



Effect of CuO on the sintering temperature and piezoelectric properties of MnO₂-doped 0.75Pb(Zr_{0.47}Ti_{0.53})O₃-0.25Pb(Zn_{1/3}Nb_{2/3})O₃ ceramics

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ABSTRACT

The sintering temperature of 0.75Pb(Zr_{0.47}Ti_{0.53})O₃-0.25Pb(Zn_{1/3}Nb_{2/3})O₃ ceramics containing 1.5 mol% MnO₂ was decreased from 930 to 850 °C with the addition of CuO. The CuO reacted with the PbO and formed a liquid phase during the sintering, which assisted the densification of the specimens. Most of the Cu²⁺ ions existed in the CuO second phase, thereby preventing any possible hardening effect from the Cu²⁺ ions. Variations of the k_p , Q_m , $\varepsilon_3^T/\varepsilon_0$ and d_{33} values with CuO were similar to that of the relative density. The specimen containing 0.5 mol% CuO sintered at 850 °C showed the good piezoelectric properties of $k_p = 0.5$, $Q_m = 1000$, $\varepsilon_3^T/\varepsilon_0 = 1750$ and $d_{33} = 300$ pC/N.

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1. Introduction

Hard piezoelectric ceramics, which can be used for ultrasonic motors, transformers and actuators, have attracted increasing research attention because of the wide range applications of these high power devices [1,2]. For such high powder applications, these hard piezoelectric ceramics require a high mechanical quality factor (Q_m), a high electromechanical coupling factor (k_p), high Curie temperature and low dielectric dissipation factors ($\tan \delta$) [3–6]. Furthermore, devices with a multilayer structure have been developed for the miniaturization and performance enhancement of electronic devices [7]. For multilayer devices, the sintering temperature of high power piezoelectric ceramics should be less than 900 °C to allow the use of cheap Ag metal as an electrode instead of expensive Ag–Pd metal. Pb(Zr_{1-x}Ti_x)O₃ (PZT)-based piezoelectric materials have been used in high power devices [8–11]. In particular, Pb(Mn_{1/2}Nb_{2/3})O₃ and Pb(Fe_{2/3}W_{1/3})O₃ or CeO₂ additives are often used to increase the Q_m value of the PZT-based materials up to 2000 [12,13]. However, the high sintering temperature of these ceramics approximately 1100 °C necessitates the use of expensive Ag–Pd metal for the electrode rather than cheap Ag for application to multilayer devices. Therefore, Li₂CO₃, BiFeO₃, LiBiO₂, and CuO additives have been used to lower the sintering temperature

[12,14–16]. However, such additives degraded the piezoelectric properties.

The solid solution of lead zinc niobate (PZN) and PZT ceramics has recently been reported to have a relatively low sintering temperature [17,18]. Moreover, the Q_m value of the PZT–PZN solid solution has been increased by MnO₂ addition because the Mn ions entered the B-sites of the PZT-based ceramic and acted as a hardener [19,20]. However, the sintering temperature of these ceramics remained too high (~930 °C) for the use of Ag metal as an electrode because of the 961 °C melting temperature of Ag. Therefore, the sintering temperature of these PZT–PZN ceramics needs to be further decreased well below 900 °C to enable the use of Ag metal as an electrode. In this work, therefore, CuO was used to reduce the sintering temperature of the 1.5 mol% MnO₂-added 0.75Pb(Zr_{0.47}Ti_{0.53})O₃-0.25Pb(Zn_{1/3}Nb_{2/3})O₃ (0.75PZT-0.25PZN–Mn) ceramics below 900 °C, while maintaining good piezoelectric properties. Furthermore, the micro-structural variation of the resulting ceramics was studied and the reaction between the Ag electrode and the CuO-added 0.75PZT-0.25PZN–Mn ceramic sintered at 850 °C was also investigated.

