Ceramics International 30 (2004) 1449–1451

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The additives for improving piezoelectric and ferroelectric properties of $0.2Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.8[PbZr\ O_3$–$PbTiO_3]$ ceramics

B.M. Jin [a], D.S. Lee [b], I.W. Kim [b,*], J.H. Kwon [c], J.S. Lee [c], J.S. Song [d], S.J. Jeong [d]

[a] *Department of Physics, Dong Eui University, Busan, South Korea*
[b] *Department of Physics, University of Ulsan, P.O. Box 18, Ulsan 680 749, South Korea*
[c] *School of Materials Science and Engineering, University of Ulsan, Ulsan, South Korea*
[d] *Electric and Magnetic Devices Group, KERI, South Korea*

Received 1 December 2003; received in revised form 10 December 2003; accepted 23 December 2003

Available online 6 May 2004

Abstract

The effects of CuO, ZnO, and Li_2O (0.2wt.%) additions on the piezoelectric and ferroelectric properties of $0.2Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.8Pb(Zr_{0.475}Ti_{0.525})O_3$ (designated as PMNZT) ceramics were investigated. The density of sintered sample was strongly affected by small amounts of CuO, ZnO, and Li_2O addition. From the X-ray diffraction analysis, single phase of polycrystalline Perovskite was confirmed. The dielectric and piezoelectric constants of PMNZT ceramics doped with CuO, ZnO, and Li_2O were higher than that of pure ones. The improvement of piezoelectric properties was maximized at various 0.2 wt.% doped PMNZT samples. The maximum dielectric constant ($\varepsilon_r = 1423$) and minimum dielectric loss ($\tan\delta = 0.0019$) at room temperature were obtained with Li_2O addition. The electromechanical coupling factor, k_{33} of 0.2 wt.% of CuO, ZnO, and Li_2O doped and pure PMNPZT ceramics were found to be 0.72, 0.68, 0.75, and 0.20, respectively. And the piezoelectric constant, d_{33} of CuO, ZnO, and Li_2O doped and pure ceramics were found to be 330, 332, 418, and 95 pC/N, respectively. These values are comparable to that of pure ones and we will discuss which impurity would be the best dopant to improve the piezoelectric and dielectric constants of pure sample.

Keywords: C. Ferroelectric properties; C. Piezoelectric properties; PMNZT

1. Introduction

Since Jaffe [1] discovered that the poled lead zirconate titanate (PZT) ceramics with composition near phase boundary between the rhombohedral and tetragonal ferroelectric phases (MPB), exhibited high piezoelectric activity and dielectric constants, PZT ceramics have been widely used to produce piezoelectric devices [2–4]. In order to reach the requirements of practical applications, a number of minor additives have been added to modify the piezoelectric properties of the PZT ceramics [5–7]. However, when two or more minor additives were added simultaneously, the piezoelectric properties obtained were not greatly improved. The ternary solid solution in the PZT-based ceramics with the Perovskite structure was synthesized to make the whole system together; its formation has been widely used to improve piezoelectric properties [8–10].

In this work, the ternary system $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbZrO_3$–$PbTiO_3$ was chosen, and modified with small amount of CuO, Li_2O, and ZnO substitutions to obtain suitable materials for making ceramic actuators. Electromechanical coupling factor (k) is the most important factor to evaluate the performance of piezoelectric ceramic actuators [11], and it has several different values depending on the sample geometry. The k_{33} that is the longitudinal expansion mode is also the most important factor for multilayered ceramic actuators [12]. It is necessary to use piezoelectric materials with a high electron-mechanical coupling factor in order to produce efficient microelectric devices. In this work, three additives were added to $0.2Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.8[PbZr\ O_3$–$PbTiO_3]$ ceramics system and the results of improvement in piezoelectric (k_{33} and d_{33}) and ferroelectric properties of those ceramics.

