Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 925–929

www.elsevier.com/locate/jeurceramsoc

Synthesis and characterization of compositionally modified PZT by wet chemical preparation from aqueous solution

Byeong Woo Lee*

Department of Materials Engineering, Korea Maritime University, Pusan 606-791, South Korea

Abstract

Compositionally modified PZT powders of Nb-doped PZT and PMN–PZT were synthesized via two processing routes, namely coprecipitation and evaporative decomposition. The new precursor of Zr_xTi_{1-x}-peroxo-nitrate solution was stable and suitable for the synthesis processes. For Nb-doped PZT, reactive fine powders of single-phase perovskite were formed at temperature as low as 600 °C in both methods and fairly high specific surface areas of 17 m^2/g (coprecipitation) and 8 m^2/g (evaporative decomposition) were obtained for the synthesized powders. For PMN–PZT, evaporative decomposition process effectively yielded the phase-pure perovskite without the pyrochlore at 700 °C.

Keywords: Perovskites; Powders–chemical preparation; PZT

1. Introduction

Wet chemical process has been extensively studied for the synthesis of various ceramic powders due to the merits of easy composition control, better homogeneity and low processing temperature in comparison to the conventional solid-state reaction process. Among the chemical processes, coprecipitation technique has been most widely investigated to prepare compositionally modified lead zirconate titanate (PZT) ceramics.[1–4] Coprecipitation uses low cost precursors of inorganic salts, such as metal chlorides or nitrates, and has considerable practical merits to prepare commercially viable powders. Although the process has achieved great successes in preparing the PZT ceramics, still some limitations, such as a preferential precipitate formation and an incomplete precipitation, may occur. For example, the preferential precipitate of lead (Pb) chloride, which is hard to re-dissolve, is easily formed in mixed chlorides and nitrates solutions prior to the coprecipitation.[3] To avoid the lead chloride precipitation and chlorine contamination in the prepared powders, aqueous solutions of metal nitrates are often used as precursors to prepare some PZT powders.[2–4] In the starting materials, however, titanium (Ti) nitrate solution is highly unstable to temperature and solution pH. Therefore, the solution must be stored in a refrigerator and kept at strong acidity.[5] Furthermore, the coprecipitates, such as metal hydroxides or oxalates, have different solubilities in the reaction solution and washing media (distilled water or alcohols), which leads to the incomplete precipitation. Especially, for PMN–PZT $\{Pb(Mg_{1/3}Nb_{2/3})O_3–PbZr_xTi_{1-x}O_3\}$ powders, Mg^{2+} has high solubility for most precipitants, and hence causes an incomplete precipitation of the magnesium component.

In the present study, compositionally modified PZT ceramics of Nb-doped PZT and PMN–PZT at near the rhombohedral–tetragonal morphotropic phase boundary (MPB) were prepared by wet chemical processes. To synthesises the single-phase powders at low temperatures and to overcome the described problems, coprecipitation and evaporative decomposition with use of modified nitrates based solutions are adapted.

2. Experimental

Nb-doped PZT ($PbZr_{0.53}Ti_{0.47}O_3$ + 0.5 wt.% Nb_2O_5) and PMN–PZT $\{0.375Pb(Mg_{1/3}Nb_{2/3})O_3–0.625PbZr_{0.4}Ti_{0.6}O_3\}$ powders of near the MPB compositions were

---

* Tel.: +82-51410-4356; fax: +82-51404-3986.
E-mail address: bwlee@kmaritime.ac.kr (B.W. Lee).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00428-X

prepared by the coprecipitation and the evaporative decomposition method.

