Effect of CuO addition on structure and electrical properties of low temperature sintered quaternary piezoelectric ceramics

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Abstract. The ceramics were prepared successfully by CuO additions to $\text{Pb}[(\text{Mn}_{1/3}\text{Sb}_{2/3})_{0.06}(\text{Ni}_{1/2}\text{W}_{1/2})_{0.02}(\text{Zr}_{0.49}\text{Ti}_{0.51})_{0.92}]\text{O}_3$. Effect of the addition on sintering temperature, structure and electrical properties of ceramics was investigated. The piezoelectric ceramics was prepared by solid-state reaction. Sintering experiments were accomplished at temperature between 950 and 1100 °C added 0.3–1.0 wt% CuO. The sintering temperature was reduced from 1250 °C (without CuO additions) to 970 °C when CuO-doped. The ceramics sintered at 970 °C for 2 h with 0.7 wt% CuO exhibited $\epsilon_r = 1845$, $\tan \delta = 0.15\%$, $d_{33} = 395$ pC/N, $k_p = 0.58$ and $Q_m = 1830$, which were the highest values. With increasing CuO doping, T_c becomes lower. Jahn–Teller effect was used to explain the contraction of *c*-axis and simultaneous extension of *a*-axis in the lattice.

Keywords. Sintering; microstructure-final; piezoelectric properties; perovskites; Jahn–Teller effect.

1. Introduction

With the miniaturization and integration of electronic circuits, small-scale devices are technologically important in the fields of smart materials and microelectro mechanical systems (MEMS), where they are mainly used by lead zirconate titanate (PZT)-based piezoelectric ceramics (Futakuchi *et al* 1999; Zhu and Zhu 1999; Li *et al* 2001; Hayashi and Tomizawa 2004). However, sintering temperature of PZT system is very high (above 1200 °C) which will cause compositional fluctuation on B-site (Kakegawa and Mohri 1985; Kakegawa *et al* 1997). Dielectric, pyroelectric and piezoelectric properties of PZT ceramics are strongly sensitive to Zr/Ti ratio. And the environment pollution due to the volatility of lead oxide during high temperature sintering is also a serious problem (Hayashi and Tomizawa 2004). The low-temperature fabrication of PZT ceramics using low-melting point additives as sintering aids can solve these problems. Many researchers have already investigated the low temperature sintering; liquid-phase sintering has been proved as an effective method for reducing sintering temperature. However, only few methods explained all the reactions and basic mechanisms of low-temperature sintering clearly and no general principles have been described (Hayashi *et al* 1999; Hu *et al* 2000; Han and Jeong 2006; Francios *et al* 2007).

In the present work, low temperature sintering of quaternary piezoelectric ceramics using CuO as sintering aid is described. It was found that the addition of CuO significantly decreased the sintering temperature from 1250 to 970 °C.

The structure, dielectric and piezoelectric properties were also investigated.

2. Experimental

The specimens were synthesized using a conventional mixed-oxide process. The quaternary compositions used in this study were as follows: $\text{Pb}[(\text{Mn}_{1/3}\text{Sb}_{2/3})_{0.06}(\text{Ni}_{1/2}\text{W}_{1/2})_{0.02}(\text{Zr}_{0.49}\text{Ti}_{0.51})_{0.92}]\text{O}_3 + x$ wt% CuO ($x = 0.0, 0.3, 0.5, 0.7, 1.0$, respectively) (abbreviated as PMS–PNW–PZT). The raw materials such as Pb_3O_4 , ZrO_2 , TiO_2 , MnO_2 , Sb_2O_3 , Ni_2O_3 and WO_3 for the given compositions were weighed by mole ratio and the powders were ball-milled for 4 h. After drying, they were calcined at 850 °C for 2 h. Thereafter, CuO was added, ball-milled and dried again. After polyvinyl alcohol (PVA: 5%) was added to the dried powders, the powders were molded by a pressure of 100 MPa in a mold which has a diameter of 15 mm, burned out at 735 °C and then sintered at 940–100 °C for 2 h.

For measuring the piezoelectric characteristics, specimens were polished to 1 mm thickness and then silver paste was printed on both sides of the polished specimens. Firstly, at 830 °C for 1 h, the electrode deposited poling was carried out at 120 °C in silicon-oil bath by applying direct current field of 3 kV/mm for 30 min. All samples were aged for 24 h before measuring the piezoelectric and dielectric properties.

Bulk density was measured using an Archimedeian method. The microstructure of the sintered bodies was observed using a scanning electron microscope (SEM Model Quanta 200, FEI Company). The calcined powders and sintered ceramics were examined by X-ray diffractometer (XRD Model DMX-2550/PC, Rigaku, Japan) to determine the crystalline phase. The dielectric properties were obtained

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by measuring capacitance and dielectric loss at 1 kHz at room temperature using LCR meter (HP Model 4294A). The piezoelectric constant (d_{33}) was measured using a quasi-static piezoelectric d_{33} meter (Model ZJ-3d, Institute of Acoustics Academic Sinica, China). The electromechanical coupling factor (k_p) and the mechanical quality factor (Q_m) were determined by the resonance–antiresonance technique on the basis of IEEE standards using an impedance analyser (HP Model 4294A) and the calculated equation of Q_m is as follows.

