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Piezoelectric properties, densification behavior and microstructural evolution of low temperature sintered PZT ceramics with sintering aids

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Abstract

$Pb(Zr_{0.53}Ti_{0.47})O_3$ Ceramics can be made densified at as low as 800°C for 2 h by incorporating $LiBiO_2+CuO$ as the sintering aids. It exhibits high dielectric constant 1000–1300 and coupling factor 55–60% over a wide temperature range 800–1000°C. The optimal properties were obtained for the ceramics sintered at 880°C for 2 h. The densification behavior was investigated by using nonisothermal techniques. In the densification curve, the three sintering stages were found for $Pb(Zr_{0.53}Ti_{0.47})O_3$ ceramics with the sintering aids at a certain addition amount. The additives were characterized by TG-DSC. The microstructure development of the ceramics was observed by SEM and compared to that of $Pb(Zr_{0.53}Ti_{0.47})O_3$ ceramics. XPS was used to analyze the distribution of the additives in sintered ceramics. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Densification behavior; Piezoelectric properties; PZT; Sintering

1. Introduction

$Pb(Zr,Ti)O_3$ ceramics (PZT) has been widely applied to various fields because of its excellent piezoelectric properties. But for conventional PZT ceramics, the vaporization of PbO in its composition during sintering is of great significance, which makes it difficult to control microstructure and the electromechanical properties of PZT and also causes the environmental pollution. The low temperature sintering of PZT ceramics can not only solve the problems from the vaporization of PbO, but also reduce the energy consumption and fabrication cost. Thus the study on lowering the sintering temperature of PZT ceramics has aroused more and more attentions from the researchers.

Previous research works have revealed that the sintering temperature of PZT ceramics can be lowered by employing the additives with low melting point.[1–5] In this way, however, it is difficult to keep the piezoelectric properties of the based composition. Therefore, it is generally believed that the employment of a proper additive as a sintering aid is favorable to low temperature sintering of $Pb(Zr_{0.53}Ti_{0.47})O_3$ ceramics (abbreviated as PZT). In this study, the additives $LiBiO_2+$ CuO (abbreviated as LBCu) were employed for facilitating the sintering process of $Pb(Zr_{0.53}Ti_{0.47})O_3$ ceramics. LBCu were chosen as a sintering aid because of their effects on enhancing the densification of PZT ceramics and improving the piezoelectric properties.[6–8]

2. Experimental

The $Pb(Zr_{0.53}Ti_{0.47})O_3$ powder was prepared via a conventional mixed-oxide route by using commercially available PbO, TiO_2 and ZrO_2 of 99.9% purity as starting materials. The calcination was done at 890°C for 2 h. The sintering aid: 1 wt.% $LiBiO_2+0.06$ wt.% CuO was added to calcined PZT powder as a mixture of Li_2CO_3, Bi_2O_3 and CuO powders. They are mixed in

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ethanol for 12 h. Disc specimens were formed at 800 kg/cm^2 in a diameter of 22 mm and thickness of 2.5 mm and sintered from 800 to 1000°C for different times at the heating rate of 5°C/min. Silver paste was fired on both faces of the specimens at 800°C as electrodes. The specimens were polarized in silicon oil bath under 3 kV/mm bias at 130°C for 10 min.

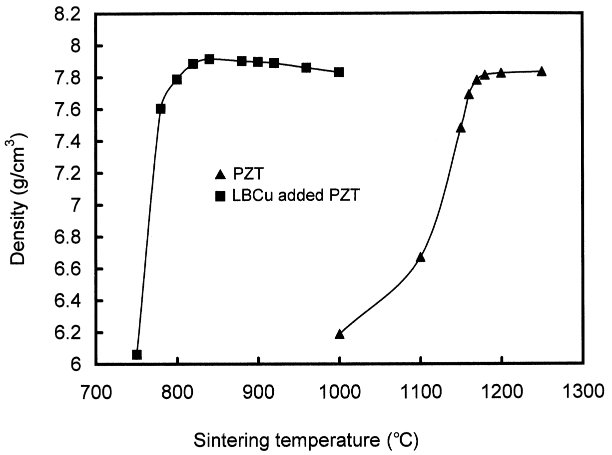

Fig. 1. Density as a function of sintering temperature for PZT ceramics with and without LBCu additives.

