Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 3709–3714

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Effects of Bi_2O_3–Li_2CO_3 additions on dielectric and pyroelectric properties of Mn doped $Pb(Zr_{0.9}Ti_{0.1})O_3$ thick films

Yike Zeng, Fei Yao, Guangzu Zhang*, Sisi Liu, Shenglin Jiang**, Yan Yu, Jungang He, Ling Zhang, Jinqiao Yi

School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, PR China

Received 4 September 2012; received in revised form 12 October 2012; accepted 12 October 2012
Available online 22 October 2012

Abstract

$Pb(Zr_{0.9}Ti_{0.1})O_3$ pyroelectric thick films adding various amounts of the sintering aids Bi_2O_3–Li_2CO_3 have been deposited on the substrates Al_2O_3 by the screen-printing process, and the dependence of microstructure, dielectric and pyroelectric properties on the content of sintering aids has been studied. When the amount of Bi_2O_3–Li_2CO_3 increases from 0 wt% to 5.4 wt%, the sintering temperature of the thick films decreases from 1100 °C to 900 °C, and the grain size and the lattice constant decrease either, but the density and the dielectric constant increase. The $Pb(Zr_{0.9}Ti_{0.1})O_3$ thick film with 5.4 wt% of Bi_2O_3–Li_2CO_3 sintered at 900 °C has the maximum pyroelectric coefficient $10.51\times10^{-8}\ \mathrm{C/cm^{-2}\,K^{-1}}$ and the highest figure-of-merit $10.58\times10^{-5}\ \mathrm{Pa^{-0.5}}$.

Keywords: B. Dielectric properties; D. PZT; Pyroelectric properties; Screen-printing

1. Introduction

As the uncooled infrared detectors develop rapidly, a series of pyroelectric materials have been explored, such as lead zirconate titanate (PZT), barium strontium titanate (BST) and so on [1–3]. As far as uncooled infrared detectors are concerned, the figure-of-merit is an important parameter for assessing the quality of pyroelectric materials. In order to achieve a better response, it is necessary to increase the pyroelectric figure-of-merit $F_D=p/C_v\sqrt{\varepsilon\tan\delta}$, which requires a combination of properties, namely high pyroelectric coefficient and low dielectric constant and loss [4]. Zr-rich $PbZr_{0.9}Ti_{0.1}O_3$ is a promising candidate because it has a high pyroelectric coefficient at room temperature when the transition from rhombohedral ferroelectric low temperature phase (F_{RL}) to rhombohedral ferroelectric high temperature phase (F_{RH}) takes place [5,6]. For obtaining a higher F_D, a proper amount of dopants (such as Mn and Nb) are added to increase the pyroelectric coefficient and decrease the dielectric loss [7–10].

Recently, PZT thick films have drawn much attention because they have better electrical properties than thin films and it is unnecessary to grind or polish them like pyroelectric ceramics [11,12]. However, the processing temperatures required to obtain dense PZT ceramics are about 1200 °C, which is too high for most of substrates and incompatible with the infrared focal plane array technologies. With this end in view, reducing the sintering temperature to 900 °C is essential for the fabrication and practical application of high performance PZT thick films [13]. Several promising approaches have been explored to reduce the sintering temperature, such as addition of sintering aids, use of chemical processing, and reduction of the particle size of the starting materials [14–16]. Among them, adding sintering aids is a simple, effective and easily controllable method. Unfortunately, the general trend indicates that the electrical properties are always deteriorated when sintering aids are added [17,18].

In this work, an interesting "discrepancy" is observed from $PbZr_{0.9}Ti_{0.1}O_3$ thick films adding the sintering aids Bi_2O_3–Li_2CO_3. When 5.4 wt% of Bi_2O_3–Li_2CO_3 sintering

---

*Corresponding author.
**Corresponding author.

