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Enhanced mechanical behaviour of lead zirconate titanate piezoelectric composites incorporating zinc oxide nanowhiskers*

Lin Hai-Bo(林海波), Cao Mao-Sheng(曹茂盛)†, Yuan Jie(袁 杰),
Wang Da-Wei(王大伟), Zhao Quan-Liang(赵全亮), and Wang Fu-Chi(王富耻)

School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, *China*

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This paper reports that the lead zirconate titanate (PZT) piezoelectric composites incorporating zinc oxide nanowhiskers (ZnO_w) were prepared by the conventional solid state processing. The whisker-dispersed PZT composites (PZT/ZnO_w) presented a significant enhancement in the mechanical properties such as Young's modulus, tensile strength and compressive strength. Especially, the compressive strength increased from 153 MPa for the PZT to 228 MPa for the PZT/ZnO_w composites. The reinforcement mechanism in strength of the composites was discussed. The mechanical quality factors of the PZT/ZnO_w composites increased considerably, while the piezoelectric constants and electromechanical coupling coefficient decreased slightly. The composites with good electrical and excellent mechanical properties are promising for further applications.

Keywords: ZnO nanowhisker, composites, mechanical property, piezoelectrics
PACC: 7760, 6220, 6200

1. Introduction

Due to their excellent electromechanical properties, lead zirconate titanate (PZT) based piezoelectric ceramics have wide applications in numerous electromechanical devices such as capacitors, actuators, sensors, resonators and high-power transducers.[1−6] With the miniaturization and integration of electronic circuits, small-scale piezoelectric devices, especially piezoelectric actuators, are technologically important in the fields of smart materials and microelectromechanical systems (MEMS).[7] Because of the inherent defect in the conventional piezoelectric devices, the high electrical driving fields needed to produce large displacements may lead to degradation of the mechanical and electrical reliabilities. Poor reliabilities have become critical limitation on the performance of the devices under severe circumstances. Advanced structural and functional composites are expected to be a good solution to this problem.

Up till now, a few approaches to improve mechanical properties have been used to study on composites incorporating fibre, whisker, particle, or metal, oxide, polymer.[8−14] Especially the addition of SiC whiskers to reinforce mechanical properties of ceramics was widely investigated.[15−17] From the above mentioned approaches, PZT ceramic composites reinforced by SiC whiskers have shown excellent mechanical properties except the electrical properties.[15] The addition of Ag metal particle possessed the improvement of the mechanical properties and the graded piezoelectric properties[7,18] whereas both Pt and Ag noble metals are too expensive to be suitable candidates for practical applications. We proposed the PZT composites incorporating ZnO nanowhiskers, which are much cheaper than the noble metal and have high strength, rigidity and chemical stability with special properties.

ZnO nanostructure has been a subject of intensive research driven by important technological applications over the past several decades owing to the specific electrical,[19] optical[20,21] and microwave absorption properties.[22,23] More recently, significant research interest has been attracted for the interesting and distinctive piezoelectric[24] and semiconducting properties.[25] Because of the high-temperature strength and excellent chemical stability,

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†Corresponding author. E-mail: caomaosheng@bit.edu.cn

ZnO whiskers have received great attention for industrial application as reinforced composite material.[26] On the other hand, conducting nanostructures dispersed in a dielectric material can improve electrical properties.[27,28] In addition, the addition of ZnO is beneficial to reduce the sintering temperature of ceramics. [29−31]

In this paper, PZT based composites dispersed with ZnO whiskers (ZnO_w) were prepared through a normal sintering process in air. In comparison with the monolithic PZT, the composites not only showed significant excellent mechanical properties, such as tensile and compressive strength, but also exhibited good electrical properties. Possible reinforcement mechanism of the ZnO_w on the mechanical responses of the composites was discussed.

2. Experiments

The ZnO_w were synthesized by combustion oxidation of fine zinc powders. The powders were placed into a quartz boat in a quartz tube with the boat located at 960° zone without any additive. After the growth of ZnO_w on the quartz boat for a period of time, the boat was taken out and cooled naturally to the ambient temperature. The soft PZT ceramics (PZT-5) with a Zr/Ti ratio of 52/48 were used as the starting materials. The PZT powders mixed with the as-fabricated ZnO_w were gently ball-milled and then rapidly dried. The mixtures of ZnO_w and the PZT powders added to an appropriate amount of polyvinyl alcohol binder were compacted under pressure of 200 MPa by die pressing. After burning out the binder in a furnace in air at 700°C, the green compacts were sintered at 1100°C in a closed alumina crucible that contained $PbZrO_3$ powders to minimize lead volatilization. The densely sintered bodies were machined to the required dimensions and sizes from the bulk for property measurements. The PZT/ZnO_w composites were polished and cleaned in acetone. Silver paste was printed to form electrodes on both sides of the samples, and then fired at 800°C for 10min. Poling treatment was carried out in silicon oil at 120°C for 20min with an electric field of 3–4 kV/mm.

