Journal of Alloys and Compounds 509 (2011) 2838–2841

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

# Microstructure and electrical properties of PLZT ceramics from $Pb_3O_4$ as the lead source

Jihua Zhang*, Shangjun Mo, Huayi Wang, Shanxue Zhen, Hongwei Chen, Chuanren Yang

*State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China*

ARTICLE INFO

*Article history:*
Received 14 July 2010
Received in revised form
16 November 2010
Accepted 22 November 2010
Available online 30 November 2010

*Keywords:*
Lead lanthanum zirconate titanate (PLZT)
Ceramics
Perovskite
Ferroelectric
$Pb_3O_4$

ABSTRACT

In this paper, $Pb_3O_4$, rather than conventional PbO, was introduced in the solid phase synthesis of $(Pb_{0.92}La_{0.08})(Zr_{0.35}Ti_{0.65})_{0.98}O_3$ (PLZT) ceramics. The microstructure and electrical properties of the PLZT ceramics were investigated. Results showed that due to the activity of $Pb_3O_4$, pyrochlore phase PLZT was depressed effectively. The PLZT ceramics with 5.0 wt.% excess $Pb_3O_4$ in the original materials had a well-crystallized pure perovskite structure when being sintered at 1100 °C for 6 h. In addition, the amount of $Pb_3O_4$ had an influence on the electrical properties of the PLZT ceramics. Residual polarization as high as 36.9 $\mu C/cm^2$ was obtained from the samples with 5.0 wt.% excess $Pb_3O_4$.

## 1. Introduction

Due to the electro-optic, birefractive, piezoelectric and electrostrictive effect, as demonstrated by several groups [1–3], lead lanthanum zirconate titanate (PLZT) ferroelectric materials play a very important role in integrated optical and photoelectronic devices. However, to develop devices, preparation of high quality PLZT materials is essential. For PLZT ferroelectric ceramics, what should be considered most are the perovskite structure and stoichiometric proportion. The main technologies to produce ceramics include: hot pressed sintering, atmosphere sintering and hot isostatic pressing sintering, etc. However, it is difficult to obtain pure perovskite phase PLZT through these conventional solid phase synthesis methods. Pyrochlore phase is often formed and thus influence the ferroelectric properties of PLZT. Furthermore, there is high content of lead in PLZT, and the lead is easy to volatile at high temperature during sintering. As a result, vacancy defects form in the lattice. The vacancy of lead influences ferroelectric properties further. Therefore, excess PbO is commonly added in the mixture as carried out by Kong et al. [4–6], and Galassi et al. [7]. Although excess PbO can compensate the loss of lead in lead-base ferroelectric materials effectively [8–11], He et al. [11] showed that excess PbO would make the ceramic composition change locally, thereby degrading the uniformity of the Pb(Zr,Ti)$O_3$ (PZT) ceramic. Lu et al. [12] found that when they prepared $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) ceramics, $Pb_3O_4$ was better than PbO in sintering character. The pure perovskite and high density PMN ceramics was obtained from $Pb_3O_4$ at 900 °C. While for PbO as the lead source, the ceramics was not single perovskite phase and the density of the sintered material was loose. As a result, because of the pure perovskite and high density, the samples synthesized from $Pb_3O_4$ had a larger dielectric constant than that of from PbO. Recently, Zhu et al. [13] also prepared pure perovskite $Pb_{0.98}Sr_{0.02}(Mn_{1/3}Sb_{2/3})_x(Zr_{0.15}Ti_{0.15})_{12x}O_3$ $(0 < x < 0.1)$ (PMSZT) using solid phase synthesis method with 1% excess $Pb_3O_4$.