E-mail addresses: zhangguangzu@gmail.com (G. Zhang), jslhust@gmail.com (S. Jiang).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.204

aids are added, the sintering temperature decreases from 1100 °C to 900 °C, and meanwhile the pyroelectric coefficient and F_D increase from $1.71 \times 10^{-8}\,\mathrm{Ccm^{-2}\,K^{-1}}$ and $1.56 \times 10^{-5}\,\mathrm{Pa^{-0.5}}$ to $10.51 \times 10^{-8}\,\mathrm{Ccm^{-2}\,K^{-1}}$ and $10.58 \times 10^{-5}\,\mathrm{Pa^{-0.5}}$, respectively. Bi_2O_3–Li_2CO_3 can decrease the sintering temperature and increase the density of thick films. Furthermore, Li^{1+} ions can enter into the grain lattice, increase the content of rhombohedral ferroelectric phase, and eventually increase the pyroelectric coefficient of the PZT materials [19]. As a result, the sintering aids Bi_2O_3–Li_2CO_3 can reduce the sintering temperature and improve the pyroelectric properties, simultaneously. In this paper, the reasons for this phenomenon are discussed in details.

2. Experimental procedure

The starting materials were analytical-grade metal oxide powders: PbO (99.9%), ZrO_2 (99.6%), and TiO_2 (99.8%). The powders were weighed according to the formula $PbZr_{0.9}Ti_{0.1}O_3$. 3.5 mol% $Mn(NO_3)_2$ solution was doped to decrease the dielectric loss, and 10 mol% excess of PbO was added to compensate the effect of lead volatilization. After that, the mixture was thoroughly milled for 4 h. The dried slurries were calcined at 850 °C for 2 h, and then ball milled again for 4 h with x wt% of Bi_2O_3–Li_2CO_3 (x is from 0 to 9) and 30 wt% of organic vehicle. The specimens with 0 wt%, 3.6 wt%, 5.4 wt%, 7.2 wt%, and 9 wt% of Bi_2O_3–Li_2CO_3 are denoted as PZT0, PZT1, PZT2, PZT3, and PZT4, respectively. Then, the films were printed on Pd/Ag coated alumina substrates. PZT0 was sintered at 1100 °C for 1 h, and PZT1, PZT2, PZT3, and PZT4 were sintered at 900 °C for 1 h. Finally, the specimens were poled at 90 °C for 1 h with the DC bias of 3 kV/mm.

The crystal structures of samples were determined by an X-ray diffractometer and the microstructures of specimens were observed by a scanning electron microscopy (SEM). The dielectric properties were measured at the frequency of