Aqueous solutions of reagent grade Pb-nitrate, Mg-nitrate and Nb-ammonium oxalate were used as precursor materials. For both the Zr and Ti components, the new precursors of $Zr_x \cdot Ti_{1-x}$-peroxo-nitrate ($x = 0.4$ and $x = 0.53$) complexes were used. The $Zr_x \cdot Ti_{1-x}$-peroxo-nitrates for the modified PZT were prepared as follows: concentration determined $ZrOCl_2$ and $TiCl_4$ aqueous solution was mixed and hydrogen peroxide (H_2O_2) was added to form a peroxo-complex solution of $Zr_x \cdot Ti_{1-x}$. The H_2O_2/Ti molar ratio was fixed at 3. $Zr_x \cdot Ti_{1-x}$-peroxo-hydroxide was precipitated by the hydrolysis of the mixed (peroxo) solution with an ammonium solution, and washed with distilled water to remove chlorine ions. $Zr_x \cdot Ti_{1-x}$-peroxo-nitrate solution was prepared by dissolving the $Zr_x \cdot Ti_{1-x}$-peroxo-hydroxide in a nitric acid solution.

The flow diagram of the powder processing methods employed in this study is shown in Fig. 1. The mixed aqueous solutions of the modified PZT compositions were prepared for both methods. For coprecipitation method, extra amount of hydrogen peroxide added again to the mixed aqueous solution for improved coprecipitation.[3] The metal peroxo-hydroxide precipitates were formed when the mixed precursor solution added to an ammonium solution by maintaining the final pH value above 12. The precipitates were filtered and washed by distilled water to remove all the soluble reaction products, and then dried at 80 °C for 12 h.

In the case of evaporative decomposition, citric acid was added in the mixed aqueous solution. The molar ratio of citric acid to metal ions was maintained at a value of 2. The clear solution with pH 6 was prepared by adding the required amount of ammonium solution. The solution was slowly evaporated at 70 °C until a viscous gel was obtained. The viscous gel was kept in vacuum oven at 80 °C for 12 h to form a solid (resin) precursor, and then the resultant solid product was heat treated at 250 °C for 10 h; this resulted in a fluffy mass as decomposed product.

The as-synthesized materials from both the methods were calcined in air at various temperatures up to 800, for 2 h. The calcined powders were sintered at 1150 °C, for 2 h by an ordinary two-crucible method with