2. Experimental procedure

The 0.75PZT-0.25PZN ceramics were prepared from oxides of with a purity > 99% using a conventional solid-state synthesis. Oxide compounds of PbO, ZrO₂, TiO₂, ZnO, and Nb₂O₅ (all from High Purity Chemicals, >99%, Japan) were mixed for 24 h in a nylon jar with zirconia balls and then dried. The dried powders were calcined at

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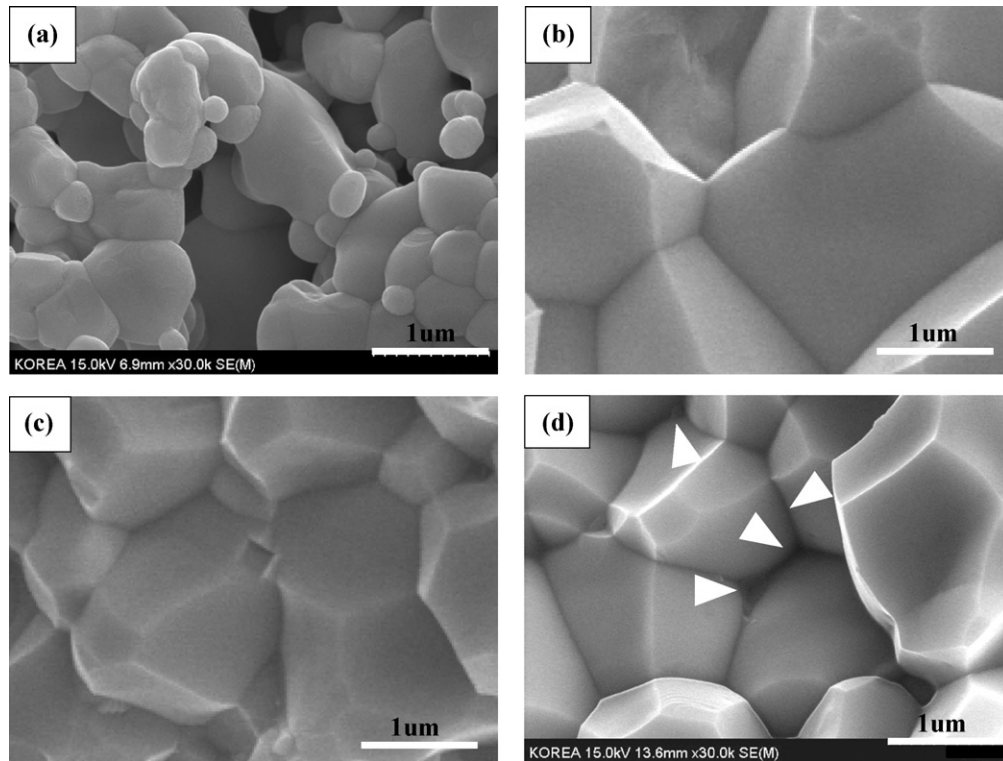


Fig. 1. SEM images of the 0.75PZT–0.25PZN–Mn+x mol% CuO ceramics sintered at 850 °C for 4 h: (a) $x=0.0$, (b) $x=0.5$, (c) $x=3.0$, and (d) $x=5.0$.

880 °C for 4 h. After re-milling with MnO₂ and CuO (High Purity Chemicals, >99%, Japan) additives, the powders were dried and pressed into discs under a pressure of 100 kgf/cm² and sintered at 850–950 °C for 4 h. The structural properties of the specimens were examined by X-ray diffraction (XRD: Rigaku D/max-RC, Tokyo, Japan) and scanning electron microscopy (SEM: Hitachi S-4300, Osaka, Japan). The densities of the sintered specimens were measured by a water-immersion, Archimedes-principle technique. A silver electrode was printed on the lapped surfaces, and the specimens were poled in silicone oil at 120 °C by applying a DC field of 4.0 kV/mm for 30 min. The piezoelectric and dielectric properties and the k_p value were determined using a d_{33} meter (Micro-Epsilon Channel Product DT-3300, Raleigh, NC) and an impedance analyzer (Agilent Technologies HP 4294A, Santa Clara, CA) on the basis of IEEE standards.