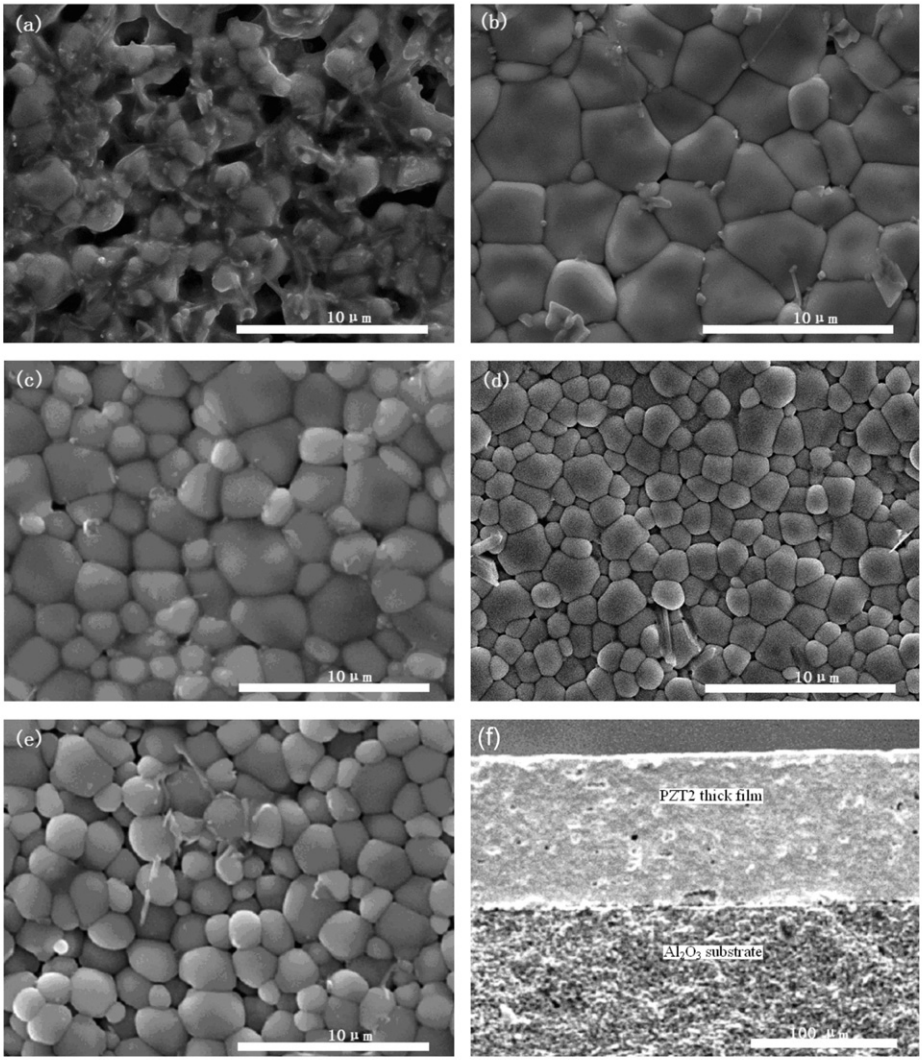

Fig. 1. Scanning electron microscopic micrographs of PZT thick films with different contents of Bi_2O_3–Li_2CO_3: (a) 0 wt%, (b) 3.6 wt%, (c) 5.4 wt%, (d) 7.2 wt%, and (e) 9 wt%, and (f) the cross-sectional scanning electron micrographs of PZT2.

1 kHz using a LCR analyzer (HP 4192; Hewlett Packard Ltd., Palo Alto, CA), and the pyroelectric coefficient was measured by the Byer–Roundy method [20].

3. Results and discussion

The SEM micrographs of all the samples are presented in Fig. 1. From Fig. 1(a) it can be observed that the porosity of PZT0 is high even though the sintering temperature reaches up to 1100 °C and the liquid phase has been formed. For Bi_2O_3–Li_2CO_3 added specimens that are sintered at 900 °C, the porosity decreases as the amount of Bi_2O_3–Li_2CO_3 increases when the Bi_2O_3–Li_2CO_3 content is less than 5.4 wt%, but further increasing Bi_2O_3–Li_2CO_3 content hinders the densification of the PZT thick films, as evidenced in Fig. 1(b–e). Fig. 1(f) is the cross section SEM picture of PZT2, it also indicates that when 5.4 wt% of sintering aids Bi_2O_3–Li_2CO_3 are added, dense PZT thick films can be obtained at the low sintered temperature. A proper amount of sintering aids Bi_2O_3–Li_2CO_3 usually aid the densification of thick films during sintering, but a too large amount of Bi_2O_3–Li_2CO_3 produce an initial rapid densification and leave closed pores in the ceramics that can not be removed by the solid state sintering. Moreover, the grain size decreases when the content of Bi_2O_3–Li_2CO_3 sintering aids increase, because Bi_2O_3–Li_2CO_3 forms a liquid phase at the grain boundary or around the grain and then restrains the grain growth. The SEM micrographs indicate that Bi_2O_3–Li_2CO_3 can optimize the microstructure of PZT thick films even at a lower sintering temperature.