The k_p and Q_m were calculated by the resonance–antiresonance method on the basis of IEEE standards using an impedance analyser (HP Model 4294A) based on the following relations and IEEE standards (1987):

$$k_p = \left[\frac{\eta_1^2 - [1 - (\sigma^E)^2]}{2(1 + \sigma^E)} \times \frac{f_a^2 - f_{s1}^2}{f_a^2} \right]^{1/2}, \quad (1)$$

$$Q_m = f_a^2 [2\pi R_f C f_r (f_a^2 - f_r^2)]^{-1}, \quad (2)$$

$$\sigma^E = \frac{5.332f_r - 1.867f_{s1}}{0.6054f_{s1} - 0.1910f_r}, \quad (3)$$

$$\eta_1 = 1.867 + 0.6054\sigma^E, \quad (4)$$

where f_a is the antiresonant frequency, f_r the resonant frequency, f_{s1} the first overtone resonant frequency, R_f and C are resonant impedance (ohm) and electrical capacitance (farad). The impedance vs frequency spectra of ceramics was measured by the impedance analyser at room temperature. The sweeping frequency is set from 150 to 215 kHz. σ^E is Poisson's ratio (the superscript 'E' means the boundary conditions are short circuited) and η_1 the frequency constant of a disk resonator.

3. Results and discussion

Figure 1 shows bulk density and porosity of PMS–PNW–PZT sintered bodies with 0.7 wt% CuO addition as a function of sintering temperature. With increase in sintering temperature, the density increases at first and reaches a high value (7.75 g/cm³). When CuO temperature is above 970 °C, the density changes a little. The addition of CuO improved sinterability and lowered their sintering temperature by more than 250 °C. The lower sintering temperature is mainly attributed to the liquid-phase sintering. The densification sintering temperature of 0.7 wt% CuO doping specimen is 970 °C, however, CuO has a high melting point of 1336 °C (Katarina and Anthony 2000), so it can be inferred that it is not CuO alone that produces the liquid phase. From the phase diagram, it can be concluded that CuO and PbO forms liquid phase eutectic at 812 °C. During post-sintering, Cu²⁺ and Pb²⁺ enter into the main crystal lattice to form perovskite solid solution. However, a large amount of this liquid

Figure 1. Bulk density and porosity as a function of sintering temperature.

phase leads to the agglomeration at grain boundary. This kind of impurity agglomeration can lower the density and deteriorate the properties of ceramics, so the appropriate amount of CuO doping is necessary. It is obvious that the radius of Cu²⁺ (0.073 nm) ions is similar to that of Zr⁴⁺ and Ti⁴⁺ ions (0.072 and 0.061 nm, respectively) (Cotton *et al* 1995). In view of the radius, Cu²⁺ ions enter the B site as acceptor. The replacement by Cu²⁺ causes distortion of lattice. The loose structure can be sintered easily and this makes the grain size to increase. A consecutive increase in the amount of Cu²⁺ addition would make the grain size decrease, because the growth of grains was significantly inhibited by the excessive content of Cu²⁺ segregating at grain boundaries which exerted a drag force against the grain boundary movement (Hou *et al* 2004).

It is clearly shown in figure 2, that the particle size of different amounts of CuO-doped samples was almost the same. With the addition of CuO, the porosity decreased and the packing density increased. Figure 2(a and b) presents mostly intergranular fracture, whereas figure 2(c and d) shows partly transgranular fracture. It is believed that the grain boundaries were mechanically weaker than the grains when CuO doping was under 0.5 wt%. As CuO doping amount is increased to 0.7 wt%, the main fracture mechanism was partly transgranular fracture, which can be explained that the solubility of Cu ion in solid solution was limited, excessive CuO concentrated in the grain boundary and enhance the intensity of the grain boundary. In particular, the introduction of CuO additive into PMS–PNW–PZT promoted the densification in the low sintering temperature of 970 °C, which was attributable to the liquid phase sintering. Binary combination of PbO and CuO in grain boundary increased the tendency to form amorphous phase below 900 °C and this amorphous phase formed during liquid-phase sintering and allowed rapid densification of PZT ceramics (Han and Jeong 2006).

Figure 3 shows XRD patterns of PMS–PNW–PZT with different amounts of CuO addition sintered at 970 °C. From

figure 3, it can be seen that all the diffraction peaks correspond to the pure perovskite XRD standard spectrum, with no second phase. At the same time, crystal structure of the specimens is modified profoundly by the addition of CuO.

The lattice parameters (a , c) of the specimens have been evaluated from the diffraction patterns which are shown in figure 4. The contraction of c -axis and simultaneous extension of a -axis are observed, which can be explained by the Jahn–Teller effect. Cu ion exists mainly in the state of

Cu^{2+} , which can enter into perovskite structure of BO_6 octahedron to substitute B -site ions (e.g. Ti^{4+} and Zr^{4+} ions). Cu^{2+} adopts the asymmetrical configuration— $(t_{2g})^6(e_g)^3$ in octahedron structure, so it is classified as a Jahn–Teller ion.

