Dielectric and Piezoelectric Properties of CuO-Doped $(\text{Na}_{0.5}\text{K}_{0.5})_{0.94}\text{Li}_{0.06}\text{NbO}_3$ Lead-Free Ceramics[†]

CHANGAN TIAN¹, JUNLIANG LIU², QIYI YIN^{1,*}, JINSONG XIE¹, CUNYANG WANG¹, BIFA JI¹ and GUANGEN SUN¹

¹Department of Chemistry and Materials Engineering, Hefei University, Hefei 230022, P.R. China

²Jiangsu Key Laboratory of Environmental Material and Environmental Engineering, Yangzhou University, Yangzhou 225009, P.R. China

*Corresponding author: E-mail: yinqiyi@163.com

AJC-13322

$(\text{Na}_{0.5}\text{K}_{0.5})_{0.94}\text{Li}_{0.06}\text{NbO}_{3-x}$ (mol %) CuO ceramics were prepared by a solid state reaction approach and their dielectric and ferroelectric properties were evaluated by conventional methods. The high piezoelectric properties of $d_{33} = 115 \text{ pC/N}$, $k_p = 0.259$, $\epsilon_r = 697$, $\tan \delta = 2.9\%$ were obtained for the $(\text{Na}_{0.5}\text{K}_{0.5})_{0.94}\text{Li}_{0.06}\text{NbO}_3$ ceramics containing 1 mol % CuO sintered at 1035 °C for 2 h. Therefore, the $(\text{Na}_{0.5}\text{K}_{0.5})_{0.94}\text{Li}_{0.06}\text{NbO}_3$ ceramics containing a small amount of CuO are a good candidate material for lead-free piezoelectric ceramics.

Key Words: Ceramics, Ferroelectric, Piezoelectric, Solid state reaction.

INTRODUCTION

Ceramics based on lead zirconate titanate (PZT) system are the most important and the most widely used piezoelectric materials because of their outstanding piezoelectric performance. However, the toxicity caused by lead evaporation leads to environmental pollution. Recently, lead-free piezoelectric materials have been attracting increasing attention as new materials in place of PZT materials for the sake of environmental protection. Recently, significant progresses have been made in $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$ -based (KNN-based) ceramics, which show that KNN-based ceramics are promising candidates as the lead-free piezoelectric materials¹⁻⁵.

In order to further enhance the properties of KNN-based ceramics and meet the requirements for practical uses, it is necessary to develop new KNN-based ceramic. In the present work, $(\text{Na}_{0.5}\text{K}_{0.5})_{0.94}\text{Li}_{0.06}\text{NbO}_{3-x}$ mol % CuO (KNNL-xCuO) ceramics are prepared and the dielectric and ferroelectric properties has been further investigated by conventional methods.

EXPERIMENTAL

KNNL-xCuO ceramics (with $x = 0.00, 0.50, 1.00, 1.50, 2.00, 2.50$, respectively) were prepared by the conventional solid-state reaction technique in ambience, using starting materials of K_2CO_3 (99.0 %), Na_2CO_3 (99.8 %), Li_2CO_3 (99.9 %) and Nb_2O_5 (99.5 %). The raw materials were dried in a vacuum oven at 120 °C for at least 8 h to remove the absorbed moisture.

After this procedure, they were weighed according to the stoichiometric ratio, ball-mixed in alcohol for 12 h and calcined at 860 °C for 8 h. After re-milling with CuO additive, the powders were dried and pressed into discs under a pressure of 60 kgf/cm² and sintered at different temperatures for 2 h in air.

The microstructure of sintered ceramics was studied by scanning electron microscope. The densities of the sintered specimens were measured by a water-immersion technique. For dielectric and piezoelectric characterization, specimens were coated with silver paint on both surfaces and fired at 700 °C for 15 min and poling was accomplished in silicon oil using a dc power supply under the dc field strength of 5.0 kV/mm at 120 °C for 0.5 h. The piezoelectric constant d_{33} was measured using a d_{33} meter (ZJ-3A, China). The electromechanical coupling factor k_p was determined by the resonance method using an impedance analyzer (HP4294A). The dielectric constant and dissipation factor of the ceramics were examined with a LCR analyzer (TH2816). Ferroelectric hysteresis loops were measured at room temperature using a ferroelectric tester (Trek 609B, Radiant Technologies, Inc., Albuquerque, NM).