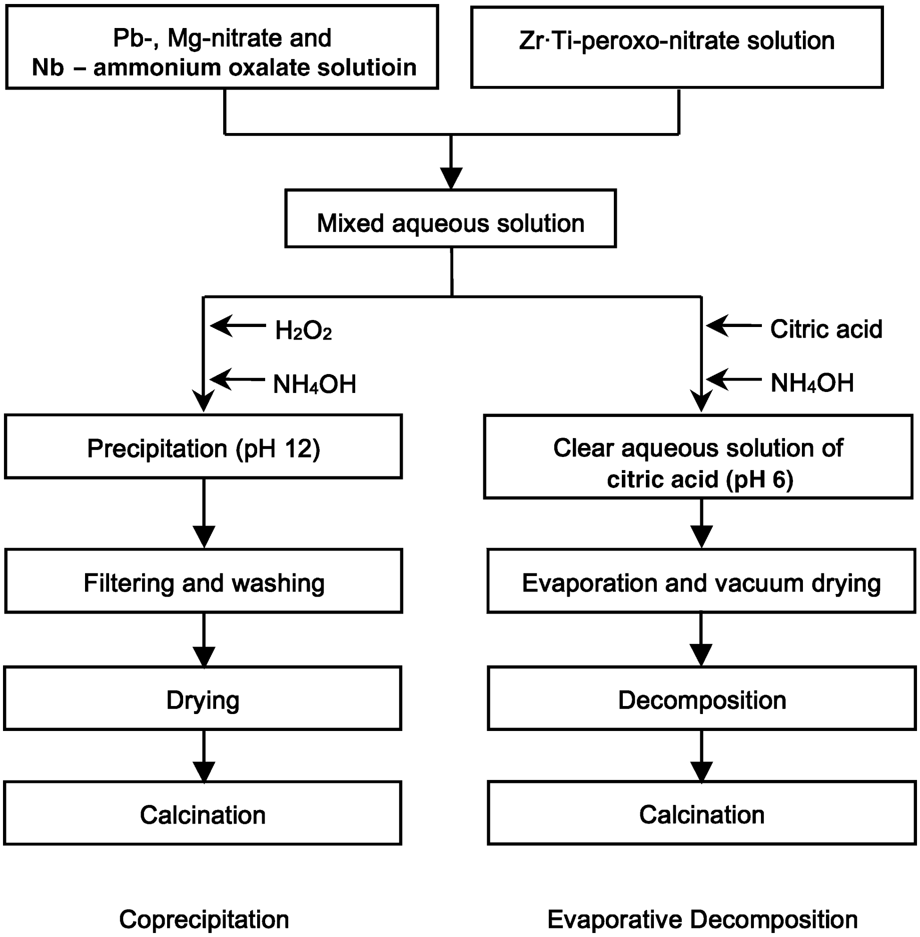

Fig. 1. Flow diagram for the powder preparation procedure.

$PbZrO_3$ atmosphere powders. For comparison, some PZT powders were also prepared by the conventional solid-state reaction of metal oxides.

ICP, TG-DTA, XRD, BET, and SEM analysis were performed on the prepared powders.

3. Results and discussion

3.1. *Stability of* $Zr_x{\cdot}Ti_{1-x}$*-peroxo-nitrates solution*

Aqueous solution of $TiO(NO_3)_2$, as a Ti source in PZT preparation, is known to be unstable under normal conditions, as mentioned.[5] Hydrous TiO_2 is easily formed in the solution and the quantity of TiO_2 increased with increasing temperature. Therefore, all the reaction temperatures during preparation process must be kept less than 15 °C and the solution stored in a refrigerator. Furthermore, the solution becomes stable only when the pH was kept at less than 0.2. In this study, it was found that the peroxo-aqueous solution of $TiO(NO_3)_2$ with H_2O_2 was far more unstable with producing higher TiO_2 product than the $TiO(NO_3)_2$ aqueous solution alone at the same temperature. By contrast, the combined peroxo-nitrate solution of Zr and Ti was quite stable and could be kept for months at room temperature without any precipitation formation. Also, there was no precipitate formed up to pH 1. The stable $Zr_x{\cdot}Ti_{1-x}$-peroxo-nitrate solution was a quite effective precursor to prepare PZT powders by the wet chemical processes.

3.2. *Preparation of Nb-doped PZT*

TG–DTA analysis of Nb-doped PZT powders prepared by the coprecipitation and the evaporative decomposition is presented in Fig. 2. For the coprecipitates [Fig. 2(a)], the reaction involving a weight loss resulting from decomposition of hydroxide was finished at around 450 °C. The endothermic peak at 510 °C was due to the transition from amorphous to perovskite. For the evaporative decomposition product [Fig. 2(b)], the consecutive reactions of the weight loss up to 500 °C, which resulted from decomposition of organic components, was found. There was decomposition oxidation with strong exothermic reaction at round 400 °C. The TG–DTA results for the Nb doped PZT powders were identical, as were the results obtained by XRD patterns (Fig. 3) of heat-treated powders at different temperatures. For the coprecipitates [Fig. 3(a)], well-developed peaks of perovskite phase were formed at 600 °C from amorphous. No intermediate impurity phase was formed. For the powders by evaporative decomposition, the well-developed perovskite phase was also formed at 600 °C [Fig. 3(b)]. Below the synthesis temperature for the perovskite phase, an impurity phase indexed as PbO was formed in the prepared powders. In this evaporative decomposition, the single-phase perovskite was formed at the low temperature without use of any complexing agents, such as ethylene glycol or ethylenediaminetetraacetic acid (EDTA), which were often used in normal evaporative decomposition process of citrate salts to help the low temperature synthesis.[6,7]