Figure 5 shows splitting of the orbital of Cu^{2+} ion from Jahn–Teller effect. As seen from figure 5, there is an uncoupled d -electron occupying the orbital of d_z^2 , thus, the electron cloud density in z -direction is lower than that in xy -plane and strength of the shielding effect on electrostatic attraction

Figure 2. SEM micrographs of different CuO contents sintered at 970 °C for 2 h: (a) 0.3 wt%; (b) 0.5 wt%; (c) 0.7 wt% and (d) 1.0 wt%.

Figure 3. XRD patterns of ceramics sintered at 970 °C as a function of CuO content.

Figure 4. Variation of lattice parameter as a function of CuO content.

Figure 5. Splitting of orbital of Cu^{2+} ion from Jahn-Teller effect.

Figure 6. ϵ_r (1 kHz) as a function of temperature with different CuO dopings.

of Cu^{2+} with two O^{2-} ligands in z -direction is weaker than that of Cu^{2+} with four O^{2-} ligands in xy -plane. Due to this uneven shielding effect in z -direction and xy -plane, the two O^{2-} ligands in z -direction are more near to the centre of CuO_6 octahedron than the four O^{2-} ligands in xy -plane, which results in the contraction of c -axis and the extension of a -axis. However, when the addition of CuO is above 0.7 wt%, variation of the lattice parameters becomes weak as the redundant CuO accumulates at the grain boundary without entering into lattice.

Figure 6 shows temperature dependence of dielectric constant as a function of CuO content. With increasing CuO doping, Curie temperature (T_c) of PZT becomes lower and consequently, the peak of the dielectric spectrum moves toward low temperature corresponding to Curie temperature. The composition with 0.7 wt% CuO shows highest peak dielectric constants, which appears at about 281 °C.

Figure 7 shows changes of $\tan \delta$ and Q_m as a function of CuO content sintered at 970 °C. To apply piezoelectric ceramics as ultrasonic wavemotors or piezoelectric transformers, it is necessary to lower $\tan \delta$ and improve Q_m as

Figure 7. Variation of $\tan \delta$ and Q_m as a function of CuO content.

Figure 8. d_{33} , k_p and ϵ_r as a function of CuO content sintered at 970 °C.

much as possible for suppressing the generation of heat during operation. As shown in figure 7, the acceptor dopant of CuO reduces dielectric loss and improves Q_m simultaneously. The lowest value (0.15%) of $\tan \delta$ and the highest value (1830) of Q_m are obtained in the ceramics with CuO amounts of 0.7 wt%, respectively. Further addition of CuO above 0.7 wt% leads to an increase in the value of $\tan \delta$. It is well known that the substitutions of $(\text{Ti}, \text{Zr})^{4+}$ by acceptor dopant Cu^{2+} ions will lead to the creation of oxygen vacancies, which pin the movement of the ferroelectric domain walls and result in an increase of Q_m and a decrease of $\tan \delta$.

Figure 8 shows changes of the piezoelectric constant (d_{33}), electromechanical coupling factor (k_p) and relative dielectric constant (ϵ_r) as a function of amount of CuO addition. As can be seen, both k_p and d_{33} show a similar variation with increasing CuO content. When the amount of CuO is higher than 0.5 and 0.7 wt%, d_{33} and k_p are rapidly decreased with increasing CuO content, respectively. The improvement of the dielectric and piezoelectric properties of the ceramics after adding small amounts of CuO is mainly due to the mechanisms of densification. During sintering, the presence of CuO liquid phase enhances the density, which leads to

the decrease of energy loss and improvement of the electrical properties and deterioration of the values ($\tan \delta$, k_p , d_{33} and ε_r) can be contributed to the decreasing density of the ceramics by adding larger amount of CuO.

4. Conclusions

The quaternary PMS–PNW–PZT piezoelectric ceramics with additions of small amounts of CuO were successfully prepared by conventional way sintered at temperatures from 950 to 1100 °C. The addition of CuO significantly lowered the sintering temperature by 250 °C. PMS–PNW–PZT ceramics sintered at 970 °C for 2 h with 0.7 wt% CuO exhibited $\varepsilon_r = 1845$, $\tan \delta = 0.15\%$, $d_{33} = 395$ pC/N, $k_p = 0.58$ and $Q_m = 1830$. With increasing CuO doping, T_c becomes less. The solubility of CuO in solid solution is limited, only a portion of CuO can enter the lattice, Cu^{2+} replaces the $(\text{Ti}, \text{Zr})^{4+}$, the constant c decreases while a increases and the ratio of c/a decreases. The remaining CuO concentrated in the grain boundary to enhance the intensity and density of ceramics. The low-temperature sintered piezoelectric ceramics revealed excellent electrical properties for application in highly reliable ceramic electronic devices.

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