

## Sinterability Enhancement in Lead Zirconate Titanate Ceramics Using $\text{Bi}_2\text{O}_3$ and $\text{Cu}_2\text{O}$ Additives

### การกระตุ้นความสามารถในการเผาผนึกของเซรามิกเลดเซอร์โคเนตทิตาเนต โดยใช้สารเจือ $\text{Bi}_2\text{O}_3$ และ $\text{Cu}_2\text{O}$

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### Abstract

The effects of  $\text{Cu}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  additives on the densification, phase formation and microstructure of lead zirconate titanate (PZT) were investigated. In this study, addition of both  $\text{Cu}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  to the PZT powder via conventional mixed-oxide techniques was examined. Before addition, PZT powder was calcined at  $850^\circ\text{C}$  for 3 h. Concentration of the additive at 1 wt.% was selected. Sintering was carried out in the range  $900\text{--}1200^\circ\text{C}$  for constant soaking time of 4 h. Microstructure, bulk density and phase analysis were carried out using XRD and SEM. High purity ceramics were identified by XRD results. SEM study of the ceramics obtained at the same sintering temperatures reveal denser bodies in those containing additives. Accordingly, high density ceramics can be obtained with 90.50% of the theoretical density after sintering at  $1074^\circ\text{C}$  for 4 h with 1 wt.%  $\text{Cu}_2\text{O}$ . Clearly, introduction of  $\text{Cu}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  additives effectively induces a higher sinterability and reasonably good densification comparing to pure PZT.

### บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อตรวจวิเคราะห์ผลของการเจือ  $\text{Cu}_2\text{O}$  และ  $\text{Bi}_2\text{O}_3$  ต่อการแน่นตัว การก่อเกิดเฟส และโครงสร้างจุลภาคของเซรามิกเลดเซอร์โคเนตทิตาเนต (PZT) โดยผงเซรามิก PZT เตรียมขึ้นด้วยวิธีผสมออกไซด์แบบดั้งเดิมและเจือด้วย  $\text{Cu}_2\text{O}$  และ  $\text{Bi}_2\text{O}_3$  ก่อนการเจือผง PZT ผ่านกระบวนการเผาแคลไซน์ที่อุณหภูมิ  $850^\circ\text{C}$  องศาเซลเซียส นาน 3 ชั่วโมง จากนั้นเติมสารเจือร้อยละ 1 โดยน้ำหนัก และเผาผนึกในช่วงอุณหภูมิ  $900\text{--}1200^\circ\text{C}$  องศาเซลเซียส โดยเผาแช่นาน 4 ชั่วโมง โครงสร้างจุลภาค ความหนาแน่น เฟสของเซรามิกตรวจวิเคราะห์ด้วยเทคนิค XRD และ SEM จากผลการตรวจวิเคราะห์เฟสด้วยเทคนิค XRD พบว่าได้เฟสเดียวของ PZT จากภาพถ่าย SEM ณ อุณหภูมิเผาผนึกเดียวกันของเซรามิก PZT และ PZT ที่เติมสารเจือพบว่า เซรามิก PZT ที่เติมสารเจือมีการแน่นตัวดีขึ้น เซรามิก PZT ที่เจือด้วย  $\text{Cu}_2\text{O}$  ร้อยละ 1 โดยน้ำหนัก ให้ค่าความหนาแน่นสูงถึงร้อยละ 90.50 ของค่าความหนาแน่นทางทฤษฎี เมื่อผ่านการเผาผนึกที่อุณหภูมิ  $1074^\circ\text{C}$  องศาเซลเซียส นาน 4 ชั่วโมง และเห็นได้ชัดว่าการเติมสารเจือ  $\text{Cu}_2\text{O}$  และ  $\text{Bi}_2\text{O}_3$  ช่วยให้สามารถเผาผนึกได้ดีขึ้นและเกิดการแน่นตัวที่ดีเมื่อเทียบกับเซรามิก PZT ที่ไม่มีสารเจือ

