Preparation of PZT Nanopowders via Sol-Gel Processing

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ABSTRACT

Lead zirconate titanate (PZT) nanopowder of molar composition 52/48 ($Pb(Zr_{0.52}Ti_{0.48})O_3$) was prepared by a modified sol-gel processing method. The starting chemicals used for the preparation of PZT precursor were lead (II) acetate trihydrate, zirconium (IV) propoxide, titanium (IV) isopropoxide, acetylacetone and 1,1,1-tris (hydroxymethyl) ethane. The as-reacted precursor and heat-treated powders at different temperatures were characterized, using thermogravimetric analysis/differential thermal analysis (TGA/DTA) and x-ray diffraction analysis (XRD) techniques. The precursors showed amorphous structure up to the calcination temperature of 500°C where perovskite PZT started to form. Scanning electron microscopy analysis (SEM) showed that PZT powder with various particle sizes in the range of nanometer could be obtained.

Key words: Lead zirconate titanate (PZT), Sol-gel processing, Nanopowder, Phase, Micro-structure

INTRODUCTION

Lead zirconate titanate (PZT) material, having a perovskite-type ABO3 formula, is an important ferroelectric material which has good piezoelectric and pyroelectric properties, relatively high Curie temperature and relatively low sintering temperatures (Haertling, 1999; Moulson and Herbert, 1999). PZT was found to be very suitable and useful for many industrial applications such as transducers, computer memory, pyroelectric sensors, electro-optical modulators, etc., (Nagao et al., 1999; Kim and Song, 2003). There are various methods that have been successfully employed for the preparation of PZT powders, for examples, mixed-oxide, hydrothermal, sputtering, spray drying and sol-gel processing (Hammer and Hoffman, 1998; Milne et al., 1999; Chen et al., 2002; Seifert et al., 2004). Among them, the sol-gel processing method has received particular interest because of its considerable advantages in producing high-purity ultrafine nanoparticle over other processing methods. The sol-gel method can produce rather reactive PZT nanopowders which gives rise to the PZT ceramics with good compositional and structural homogeneity (Xu et al., 2004). The most common method for sol-gel synthesis involves hydrolysis and condensation of metal alkoxides with different modifiers including methoxylethanol (Budd et al., 1985), acetic acid (Yi and Sayer, 1996) and acetlyacetone (Tu et al., 1996). The modifiers were used to stabilize titanium and zirconium alkoxides against hydrolysis caused by moisture in air. Recently, two different sol processing routes have been developed. The first one is known as a diol route while the other is named a triol route (Kurchania and Milne, 1998; Nakasata and Milne, 2001). The triol route used a triol, 1,1,1- tris (hydroxymethyl) $CH_3C(CH_2OH)_3$, which undergoes ligand-exchange reaction with propoxy and pentanedione groups on the Ti and Zr starting reagents and links together metal components to form a polymeric precursor solution (Nakasata and Milne, 2001).

The purpose of this research is to prepare PZT nanopowders by a triol sol-gel route. Preliminary study on phase formation and transition temperature of the as-synthesized powder is carried out. The relationship between synthesis conditions and microcstructure of these powders are also investigated and discussed.

MATERIALS AND METHODS

The starting materials used were zirconium (IV) propoxide (70%, Aldrich) 9.621 g and acetylacetone (99%, Fluka) 6.206 g in a dry nitrogen atmosphere. The mixture was refluxed in an oil bath at 90°C for 2 h. The solution was then cooled down to room temperature before adding 5.562 g of titanium (IV) isopropoxide (99%, Aldrich), 16.498 g of lead (II) acetate trihydrate (99%, Riedel) and 4.798 g of 1,1,1- tris (hydroxymethyl) ethane (99%, Aldrich) into the solution. The mixture was heated at 70°C for 4 h. The final product was a viscous golden solution, *so called* a sol. After the resulting sol was dried at 120°C for 24 h, the powders were formed and then were subjected to a calcination process at various temperatures between 300-700°C for 2 h with heating/cooling rates of 5°C/min. Thermal characteristics of powders were studied, using thermogravimetric analysis/differential thermal analysis (DTA and TGA). The phase formation to a perovskite PZT was determined, using X-ray diffraction analysis (XRD, Phillip Model X-pert) with CuKα radiation. Scanning electron microscopy (SEM, JEOL JSM-6335F) was used for examining the microstructure and particle size of the PZT powders.