The shrinkage behavior of green rods as a function of temperature was detected by using a thermomechanical analyzer (TMA) with a 0.01 N nominal load applied at a heating rate of 5°C /min until 1000°C. A JEOL JSM-T330 scanning electron microscope (SEM) was used for the observation of morphology of the free surface of sintered body. Piezoelectric and dielectric properties were measured by using an impedance analyzer (YHP-4194A) on the bar-shaped (12×3×1 mm) specimens. Apparent density was determined by the Archimedes method.

3. Results and discussion

Fig. 1 gives the density as a function of sintering temperature for PZT and PZT composition with 1.06 wt.% $LiBiO_2+CuO$ added. The initial sintering temperature for the PZT based composite is higher than 1150°C. In contrast to that, the LBCu added PZT powders has attained a high density at 800°C. With a

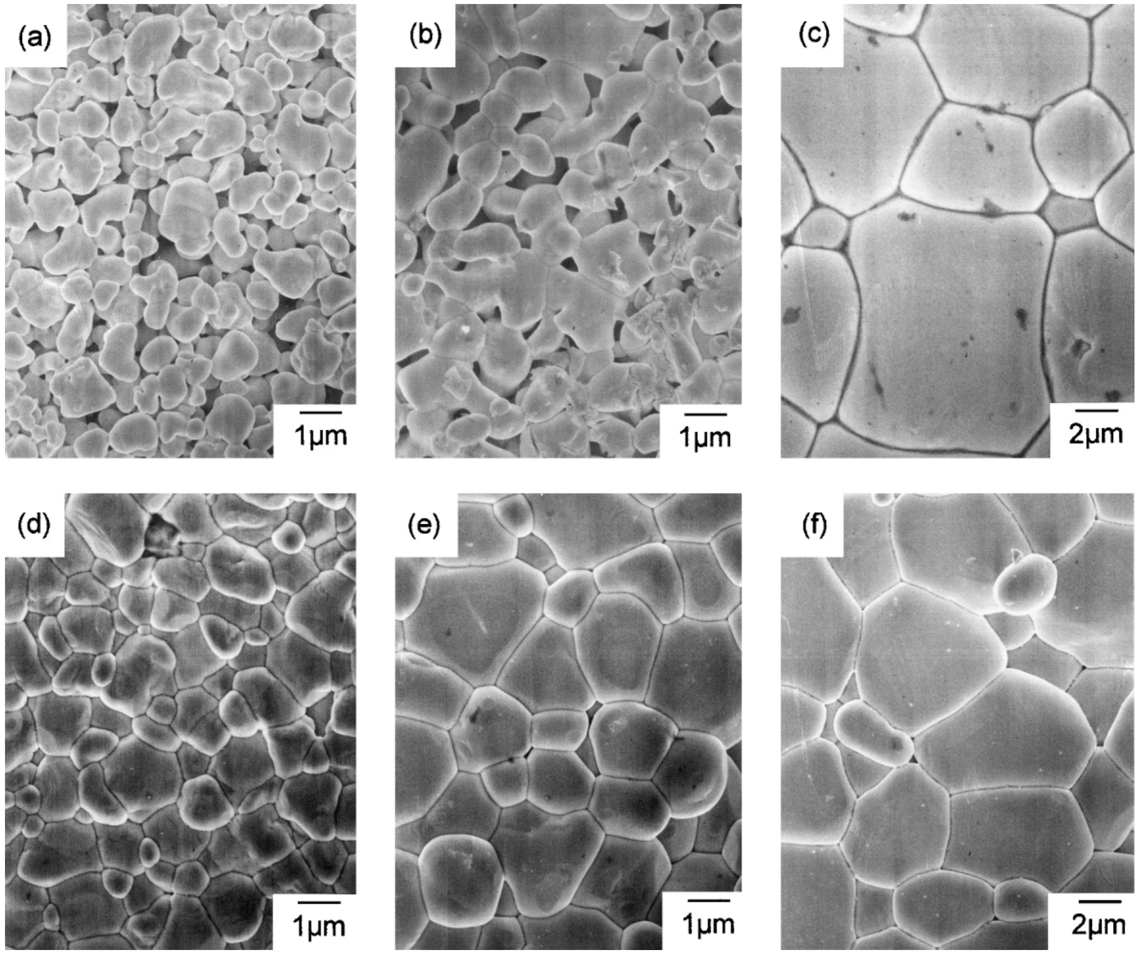

Fig. 2. SEM micrographs of as-fired surfaces of PZT ceramics sintered at (a) 800°C, (b) 900°C, (c) 1200°C, and LBCu added PZT ceramics sintered at (d) 800°C, (e) 880°C, (f) 1000°C for 2 h.

minor addition of LBCu additives, the sintering temperature of PZT powders can be reduced by 350°C.