**Keywords:** Liquid Phase Sintering, Densification, Lead Zirconate Titanate

**คำสำคัญ:** การเผาผนึกด้วยเฟสของเหลว การแน่นตัว เลดเซอร์โคเนตทิตาเนต

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## Introduction

The Lead zirconate titanate (Pb(Zr,Ti)O<sub>3</sub> or PZT) ceramic is an important ferroelectric material with perovskite structure. The excellent dielectric and piezoelectric properties make it a useful material for transducers, computer memory and display and pyroelectric sensors (Zahi et al., 2003). However, sintering of PZT at high temperatures gives rise to loss of Pb content, which drastically degrades the chemical compositions and properties. Many works (Jaffe et al., 1971; Setter and Waser, 2000) have been concerned the PZT prepared via solid phase sintering in order to study its phase transitions, piezoelectric properties and applications. In principle, fast densification is also an effective way to minimize the lead loss during sintering. It is very important to obtain desirable composition and provide excellent properties after using a low sintering temperature. Generally, lead loss at high temperature can be prevented by atmospheric control or decreasing the sintering temperature. Accordingly, excess Cu<sub>2</sub>O has been reported (Zuo et al., 2006; Lim et al., 2006; Kim et al., 2006) to lower the sintering temperature of BaSm<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub>, Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> and Ba(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> ceramic materials. Zuo et al. (2006) reported that the density of the BaSm<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> increases with increasing CuO additive up to 2 wt.%. Bi<sub>2</sub>O<sub>3</sub> can be also used as a sintering additive to reduce the sintering temperature. Chu (2000) and Ha et al. (2003) reported that high densities and improved properties in 0.25 Pb(Ni<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.75Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> (PNN-PZT) and (Pb<sub>0.45</sub>Ca<sub>0.55</sub>)[(Fe<sub>0.05</sub>Nb<sub>0.5</sub>)<sub>0.9</sub>Sn<sub>0.1</sub>]O<sub>3</sub> (PCFNS) ceramics can be achieved by doping with Bi<sub>2</sub>O<sub>3</sub>. In the present work, the same effect was also investigated for PZT ceramics. The main aim was to study the

effects of additive to lower the sintering temperature. Thus, concentration of additives was kept constant at 1 wt.% for both Cu<sub>2</sub>O and Bi<sub>2</sub>O<sub>3</sub>. The effect was evaluated in terms of phase formation, microstructure development and densification.

## Material and Methods

The Pb(Zr,Ti)O<sub>3</sub> powder was prepared by conventional solid state reaction using reagent grade powders of PbO, ZrO<sub>2</sub> and TiO<sub>2</sub>. They were mixed by ball milling for 24 h and were calcined at 850 °C for 3 h with a heating and cooling rate of 10 °C/min. The PZT powders were mixed with Cu<sub>2</sub>O 1 wt.% or Bi<sub>2</sub>O<sub>3</sub> 1 wt.% and then were uniaxially pressed at 1.5 ton. The pellets with and without Cu<sub>2</sub>O and Bi<sub>2</sub>O<sub>3</sub> were sintered at 902, 999, 1035, 1075 and 1200 °C with constant dwell time of 4 h. The phase constitution was characterized by X-ray diffraction (XRD) analysis using Cu<sub>Kα</sub> radiation (Philips, X'Pert). The density of the sintered ceramics was measured using the Archimedes method. The microstructure was observed using a scanning electron microscope (JEOL, JSM-541).

## Results and Discussion

Figure 1 shows the XRD patterns of Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> ceramics with and without additives as a function of sintering temperature. All XRD patterns show that the majority phases have the perovskite structure under all conditions, and all the reflections could be indexed satisfactorily in the tetragonal cell which could be matched with JCPDS file 06-0452. Although changes of peak profile can be observed in XRD patterns of ceramics samples with additives, the peak positions when converted into lattice parameters indicate no deviation. The same

observation has also been reported elsewhere (Corker et al., 2000). However, the secondary phase can also be found and identified as  $\text{ZrO}_2$  which may be a consequence of  $\text{ZrO}_2$  aggregation during sintering (Tipakontitukul et al., 2006). This is because of its inert nature. The relative amounts of perovskite and secondary phases can be determined from the integrated intensities of XRD peaks and the results are summarized in Table 1. The maximum amount of the perovskite phase up to 98.33 wt.% was found in the PZT doped with  $\text{Cu}_2\text{O}$  ceramic and sintered at 999 °C for 4 h. It can also be seen that presence of  $\text{Cu}_2\text{O}$  in PZT can reduce the amount of the  $\text{ZrO}_2$  which presents as a secondary phase compared with PZT without additives. It is possible that the presence of  $\text{Cu}_2\text{O}$  content can minimize loss of  $\text{PbO}$ , which can be responsible for  $\text{ZrO}_2$  aggregation (Zhu et al., 2005).