Fig. 2(a) shows the X-ray diffraction patterns of all specimens. From XRD patterns it can be seen that there is only the perovskite structure in the samples. The lattice constants calculated on the basis of the least square refinement with over six peaks of diffraction patterns [21] are listed in Fig. 3. The lattice constant and unit-cell volume decrease as the content of Bi_2O_3–Li_2CO_3 increases, due to the substitution of smaller Bi^{3+} and Li^{1+} ions for larger A and B site ions [19,22,23]. It has been reported that, for PZT thick films at room temperature, the ratio of rhombohedral phase to tetragonal phase is characterized by a (002)/(200) peak splitting near 44°, the splitting of (002) and (200) peaks indicates that the ferroelectric tetragonal and rhombohedral phases coexist in the PZT, and the proportion of rhombohedral phase increases while the peak splitting effect is weakening. The enlarged pictures of the typical peaks when 2θ is about 44° are shown in Fig. 2(b). The splitting of (002) and (200) peaks can be seen in PZT0. As the amount of Bi_2O_3–Li_2CO_3 increases, the split peaks gradually merge into one peak. This means that the proportion of rhombohedral phase in PZT increases as the content of Bi_2O_3–Li_2CO_3 increases. The result is consistent with the investigation performed by Gao who attributed the increase of the rhombohedral phase content to the substitution of Li^{1+} ions for B site ions [19]. The high pyroelectric coefficient of Zr-rich PZT materials comes from the rhombohedral ferroelectric F_{RL}–F_{RH} phase transition; therefore, the proportion of rhombohedral phase is crucial [5,6]. The PZT thick films containing sintering aids Bi_2O_3–Li_2CO_3 have a higher content of rhombohedral phase, which indicates that the higher pyroelectric coefficient can be expected.

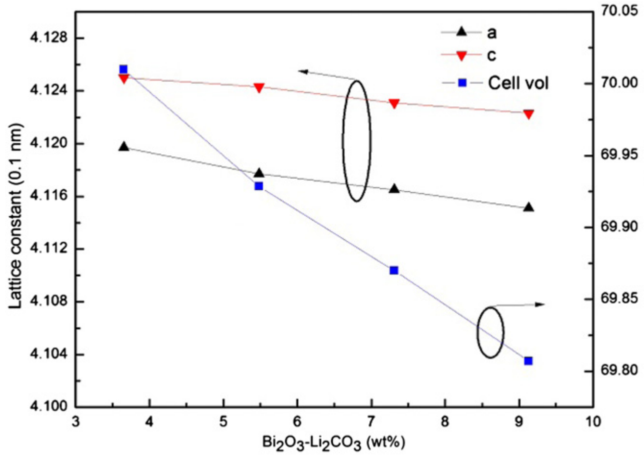

Fig. 3. The lattice constant and unit-cell volume of PZT thick films with different contents of Bi_2O_3–Li_2CO_3.

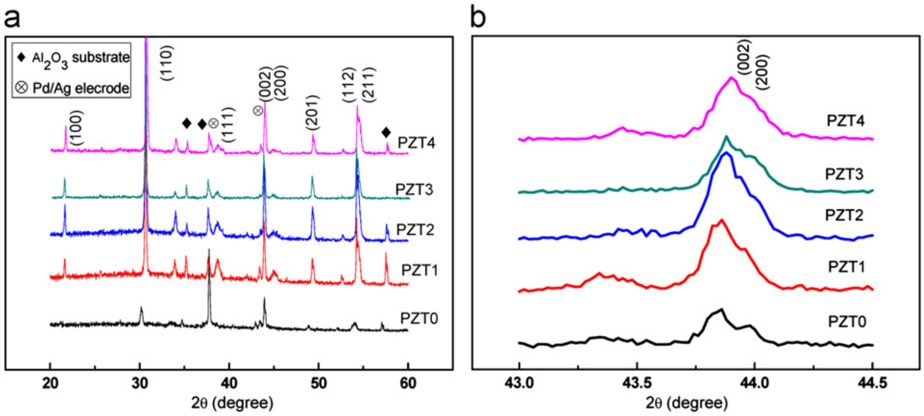

Fig. 2. (a)X-ray diffraction patterns and (b) the enlarged picture around $2\theta=44°$of PZT thick films with different contents of Bi_2O_3–Li_2CO_3.