The bulk density was determined by the Archimedes method in water. The crystalline phases of the sintered materials were examined by x-ray diffraction (XRD) with Ni-filtered CuKα radiation. The morphology of the as-prepared whiskers and composites was studied by a field-emission JSM-6700F scanning electron microscope (SEM). The piezoelectric properties of the polarized specimens were measured using a piezoelectric tester (ZJ-3AN), and electromechanical and dielectric characteristics were calculated with the Model HP 4194 impedance analyser. Compression tests were performed on a CSS-2220 testing machine using cylinders 12 mm in diameter and 4.2 mm in thickness at room temperature.

3. Results and discussion

Figure 1 shows the SEM image of ZnO nanowhiskers synthesized by the simple combustion oxidation method without any catalysts or additives. It is clearly seen that the nanostructures are definitely uniform. The individual structure consists of needle-shaped legs with high aspect ratio. The thickness of narrow tips are some decades of nanometre, whereas the lengths are in the range of 10–30 μm.

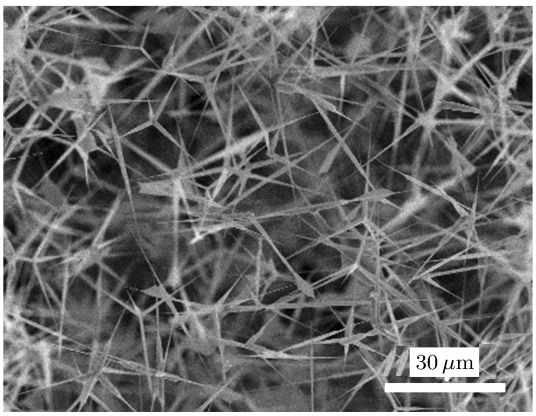


Fig.1. SEM image of ZnO nanowhiskers synthesized by conventional solid state processing.

Figure 2 shows the XRD patterns of the ZnO_w, PZT and the PZT/ZnO_w composites. The diffraction peaks characteristics of perovskite-structured PZT can be identified from the PZT and the PZT/ZnO_w composites. The zinc oxide phases are demonstrated from the pure ZnO_w and the composites. A comparison of the diffraction peaks in the samples indicates that no significant chemical reaction occurred between the PZT and ZnO_w during sintering at 1100°C. There are no characteristic peaks from other impurities and no conspicuous change of lattice constants detected. This result confirms that the PZT is chemically inert to ZnO_w in PZT/ZnO_w composites. The sintering temperature is decreased from the temperature 1300°C for monolithic PZT to 1100°C for the com-

posites added with ZnO_w.

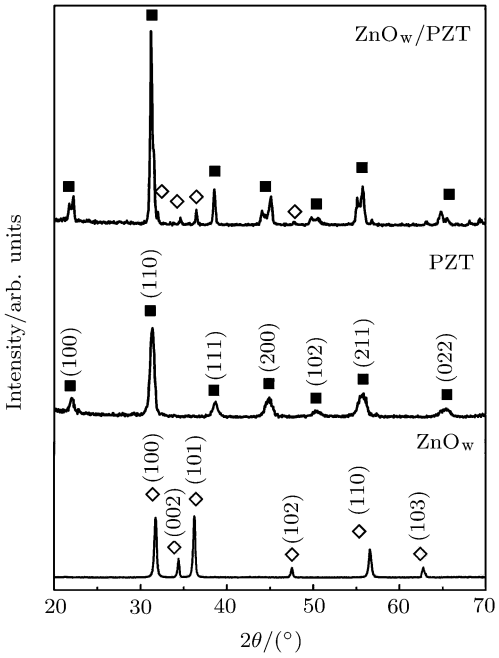


Fig.2. X-ray diffraction patterns of the ZnO_w, PZT and PZT/ZnO_w composite samples.