Based on the possible superiority of $Pb_3O_4$ in synthesis of lead-base ferroelectric materials, in this paper, we adopted $Pb_3O_4$ to replace conventional PbO as the lead source in preparation of PLZT ceramics. The effect of excess $Pb_3O_4$ on the microstructure and electrical properties of PLZT was studied. We found that the pyrochlore phase was depressed and pure perovskite phase was obtained with 5.0 wt.% excess $Pb_3O_4$. The resultant PLZT ceramics crystallized well with uniform grain. Moreover, electrical properties of the PLZT ceramics were also improved with optimized amount of $Pb_3O_4$.

## 2. Experiment

PLZT was synthesized from $Pb_3O_4$, $TiO_2$, $ZrO_2$ and $La_2O_3$ using conventional ceramics process. What should be noted that we adopted $Pb_3O_4$ rather than commonly used PbO as the lead source. All the original materials were analytically pure. To compensate the loss of lead during the sintering, excess $Pb_3O_4$ was added in the original materials. Dosing was adopted according to the stoichiometry of $(Pb_{0.92}La_{0.08})(Zr_{0.35}Ti_{0.65})_{0.98}O_3 + xPb_3O_4$, where $x = 0.0$ wt.%, 2.0 wt.%, 5.0 wt.%, 8.0 wt.%, 10.0 wt%, respectively. The molded samples were sintered at 1100 °C for

---

* Corresponding author. Tel.: +86 28 83206506; fax: +86 28 83201632.
*E-mail address:* jhzhang@uestc.edu.cn (J. Zhang).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.11.135

6 h. To further inhibit the vaporization of lead during the sintering process, samples were surrounded by $PbZrO_3$ atmosphere.

This paper focused on the effect of different amount of excess $Pb_3O_4$. The phase structure of the presintered powder and the sintered ceramics were characterized by Bede D1 high resolution XRD system with Cu Kα source. Microstructure and surface topography were examined through Hitachi S-450 scanning electronic microscope (SEM). To measure the electrical properties, both sides of the samples were coated with sliver paste and were sintered at 800 °C. The dielectric properties were measured using Hioki3532-50 LCR meter at frequency of 1 MHz and on temperature between −50 °C and 140 °C. Ferroelectric properties were measured using Radiant Precision LC 2000 meter.

## 3. Results and discussion

### 3.1. Effect of excess $Pb_3O_4$ on the microstructures

In order to depress the volatilization of lead in PLZT, this work introduced $Pb_3O_4$ as flux to reduce the sintering temperature. Excess $Pb_3O_4$ was also used to compensate the loss of lead. Fig. 1 presents the XRD spectra of the presintered powder and the sintered ceramics for excess 5.0 wt.%, 8.0 wt.% and 10.0 wt.% of $Pb_3O_4$, respectively. It was shown that, when presintering at 910 °C for 2 h, all PLZT powder with different content of $Pb_3O_4$ were perovskite phase. In addition, there were some peaks corresponded to PbO. It is well known that $Pb_3O_4$ will decomposed on the temperature higher than 500 °C as

$$Pb_3O_4 \rightarrow 3PbO + 1/2O_2$$

This fact demonstrated that there remained PbO and it did not take part in the solid reaction. The remained PbO was helpful to compensate the volatilization of lead during the subsequent sintering process. This result indicated that, presintering at 910 °C for 2 h was a suitable condition for the preparation of PLZT ceramics. Because the PbO obtained from the as-decomposed $Pb_3O_4$ had extremely small particles and fresh surface, it was more active and favorable to synthesize perovskite PLZT. After presintering, the PLZT powder was ball milled and molded into discs with Ø10mm × 1 mm, and then the samples were sintered at 1100 °C for 6 h. Fig. 1(b) is the XRD spectra of sintered PLZT ceramics. It can be seen that, for the samples from 8.0 wt.% and 10.0 wt.% excess $Pb_3O_4$, there was also a peak around $2\theta = 28^\circ$ besides the peaks of perovskite phase as indicated. It was corresponded to the pyrochlore phase. Additionally, PbO peaks could also be observed on these two XRD spectra. The PbO is come from the decomposition of $Pb_3O_4$, and implied that $Pb_3O_4$ was over dosing. However, for the sample from 5.0 wt.% excess $Pb_3O_4$, the PLZT was pure perovskite structure, no pyrochlore phase was observed from the XRD spectrum. According to the XRD results, the PLZT8/65/35 ceramics was a tetragonal structure with lattice parameter $a = b = 0.4015$nm, $c = 0.4117$ nm and $c/a = 1.0254$. Therefore, 5.0 wt.% excess $Pb_3O_4$ in the original material is optimized, which can synthesize pure perovskite phase PLZT ceramics.