RESULTS AND DISCUSSION

Fig. 1 shows the SEM micrograph of the fracture surface of the KNNL-xCuO piezoelectric ceramics with the different sintering temperature. It can be seen from Fig. 1(a) that many

[†]Presented to the 6th China-Korea International Conference on Multi-functional Materials and Application, 22-24 November 2012, Daejeon, Korea

distinct pores exist in the grain boundary of KNNL-1.00 CuO ceramics sintered at 1000 °C for 2.0 h. The microstructure is inhomogeneous and the fracture surface is the typical transgranular fracture mode for the sample sintering at 1000 °C. This result demonstrates that the grains of KNNL-1.00 CuO ceramics sintered at 1000 °C do not grow sufficiently. With the sintering temperature increases, the pores significantly decrease. The microstructure of the sample sintering at 1035 °C is much uniform and fine, the average grain size is about 0.5–3.0 μm as seen in Fig. 1(b). This result indicates that KNNL-1.00 CuO grains of the sample sintered at 1035 °C grow sufficiently and the atomic binding force is greater than intergranular force. The relatively density of the KNNL ceramics doped with CuO sintered at 1035 °C for 2.0 h are generally larger than 96 %. These clearly show that the doping of CuO is effective in promoting the densification of the ceramics^{6–8}. Take into account above results, it can be concluded that the optimum sintering temperature for KNNL- x CuO ceramics should be 1035 °C.

Fig. 1. SEM images of the fractured surface of the KNNL-1.00 CuO ceramics sintered at various temperatures: (a) 1000 °C, (b) 1035 °C

Fig. 2 show the piezoelectric constant d_{33} and the planar electromechanical coefficient k_p of KNNL- x CuO ceramics sintered at 1035 °C for 2.0 h as a function of x . The d_{33} increases with the increasing x and reaches maximum (115 pC/N) at $x = 1.00$, then it drops with further increasing x . Similar to d_{33} , it is also found that the k_p increases with the increasing x and reaches maximum ($k_p = 25.9\%$) at $x = 1.00$, then it decreases with further increasing x . These results indicate that the KNNL-1.00 CuO ceramics possess good electrical properties at room temperature, *i.e.*, the piezoelectric constant d_{33} of 115 pC/N and planar electromechanical coefficient k_p of 25.9 %. Over this boundary ($x = 1.00$), the electrical properties decrease with the increasing x . So it is found that the MPB plays an important role in improving the piezoelectric properties of KNNL-1.00 CuO ceramics^{9–11}.

Fig. 3 shows the dielectric constant ϵ_r and dielectric loss $\tan \delta$ at room temperature of KNNL- x CuO ceramics sintered at 1035 °C for 2 h as a function of x . The dielectric constant ϵ_r increases with increasing CuO fraction up to $x = 1.00$ with $\epsilon_r = 697$, then decreases. while the dielectric loss $\tan \delta$ decreases with increasing x and reaches minimum ($\tan \delta = 2.9\%$) at $x = 1.00$, then it increases with further increasing x .

In order to characterize the ferroelectric properties, the P-E hysteresis loops of KNNL- x CuO ceramics were measured. Fig. 4 shows typical P-E hysteresis loops of KNNL- x CuO ($0.00 \leq x \leq 2.00$) ceramics. From the P-E hysteresis loops in Fig. 4, well saturated hysteresis loops were observed over a wide

composition range. Usually, the existence of P-E hysteresis loops is considered as evidence that material is ferroelectrics¹¹. In this work, the saturated P-E hysteresis loops confirm good ferroelectric nature of the KNNL- x CuO ceramics.

