12 mm in diameter and 1 to 4 mm in height after mixing by planetary ball

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milling for 3 h. Finally, the compacts were sintered at the temperatures of 1000 to 1200°C in air for 3 h.

Powder X-ray diffraction (XRD) analysis using Cuα radiation, scanning electron microscopy (SEM) observation, and differential thermal analysis (DTA) were carried out for microstructural characterization, and the dielectric properties were measured by a LCR meter (WK4210) at 1 kHz, Young's modulus E and electro-mechanical coupling coefficient k_p were determined by a routine resonant technique.

The fracture toughness of the present composite ceramics was evaluated through the indentation method[8,9] and the following modified version of Evans-Charles Equation[9] was adopted in the calculations.

$$(K_{IC}\phi/Ha^{1/2})(H/E\phi)^{0\cdot 4} = 0\cdot 142(c/a)^{-1\cdot 56} \qquad (1)$$

where K_{IC} is the fracture toughness, H is the hardness, E is Young's modulus, ϕ is the constraint factor (~3), 'a' is the half-diagonal of the Vickers indent and c is the radius of the surface crack.

3 Results and Discussion

As shown in Fig. 1, the densification temperature of (1–x)PZT/xBIT composite ceramics significantly decreases with increasing the concentration of BIT secondary phase and shows the minimum at some point between x = 6 mol% and x = 9 mol%, and this can be interpreted as the result of liquid phase sintering.[7,10] The densification can be performed well at 1050 to 1100°C for x = 3 mol%, 1000°C or below for x = 6 mol% and x = 9 mol%, and 1100°C for x = 12 mol% and x = 15 mol%. It must be mentioned here that the excessively high sintering temperature generally leads to significant decrease of density of the present composite ceramics.

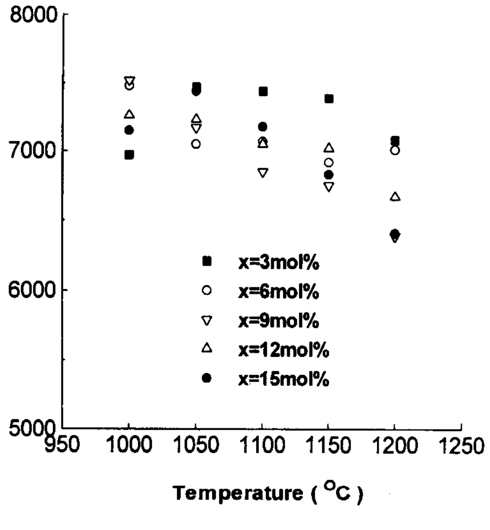

Fig. 1. Bulk density of (1–x)PZT/xBIT composite ceramics with various composition versus sintering temperature, for an identical time of 3 h in air.

As indicated in Fig. 2, fracture toughness of the present composite ceramics increases significantly with increasing the concentration of BIT secondary phase, and the fracture toughness even reaches 2·8MPa m$^{1/2}$, whereas a much lower value of about 1·0MPa m$^{1/2}$ is measured for the pure PZT ceramics. In other words, fracture toughness of PZT ceramics can be enhanced by incorporating BIT secondary phase into PZT matrix to create composite ceramics. The sintering temperature significantly affects this toughening process through affecting the bulk density and microstructures, and the composite ceramics sintered at 1050°C generally have the highest fracture toughness.

Figure 3 shows the expected in-situ formed complex structure in (1–x)PZT/xBIT composite ceramics (x = 9 mol%), where the developed plate-like grains of secondary phase are homogeneously dispersed within the PZT matrix. It is considered that the toughening of PZT ceramics described

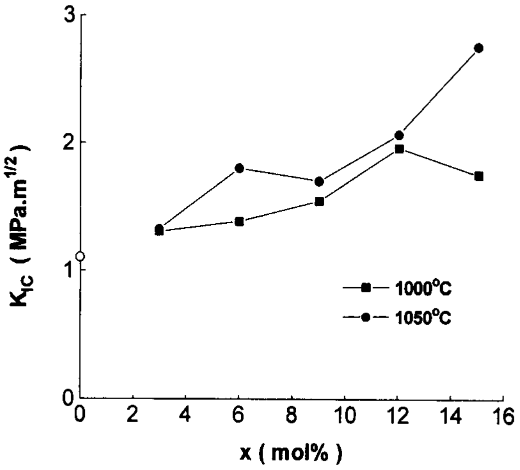

Fig. 2. Fracture toughness of (1–x)PZT/xBIT composite ceramics as function of concentration of BIT and sintering temperature.