RESULTS AND DISCUSSION

After the as-reacted precursor was dried, the as-received powder was characterized, using DTA and TGA. The DTA curve in Figure 1 shows four endothermic and exothermic peaks. The first peak at 95°C was primarily due to the removal of water and/or the organic species within micropores of the powder (Linardos et al., 2004), corresponding to the TGA result shown in the same figure, a continuous mass decreasing before 370°C occurred. The second DTA peak at 370°C corresponds to a weight loss as shown by the TGA curve. This is probably attributed to the oxidation of acetate as suggested by other researchers (Xu et al., 2004). The third DTA peak at 600°C is not accompanied by a significant decrease in weight and this therefore may reflect the crystallization of PZT powder (Weng et al., 2002), while the DTA peaks at about 800oC may be caused by the decomposition of PbO which is also related to weight loss in TGA curve over the same temperature range (Nothrop, 1968).

The XRD patterns of as-synthesized PZT and PZT powders calcined at 300, 400, 500, 600 and 700°C are shown in Figure 2. The results suggested that the as-received powder and those calcined up to 400°C comprised only amorphous structure which was indicated by the broadened XRD peak. At 500°C, the crystalline perovskite-type structure of PZT started to form and the degree of crystallinity increased with the calcination temperature. The complete crystalline PZT powder was achieved at the calcination temperature of about 600–700°C and its XRD peaks corresponded to a tetragonal structure (JCPDS file number. 33–784). However, a very small amount of unknown phase also existed in the powder along with the perovskite PZT. The formation of the unknown phase at $2\theta \sim 29($ is believed to be caused by an inhomogeneous distribution of Pb, Ti, Zr component in the sol (Bursill et al., 1994; Weng et al., 2002). Some researchers referred to this unknown phase as a pyrochlore phase (Kwok and Desu, 1992; Tiwari et al., 1998).

