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Piezoelectric properties of low temperature sintering in $Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$ ceramics for piezoelectric transformer applications

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Abstract

In this study, in order to develop low-temperature sintering ceramics for a multilayer piezoelectric transformer application, we explored CuO and Bi_2O_3 as sintering aids at low temperature (900 °C) sintering condition for Sb, Li and Mn-substituted $0.8Pb(Zr_{0.48}Ti_{0.52})O_3$–$0.16Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.04Pb(Ni_{1/3}Nb_{2/3})O_3$ ceramics. These substituted ceramics have excellent piezoelectric and dielectric properties such as $d_{33} \sim 347$ pC/N, $k_p \sim 0.57$ and $Q_m \sim 1469$ when sintered at 1200 °C. The addition of CuO decreased the sintering temperature through the formation of a liquid phase. However, the piezoelectric properties of the CuO-added ceramics sintered below 900 °C were lower than the desired values. The additional Bi_2O_3 resulted in a significant improvement in the piezoelectric properties. The composition Sb, Li and Mn-substituted $0.8Pb(Zr_{0.48}Ti_{0.52})O_3$–$0.16Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.04Pb(Ni_{1/3}Nb_{2/3})O_3$ + 0.5 wt% CuO + 0.5 wt% Bi_2O_3 showed the value of $k_p = 0.56$, $Q_m = 1042$ (planar mode), $d_{33} = 350$ pC/N, when it was sintered at 900 °C for 2 h. These values indicated that the newly developed composition might be suitable for multilayer piezoelectric transformer application.

Keywords: Low temperature sintering; Piezoelectric transformer and vibration velocity

1. Introduction

The materials for piezoelectric actuators, ultrasonic motors and piezoelectric transformers applications should have compromised characteristics between hard and soft piezoelectrics, implying high electromechanical coupling factor (k) and piezoelectric constant (d) with high mechanical quality factor (Q_m) [1].

However, the sintering temperature of lead zirconate titanate (PZT)-based high-power compositions is usually too high, approximately 1200 °C, to use base metal electrodes such as Ag and Cu. Therefore, Ag/Pd alloy is generally used as the electrode to suppress the migration of Ag into the ceramics at high temperature. Consequently, lowering of the sintering temperature of piezoelectric ceramics is essential for the fabrication of cost-effective multilayer piezoelectric devices. Furthermore, low temperature sintering can provide advantages such as compatibility with low temperature cofired ceramics (LTCC), the reduction of energy consumption, and the reduced PbO volatilization.

Previously, various techniques were employed to obtain the low temperature sinterable PZT composition. The addition of dopants, which improves solid-state sintering, and the addition of oxides and compounds, which have low melting points for liquid-phase sintering are the most popular methods [2–4]. Some of the oxides and compounds that have been used for assisting liquid-phase sintering [5–9]. Even though these techniques were able to obtain dense ceramics at low sintering temperature, piezoelectric properties were not satisfactory enough to be used in industry.

Previously, we developed the Sb, Li and Mn-substituted $Pb(Zr_{0.48}Ti_{0.52})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$ ceramics with excellent dielectric and piezoelectric properties when sintered at 1200 °C [10]. The aim of this study was to

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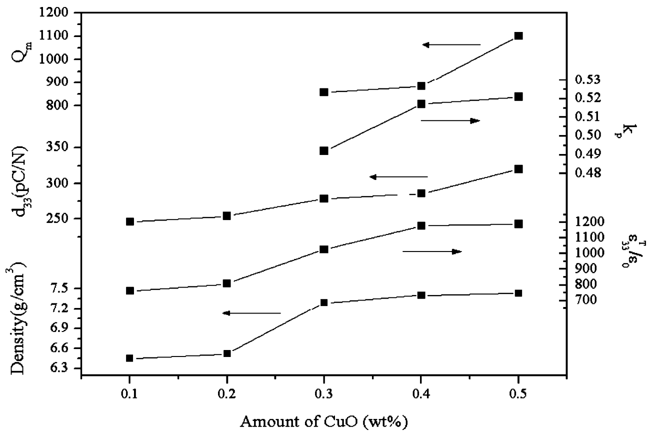

Fig. 1. Density, dielectric permittivity ($\varepsilon_{33}^{T}/\varepsilon_0$), piezoelectric constant (d_{33}), electromechanical coupling factor (k_p) and mechanical quality factor (Q_m) and of the specimens sintered at 900 °C for 2 h in $Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$ + x wt% CuO ceramics.

lower the sintering temperature of this composition for providing Ag or Cu cofiring compatible high-power piezoelectric ceramics, aiming at layered structure piezoelectric actuators and transformer applications. We therefore investigated the effect of CuO and Bi_2O_3 addition in the Sb, Li and Mn-substituted $Pb(Zr_{0.48}Ti_{0.52})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$ ceramics as a solution for low temperature sinterable high power ceramics.