* Corresponding author. Tel.: +82-52-259-2323; fax: +82-52-259-1623.
E-mail address: kimiw@mail.ulsan.ac.kr (I.W. Kim).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.070

2. Experimental

The $0.2Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.8Pb(Zr_{0.475}Ti_{0.525})O_3$ (abbreviated as PMNZT) ceramics doped with 0.2 wt.% CuO, 0.2 wt.% Li_2O, and 0.2 wt.% ZnO were prepared by a two-step calcination method. In the first step, MgO, Nb_2O_5, ZrO_2, and TiO_2 powders were properly weighed and ball milled with zirconia balls for 24 h. The mixed powders were dried and calcined at 1000 °C for 4 h to form a columbite phase of $MgNb_2O_6$. In the second step, the appropriate amount of PbO was weighed and mixed with calcined powder by ball milling for 24 h. After drying, it was calcined at 850 °C for 2 h. The calcined powders were mixed again with the additives. They were pressed into disk shape of 18 mm in diameter at 100 MPa. The specimens were sintered at 1000 °C for 2 h in a covered alumina crucible. To prevent PbO evaporation from the pellets, a powder of $PbZrO_3$ was used as the bedding powder.

Silver paint was pasted on both sides of the disk shaped samples and fired at 700 °C for 30 min. Before measuring the piezoelectric properties, the samples were poled in silicon oil bath at 120 °C by applying a DC electric field of 3 kV/mm.

The microstructure was analyzed using a scanning electron microscope (SEM). The dielectric constant of as-sintered samples was measured with Impedance Analyzer (HP 4192A, USA) as a function of temperatures at several frequencies. A longitudinal vibration mode, k_{33} was measured using rectangular sample of $1.3 \times 1.3 \times 3.5$ ($W \times D \times H$) mm. The piezoelectric coefficients for longitudinal (k_{33}, d_{33}, and g_{33}) modes were determined by the resonance–antiresonance method.

3. Result and discussion

Fig. 1 shows XRD patterns of CuO, Li_2O, and ZnO doped PMNZT ceramics sintered at 1000 °C. All peaks are well matched with the Perovskite structure. The secondary phase was not observed at all. It is reported that tetragonal (T) and rhombohedral (R) and T–R phase were identified by an analysis of the peaks of tetragonal (0 0 2), tetragonal (2 0 0), rhombohedral (2 0 0) that are in the 2q range of 43–47°. The splitting of (0 0 2) and (2 0 0) peaks indicates that they are the ferroelectric tetragonal phase, while the single (2 0 0) peak indicates the ferroelectric rhombohedral phase. Triplet peak indicates that the samples are consists of a mixture of tetragonal and rhombohedral phases.

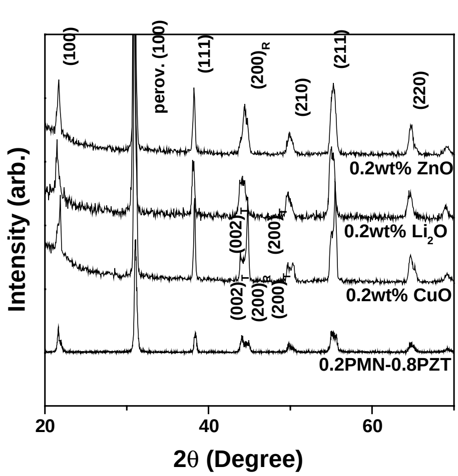

Fig. 1. XRD patterns of CuO, Li_2O, and ZnO doped PMNZT ceramics sintered at 1000 °C.