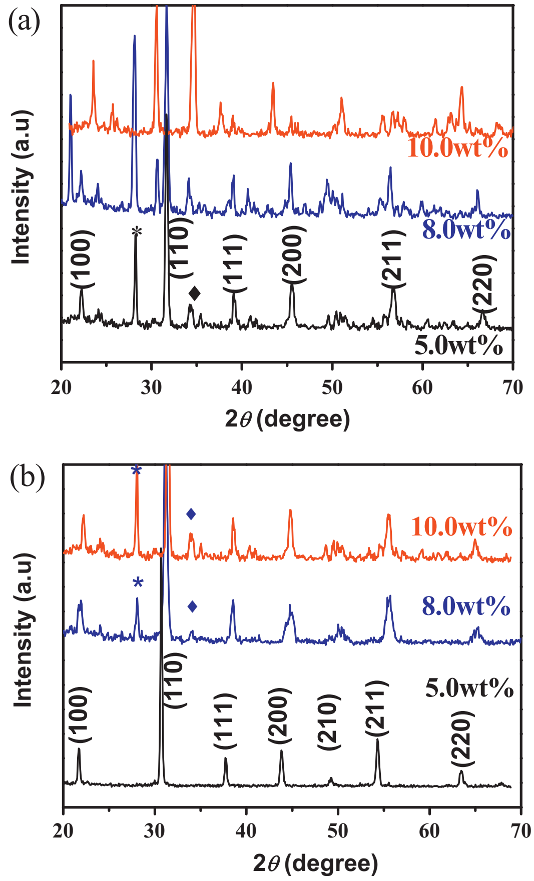

**Fig. 1.** XRD patterns of PLZT with different amount of excess $Pb_3O_4$: (a) calcined at 910 °C for 2 h and (b) sintered at 1100 °C for 6 h. Peaks marked with (*) are pyrochlore phase PLZT, and marked with (♦) are PbO.

The content of $Pb_3O_4$ not only influences the phase composition of PLZT ceramics, but also the microstructure and surface morphology. Fig. 2 depicts the SEM photographs of PLZT ceramics for different amount of $Pb_3O_4$. All samples were sintered at 1100 °C for 6 h. It showed that for the samples synthesized from 5.0 wt.% excess $Pb_3O_4$, the grain was well crystallized. The grain boundary was sharp and the grain size was uniform. As the content of $Pb_3O_4$ increased, the grain of the PLZT ceramics was not well developed, the porosity increased and thus the density decreased. These results indicated that 5.0 wt.% of $Pb_3O_4$ was optimal for preparation of well crystallized PLZT ceramics. This is well consistent with the XRD result and the electrical properties discussed later.