2. Experimental procedure

The specimens studied in this research were fabricated according to the formula: $0.8Pb(Zr_{0.48}Ti_{0.52})O_3$–$0.16Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.04Pb(Ni_{1/3}Nb_{2/3})O_3$ with Sb, Li and Mn substitution ($Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$) + x wt% CuO + y wt% Bi_2O_3, where $x = 0.1$–0.5; $y = 0$–0.5, respectively. Raw materials of PbO, ZrO_2, TiO_2, ZnO, NiO, Nb_2O_5, Sb_2O_5, Li_2CO_3, MnO_2, CuO and Bi_2O_3 with >99% purity were used to prepare samples by a conventional ceramic sintering process. The obtained mixture was ball-milled using zirconia ball media with isopropanal as a medium in a polyethylene jar for 24 h. The mixed slurry was dried and calcined at 750 °C for 2 h. The calcined powders were ball-milled again with additives and consolidated into disks of 12.5 mm diameter and rectangular plates using isostatic pressing about 150 MPa. PbO-rich atmosphere sintering of the ceramics was performed in a high-purity alumina crucible at the temperature of 850–900 °C for 2 h. The crystal structure and symmetry of the sintered bodies were examined by X-ray diffraction (XRD) and sintered densities were measured by the Archimedes method. Silver electrode (Dupont, QS 171) was printed on the lapped surfaces for electrode. The electrode specimens were poled in silicone oil at 150 °C by applying a dc field of 3 kV/mm for 30 min. 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 planar coupling coefficient (k_p)

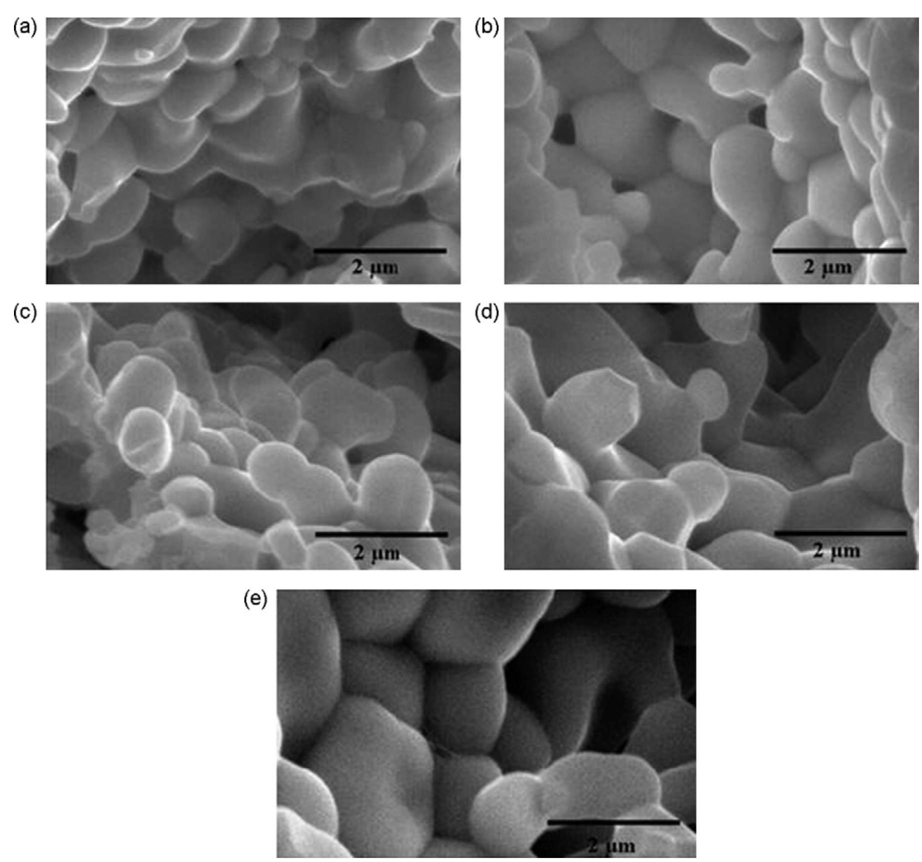

Fig. 2. SEM images of the samples sintered at 900 °C for 2 h in $Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$ + x wt% CuO ceramics.: (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$, (d) $x = 0.4$ and (e) $x = 0.5$.