3. Results and discussion

Fig. 1(a)–(d) shows the SEM images of the 0.75PZT–0.25PZN–Mn+x mol% CuO ceramics, with $0.0 \leq x \leq 5.0$, sintered at 850 °C for 4 h. For the specimen with $x=0.0$, a porous microstructure was developed, as shown in Fig. 1(a), but a dense microstructure was formed when CuO was added (see Figs. 1(b)–(d)). A homogeneous phase was formed for the specimens containing up to 3.0 mol% CuO. However, at 5.0 mol% a second phase was formed along the grain boundary and the triple point of the specimen, as indicated by the arrowhead in Fig. 1(d), revealing that liquid phase sintering was responsible for the formation of the dense microstructure for the CuO-added specimens sintered at 850 °C. Moreover, since CuO and PbO form the eutectic point at approximately 790 °C [21], the second phase found in the specimen with $x=5.0$ was considered to contain both CuO and PbO.

Fig. 2(a)–(e) shows the XRD patterns of the 0.75PZT–0.25PZN–Mn+x mol% CuO ceramics with $0.0 \leq x \leq 5.0$ sintered at 850 °C for 4 h. All the specimens had a tetragonal perovskite structure and a homogeneous tetragonal perovskite phase was observed for the specimens with $x \leq 3.0$. However, a CuO peak was observed for the specimen with $x=5.0$, indicating that the second phase found in the SEM image shown in Fig. 1(d) is CuO.

Therefore, the added CuO reacted with the PbO to form a liquid phase, which assisted the densification of the specimen during the sintering. Moreover, most of the Pb²⁺ ions were incorporated into the matrix during the cooling and only the CuO remained in the grain boundary, as shown in Fig. 1(d). Since the most of the Cu²⁺ ions remained in a CuO second phase instead of being incorporated into the matrix, the hardening effect of the Cu²⁺ ions was negligible in the 0.75PZT–0.25PZN–Mn ceramics, as discussed below.

Fig. 3(a) show a plot of the induced polarization versus electric field for the 0.75PZT–0.25PZN–Mn+x mol% CuO ceramics with $0.0 \leq x \leq 3.0$ sintered at 850 °C for 4 h. A low remnant polarization (P_r) of 7.9 $\mu\text{C}/\text{cm}^2$ was observed for the specimen with $x=0.0$ because of the porous microstructure. The P_r value increased with

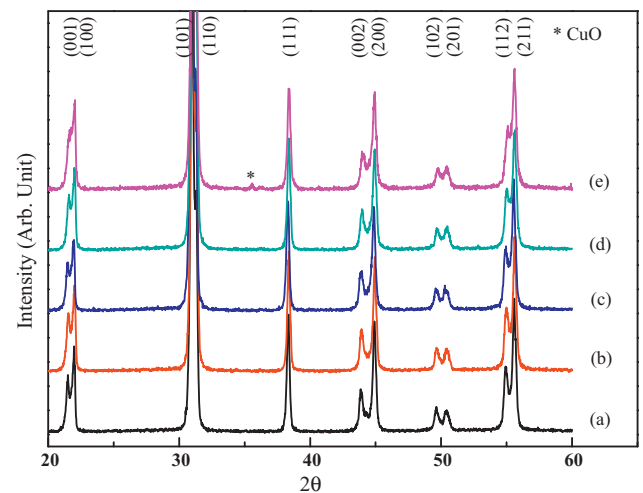


Fig. 2. XRD patterns of the 0.75PZT–0.25PZN–Mn+x mol% CuO ceramics sintered at 850 °C for 4 h: (a) $x=0.0$, (b) $x=0.5$, (c) $x=1.5$, (d) $x=3.0$ and (e) $x=5.0$.