### 3.2. Effect of excess $Pb_3O_4$ on dielectric properties

Temperature dependence of the relative dielectric constant ($\varepsilon_r$–$T$ plots) of PLZT ceramics from various amount of excess $Pb_3O_4$ is shown in Fig. 3. Compared to single phase ferroelectric materials, the $\varepsilon_r$–$T$ plots changed gradually for this PLZT compound. The transformation temperature zone widened obviously. The Curie temperature $T_C$ and maximal dielectric constant $\varepsilon_{max}$ were greatly affected by the amount of $Pb_3O_4$. For 5.0 wt.% excess $Pb_3O_4$, $\varepsilon_{max} = 7521$, $T_C = 74$ °C, For 8.0 wt.% excess $Pb_3O_4$, $\varepsilon_{max} = 5484$, $T_C = 72$ °C and for 10.0 wt.% excess $Pb_3O_4$, $\varepsilon_{max} = 3584$, $T_C = 68$ °C. That is to say, the Curie temperature $T_C$ reduced as the amount of $Pb_3O_4$ increases. Accordingly, the maximal dielectric constant $\varepsilon_{max}$ reduced. Of course, it was not found significant effect of excess $Pb_3O_4$ on ferroelectric to paraelectric transition temperature $T_C$, which is similar to Bongkarn's [14] result for lead barium zirconate ceramics.

As discussed above, the grain size, the porosity, the density and the grain boundary are determined by the content of $Pb_3O_4$ in the original materials. Compared with the samples synthesized from 5.0 wt.% of $Pb_3O_4$, PLZT from 8.0 wt.% and 10.0 wt.% of $Pb_3O_4$ have a smaller grain size, and the non-ferroelectric grain boundary is thicker. Because of the presence of the minor non-ferroelectric phases (as is also seen from XRD), dielectric constant reduced. In order to compensate the loss of lead during the sintering of ceramics target and the deposition of thin films, Zeng et al. [15] also added excess $Pb_3O_4$ in the target material when sputtering $PbZrTiO_3$ (PZT) thin films. They found that PZT films without pyrochlore phase were obtained when the PZT ceramics target was synthesized from 5.0% excess $Pb_3O_4$ in mass percentage. This is consistent with our results.

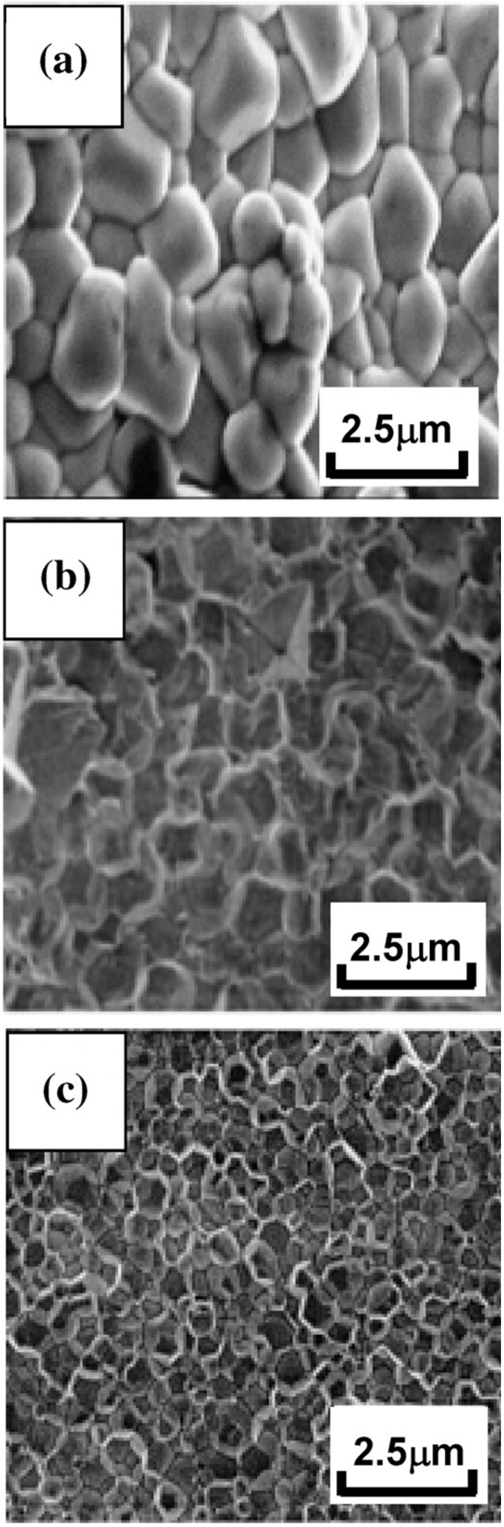

**Fig. 2.** SEM photographs of the fractured surface of the PLZT ceramics with different amount of excess $Pb_3O_4$: (a) $x = 5.0$ wt.%, (b) $x = 8.0$ wt.%, and (c) $x = 10.0$ wt.%.