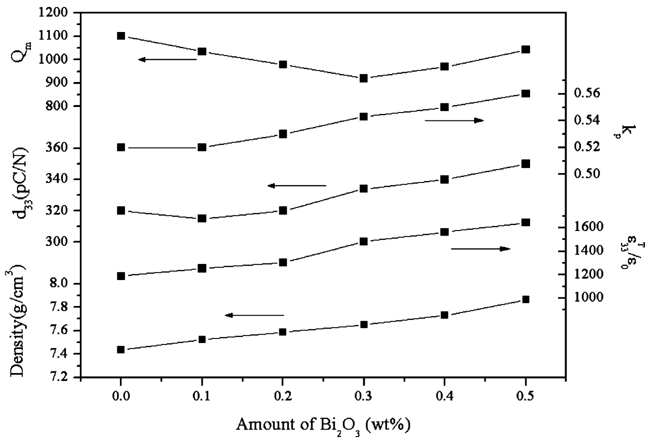

Fig. 3. Density, dielectric permittivity ($\varepsilon_{33}^T/\varepsilon_0$), piezoelectric constant (d_{33}), electromechanical coupling factor (k_p) and mechanical quality factor (Q_m) and of the specimens sintered at 900 °C for 2 h in $Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$ + 0.5 wt% CuO + y wt% Bi_2O_3 ceramics.

and the mechanical quality factor (Q_m) were determined by the resonance and anti-resonance technique using an impedance analyzer (Model HP4294A, Hewlett-Packard, CA).

3. Results and discussion

3.1. Effect of CuO addition

Initially, the effect of the addition of CuO on the sinterability, crystal structure, piezoelectric and dielectric properties was investigated in $Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$-based ceramics. The sintering temperature of all the specimens was fixed at 900 °C, which is cofiring compatible temperature for Ag and low temperature cofired ceramics (LTCC) substrate. Density, dielectric permittivity ($\varepsilon_{33}^T/\varepsilon_0$), electromechanical coupling factor (k_p), mechanical quality factor and piezoelectric constant (d_{33}) were plotted as a function of the amount of CuO addition in Fig. 1. The density was increased with the increase of CuO contents approximately from 6.4 to 7.8 g/cm^3. This improvement of the density might be related to the formation of the liquid phase. Moreover, the variation of piezoelectric and dielectric properties showed similar trend to that of density. Therefore, the improved piezoelectric and dielectric properties, which were observed in the range of $x \geq 0.3$, might be due to the increased density as well as increased grain size shown in Fig. 2. This hardening effect that could be confirmed by the enhancement of Q_m value approximately from 600 to 1200 as shown in Fig. 1. Therefore, Cu ions could be expected to enter B site and act as a hardener. Fig. 2 shows the SEM images of the $Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$ + x wt% CuO ceramics sintered at 900 °C for 2 h. As the CuO addition amount increased, grain growth happened whereas small grains disappeared. This grain growth with CuO addition can be explained with liquid phase sintering. Previously, we showed that the addition of CuO can reduce the sintering temperature of the $Pb(Zr,Ti)O_3$–$Pb(Ni,Nb)O_3$ system by the formation of a liquid phase [11]. Thus, this liquid phase formation can also be an explanation for the $Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$ + x wt% CuO ceramics.

3.2. Effect of Bi_2O_3 addition

Bi_2O_3 has low melting temperature (817 °C) and it was reported Bi_2O_3 can form liquid phase with ZnO at approximately 750 °C. Therefore, Bi_2O_3 was added to $Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$ + 0.5 wt% CuO in order to further improve the piezoelectric properties of the specimens sintered at low temperature. Density, dielectric permittivity ($\varepsilon_{33}^T/\varepsilon_0$), electromechanical coupling factor (k_p), mechanical quality