Fig. 2 shows the SEM micrographs of the surfaces of PZT and LBCu added PZT compositions. An addition of 1.06 wt.% LBCu to PZT composition promoted grain growth considerably at the same firing temperature. This result is consistent with those obtained before by other researchers using Li_2CO_3 or $LiBiO_2$ as the sintering aids.[7,8]

Fig. 3 illustrates the dielectric constant and coupling factor of LBCu added PZT composition sintered at different temperatures. Comparing those of PZT composition: dielectric constant ε_r is 1016, coupling factor Kp 57.1%. The introduction of LBCu into PZT composition improves them in the temperature range of 850–950°C. Generally, if only $LiBiO_2$ is employed, the optimal properties can be obtained at a sintering temperature higher than 1000°C.[7,8] When one more CuO component is used, the sintering temperature at which the optimal properties are exhibited is shifted to below 900°C.

Fig. 4 shows a comparison of the densification behavior between $Pb(Zr_{0.53}Ti_{0.47})O_3$ and LBCu added $Pb(Zr_{0.53}Ti_{0.47})O_3$ compositions. The shrinkage rate reveals two peaks for the latter composite whereas the former composition reveals only one peak,[9] which indicates that the densification mechanisms of these two compositions should be different. For $Pb(Zr_{0.53}Ti_{0.47})O_3$ composition, densification starts at temperature above 800°C owing to volume diffusion. For LBCu added $Pb(Zr_{0.53}Ti_{0.47})O_3$ composition, the densification starts at about 600°C and approaches its end at about 950°C. It is evident that addition of LBCu additives can enhance the densification remarkably. According to the shrinkage behavior shown in Fig. 4, the densification process of the LBCu added composition should consist of three stages. Taking into account the melting temperature of LBCu additives shown in Fig. 5, it should be reasonable to consider that the main densification process in the early stage of sintering can be related to particle arrangement[10,11] even though the first peak is much smaller than the second one. The main densification occurs in the intermediate stage in which the shrinkage rate is comparable to that of $Pb(Zr_{0.53}Ti_{0.47})O_3$ composition. The major densification process in this stage is probably also volume diffusion.

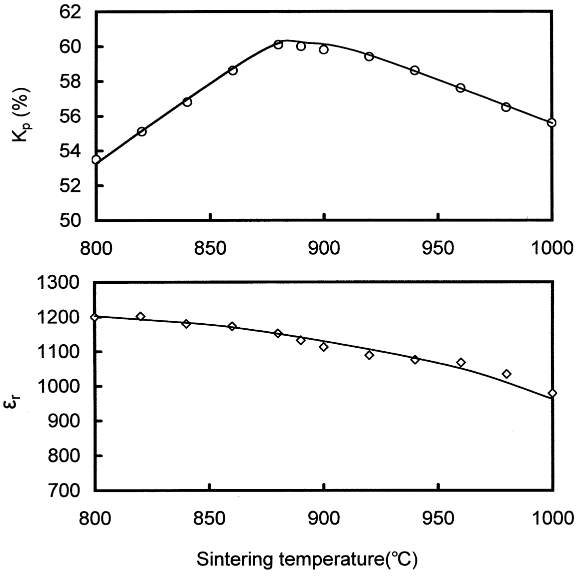

Fig. 3. Variation of sintering temperature with piezoelectric properties for LBCu-added PZT ceramics sintered for 2 h.