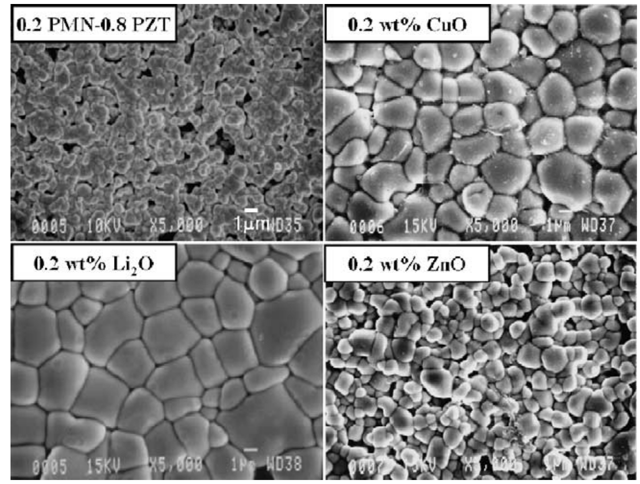

Fig. 2. SEM micrograph of CuO, Li_2O, and ZnO doped PMNZT ceramics sintered at 1000 °C.

Fig. 2 shows the SEM micrograph of CuO, Li_2O, and ZnO doped PMNZT ceramics sintered at 1000 °C. The average grain size of PMNZT:Cu, PMNZT:Li, and PMNZT:Zn are about 2, 3, and 1 mm, respectively. In this figure, grain size of PMNZT:Li ceramic is larger than that of other ceramics.

Dielectric constants of PMNZT, PMNZT:Cu, PMNZT:Li, and PMNZT:Zn ceramics as a function of temperature were also measured (not shown here). The dielectric constant of

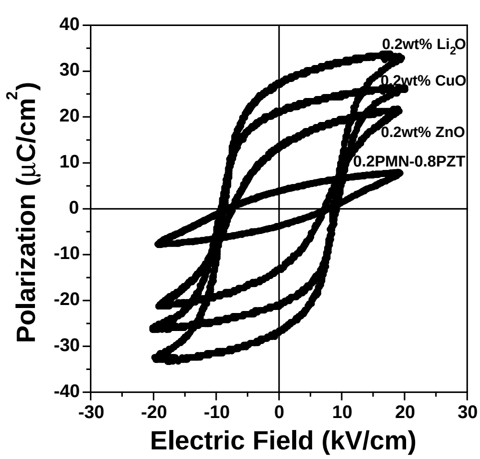

Fig. 3. The ferroelectric polarization–electric field (P–E) loops of PMNZT:Li, PMNZT:Cu, PMNZT:Zn, and PMNZT ceramics (from top to bottom).

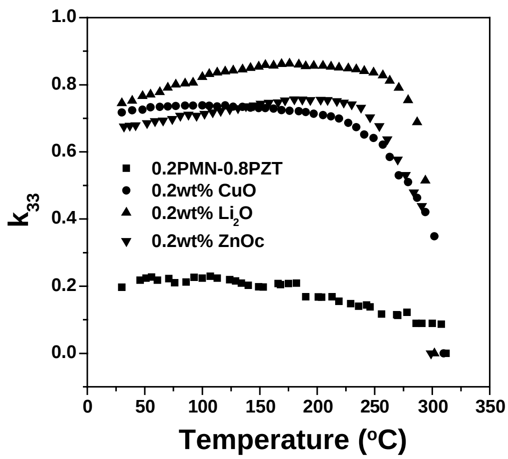

Fig. 4. A k_{33} values of PMNZT, PMNZT:Cu, PMNZT:Li, and PMNZT:Zn ceramics.

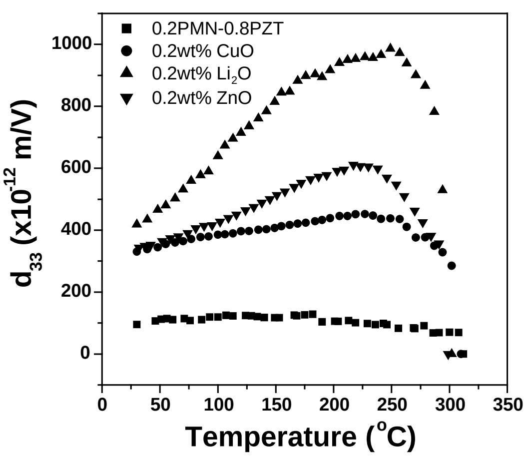

Fig. 5. A d_{33} values of PMNZT, PMNZT:Cu, PMNZT:Li, and PMNZT:Zn ceramics.