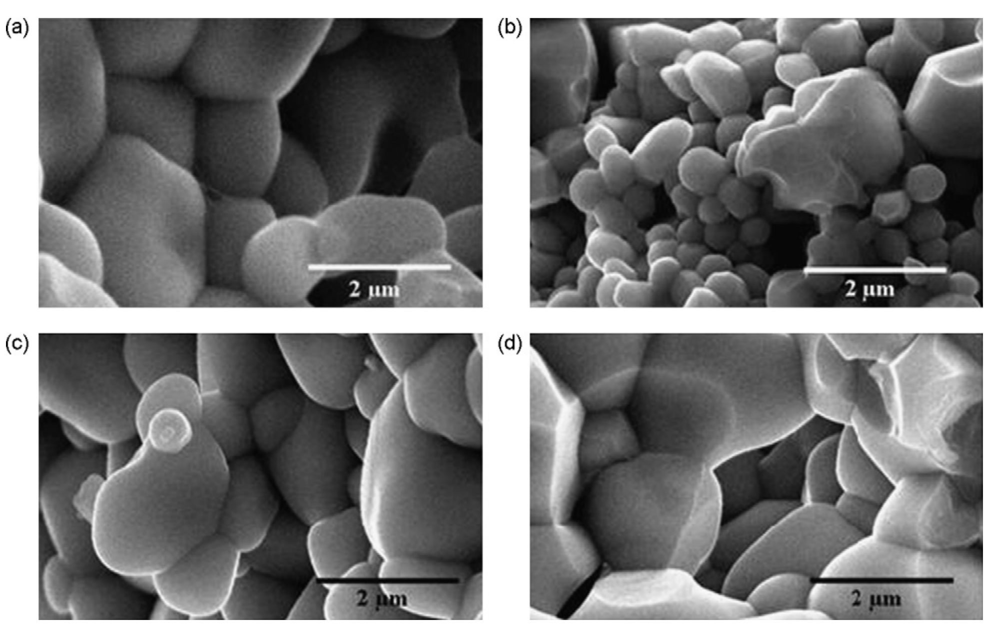

Fig. 4. SEM images of the samples sintered at 900 °C for 2 h in $Pb(Zr,Ti)O_3$–$Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$ + 0.5 wt% CuO + y wt% Bi_2O_3 ceramics.: (a) $y = 0$, (b) $y = 0.1$, (c) $y = 0.3$ and (d) $y = 0.5$.

factor and piezoelectric constant (d_{33}) of Pb(Zr,Ti)O_3–Pb(Zn,Ni)$_{1/3}$Nb$_{2/3}$$O_3$ + 0.5 wt% CuO + *y* wt% Bi_2O_3 ceramics sintered at 900 °C for 2 h are plotted as a function of the amount of Bi_2O_3 addition in Fig. 3. When Bi_2O_3 was added, density was increased and this increased density improved the dielectric and piezoelectric properties as seen in Fig. 3. The density of the specimens was improved when the amount of Bi_2O_3 was added and this increase might be due to the formation of liquid phase. In addition, Q_m was decreased and $\varepsilon_{33}^T/\varepsilon_0$ and d_{33} were increased with the amount of Bi_2O_3 addition in the range of $0.0 \leq y \leq 0.3$. Therefore, their variations could happen because Bi ions entered A site, since they acted as softener in this range. On the contrary, Q_m exhibits a minimum profile at 0.3 wt% of Bi_2O_3 addition. In addition, $\varepsilon_{33}^T/\varepsilon_0$, d_{33} and Q_m were increased with the amount of Bi_2O_3 addition above 0.3 wt%. Thus, Bi ions might act as both hardener and softener in this range and their variations might be able to occur because Bi ions entered B site and A site, respectively. Fig. 4 shows the SEM images of the Pb(Zr,Ti)O_3–Pb(Zn,Ni)$_{1/3}$Nb$_{2/3}$$O_3$ + 0.5 wt% CuO + *y* wt% Bi_2O_3 ceramics sintered at 900 °C for 2 h. When the amount of Bi_2O_3 was more than 0.3 wt%, the small grains almost disappeared and average grain size increased. Even though apparent liquid phase formation was not observed in the SEM images, Bi_2O_3 addition might induce small amount of liquid phase and it could be expected to help grain growth due to its low melting point.

4. Conclusions

In this study, we developed CuO and Bi_2O_3 as sintering aids at low temperature sintering condition (900 °C) for Sb, Li and Mn-substituted Pb(Zr,Ti)O_3–Pb(Zn,Ni)$_{1/3}$Nb$_{2/3}$$O_3$ ceramics. The addition of CuO decreased the sintering temperature through the formation of a liquid phase. However, the piezoelectric properties of the CuO-added ceramics sintered below 900 °C were lower than the desired values. The additional Bi_2O_3 resulted in a significant improvement in the piezoelectric properties.

At the sintering temperature of 900 °C, the electromechanical coupling factor (k_p), piezoelectric constant (d_{33}), mechanical quality factor (Q_m) of Sb, Li and Mn-substituted 0.8Pb($Zr_{0.48}Ti_{0.52}$)O_3–0.16Pb($Zn_{1/3}Nb_{2/3}$)O_3–0.04Pb($Ni_{1/3}Nb_{2/3}$)O_3-based ceramics with 0.5 wt% CuO and 0.5 wt% Bi_2O_3 show the optimal value of 0.56, 350 pC/N and 1042, respectively. These values indicated that the newly developed composition might be suitable for multilayer piezoelectric transformer application.

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