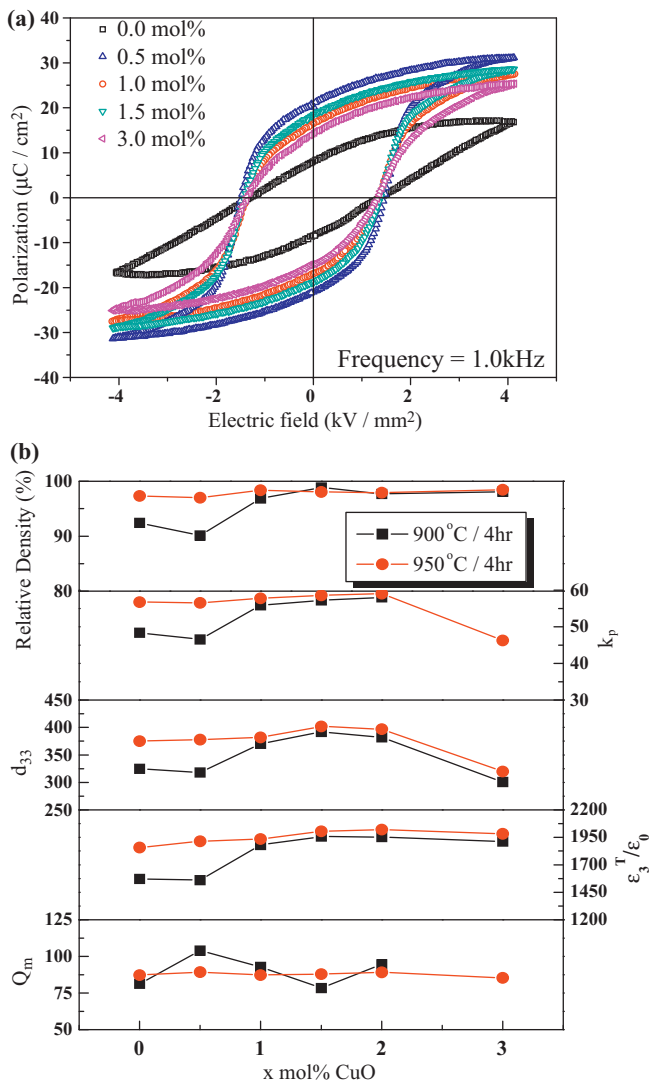


Fig. 3. (a) Plot of the induced polarization versus electric field for the 0.75PZT–0.25PZN–Mn+x mol% CuO ceramics with $0.0 \leq x \leq 3.0$ sintered at 850°C for 4 h and (b) variations of relative density, and k_p , d_{33} , ϵ_3^T/ϵ_0 , and Q_m values of the CuO-added 0.75PZT–0.25PZN ceramics sintered at 900 and 950°C .

small CuO addition to a maximum of $20.0 \mu\text{C}/\text{cm}^2$ for the specimen with $x=0.5$, due to the formation of a dense microstructure. However, it decreased with further increase of the CuO content, probably due to the existence of the CuO second phase. The coercive electric field (E_c) of the 0.75PZT–0.25PZN–Mn was approximately $1.2 \text{ kV}/\text{mm}$ and its variation was insignificant with CuO addition. If Cu^{2+} ions replaced the Ti^{4+} (or Nb^{5+}) ions, then it would be considered that E_c had increased because of the hardening effect of the Cu^{2+} ions. However, the negligible increase of E_c with CuO addition confirmed that most of the Cu^{2+} ions existed in the CuO second phase. In order to clarify the effect of CuO, the CuO-added 0.75PZT–0.25PZN ceramics were sintered at 900 and 950°C and their relative density, and k_p , d_{33} , ϵ_3^T/ϵ_0 , and Q_m values were measured, as shown in Fig. 3(b). The relative density of the 0.75PZT–0.25PZN ceramics sintered at 900°C was low but increased with CuO addition, probably due to the formation of the CuO–PbO related liquid phase during the sintering. The d_{33} and k_p values were low for the 0.75PZT–0.25PZN ceramics sintered at 900°C but they increased with CuO addition up to 2.0 mol% because of the increased relative density. However, they decreased when the CuO content exceeded 2.0 mol%, probably due to the formation