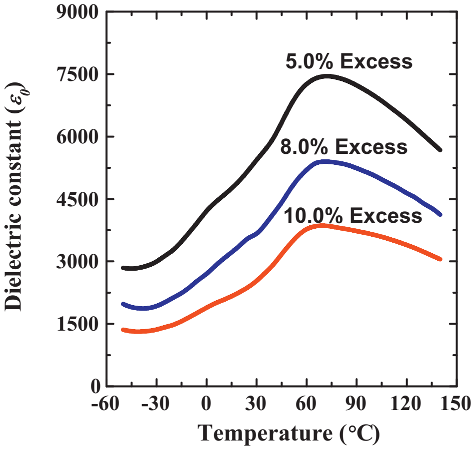

**Fig. 3.** Temperature dependence of the relative dielectric constant of PLZT ceramics with different amount of excess $Pb_3O_4$.

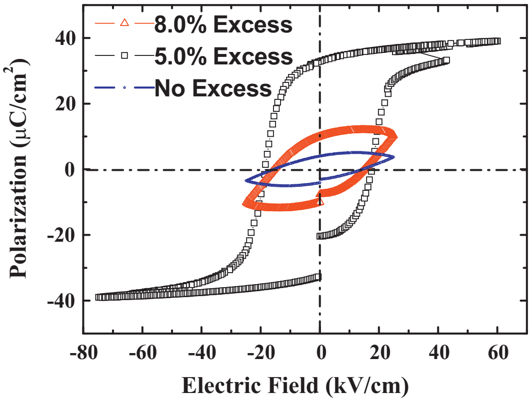

**Fig. 4.** Ferroelectric hysteresis loops of PLZT ceramics with different amount of excess $Pb_3O_4$.

### 3.3. Effect of excess $Pb_3O_4$ on ferroelectric properties

Ferroelectric hysteresis loops were carried out by Radiant Precision LC 2000 meter at 10 kHz and on room temperature. Fig. 4 presents the ferroelectric hysteresis loop of samples with different content of $Pb_3O_4$. It was found that the ferroelectric properties were significant different. For samples of $x = 0$ and $x = 8\%$, due to the large leakage currents at high voltage, the maximum electric field could only be applied to 25 kV/cm. While for samples of $x = 5.0$ wt.%, leakage currents remained small enough that electric field as high as 80 kV/cm could be applied. It presented superior insulator characteristics. Table 1 lists the ferroelectric performance parameters of PLZT ceramics samples from five proportions of 0 wt.%, 2.0 wt.%, 5.0 wt.%, 8.0 wt.% and 10.0 wt.%, respectively. It was found that the sample of $x = 5.0$wt% exhibited the best ferroelectric properties, which had a saturation polarization $P_s$ of 41.1 μC/cm$^2$ and residual polarization $P_r$ of 36.9 μC/cm$^2$.