To understand the densification of PZT with and without additives at different sintering temperatures, investigation of linear shrinkage and bulk density coupled with the SEM micrographs are employed. The results are demonstrated by plots of linear shrinkage and apparent density as a function of sintering temperature in Figure 2. Increasing sintering temperature induces a higher shrinkage to the PZT. Also, under the same sintering conditions, the presence of small amounts of  $\text{Cu}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  seems to promote a higher densification as a higher degree of shrinkage was clearly observed. The shrinkage curve of PZT ceramics reveals a rapid sintering in the range of 900–1200 °C. The present results are consistent with other reports of PZT doped with several additives, such as  $\text{Li}_2\text{CO}_3$  (Yoo et al., 2005),  $\text{MgO}$  (Saha et al., 1999),  $4\text{PbO}\cdot\text{B}_2\text{O}_3$  (Wang, 2002) and  $\text{PbO-SiO}_2$  glass (Pérez et al., 2005) etc. Related SEM micrographs are shown in Figure 3. The SEM

of PZT without additive (Figure 3a and b) shows practically no shrinkage as their grains in the microstructure reflect the particle morphology of the starting powder.

On the other hand, the presence of  $\text{Cu}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  induces a higher shrinkage and development of the grain. This was seen as a change in grain morphology in Figures 3c, d, e and f. The morphology of the PZT ceramics with additive has a smaller grain size than one without additive sintered under the same sintering conditions. The present observation reveals that  $\text{Cu}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  addition results in an inhibition of grain growth as has been found in the case of  $\text{Nb}_2\text{O}_5$  addition (Huang et al., 2004). The results of SEM are also consistent with those of shrinkage measurement. Occurrence of porosity can be clearly observed for both PZT ceramics with and without doping. However, density values of the ceramic samples with doping are considerably higher than those with no doping. These results suggest that the densification of PZT may be driven by the liquid phase since the melting point of  $\text{Bi}_2\text{O}_3$  is ca. 820 °C. The % theoretical density also increased to denser with increasing sintering temperature. The present results are consistent with another report on doping agent distribution methods (Bourgeois et al., 2001). However, drop of shrinkage was found at a temperature of 1035 °C before rising to higher shrinkage again when the sintering temperature exceeded this range. This discrepancy may be the effect of abnormal grain growth observed at 1035 °C (Figure 3f). Following this growth, a homogeneous grain structure is obtained at higher temperatures. There is thus a close correlation between the appearance of abnormal grain growth stage and the re-acceleration of shrinkage rates.

## Conclusion

Thus, it may be concluded that adding Cu<sub>2</sub>O and Bi<sub>2</sub>O<sub>3</sub> (1 wt.%) as a sintering aid during sintering of the PZT provides better sintering conditions at somewhat lower temperature compared with un-doped PZT. The presence of these aids also enhances the linear shrinkage, density and microstructural development. However, this enhancement would be a great deal if it also gave rise to reasonable piezoelectric response or even provided a better piezoelectric constant. This has been considered by the authors and work on electrical properties is under progress and will be in a future report.