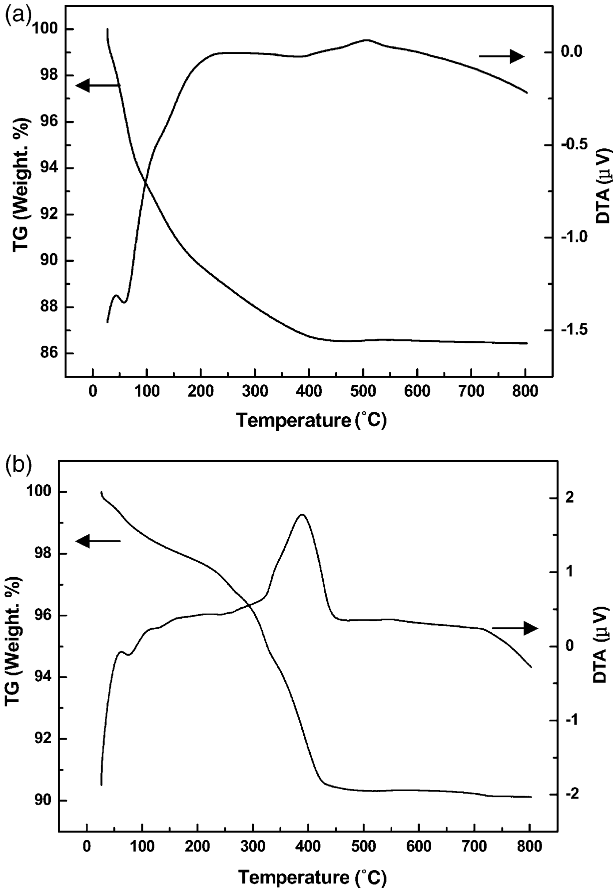

Fig. 2. TG–DTA curves of the Nb-doped PZT powders prepared by (a) coprecipitation and (b) evaporative decomposition.

The results show that the synthesis temperature was as low as around 600 °C in both the preparation methods and the temperature was substantially lower than those (800–1000 °C) of the conventional solid state reaction process.[8] In both methods, the composition between the starting solution and the prepared powders determined by ICP analysis was identical.

Fig. 4 shows morphologies of the synthesized powders prepared at 600 °C for 2 h. Coprecipitation method yielded very fine powder with a median particle size of around 0.1 μm. The powder obtained by evaporative decomposition contained a large portion of agglomerates with small particulates. The values of specific surface area determined by BET analysis were 17 m^2/g (coprecipitation) and 8 m^2/g (evaporative decomposition). The results indicate that the powder prepared by coprecipitation is a much more reactive fine powder with a uniform size distribution than the powder by

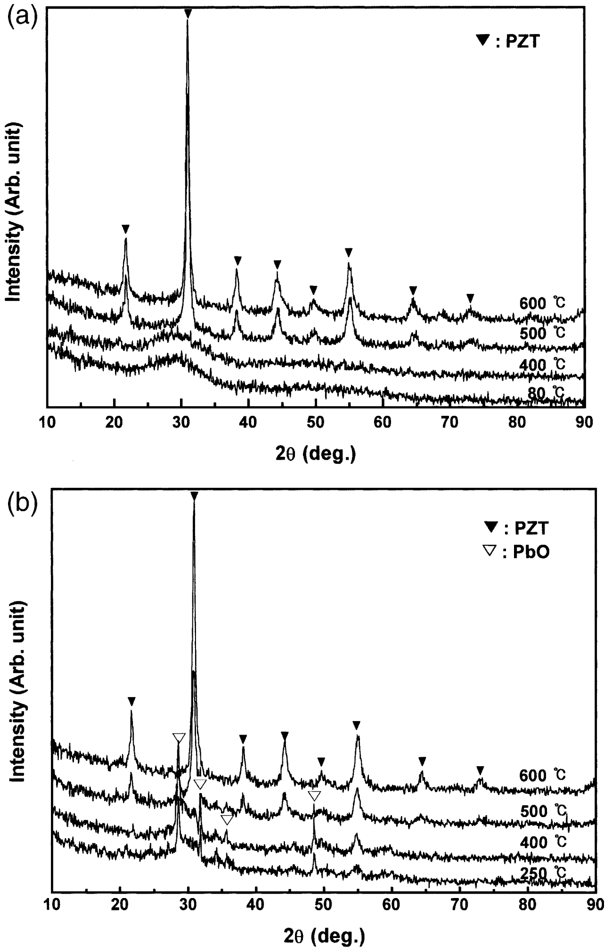

Fig. 3. XRD patterns of the prepared Nb-doped PZT powders heat-treated at different temperatures: (a) coprecipitation and (b) evaporative decomposition.