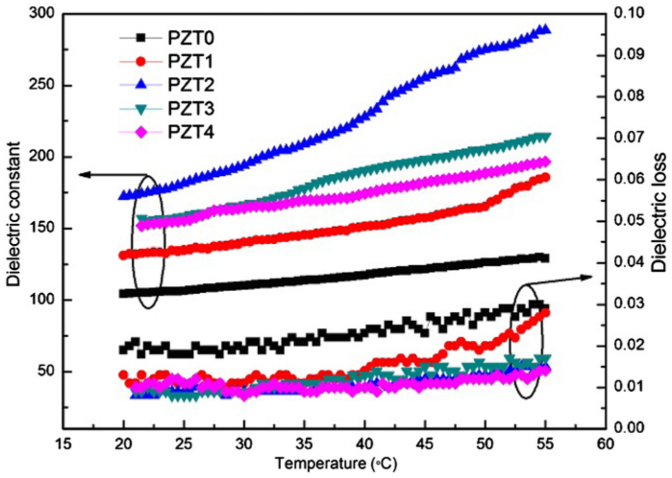

Fig. 4. Temperature dependence of dielectric constant and loss of PZT thick films with different contents of Bi_2O_3–Li_2CO_3.

The temperature-dependent dielectric constant and loss curves of the PZT thick films with various contents of Bi_2O_3–Li_2CO_3 are shown in Fig. 4. The dielectric constant increases when the content of Bi_2O_3–Li_2CO_3 increase from 0 wt% to 5.4 wt%, but then decreases as the content of the sintering aids increase to 9 wt%. PZT0 has the lowest dielectric constant due to its high porosity. The density of PZT thick films increases as the Bi_2O_3–Li_2CO_3 content increases, resulting in the increase of the dielectric constant of PZT1 and PZT2. On the other hand, the internal stress between the grains increases as the grain size decreases. When the grain size is larger than 0.8 μm, the content of 90° domain increases as the internal stress increases, and this leads to the increase of dielectric constant. [24] The grain size of PZT thick films decreases as the Bi_2O_3–Li_2CO_3 content increases, and this also results in the increase of the dielectric constant. However, when the content of Bi_2O_3–Li_2CO_3 is more than 5.4 wt%, the grain size decreases and the proportion of grain boundary increases dramatically, as evidenced in Fig. 1. The dielectric constant of grain boundary is much lower than that of grains, and hence the dielectric constant of the PZT thick films decreases with the further increase of Bi_2O_3–Li_2CO_3 [25,26]. The phenomenon that PZT0 shows the highest dielectric loss can also be attributed to its low density. Because of their high densities, samples sintered at 900 °C with 5.4 wt% or more Bi_2O_3–Li_2CO_3 have low dielectric losses, which are favorable to the increase of the pyroelectric figure-of-merit.