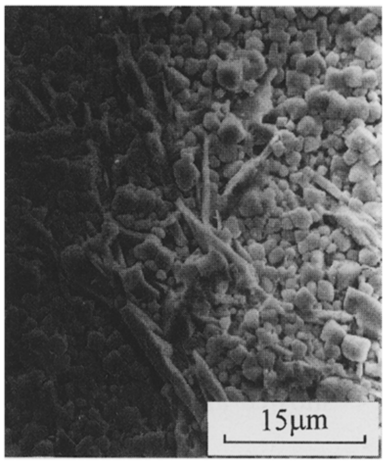

Fig. 3. In-situ complex structure in (1–x)PZT/xBIT composite ceramics (x = 9 mol%).

above is primary contributed by this in-situ complex structure through the complex structure toughening mechanism,[11] the typical fracture morphology of the composite ceramics (see Fig. 4) can give strong evidence for this consideration. The formation and development of such in-situ complex structure is strongly dependent on the concentration and sintering temperature, therefore the toughness of (1–x)PZT/xBIT composite ceramics are dominated by these parameters. High concentration and suitable sintering temperature lead to high levels of toughness because the desired in-situ complex structure is formed under such conditions. Meanwhile, lower toughness levels observed for the samples sintered at excessively high sintering temperatures is considered due to the large porosity.

The harmful influence of the secondary phase upon the piezoelectric properties has been a serious problem when the enhancement of mechanical performance of PZT ceramics were considered by using conventional approaches.[1–6] However, the results in the present work are quite heartening. As shown in Fig. 5, although the piezoelectric properties of (1–x)PZT/xBIT composite ceramics decrease with increasing the concentration of secondary phase, such properties are much better than those in the previous work using conventional approaches.[5]

The XRD pattern for the composite ceramics suggests that BIT secondary phase seems to coexist with the PZT major phase (see Fig. 6). However, there is no evidence of the ferroelectric phase transition for BIT observed on the DTA curve, but two clear phase transition peaks appear at 330°C and 570°C, respectively (Fig. 7). The former corresponds to the Curie point of PZT major phase, and the latter just equals to the Curie point of $PbBi_4Ti_4O_{15}$ which also belongs to the Bismuth layer structure compound family and has the XRD pattern very close to that of BIT. These results

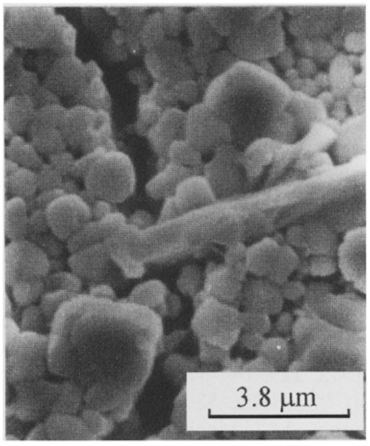

Fig. 4. Typical fracture morphology in (1–x)PZT/xBIT composite ceramics.

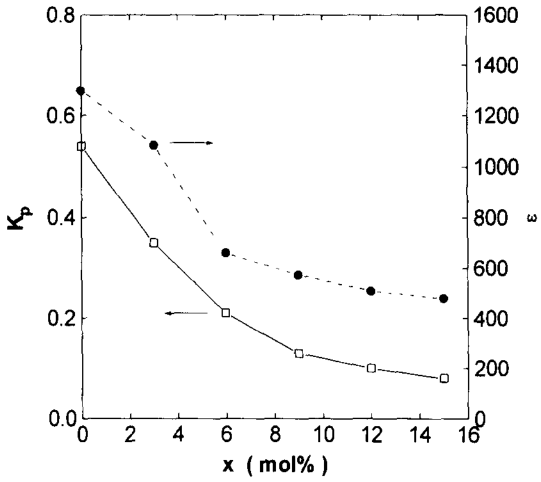

Fig. 5. Variation of dielectric constant and kp in (1–x)PZT/xBIT composite ceramics with concentration of BIT.