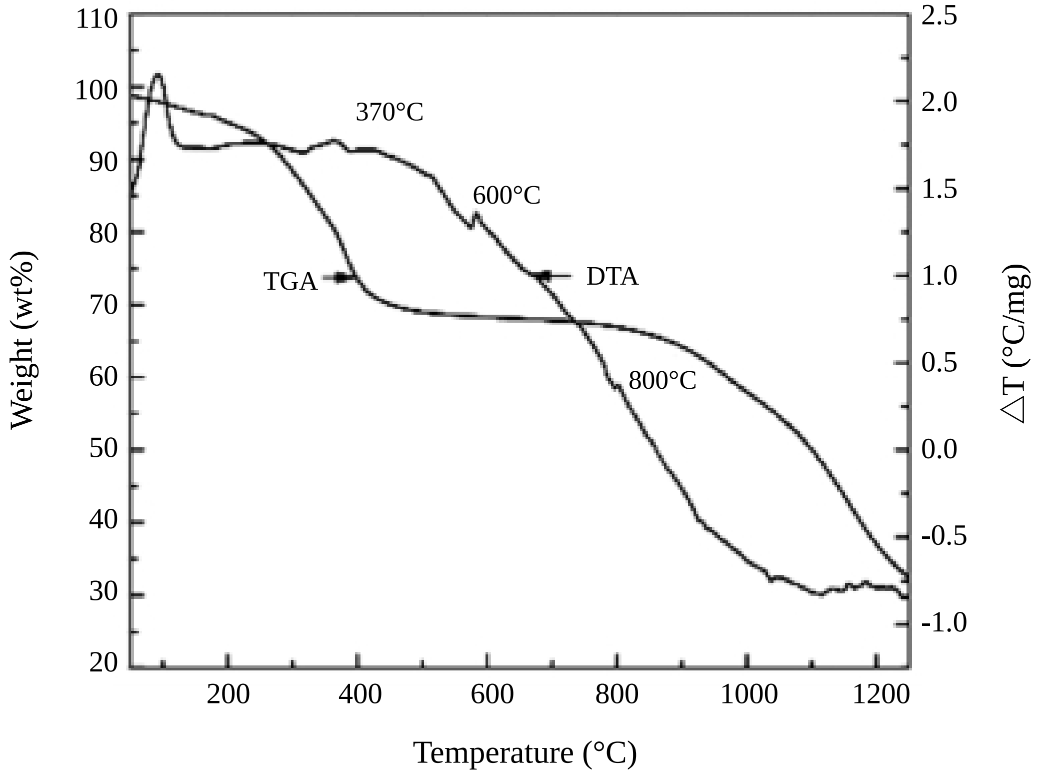

Figure 1. A D

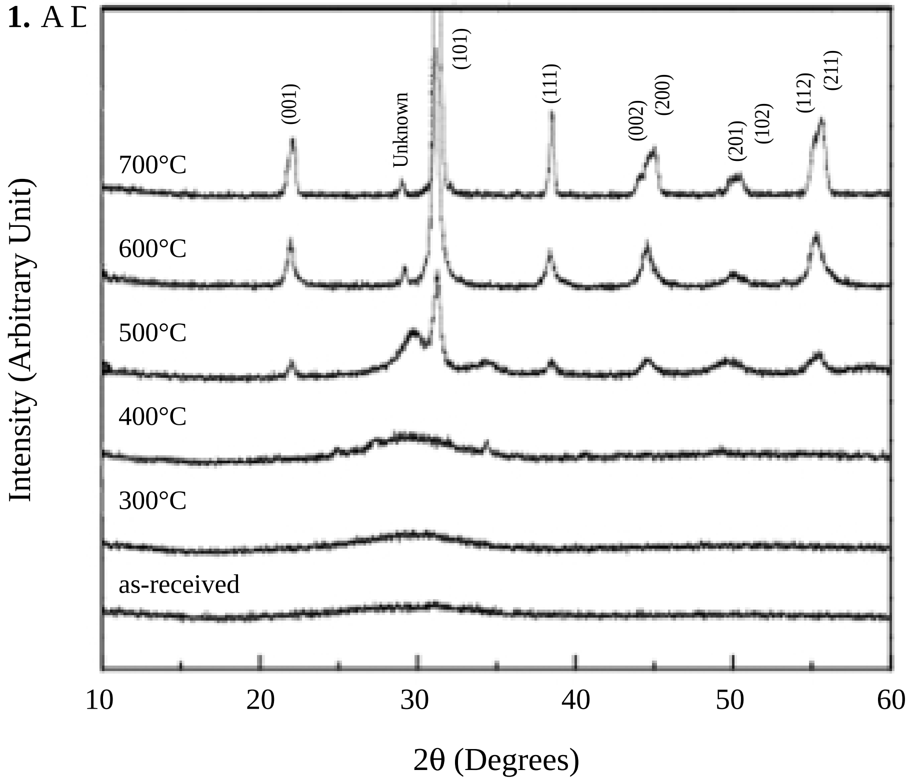

Figure 2. X-ray diffraction patterns of as-received PZT powder and PZT powders calcined at 300, 400, 500, 600 and 700°C.

SEM micrographs of synthesized PZT and calcined PZT powders are shown in Figure 3. It is seen that below 600°C, the powders are likely to melt to form an amorphous clot, in good agreement with the XRD results. After 500°C, the particle sizes of all powders rapidly increase with increasing calcining temperatures. This observation could be attributed to the crystallization of PZT compounds in consistent with the TGA/DTA and XRD results reported earlier. The results in this study suggested that the sol-gel PZT powder calcined at 600°C showed a potential to form a good ceramic due to its nano-sized particles with high crystallinity of perovskite-type structure.