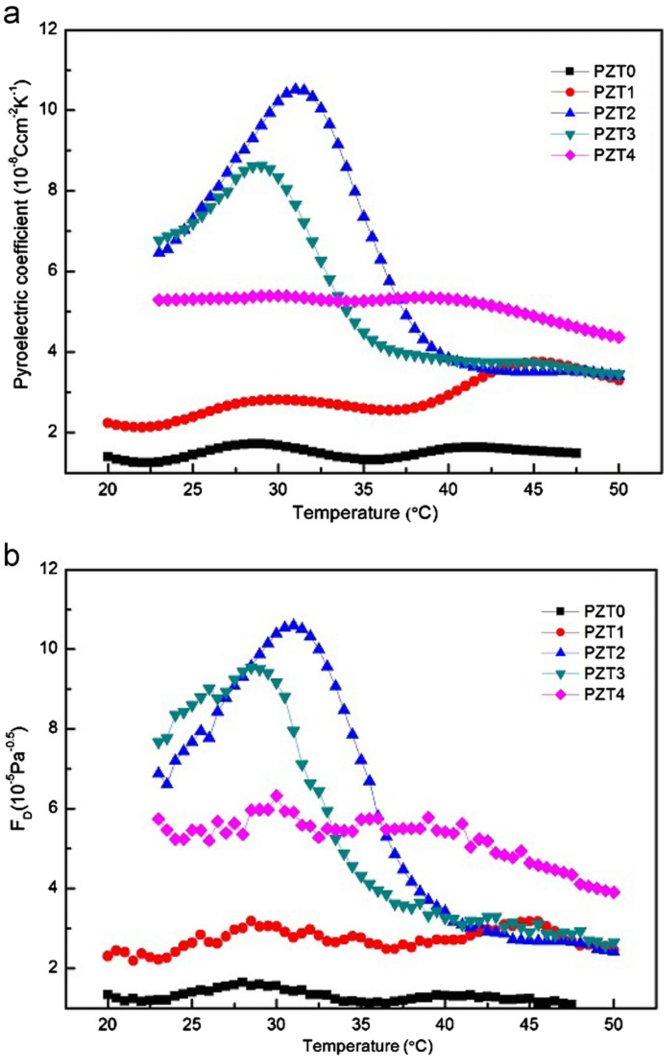

Fig. 5. Temperature dependence of (a) pyroelectric coefficient and (b) pyroelectric figure-of-merit.

Fig. 5(a) shows the curves of pyroelectric coefficient versus temperature of samples with different contents of Bi_2O_3–Li_2CO_3. The thick films sintered at 1100 °C without adding the sintering aids Bi_2O_3–Li_2CO_3 show a low pyroelectric coefficient on account of its high porosity and low content of rhombohedral phase. The pyroelectric coefficient increases dramatically. A steep pyroelectric coefficient peak can be observed as the Bi_2O_3–Li_2CO_3 content increases to 5.4 wt%. There are two reasons for the obvious increase of the pyroelectric coefficient of PZT2. Firstly, an appropriate amount of Bi_2O_3–Li_2CO_3 as sintering aid can decrease the porosity and increase the density of the PZT thick films, and finally increase the pyroelectric coefficient. Secondly, for Zr-rich PZT, the F_{RL}–F_{HL} phase transition occurs when the temperature varies near 30 °C. It is well known that the high pyroelectric coefficient can be obtained when the rhombohedral ferroelectric F_{RL}–F_{RH} phase transition occurs [5,6], and therefore the Zr-rich PZT samples with the large proportion of rhombohedral phase can exhibit a high pyroelectric coefficient. Thick films adding 5.4 wt% of Bi_2O_3–Li_2CO_3 have a greater proportion of rhombohedral phase owing to the substitution of Li^{1+} ions for B site ions, as evidenced by the XRD pattern. Consequently, it shows a steep pyroelectric coefficient peak. This result reveals that the Bi_2O_3–Li_2CO_3 sintering aids can not only reduce the sintering temperature and increase the density, but also lead to the increase of pyroelectric coefficient by 6 times. When the content of Bi_2O_3–Li_2CO_3 increases to 9 wt%, the pyroelectric coefficient decreases and the pyroelectric coefficient peak is suppressed. When the grain size decreases, the internal stresses among the grains increase. The large internal stresses can increase the dispersity of the $F_{R(LT)}$–$F_{R(HT)}$ phase transition and suppress the pyroelectric coefficient peak [27]. Also, the grain boundary content increases as the grain size decreases, and the high content of non-ferroelectric grain boundary results in the decrease of pyroelectric coefficient.

Fig. 5(b) exhibits the figure-of-merit F_D of all samples. PZT2 has the largest pyroelectric coefficient and a low dielectric loss, and therefore it shows the highest F_D of 10.58×10^{-5} $Pa^{-0.5}$, which is about 7 times as that of PZT thick films without adding Bi_2O_3–Li_2CO_3.