Li_2O added PMNZT ceramics was higher than that of other ceramics. The relatively higher dielectric constants of additives doped samples can be explained by the increase of grain size. If the grain size increases, then the cavities that can dissipate the energy will be reduced, therefore the dielectric constant would be increased [13].

The ferroelectric polarization–electric field (P–E) loops of PMNZT, PMNZT:Cu, PMNZT:Li, and PMNZT:Zn ceramics were shown in Fig. 3. The remnant polarization of PMNZT, PMNZT:Cu, PMNZT:Li, and PMNZT:Zn ceramic was 3.8, 21.1, 27.2, and 13.4 $\mu C/cm^2$, respectively. When the Li_2O, CuO, and ZnO were added, the hysteresis loops were fully saturated at the lower sintering temperatures than that of pure PMNZT.

Fig. 4 shows temperature dependences of k_{33} of PMNZT, PMNZT:Cu, PMNZT:Li, and PMNZT:Zn ceramics. A k_{33} of PMNZT ceramic is 40% when the ceramic was sintered at higher temperature of 1200 °C. The value of k_{33} of PMNZT is 20% when it is sintered at 1000 °C. The samples doped with Li_2O, CuO, and ZnO had the values of k_{33} that were increased about three times.

Fig. 5 shows temperature dependences of d_{33} of PMNZT, PMNZT:Cu, PMNZT:Li, and PMNZT:Zn ceramics. The abrupt d_{33} increase of PMNZT:Li is related to the abrupt change of the dielectric constant around the phase transition region. PMNZT:Li sample has highest piezoelectric properties among the additives.

4. Conclusion

Regardless of low-sintering temperature of 1000 °C, single phases of Li_2O, CuO, ZnO added PMNZT ceramic were formed by confirmed from X-ray diffraction. The triplet peaks shows the co-existence of tetragonal and rhombohedral phases although the tetragonal phase is dominant. PMNZT does not have a saturated hysteresis loop because of low sintering temperature. The samples which are doped with several additives have strongly saturated hysteresis loops even though the same low sintering temperatures which is the proof that the additive can reduced the sintering temperature. The piezoelectric properties that are also strongly dependent on the mechanical geometry will be also enhanced like in Figs. 4 and 5.

Acknowledgements

This research was supported by a grant from ‘Center for Advanced Materials Processing’ of ‘21st Century Frontier R&D Program’, funded by Ministry of Science and Technology, Republic of Korea.

References

[1] B. Jaffe, W. R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press, London, 1971.
[2] M. Adachi, A. Hachisuka, N. Okumura, T. Shiosaki, A. Kawabata, Jpn. J. Appl. Phys. 29 (1987) 68.
[3] W.P. Robbins, D.L. Polla, D.E. Glumac, IEEE Trans. Ultrason. Ferroelec. Frq. Contr. 38 (1991) 454.
[4] L. Jonts, E. Garcia, H. Waites, Smart. Mater. Struct. 3 (1994) 147.
[5] R. Gerson, J. Appl. Phys. 31 (1960) 188.
[6] F. Kulcsar, J. Am. Ceram. Soc. 42 (1959) 343.
[7] M. Takahashi, Jpn. J. Appl. Phys. 9 (1970) 1236.
[8] H. Ouchi, J. Am. Ceram. Soc. 51 (1968) 169.
[9] H. Ouchi, K. Nagano, S. Hayakara, J. Am. Ceram. Soc. 48 (1965) 169.
[10] J.H. Moon, H.M. Jang, J. Mater. Res. 8 (1993) 3184.
[11] K. Uchino, Ceram. Bull. 65 (1986) 647.
[12] S. Takahashi, Piezoelectric Ceramic Actuator, Ohmsha, Tokyo, 1987, pp. 62–74.
[13] B.M. Jin, A.S. Bhalla, J.B. Kim, J.N. Kim, J. Mater. Sci. 4 (1993) 225.