Figure 3(a) shows the SEM image of the polished surface of the PZT/ZnO_w composites sintered at 1100° for 2 h. The whiskers with a few micrometres in size are homogeneously dispersed in the PZT. Energy dispersive x-ray spectroscopy (EDS) results indicate that the black area marked with the white square is composed of the secondary phase ZnO and the area marked with circle is composed of the PZT phase as shown in Figs.3(b) and 3(c), respectively. The Au peaks came from metal Au deposited on the surface of the as-prepared samples before measurement. It should be noted that some cavities are observed in the composites. We speculate that it is related to whisker pullout under the cracks reaching the tip of whiskers.

Figure 4(a) shows a full leg of ZnO_w in the composites detected from the fracture surfaces after the mechanical test. Figure 4(b) illustrates the cavities in the fracture surfaces of the composites with the diameters 0.7–1.2 μm, and Fig.4(c) shows a single leg of the sintered ZnO_w with the diameters approximate 0.8 μm at the tip and the width ranging from 1.5 to 2 μm at the root. The cavities are believed to be induced by the pinning effect of ZnO_w on the PZT under the applied stress conditions. The observations indicate that the cracks reach the interface and then proceed without fracturing the whisker. Accordingly, it can be

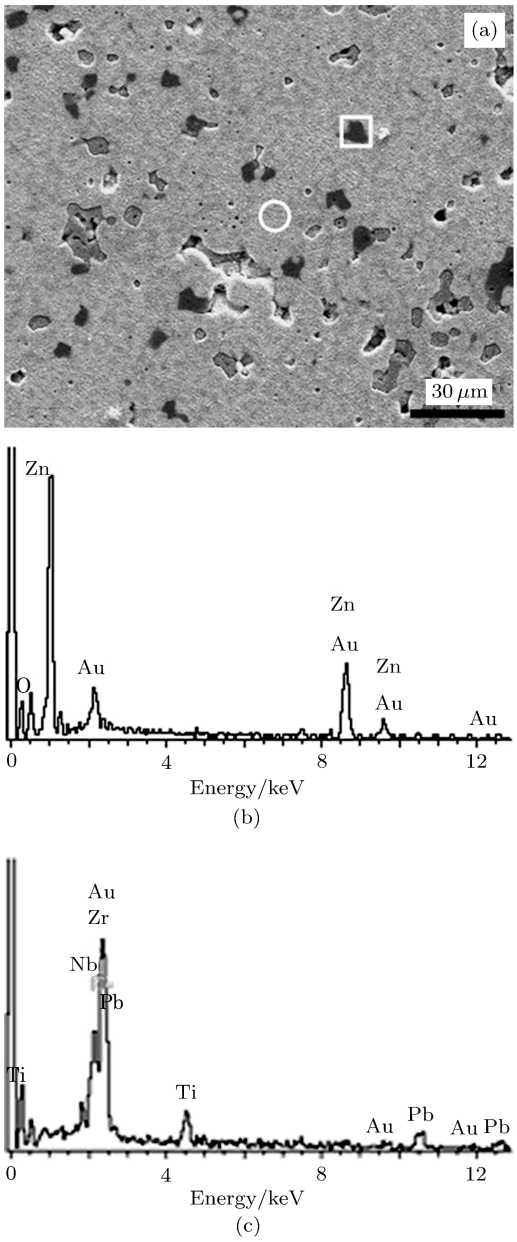


Fig.3. (a) SEM image of the polished surface of the as-fabricated PZT/ZnO_w composites; (b) and (c) EDS patterns at the locations indicated with the square and circle in (a), respectively.

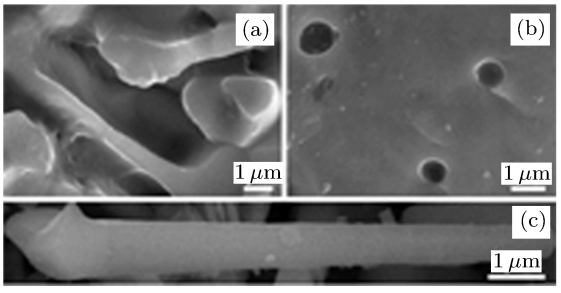


Fig.4. (a, b) SEM images of the fracture surface of the as-fabricated PZT/ZnO_w composites and (c) SEM image of a single leg of the sintered ZnO_w.

ascertained that the whisker pullout effect could make the composites reinforced. It suggests that the PZT composites containing a whole leg of whisker led to degradation of brittle behaviour and the improvement of the mechanical properties.