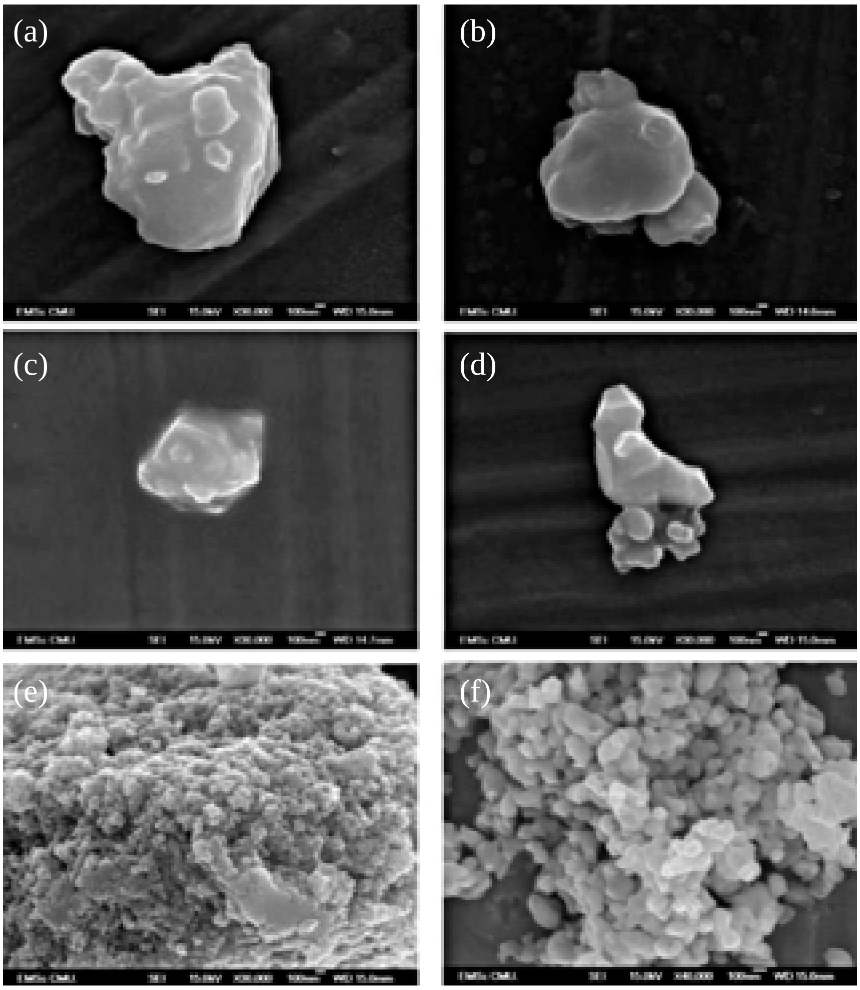

Figure 3. SEM micrographs of (a) as-received PZT powder and PZT powders calcined at (b) 300, (c) 400, (d) 500, (e) 600 and (f) 700°C.

CONCLUSION

PZT nanopowder was successfully synthesized by a triol sol-gel route. According to the results of TGA/DTA analysis, crystalline perovskite-type PZT nanopowder could be obtained at the calcination temperature of 500°C. XRD patterns confirmed the formation of perovskite-phase PZT nanopowder. However, a small amount of unknown phase was often found to exist along with the perovskite PZT phase. The particle size in the range of nanometer was obtained at all calcination temperatures. From this study, it could be seen that the calcination temperature showed rather strong effect on the phase composition and microstructure of the sol-gel-derived PZT powder.

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REFERENCES

Budd, K. D., S. K. Dey, and D. A. Payne. 1985. Sol-gel processing of $PbTiO_3$, $PbZrO_3$, PZT, PLZT thin film. Proceedings British Ceramics Society 36 : 107–121.