evaporative decomposition. These BET values are quite larger than the value below 2 m^2/g for the ordinary solid-state reaction product.[8]

The sinterability of calcined powders was in proportion with their specific surface areas. The higher surface area lead to the higher sintered density. It was shown that the fairly high densities of 99% (coprecipitation) and 95% (evaporative decomposition) of theoretical were obtained for the ceramics sintered at 1150 °C and the sintering temperature was also a lower temperature than that (around 1250 °C) of the solid state reaction.

3.3. Preparation of PMN–PZT

The powders obtained by different processing routes were characterized by XRD as shown in Fig. 5. Phase-pure perovskite PMN–PZT was synthesized at 700 °C only by evaporative decomposition process. For the powders prepared by coprecipitation and solid-state reaction process, the pyrochlore phase was found at 800 °C and did not disappear even after calcinations at 1000 °C. The formation of pyrochlore at high temperatures in the solid-state reaction powder was mainly due to a compositional in-homogeneity resulting from an insufficient mixing.[9,10] On the other hand, for the powder prepared by coprecipitation, the pyrochlore was formed by an incomplete magnesium precipitation.

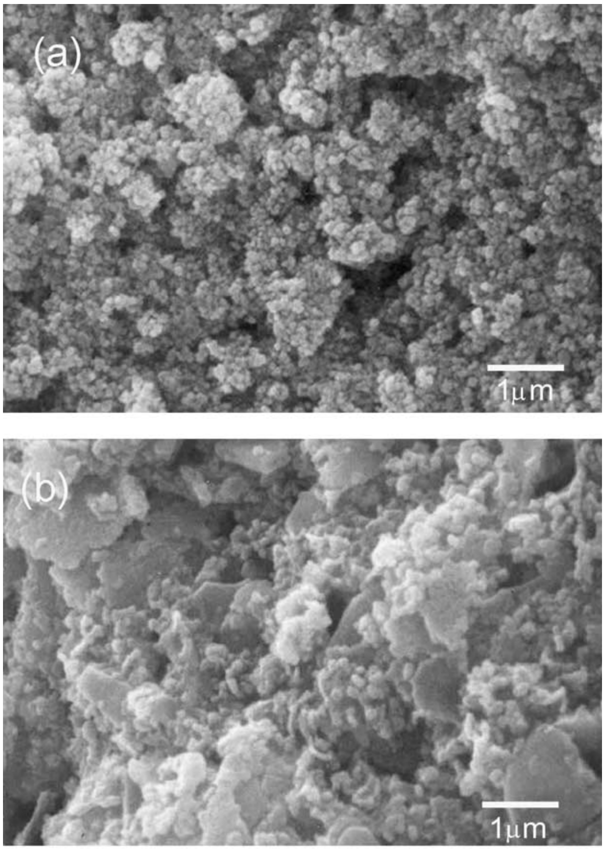

Fig. 4. SEM micrographs of the prepared Nb-doped PZT powders calcined at 600 °C for 2 h: (a) coprecipitation and (b) evaporative decomposition.

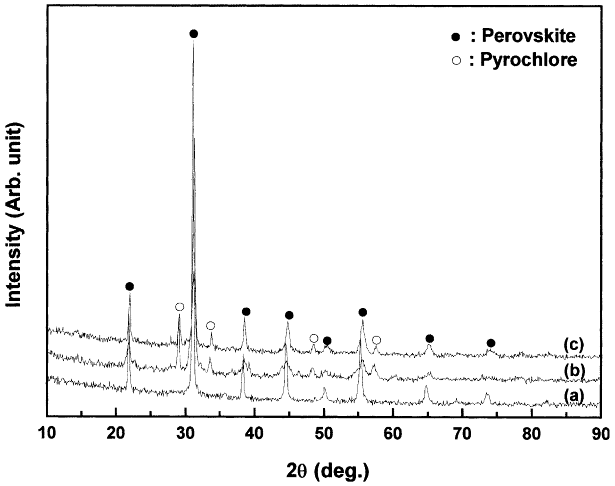

Fig. 5. XRD patterns of the PMN–PZT powders prepared by (a) evaporative decomposition at 700 °C for 2 h, (b) coprecipitation at 800 °C for 2 h, and (c) solid state reaction at 800 °C for 2 h.