Table 1 shows electrical properties of the monolithic PZT sintered at 1300°C for 2 h and PZT/ZnO_w composites sintered at 1100°C for 2 h. The PZT shows typical soft-type properties: a low mechanical quality factor Q_m (∼70); relatively good piezoelectric properties; the piezoelectric coefficient d_{33} (∼500) and electromechanical coupling coefficient k_p (∼62%). As listed in Table 1, the composites exhibit that a very high Q_m value (∼148) is about two times greater than those of the PZT, while the dielectric and piezoelectric properties are found to be slightly lower than these of the PZT. The mechanical quality factor Q_m, which is the reciprocal of the mechanical loss, increases considerably by conducting the whiskers, implying that the addition of the ZnO_w will cause less mechanical loss when the composites are used in an actuator machine. The electrical properties of the composites can be obviously adjusted within a relatively broad range

Table 1. Comparison of electrical properties of PZT/ZnO_w composites with PZT materials.

material	PZT	PZT/ZnO_w
d_{33}(pC/N)	500	401
Q_m	70	148
k_p	0.62	0.49
ε_{33}^T	3800	2780

according to their practicality and the PZT/ZnO_w composites are of promising importance for various piezoelectric applications.

The mechanical properties of the PZT/ZnO_w composites are listed in Table 2 and compared with those of the monolithic PZT obtained from our calculations. Observations show that the incorporation of ZnO_w gives rise to increase in Young's modulus (E), compressive strength (σ_c) and tensile strength (σ_t). The compressive strength of the PZT is found to be 153 MPa and substantially increases to 228 MPa after incorporating the ZnO_w, indicating strain hardening. Similar increase in the Young's modulus is observed in the composites comparison with the PZT. The tensile strength of the obtained composites is superior to that of the PZT, perhaps due to restrict slide of the whisker–ceramic interface. These results reveal that substantial reinforcements in strength and resistance to slow crack growth are achieved via the incorporation of strong, small-diameter whiskers into the PZT. The ZnO_w acts as active barrier to prevent sudden brittle rupture. Hence, crack propagation is greatly suppressed by the dispersed ZnO_w, which also bridged and deflected the crack, leading to reinforcement in the observed mechanical properties. This result is in good agreement with the pinning effect of ZnO_w from the SEM observations mentioned above. Therefore, the observed enhancement in tensile strength and compressive strength may be induced by the existence of conducting ZnO_w.

Table 2. Comparison of mechanical properties of PZT/ZnO_w composites with PZT materials.

material	PZT	PZT/ZnO_w
RD/%	97	96.9
E/GPa	60	83
σ_t	18	30
σ_c	153	228

Under loading conditions, cracks are arrested upon reaching the tip or root of the whisker from the whisker-PZT interface and then extend along the interface.[32] Cracks reach the whisker and then continue in the PZT, keeping the whisker intact (Fig.4(c)). These processes alleviate the high stress concentration at the crack tip which would normally result in the crack propagating through the whisker. In other words, whisker bridging can occur as the whisker-PZT interface debonds when the crack tip approaches the interface. Cracks propagate past the whisker and keep whisker intact which pullouts from the PZT. It is believed that the influence of ZnO_w dispersion on the strength is related to the whisker bridging and whisker pullout.

4. Conclusions

In summary, the PZT-based ceramic composites incorporating ZnO whiskers were prepared by the conventional solid state processing. There were no unwanted reaction phases between the monolithic PZT and ZnO_w at high temperature and it was easily prepared for the composites of ZnO whisker. The study indicated that the PZT/ZnO_w composites had the following merits. First, the composites added with ZnO whiskers had better mechanical properties than monolithic PZT ceramics. However the mechanical properties are not the main concern when PZT ceramics are used for electrical devices, the above enhance-

ments in tensile strength and compressive strength are very beneficial to expand the application. Second, the piezoelectric properties of the composites could be adjusted within a relatively wide range according to their practical use. Third, the addition of ZnO whiskers increased the Young's modulus and the mechanical quality factors significantly, which make the composites interesting. The PZT/ZnO_w composites with good electrical and mechanical properties are promising for further applications. PZT/ZnO_w composites were chosen as a model material to investigate the influences of the incorporation of a secondary phase whisker on the piezoelectric and mechanical properties. Since no theoretical studies have been investigated on the influence of the piezoelectric whiskers dispersion on the piezoelectric and dielectric properties of PZT ceramics, it is hard to further discuss about relationship between the whisker amount and the piezoelectric properties in detail. In order to develop the PZT/ZnO_w composites for the applications, it is fundamentally important to characterize completely the corresponding microstructure and the special properties.

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