Bursill. L. A., I. M. Reaney, D. P. Vijay, and S.B. Desu. 1994. Comparison of lead zirconate titanate thin films on ruthenium oxide and platinum electrodes. Journal of Applied Physics 75 : 1521–1525.

Chen. Y. Z., L. B. Ma, J. Kong, and R. F. Zhang. 2002. Seeding in sol-gel process for $Pb(Zr_{0.52}Ti_{0.48})O_3$ powder fabrication. Materials Chemistry and Physics 75 : 225–228.

Haertling, G. H. 1999. Ferroelectric ceramics, history and technology. Journal of the American Ceramics Society 82 : 797–818.

Hammer, M., and M. J. Hoffmann. 1998. Sintering model for mixed-oxide-derived lead zirconate titanate ceramics. Journal of the American Ceramics Society 81 : 3277–3284.

Kim, K., and Y. J. Song. 2003. Integration technology for ferroelectric memory devices. Microelectron Relib 43(3) : 385–398.

Kurchania, R., and S. J. Milne. 1998. Synthesis of PZT thin films using a diol based sol-gel route. Journal of Materials Science 33 : 659–667.

Kwok, C. K., and S. B. Desu. 1992. Pyrochlore to perovskite phase transformation in sol-gel derived PZT thin film. Applied Physics Letters 60 : 1430–1432.

Linardos, S., Q. Zhang, and J. R. Alcock. 2004. Preparation of sub-micron PZT particles with the sol-gel technique. Journal of the European Ceramic Society. (in press).

Milne, S. J., R. Kurchania, J. D. Kenedy, M. Naksata, S. Arscott, D. Kaewchinda, N. Sriprang, and R. Miles. 1999. Triol sol-gel route for preparing PZT thin films. Ceramics Transactions 95 : 95–101.

Moulson, A. J., and J. M. Herbert. 1999. Electroceramics. Chapman and Hall, London.

Nagao, M., K. Minami, and M. Esashi. 1999. Silicon angular rate sensor using PZT thin film. Sensor Materials 11(1) : 31–39.

Nakasata, M., and S. J. Milne. 2001. Phase development and ferroelectric properties of lead zirconate titnate thin films prepared from a triol sol-gel route. International Journal of Inorganic Materials 3 : 169–173.

Nothrop, D. A. 1968. Vaporization of lead zirconate-lead titanate materials : Hot-pressed compositions near theoretical density. Journal of the American Ceramic Society 51 [7] : 357–368.

Philips, N. J., and S. J. Milne. 1992 Sol-gel-derive lead titanate films. Journal of Non-Crystalline Solids 147 : 285–290.

Seifert, S., D. Sporn, T. Hauke, G. Muller, and H. Beige. 2004. Dielectric and electromechanical properties of sol-gel prepared PZT thin films on metallic substrates. Journal of the European Ceramic Society 24 : 2553–2566.

Tiwari, V. S., A. Kumar, and V. K. Wadhawan 1998. Kinetics of formation of the pyrochlore and perovskite phases in sol-gel derived lead zirconate titanate powder. Journal of Materials Research 13: 2170–2173.

Tu, Y. L., M. L. Calzada, S. J. Milne, N. J. Phillips, and Y. L. Tu. 1996. Synthesis and electrical characterisation of thin films of PT and PZT made from a diol based sol-gel route Journal of the American Ceramic Society 79 : 441–448.

Weng, L., X. Bao, and C. K. Sagoe. 2002. Effect of acetylacetone on the preparation of PZT materials in sol-gel processing. Materials Science and Engineering B96 : 307–312.

Xu, Z. J., R. Q. Chu, G. R. Li, X. Shao, and Q. R.Yin. 2004. Preparation of powders and ceramics via a hybrid method of sol-gel and ultrasonic atomization. Materials Science and Engineering B117 : 113–118.

Yi, G., and M. Sayer. 1996. An acetic acid/water based sol-gel PZT process Zr and Ti alkoxides with acetic. Journal of Sol-Gel Science Technology 6 : 65–74.