Conclusion

Effect of the content of CuO and the sintering temperature on the microstructure and piezoelectric properties of

Fig. 2. Piezoelectric constant d_{33} and planar electromechanical coefficient k_p of KNNL- x CuO ceramics as a function of x

Fig. 3. Dielectric constant ϵ_r and dielectric loss $\tan \delta$ of KNNL- x CuO ceramics as a function of x

Fig. 4. Polarization versus electric field curves for KNNL- x CuO ceramics sintered at 1035 °C for 2 h

(Na_{0.5}K_{0.5})_{0.94}Li_{0.06}NbO₃ ceramics were investigated. The results are summarized as follows:

1. Lead-free piezoelectric ceramics KNNL-xCuO have been synthesized by a solid state reaction approach. CuO can be effective in promoting the densification of the ceramics, the optimum sintering temperature for KNNL-xCuO ceramics should be 1035 °C.

2. The optimum composition for KNNL-xCuO ceramics is KNNL-1.00 CuO. Piezoelectric properties of KNNL-1.00 CuO ceramics under condition the optimum composition and sintering temperature are piezoelectric constant d_{33} of 115 pC/N, planar electromechanical coupling factor k_p of 25.9 % and the dielectric constant ϵ_r of 697 and dielectric loss $\tan \delta$ of 2.9 %, respectively. The results show that KNNL-1.00 CuO is an excellent candidate for lead-free piezoelectric ceramics.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support of the National Science Foundation of China (No. 51102073), the Natural Science Foundation of Anhui Province of China (No. 10040606Q53, 1308085QB35), Natural Science Foundation of Education Department of Anhui Province (No. KJ2012B154, KJ2013B229), the Open Project of Key Laboratory for Ecological-

Environment Materials of Jiangsu Province of China (No. K11031) and the College Students' Innovation and Entrepreneurship Training Program of China (No. 201211059006, 201211059007, 201211059011, 201211059009, 201211059005).

REFERENCES

1. G.L. Yuan, S.W. Or, Y.P. Wang, Z.G. Liu and J.M. Liu, *Solid State Commun.*, **138**, 76 (2006).
2. J.G. Wu, D.Q. Xiao, Y.Y. Wang, W.J. Wu, B. Zhang, J. Li and J.G. Zhu, *Scripta Materialia*, **59**, 750 (2008).
3. E.D. Yilmaz, H.E. Mgbemere, H. Özcoban, R.P. Fernandes and G.A. Schneider, **32**, 3339 (2012).
4. I.-Y. Kang, I.-T. Seo, Y.-J. Cha, J.-H. Choi, S. Nahm, T.-H. Sung and J.-H. Paik, *J. Eur. Ceram. Soc.*, **32**, 2381 (2012).
5. W. Supattra, A. Supon and Y. Rattikorn, *Ceram. Int.*, **38**, 147 (2012).
6. L.-Q. Cheng, J.-J. Zhou, K. Wang, J.F. Li and Q.M. Wang, *J. Mater. Sci.*, **47**, 6908 (2012).
7. J.G. Hao, Z.J. Xu, R.Q. Chu, Y.J. Zhang, G.R. Li and Q.R. Yin, *Physica B*, **404**, 1974 (2009).
8. J.G. Hao, W.F. Bai, B. Shen and J.W. Zhai, *J. Alloys Comp.*, **534**, 13 (2012).
9. Y.M. Li, Z.Y. Shen, L. Jiang, R.H. Liao, Z.M. Wang and Y. Hong, *J. Electron. Mater.*, **41**, 546 (2012).
10. J.G. Hao, R.Q. Chu, Z.J. Xu, G.Z. Zang and G.R. Li, *J. Alloys Comp.*, **479**, 376 (2009).
11. Y.Y. Wang, J.G. Wu, D.Q. Xiao, J.G. Zhu, P. Yu, L. Wu and X. Li, *J. Alloys Comp.*, **462**, 310 (2008).