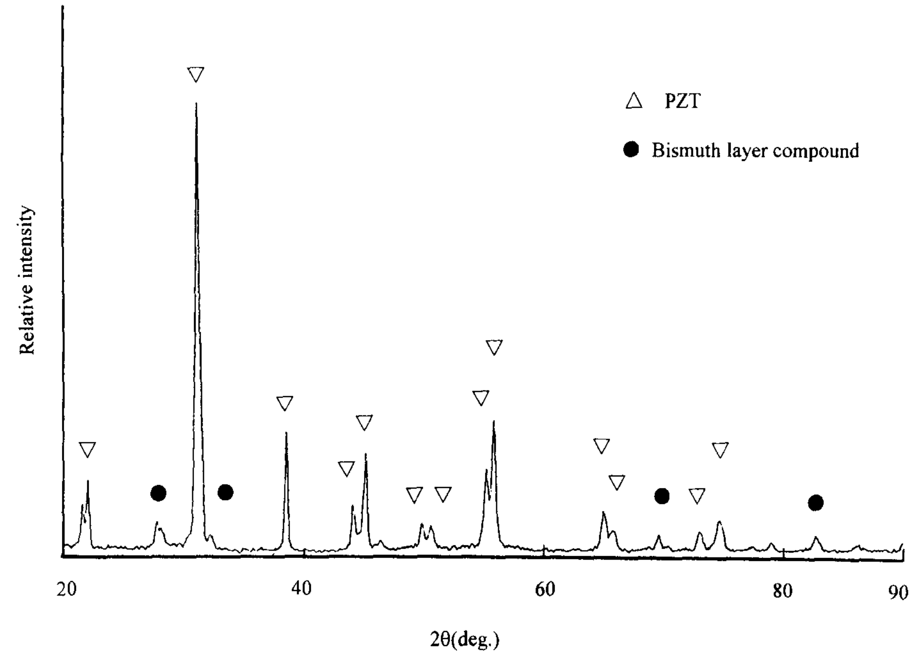

Fig. 6. XRD pattern of (1–x)PZT/xBIT composite ceramic (x = 0·06).

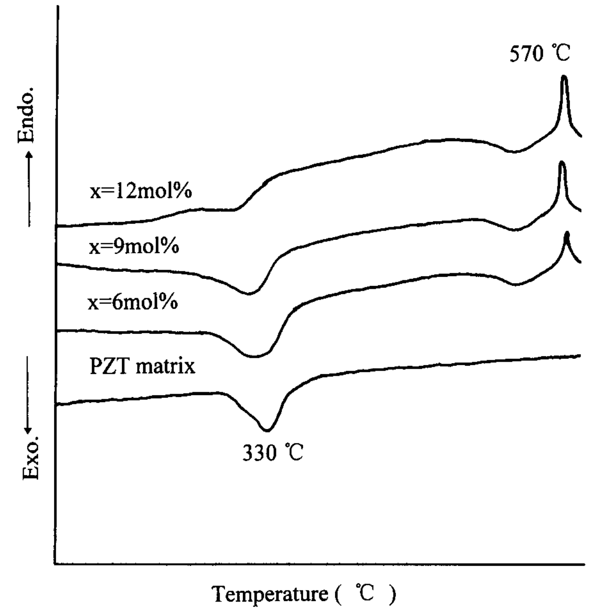

Fig. 7. DTA curves for (1-x)PZT/xBIT composite ceramics with various composition.

conclude that, PbBi4Ti4O15 is the stable secondary phase which coexists with the PZT matrix as a sequence of the following reaction:

$$\mathrm{Pb(Zr1-x'Tix')O_3+xBi_4Ti_3O_{12}\rightarrow(1-x)}$$
$$\mathrm{Pb(Zr(1-x')/(1-x)Ti(x'-x)/(1-x))O_3+}$$
$$\mathrm{xPbBi_4Ti_4O15}$$

where, x is the concentration of BIT. Due to this reaction during sintering, the ratio of Zr/Ti will deviate from the initial value and shift to Zr rich side. The deviation of Zr/Ti ratio from MPB is considered to be the primary factor causing the degradation of piezoelectric performance, i.e. decrease of *kp*, and therefore the negative effects of secondary phase on the piezoelectric properties is expected to be almost suppressed if a more stable Bismuth layer structure compound such as $PbBi_4Ti_4O_{15}$ is incorporated into the PZT matrix as the secondary phase.

4 Conclusion

A new approach for toughening PZT piezoelectric ceramics has been developed, and the fracture toughness of PZT piezoelectric ceramics can be enhanced through introducing piezoelectric secondary phase to generate in-situ complex structures, while the piezoelectric properties suffer decrease much less than that in the previous work.[5] It is believed that further improvement of fracture toughness without damage of piezoelectric properties can be achieved by adopting a more stable secondary phase and optimizing in-situ complex structures. The remaining challenge issue is to achieve the synergistic improvement of toughness and piezoelectric performance.

Acknowledgements

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