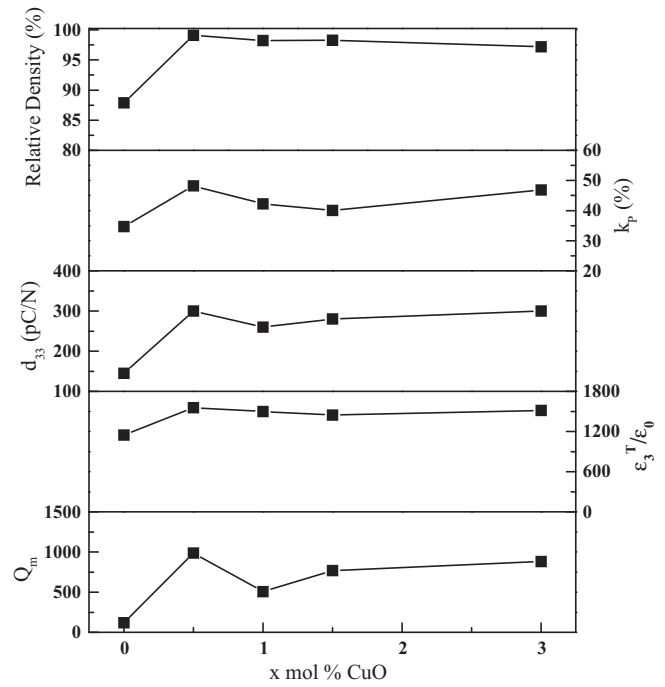


Fig. 4. Relative density, and k_p , d_{33} , ϵ_3^T/ϵ_0 , and Q_m values of the 0.75PZT–0.25PZN–Mn+x mol% CuO ceramics with $0.0 \leq x \leq 3.0$ sintered at 850°C for 4 h.

of a large amount of liquid phase. On the other hand, the Q_m value of the 0.75PZT–0.25PZN ceramics was low and its variation with the CuO content was not significant, as shown in Fig. 3(b), revealing the negligible hardening effect of the Cu^{2+} ions in the CuO-added 0.75PZT–0.25PZN ceramics.

Fig. 4 shows the variations in the relative density, and k_p , d_{33} , ϵ_3^T/ϵ_0 , and Q_m values of the 0.75PZT–0.25PZN–Mn+x mol% CuO ceramics with $0.0 \leq x \leq 3.0$ sintered at 850°C for 4 h. The relative density of the specimen with $x=0.0$ was very low but increased with increasing CuO content to a maximum value of 99.0% of the theoretical density for the specimen with $x=0.5$. Variations of the d_{33} , k_p and ϵ_3^T/ϵ_0 values according to CuO content were very similar to that of the relative density, and maximum values of 300 pC/N, 0.5 and 1750, respectively, were found in the specimen with $x=0.5$, revealing the strong dependence of these values on the relative density. The Q_m value of the specimen with $x=0.0$ was very low, due to the low density. It increased with CuO addition because of the increased relative density to a maximum Q_m value of 1000 for the specimen with $x=0.5$. This Q_m value, however, was similar to that of the 0.75PZT–0.25PZN–Mn ceramics sintered at 930°C [19], indicating that the high Q_m value of the CuO-added 0.75PZT–0.25PZN–Mn ceramics was mainly due to the hardening effect of the Mn ions. According to the previous works, most of the Mn ions existed as Mn^{3+} in the PZT-based piezoelectric ceramics at the temperatures between 535 and 1080°C [22,23]. Moreover, since all the specimens in this work were sintered at 850 – 950°C , most of the Mn ions were considered to exist as the Mn^{3+} ions and behave as the hardeners in the CuO-added 0.75PZT–0.25PZN–Mn ceramics.

The reaction between the Ag electrode and the CuO-added 0.75PZT–0.25PZN–Mn ceramics was also investigated. Fig. 5(a) shows the XRD pattern of the 0.5 mol% CuO-added 0.75PZT–0.25PZN–Mn (Cu–0.75PZT–0.25PZN–Mn) ceramics sintered with Ag metal at 850°C . Peaks for the Cu–0.75PZT–0.25PZN–Mn ceramic and the Ag metal were observed without any peaks for a second phase. The interface between the Ag metal and the Cu–0.75PZT–0.25PZN–Mn ceramic was also studied using SEM and energy dispersive X-ray spectroscopy (EDS) line