An ICP analysis in this study has shown that the Mg still remained unreactive in the solution after precipitation. It has been known that the magnesium deficiency in the prepared powders resulted in the lead niobate based pyrochlore.[10]

Since there was no compositional difference between the starting solution and the prepared powder, the evaporative decomposition process provided a precise composition control, which was hardly obtainable in the coprecipitation method involving the high solubility component.

4. Conclusion

Compositionally modified PZT powders were prepared by coprecipitation and evaporative decomposition process. In this study, the modified wet chemical approaches by using the $Zr_x \cdot Ti_{1-x}$-peroxo-nitrate solutions were found to be quite applicable routes for the powder synthesis at lower temperatures.

For Nb-doped PZT, the processing temperatures of perovskite phase synthesis and dense ceramic formation were substantially lowered in both wet chemical methods. Coprecipitation was more effective to prepare reactive fine powders of higher surface area.

In the case of PMN–PZT, the evaporative decomposition process effectively yielded homogeneous powders of the phase-pure perovskite with a precise control of the desired composition of exact Mg content.

Acknowledgements

This article was financially supported by the Research Center for Electronic Ceramics (RCEC) of Dongeui University funded by the Korea Science and Engineering Foundation (KOSEF), Ministry of Science and Technology (MOST) and the Busan Metropolitan City Government.

References

1. Rao, K., Rao, A. V. and Komarneni, S., Reactive PZT precursor powder by coprecipitation. *Mater. Lett.*, 1996, **28**, 463–467.
2. Yoshikawa, Y. and Tsuzuki, K., Susceptibility to agglomeration of fine PLZT powders prepared from nitrate solution. *J. Euro. Ceram. Soc.*, 1990, **6**, 227–235.
3. Yoshikawa, Y. and Tsuzuki, K., Fabrication of transparent lead lanthanum zirconate titanate ceramics from fine powders by two-stage sintering. *J. Am. Ceram. Soc.*, 1992, **75**(9), 2520–2528.
4. Guo, L., Lyashchenko, A. and Dong, X. L., Synthesis of zirconium-rich PZT ceramics by hydroxide coprecipitation under hot-press. *Mater. Lett.*, 2002, **56**, 849–855.
5. Bhattacharjee, S., Paria, M. K. and Maiti, H. S., Preparation of $PbTiO_3$ powder through oxalate precipitation route. *Mater. Lett.*, 1992, **13**, 130–134.
6. Rukmini, H. R., Choudhary, R. N. P. and Rao, V. V., Structural and electrical properties of sol-gel prepared (La,Li) modified PZT ceramics. *Mater. Lett.*, 1998, **37**, 268–275.
7. Wang, H. W., Hall, D. A. and Sale, F. B., Phase homogeneity and segregation in PZT powders prepared by thermal decomposition of metal-EDTA complexes derived from nitrate and chloride solutions. *J. Am. Ceram. Soc.*, 1992, **75**(1), 124–130.
8. Cho, S. H. and Biggers, J. V., Characterization and sintering of lead zirconate–titanate powders. *J. Am. Ceram. Soc.*, 1983, **66**(10), 743–746.
9. Bouquin, O., Lejeune, M. and Boilot, J. P., Formation of the perovskite phase in the $PbMg_{1/3}Nb_{2/3}O_3$–$PbTiO_3$ system. *J. Am. Ceram. Soc.*, 1991, **74**(5), 1152–1156.
10. Watanabe, A., Haneda, H., Moriyoshi, Y., Shirasaki, S., Kuramoto, S. and Yamamura, H., Preparation of lead magnesium niobate by a coprecipitation method. *J. Mater. Sci.*, 1992, **27**, 1245–1249.