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## References

- Bourgeois, L., Dehaut, Ph., Lemaignan, C. and Hammou, A. 2001. Factors governing microstructure development of Cr<sub>2</sub>O<sub>3</sub>-doped UO<sub>2</sub> during sintering. **J Nucl Mater** 297: 313-326.
- Chu, S.-Y. 2000. Doping effects on the dielectric properties of low temperature sintered lead-based ceramics. **Mater Res Bull** 35(7): 1067-1076.
- Corker, D.L., Whatmore, R.W., Ringgaard, E. and Wolny, W.W. 2000. Liquid-phase sintering of PZT ceramics. **J Euro Ceram Soc** 20(12): 2039-2045.
- Ha, J.-Y., Choi, J.-W., Kim, H.-J., Yoon, S.-J. and Yoon, K.H. 2003. The effect of sintered aid CuO-Bi<sub>2</sub>O<sub>3</sub> on microwave dielectric properties of (Pb<sub>0.45</sub>Ca<sub>0.55</sub>)(Fe<sub>0.5</sub>Nb<sub>0.5</sub>)<sub>0.9</sub>Sn<sub>0.1</sub>O<sub>3</sub>. **Mater Chem Phys** 79(2-3): 261-265.
- Huang, C.-L., Chen, B.-H., Wu, L. 2004. Variability of impurity doping in the modified Pb(Zr,Ti)O<sub>3</sub> ceramics of type ABO<sub>3</sub>. **Solid State Comm** 130: 19-23.
- Jaffe, B., Cook, W.R., Jaffe, H. 1971. **Piezoelectric Ceramics**. New York: Academic Press.
- Kim, M.-H., Jeong, Y.-H., Nahm, S., Kim, H.-T. and Lee, H.-J. 2006. Effect of B<sub>2</sub>O<sub>3</sub> and CuO additives on the sintering temperature and microwave dielectric properties of Ba(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> ceramics. **J Eur Ceram Soc** 26(10-11): 2139-2142.
- Lim, J.-B., Kim, D.-H., Nahm, S., Paik, J.-H. and Lee, H.-J. 2006. Effect of B<sub>2</sub>O<sub>3</sub> and CuO additives on the sintering temperature and microwave dielectric properties of Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> ceramics. **Mater Res Bull** 41(6): 1199-1205.
- Pérez, J.A., Soares, M.R., Mantas, P.Q. and Senos, A.M.R. 2005. Microstructural design of PZT ceramics. **J Euro Ceram Soc** 25: 2207-2210.
- Setter, N. and Waser, W., 2000. Electroceramic Materials. **Acta Mater** 48: 151-178.
- Saha, D., Sen, A. and Maiti, H.S. 1999. Low temperature liquid phase sintering of lead magnesium niobate. **Ceram Inter** 25: 145-151.

Tipakontitkul, R., Ananta, S. and Yimnirun, R. 2006. Phase formation and transitions in the lead magnesium niobate–lead zirconate titanate system. **Curr Appl Phys** 6: 307–311.

Wang, C.-H. 2002. The microstructure and characteristics of 0.875PZT–0.125PMN ceramics with addition of Pb-based flux. **J Euro Ceram Soc** 22:2033–2038.

Yoo, J., Lee, C., Jeong, Y., Chung, K., Lee, D. and Paik D. 2005. Microstructural and piezoelectric properties of low temperature sintering PMN–PZT ceramics with the amount of  $\text{Li}_2\text{CO}_3$  addition. **Mater Chem Phys** 90: 386–390.

Zahi, S., Bouaziz, N., Abdesslem, N. and Boutarfaia, A., 2003. Dielectric and piezoelectric properties of  $\text{PbZrO}_3$ – $\text{PbTiO}_3$ – $\text{Pb}(\text{Ni}_{1/3}, \text{Sb}_{2/3})\text{O}_3$  ferroelectric ceramic system. **Ceram Inter** 29: 35–39.

Zhu, Z.G., Li, G.R., Zheng, L.Y. and Yin, Q.R. 2005. Microstructure, domain morphology and piezoelectric properties of Si-doped  $\text{Pb}(\text{Mn}_{1/3}, \text{Sb}_{2/3})\text{O}_3$ – $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  system. **Mater Sci Eng B** 119: 46–50.

Zuo, M.-K., Li, W., Shi, J.-L. and Zeng, Q. 2006. Influence of  $\text{CuO}$  addition to  $\text{BaSm}_2\text{Ti}_4\text{O}_{12}$  microwave ceramics on sintering behavior and dielectric properties. **Mater Res Bull** 41(6): 1127–1132.