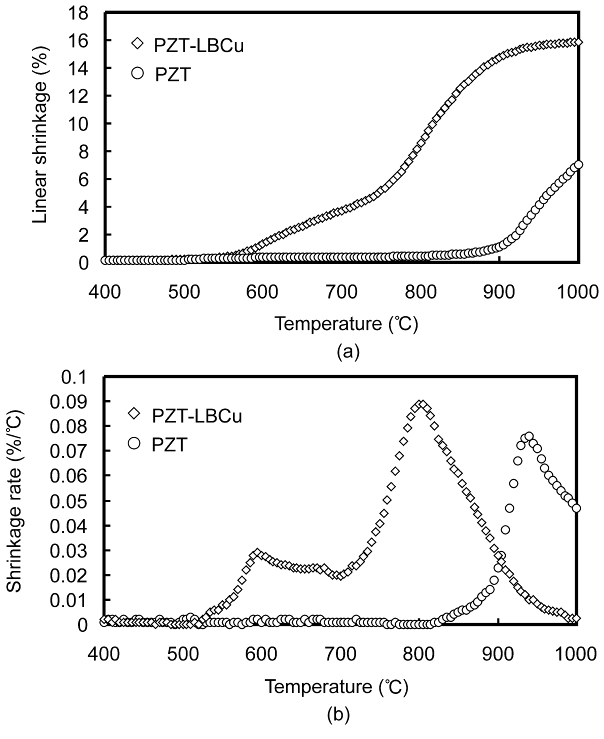

Fig. 4. Non-isothermal shrinkage behavior of $Pb(Zr_{0.53}Ti_{0.47})O_3$ with and without LBCu additives: (a) linear shrinkage versus temperature, (b) shrinkage rate versus temperature.

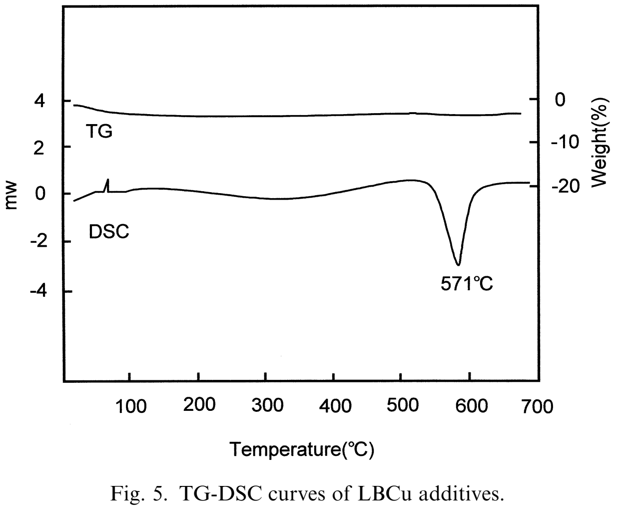

Fig. 5. TG-DSC curves of LBCu additives.

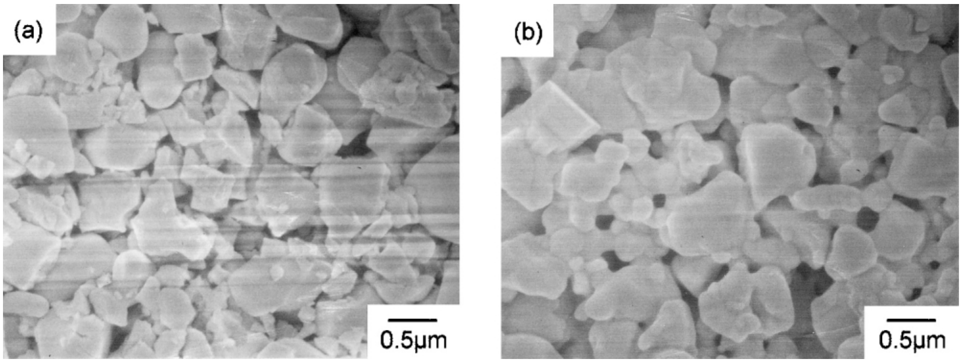

Fig. 6. Microstructure of LBCu added PZT ceramics fired at (a) 600°C, (b) 800°C, corresponding to sintering stages shown in Fig. 4.

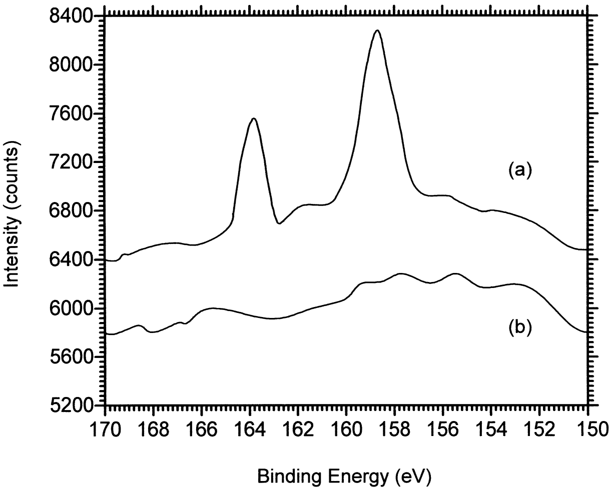

Fig. 7. Bi4f XPS spectra of fracture surface of LBCu added PZT ceramics: (a) before argon ion etching, (b) after argon ion etching for 30s.