4. Conclusions

The effects of the sintering aids Bi_2O_3–Li_2CO_3 on the microstructure, dielectric and pyroelectric properties of PZT thick films have been systematically investigated. The results indicate that unlike other sintering aids, a proper amount of Bi_2O_3–Li_2CO_3 can reduce the sintering temperature from 1100 °C to 900 °C, decrease the porosity of the PZT thick films, and lead to more-than-6-times increase of the pyroelectric coefficient and figure-of-merit, simultaneously.

Acknowledgment

The present study was supported by the National Science and Technology Support Program (2012BA113B00), National Nature Science Foundation of China (51102102), Research Fund of the Doctoral Program of Higher Education of China (20110142120074), Science and Technology Projects of Wuhan (201210321103), SME Technology Innovation Fund (12C26214405276, 12C26114405436) and Innovation Research Fund of Huazhong University of Science and Technology (2011TS048, 2011QN002, 2011QN008). The authors also wish to thank Zhenxing Yuan and the Analytical and Testing Center of Huazhong University of Science and Technology.

References

[1] R.W. Whatmore, P.C. Osbond, N.M. Shorrocks, Ferroelectric materials for thermal IR detectors, Ferroelectrics 76 (1987) 351–367.

[2] P. Guggilla, A.K. Batra, J.R. Currie, M.D. Aggarwal, M.A. Alim, R.B. Lal, Pyroelectric ceramics for infrared detection applications, Materials Letters 60 (2006) 1937–1942.

[3] B.M. Kulwicki, A. Amin, H.R. Beratan, C.M. Hanson, Pyroelectric imaging, Proceedings of the Eighth IEEE International Symposium on Applications of Ferroelectrics (1992) 1–10.

[4] R.W. Whatmore, Pyroelectric devices and materials, Reports on Progress in Physics 49 (1986) 1335–1386.

[5] T. Zeng, G. Wang, X. Dong, H. He, X. Chen, Investigation on $FR_{(LT)}$–$FR_{(HT)}$ phase transition and pyroelectric properties of porous Zr-rich lead zirconate titante ceramics, Materials Science and Engineering B 140 (2007) 5–9.

[6] N. Duan, D. Sun, X. Dong, S. Lin, Y. Wang, F_{RL}–F_{RH} phase transition behavior in the stacked $Pb(Zr_{1-x}Ti_x)O_3$ perovskite ceramics, Journal of the European Ceramic Society 19 (1999) 1207–1211.

[7] L. Liu, X. Li, X. Wu, Y. Wang, W. Di, D. Lin, X. Zhao, H. Luo, N. Neumann, Dielelctric, ferroelectric, and pyroelectric characterization of Mn-doped $0.74Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.26PbTiO_3$ crystals for infrared detection applications, Applied Physics Letters 95 (2009) 192903.

[8] Q. Zhang, R.W. Whatmore, Improved ferroelectric and pyroelectric properties in Mn-doped lead zirconate titanate thin films, Journal of Applied Physics 94 (2003) 5228–5233.

[9] C.P. Shaw, S. Gupta, S.B. Stringfellow, A. Navarro, J.R. Alcock, R.W. Whatmore, Pyroelectric properties of Mn-doped lead zirconate–lead titanate–lead magnesium niobate ceramics, Journal of the European Ceramic Society 22 (2002) 2123–2132.

[10] Z. Ujma, L. Szymczak, J. Handerek, K. Szot, H.J. Penkalla, Dielectric and pyroelectric properties of Nb-doped $Pb(Zr_{0.92}Ti_{0.08})O_3$ ceramics, Journal of the European Ceramic Society 20 (2000) 1003–1010.

[11] C. Lucat, F. Menil, R.V.D. Muhll, Thick-film densification for pyroelectric sensors, Measurement Science & Technology 8 (1997) 38–41.