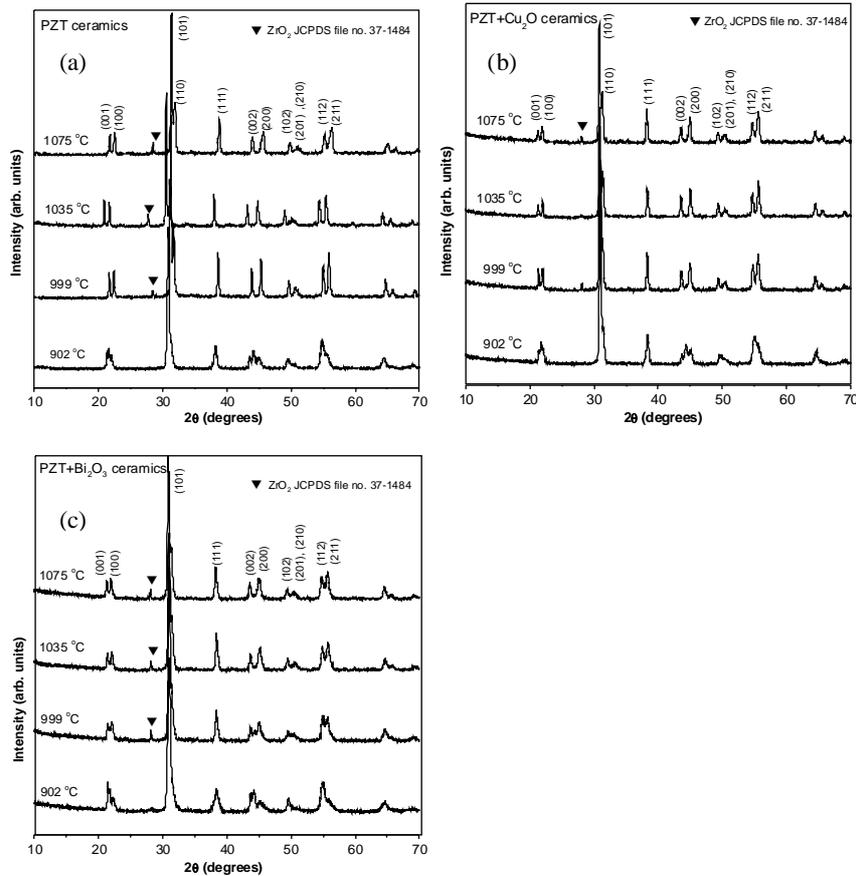
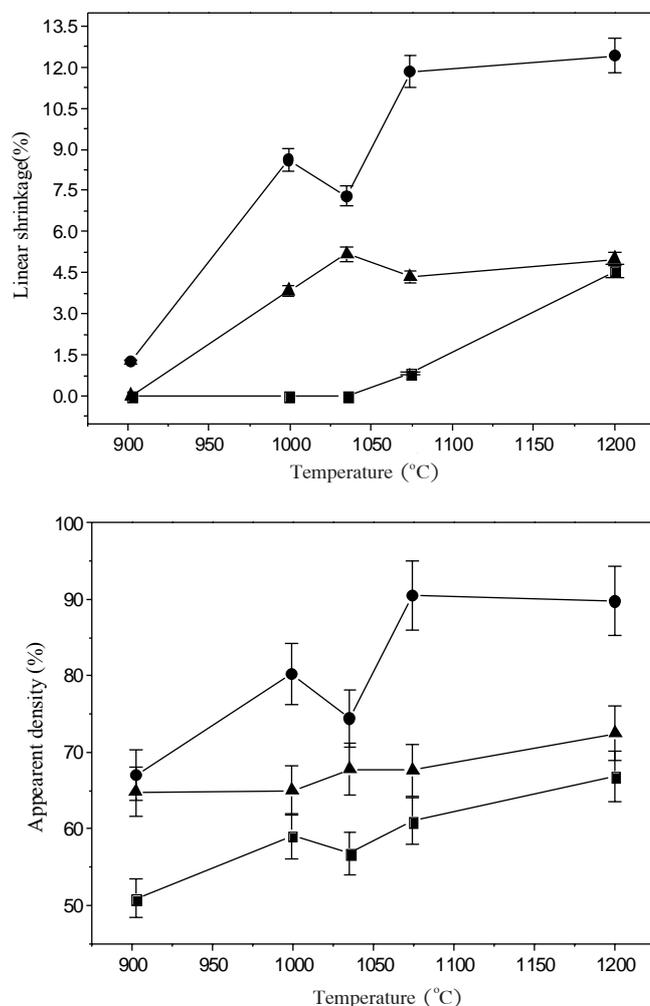