Fig. 6 shows SEM micrographs of LBCu added $Pb(Zr_{0.53}Ti_{0.47})O_3$ composition fired until 600 and 800°C without keeping time at a heating rate of 5°C/min, corresponding to the early and intermediate sintering stages mentioned above. The microstructure in the early stage is composed of irregular and separated particles. No grain growth was observed. In the intermediate stage, the irregular particles were rounded, and held together. The compacted body becomes denser.

Fig. 7 shows Bi4f XPS spectra of fracture surface of LBCu added $Pb(Zr_{0.53}Ti_{0.47})O_3$ composition sintered at 880°C for 2 h. Before Ar ion etching, Bi4f XPS spectra can be observed. After Ar ion etching for 30 s, Bi4f peaks disappeared. Thus it seems that there are some additives existing on the grain boundaries after sintering.

4. Conclusion

Low temperature sintering of $Pb(Zr_{0.53}Ti_{0.47})O_3$ composition has been successfully attempted by using $LiBiO_2 + CuO$ additives as sintering aids. The densification of $LiBiO_2 + CuO$ added $Pb(Zr_{0.53}Ti_{0.47})O_3$ composition occurs at around 600°C through particle rearrangement process due to the formation of a small amount of liquid phase from the melting of the additives. The main densification mechanism at relatively higher temperature is similar to solid-state sintering by volume diffusion. The additives promote the densification and grain growth greatly. According to XPS analysis, some additives remain on the grain boundaries of sintered ceramics.

References

1. Wittmer, D. E. and Buchanan, R. C., Low-temperature densification of lead zirconate-titanate with vanadium pentoxide additive. *J. Am. Ceram. Soc.*, 1981, **64**, 485–490.
2. Gui, Z., Li, L., Gao, S. and Zhang, X., Low-temperature sintering pf lead-based piezoelectric ceramics. *J. Am. Ceram. Soc.*, 1989, **72**, 486–491.
3. Takahashi, S., Sintering Pb(Zr, Ti)O_3 ceramics at low temperature. *Jpn. J. Appl. Phys.*, 1980, **19**(4), 771–772.
4. Wang, X., Lu, P. and Xue, W., The mechanism of low temperature sintering of PZT ceramics with additives of Li_2O–Bi_2O_3–CdO. In *Proceedings of the Sixth International Symposium on the Applications of Ferroelectrics*, USA. 1992, pp. 585-587.
5. Wang, X., Murakami, K. and Kaneko, S., Low temperature sintering of high performance piezoelectric ceramics. In *Proceedings of Fourth International Conference on Intelligent Materials*. The Society of Non-Traditional Technology, Japan, 1998, pp. 72–73.
6. Kaneko, S., Dong, D. and Murakami, K., Effect of simultaneous addition of $BiFeO_3$ and $Ba(Cu_{0.5}W_{0.5})O_3$ on lowering of sintering temperature of Pb(Zr, Ti)O_3 ceramics. *J. Am. Ceram. Soc.*, 1998, **81**(4), 1013–1018.
7. Hayashi, T., Inoue, T. and Akiyama, Y., Low temperature sintering and properties of (Pb,Ba,Sr)(Zr,Ti,Sb)O_3 piezoelectric ceramics using sintering aids. *Jpn. J. Appl. Phys.* 1999, **38** (Part 1, No. 9B), 5549-5552.
8. Cheng, S. Y., Fu, S. L., Wei, C. C. and Ke, G. M., The properties of low-temperature fired piezoelectric ceramics. *J. Mater. Sci,*, 1986, **21**, 572–576.
9. Hammer, M. and Hoffmann, MichaelJ., Sintering model for mixed-oxide-derived lead zirconate titanate ceramics. *J. Am. Ceram. Soc.*, 1998, **81**(12), 3277–3284.
10. Kingery, W. D., Densification during sintering in the presence of a liquid phase. I. Theory. *J. Appl. Phys.*, 1959, **30**(3), 301–306.
11. German, R. M., *Liquid Phase Sintering*. Plenum Press, New York, 1985.