The results indicated that, for lead-base ferroelectric PLZT, if the excess $Pb_3O_4$ was less than 5.0 wt.%, lead was not enough to compensate the loss during the high temperature sintering process. The lack of lead in the PLZT samples made the ferroelectric properties inferior. While for $x > 5.0$ wt.%, there remained much PbO impurity at the PLZT lattice boundary, which created a non-ferroelectric layer in the samples and reduce the dielectric constant. Additionally, the excess impurity made the local composition distribute non-uniformly and further reduced the ferroelectric properties. These results also proved that, in the process of our work, 5.0 wt.% excess

**Table 1**
Ferroelectric parameters of PLZT ceramics with different amount of excess $Pb_3O_4$.

| | 0 wt.% | 2.0 wt.% | 5.0 wt.% | 8.0 wt.% | 10.0 wt.% |
|---|---|---|---|---|---|
| $P_S$ (μC/cm$^2$) | 7.38 | 16.7 | 41.1 | 15.75 | 7.43 |
| $P_r$ (μC/cm$^2$) | 7.51 | 9.34 | 36.9 | 9.18 | 7.14 |
| $E_c$ (kV/cm) | 13.72 | 15.24 | 17.64 | 14.34 | 14.18 |

$Pb_3O_4$ in the original materials was an optimized formula for the synthesis of high performance PLZT ceramics.

## 4. Conclusion

In conclusion, this paper introduced $Pb_3O_4$ as the lead source in the synthesis of PLZT8/65/35 ceramics. As $Pb_3O_4$ can be decomposed into PbO with small particle and fresh surface, the activity of $Pb_3O_4$ is higher than that of common PbO powder in original materials. It can effectively promote the pure perovskite phase, and depress the formation of pyrochlore phase. Of course, because of the volatility of lead, excess $Pb_3O_4$ needs to be added to original materials. When the amount of excess $Pb_3O_4$ is 5.0 wt.%, the resultant PLZT ceramic has high density and is well crystallized. The grain size is uniform and has a higher dielectric constant and superior ferroelectric properties.

## Acknowledgment

This work is sponsored by the National Natural Science Foundation of China (grant no. 60607004.)

## References

[1] O. Maris, H. Dag, Proc. SPIE 4829 I (2003) 46–47.
[2] T. Aoki, M. Kondo, M. Ishii, A. Sugama, M.K. Tsukada, K.M. Kuwabara, J. Eur. Ceram. Soc. 25 (2005) 2917–2920.
[3] A. Khodorov, M.J.M. Gomes, Vacuum 82 (2008) 1495–1498.
[4] L.B. Kong, J. Ma, W. Zhu, O.K. Tan, J. Alloys. Compd. 322 (2001) 290–297.
[5] L.B. Kong, J. Ma, H. Huang, R.F. Zhang, J. Alloys. Compd. 345 (2002) 238–245.
[6] L.B. Kong, J. Ma, R.F. Zhang, T.S. Zhang, J. Alloys. Compd. 339 (2002) 167–174.
[7] C. Galassi, D. Piazza, F. Craciun, P. Verardi, J. Eur. Ceram. Soc. 24 (2004) 1525–1528.
[8] W. Tangkawsakul, P. Sittiketkron, T. Bongkarn, Adv. Mater. Res. 55-57 (2008) 193–196.
[9] Y.C. Zhang, Z.Z. Yang, W.N. Ye, C.J. Lu, L.H. Xia, J. Mater. Sci. Mater. Electron. (2010), doi:10.1007/s10854-010-0134-7.
[10] C.-S. Park, S.-M. Lee, H.-E. Kim, J. Am. Ceram. Soc. 91 (2008) 2923–2927.
[11] L. He, G. Peng, W. Yang, C. Zheng, J. Yu, Y. Wang, Chin. J. Semicond. 28 (2007) 711–716.
[12] C.H. Lu, D.P. Chang, J. Mater. Sci. 11 (2000) 363–367.
[13] L. Zhu, P.-Y. Liu, Y.-J. Chen, P. Chang, J. Jilin Univ. Eng. Technol. Ed. 30 (2009) 518–522.
[14] T. Bongkarn, G. Rujijanagul, Ferroelectrics 358 (2007) 67–73.
[15] Y.K. Zeng, S.L. Jiang, C.Y. Deng, S. Chen, M.D. Liu, J. Chin. Ceram. Soc. 33 (2005) 358–361.