[12] C. Mao, S. Cao, C. Yao, F. Cao, K. Li, W. Liu, G. Wang, X. Dong, X. Hu, C. Yang, Effect of sintering atmosphere on the microstructure and electrical properties of donor-doped barium strontium calcium titanate pyroelectric ceramics, Journal of the American Ceramic Society 94 (2011) 2003–2006.

[13] M. Hrovat, J. Holc, S. Drnovsek, D. Belavic, J. Cilensek, M. Kosec, PZT thick films on LTCC substrates with an interposed alumina barrier layer, Journal of the European Ceramic Society 26 (2006) 897–900.

[14] K. Yao, X. He, Y. Xu, M. Chen, Screen-printed piezoelectric ceramic thick films with sintering additives introduced through a liquid-phase approach, Sensors and Actuators A 118 (2005) 342–348.

[15] B. Su, C.B. Ponton, T.W. Button, Hydrothermal and electrophoretic deposition of lead zirconate titanate (PZT) films, Journal of the European Ceramic Society 21 (2001) 1539–1542.

[16] T. Hayashi, T. Inoue, Y. Akiyama, Low temperature sintering of PZT powders coated with $Pb_5Ge_3O_{11}$ by sol–gel method, Journal of the European Ceramic Society 19 (1999) 999–1002.

[17] C. Nam, H. Park, I. Seo, J. Choi, S. Nahm, H. Lee, Effect of CuO on the sintering temperature and piezoelectric properties of MnO_2-doped $0.75Pb(Zr_{0.47}Ti_{0.53})O_3$–$0.25Pb(Zn_{1/3}Nb_{2/3})O_3$ ceramics, Journal of Alloys and Compounds 509 (2011) 3686–3689.

[18] W. Zhang, R.E. Eitel, Low-temperature sintering and properties of 0.98PZT–0.02SKN ceramics with $LiBiO_2$ and CuO addition, Journal of the American Ceramic Society 94 (2011) 3386–3390.

[19] F. Gao, R. Hong, J. Liu, Z. Li, C. Tian, Effects of ZnO/Li_2O codoping on microstructure and piezoelectric properties of low-temperature sintered PMN–PNN–PZT ceramics, Ceramics International 35 (2009) 1863–1869.

[20] R.L. Byer, C.B. Roundy, Pyroelectric coefficient cirect measurement technique and application to a *n* sec response time detector, Ferroelectrics 3 (1972) 333–338.

[21] J.W. Liou, B.S. Chiou, Effect of direct-current biasing on the dielectric properties of barium strontium titanate, Journal of the American Ceramic Society 80 (2011) 3093–3099.

[22] Z. Ujma, J. Handerek, Peculiarities of the pyroelectric effect and of the dielectric properties in Bi-doped $Pb(Zr_{0.95}Ti_{0.05})O_3$, Journal of the European Ceramic Society 23 (2003) 203–212.

[23] S. Dutta, R.N.P. Choudhary, P.K. Sinha, Ferroelectric phase transition in Bi-doped PLZT ceramics, Materials Science and Engineering B 98 (2003) 74–80.

[24] Z. Zhao, V. Buscaglia, M. Viviani, M.T. Buscaglia, L. Mitoseriu, A. Testino, M. Nygren, M. Johnsson, P. Nanni, Grain-size effects on the ferroelectric behavior of dense nanocrystalline $BaTiO_3$ ceramics, Physical Review B 70 (2004) 024107-1–024107-8.

[25] H.T. Martirena, J.C. Burfoot, Grain-size effects on properties of some ferroelectric ceramics, Journal of Physics C: Solid State Physics 7 (1974) 3182–3192.

[26] A. Chaipanich, Effect of PZT particle size on dielectric and piezoelectric properties of PZT–cement composites, Current Applied Physics 7 (2007) 574–577.

[27] B. Kang, D. Gu-Choi, S. Choi, Effects of grain size on pyroelectric and dielectric properties of $Pb_{0.9}La_{0.1}TiO_3$ ceramics, Journal of Materials Science: Materials in Electronics 9 (1998) 139–144.