

Synthesis and thermal stability of perovskite $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) powders via precipitation routes

Gang Xu · Gaorong Han

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Abstract Synthesis of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) powders was realized via coprecipitation route or two-stage precipitation route. The thermal behavior and phase evolution of the PZT precursor were investigated with DTA/TG and followed with XRD, respectively. The thermal stabilities of the synthesized PZT powders were evaluated with TG. It concluded that the PZT powder prepared via two-stage precipitation route is of pure perovskite phase and of good thermal stability because the combination of Zr^{4+} and Ti^{4+} ions is enhanced and $\text{Pb}(\text{OH})_2$ is encapsulated by $(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}(\text{OH})_2$. However, the PZT powder obtained via coprecipitation route is of poor thermal stability due to the formation and evaporation of PbO .

Keywords Ferroelectrics · PZT · Thermal stability · Synthesis · Powder

1 Introduction

Lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, $0 \leq x \leq 1$, PZT), which is a solid solution of lead zirconate (ZT) and lead titanate (PT), is an important ferroelectric material for a variety of applications in high energy capacitors, nonvolatile memories, ultrasonic sensors, infrared detectors and electro-optic devices [1–3]. The highest piezoelectric coupling coefficient as well as maximum permittivity of PZT are obtained for compositions close to the morphotropic phase boundary (MPB) between tetragonal and rhombohedral phases [4]. In

order to fabricate PZT components of good properties, in generally, the PZT ceramics used should be of narrow MPB and stoichiometrical homogeneous composition, which require the PZT powder of well thermal stability and high sintering activity.

Over the last few decades, a number of chemical synthesis techniques [5–9] have been reported to yield pure homogeneous PZT powders. However, few studies on the thermal stability of the synthesized PZT powder are performed till now. In this paper, coprecipitation route and two-stage precipitation route were explored to synthesized pure perovskite PZT powder and the thermal stabilities of the prepared powders were evaluated.

2 Experimental procedure

Chemical composition as $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$, which closes to the MPB, was selected for synthesis. Starting materials used were chemical grade tetrabutyl titanate ($(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$), zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and lead nitrate (PbNO_3), precipitant was ammonia, solvents were ethanol and distilled water.

To the coprecipitation route, the detail presentation of the procedure for the synthesis of PZT powder was reported in our precious work [10]. The precursor solution, which dissolved $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, PbNO_3 and $(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$, was introduced into ammonia solution for coprecipitation, attaining the co-precipitates of zirconium, titanium and lead hydroxides ($\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}(\text{OH})_4$). In the two-stage precipitation route, the well mixed precipitates of zirconium and titanium hydroxides ($(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}(\text{OH})_2$) were prepared by coprecipitation method firstly, and then lead hydroxide was precipitated in an ammonia solution containing $(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}(\text{OH})_2$, attaining a mixed precipitates

G. Xu · G. Han (✉)
State Key Laboratory of Silicon Materials, Department of
Materials Science and Engineering, Zhejiang University,
Hangzhou 310027, People's Republic of China
e-mail: msegxu@zju.edu.cn

of $\text{Pb}(\text{OH})_2$ and $(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}(\text{OH})_2$. The two precipitates were filtered and washed with distilled water for six times and ethanol for two times and then dried respectively, attaining two precursors for synthesizing PZT powder. The chemical compositions of the prepared precursors were well fitted the selected stoichiometric composition for synthesis by verified with ICP.

The thermal behavior of the prepared precursors was studied with DTA and TG, the phase evolution was followed by XRD and the thermal stability of the PZT powders obtained was investigated with TG and ICP.

3 Results and discussion

Figure 1 shows the DTA and TG curves of the PZT precursors prepared via coprecipitation or two-stage precipitation route, respectively. It demonstrates that when the temperature is below about 600°C the two precursors are of similar thermal behavior. In the temperature range of room temperature to 500°C , because of the release of adsorbed water and dehydration of hydroxides two large endothermic peaks respectively appear at about the temperature of 100