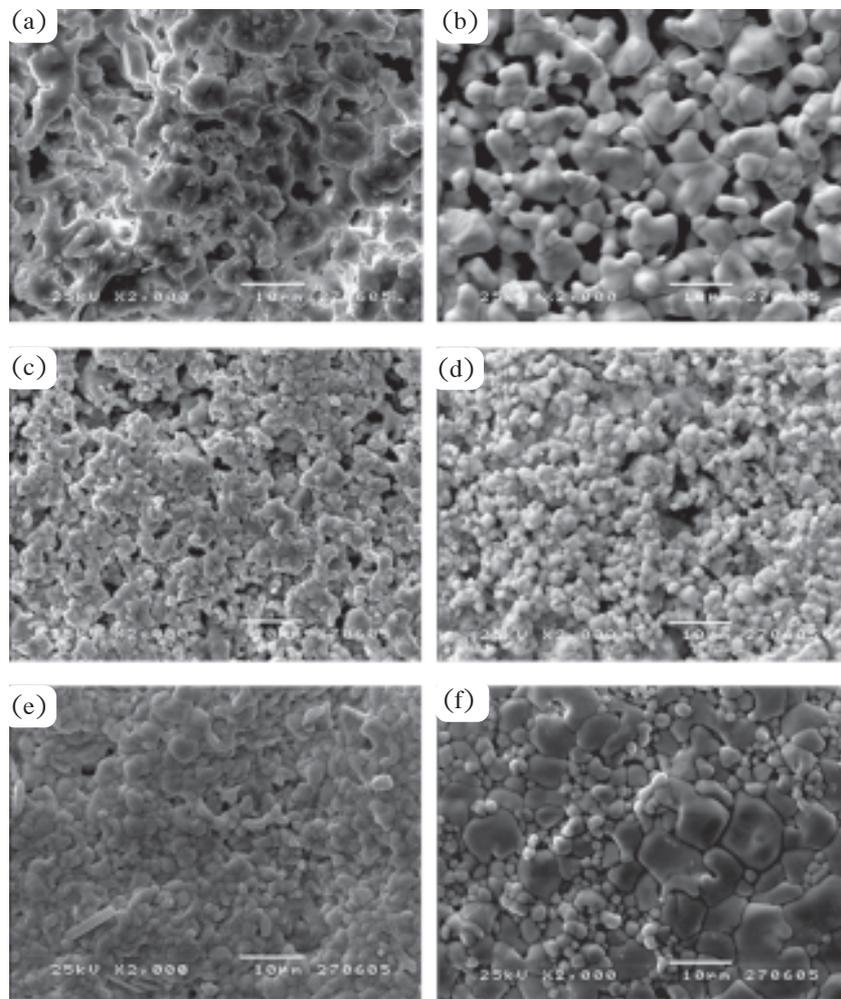
Figure 1. XRD patterns of (a) PZT ceramics, (b) PZT with 1 wt.% of  $\text{Cu}_2\text{O}$  and (c) PZT with 1 wt.% of  $\text{Bi}_2\text{O}_3$  with various sintering temperatures.

**Table 1.** Summary of relative concentration of the main PZT and secondary components as a function of sintering temperature.

Sintering conditions		% PZT perovskite phase (wt.%)		% perovskite phase of PZT+ Bi <sub>2</sub> O <sub>3</sub> phase (wt.%)		% perovskite phase of PZT+ Cu <sub>2</sub> O phase (wt.%)	
Temperature (°C)	Dwell time (h)	PZT	Secondary phase	PZT	Secondary phase	PZT	Secondary phase
902	4	96.41	3.59	94.30	5.70	97.54	2.46
999	4	91.95	8.05	93.42	6.58	98.33	1.67
1035	4	91.86	8.14	93.70	6.30	94.22	5.78
1075	4	87.80	12.20	95.17	4.83	78.34	21.66



**Figure 2.** Variation of linear shrinkage and apparent density of (■) PZT , (▲) PZT+ 1 mol% of Bi<sub>2</sub>O<sub>3</sub> and (●) PZT + 1 wt.% of Cu<sub>2</sub>O during sintering at 900 – 1200 °C for 4 h.



**Figure 3.** Microstructure of PZT (a) and (b), PZT with  $\text{Bi}_2\text{O}_3$  additive (c) and (d) and PZT with  $\text{Cu}_2\text{O}$  additive (e) and (f) sintered at 1,035 and 1,075 °C for 4 h with heating/cooling rate of 10 °C/min.