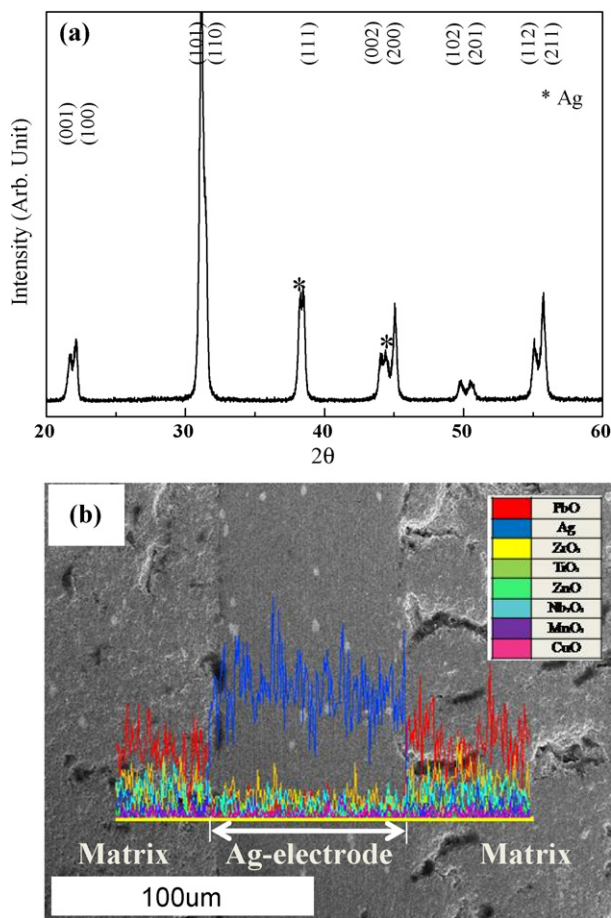


Fig. 5. (a) XRD pattern of the Cu-0.75PZT-0.25PZN-Mn ceramics sintered with Ag metal at 850 °C and (b) SEM image and EDS line scan of the interface between the Cu-0.75PZT-0.25PZN-Mn ceramics and the Ag metal.

scan, as shown in Fig. 5(b). This interface was well developed and the silver profile sharply decreased at the interface, indicating the absence of any silver diffusion into the Cu-0.75PZT-0.25PZN-Mn ceramic. Moreover, the very low concentrations of Pb, Zr, Zn, Ti and Nb in the Ag metal suggested the absence of any reaction between the Ag metal and the Cu-0.75PZT-0.25PZN-Mn ceramic. This demonstrated the potential of the Cu-0.75PZT-0.25PZN-Mn ceramic as a promising hard piezoelectric material candidate for low temperature co-fired ceramic (LTCC) devices.

4. Conclusions

The 0.75PZT-0.25PZN-Mn ceramics were well sintered at 850 °C with small CuO addition. A second phase identified as CuO was found in the specimen containing 5.0 mol% CuO. Therefore, the CuO was considered to react with PbO and form a liquid phase during the

sintering, which assisted the densification of the specimen. Moreover, most of the Pb^{2+} ions entered the matrix of the specimen, resulting in the CuO second phase. The P_r value increased with CuO addition due to the increased relative density but the variation of E_c with CuO content was insignificant. The relative density, and k_p and d_{33} values of the CuO-added 0.75PZT-0.25PZN ceramics increased with CuO addition, due to the densification of the specimen. However, the Q_m value of these ceramics was unaffected by CuO addition, revealing the negligible hardening effect of the Cu^{2+} ions in this specimen. The variations of the d_{33} , k_p and ϵ_3^T/ϵ_0 values of the 0.75PZT-0.25PZN-Mn ceramics sintered at 850 °C with respect to CuO content were very similar to that of the relative density, and maximum d_{33} , k_p and ϵ_3^T/ϵ_0 values of 300 pC/N, 0.5 and 1750, respectively, were found in the specimen with $x=0.5$. A maximum Q_m value of 1000 was obtained for the specimen with $x=0.5$. The CuO-added 0.75PZT-0.25PZN-Mn ceramics were sintered with Ag metal at 850 °C and no reaction between the Ag metal and the Cu-0.75PZT-0.25PZN-Mn ceramic was found.

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