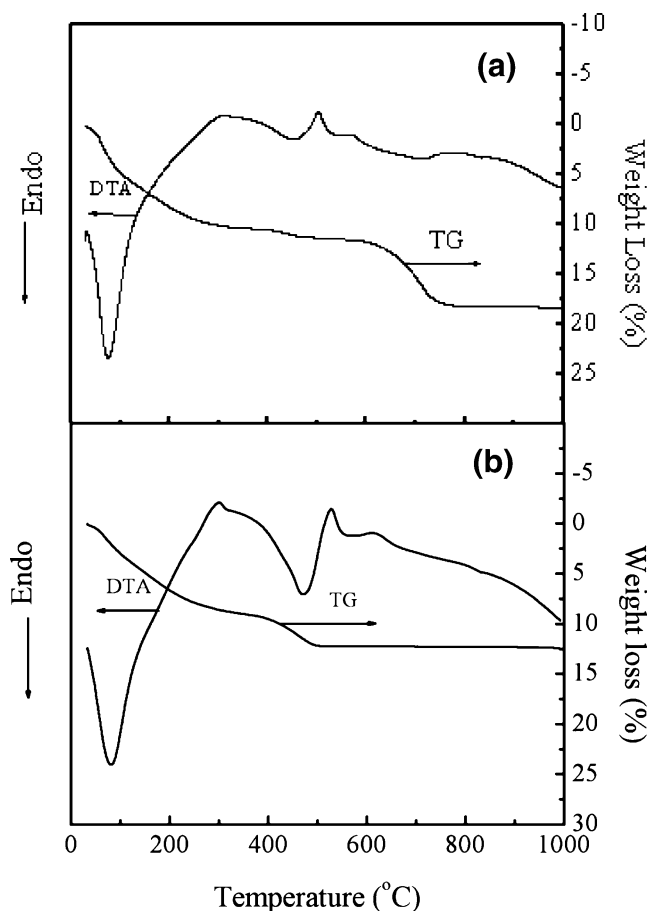


Fig. 1 DTA and TG curves of PZT precursor prepared via (a) coprecipitation route or (b) two-stage precipitation route

or 450°C , and because of the combustion of butyl–ethanol that is the by-product of dehydration of $(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$ a weak exothermic peak appears at about 300°C , all accompanying large weight loss. Two exothermic peaks at the temperature range of 450 and 600°C , which have no associated weight loss manifestation in the TG curves, may be attributed to the crystallization of perovskite PZT phase. It is obvious that the crystallization temperature with regard to the PZT precursor prepared via coprecipitation route is lower than that prepared via two-stage precipitation route.

Higher than the crystallization temperature of perovskite PZT phase, however, the thermal behaviors of the two PZT precursor is much more differential. The PZT precursor prepared via coprecipitation route occurs large weight loss, but the PZT precursor prepared via two-stage precipitation has no weight loss at the higher temperature than 600°C .

Figure 2 shows the XRD patterns of the PZT powder calcined at different temperature. It is revealed that after calcined at 400°C , the both powders obtained via the two routes are still of amorphous phase, and perovskite PZT

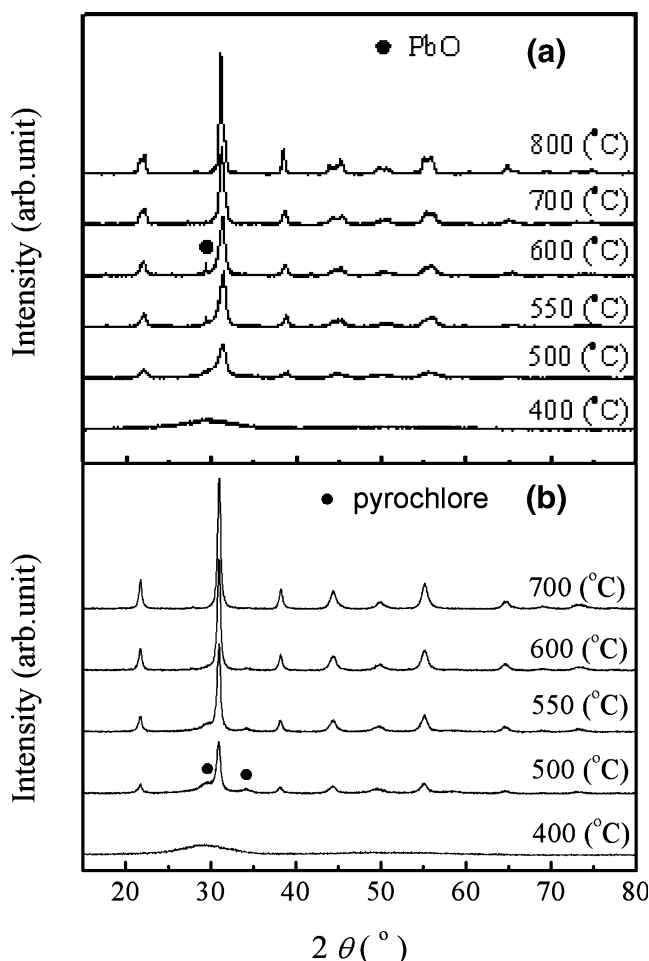


Fig. 2 XRD patterns of the PZT powder by calcinations the precursor prepared via (a) coprecipitation route or (b) two-stage precipitation route at the temperature for 2 h

phase initially occurs over 500°C. With regard to the coprecipitation route, the powder calcined at 550 or 600°C contains a little PbO phase except for the main phase of perovskite PZT. Calcined at over 700°C, the powder obtained only contains perovskite PZT phase. To the two-stage precipitation route, however, the powder calcined at the temperature over 500°C only contains perovskite PZT phase but for PbO phase. Two broad peaks of pyrochlore obviously appear at the XRD patterns of the PZT powder calcined at low temperature as 500 or 550°C, which demonstrates that the formation of perovskite PZT phase follows a consecutive mechanism [11, 12] and illustrate why there two exothermic peaks related to the crystallization appear on the DTA curve.

Figure 3 shows the TG curves of the PZT powders obtained by calcined the coprecipitation PZT precursor at 500 or 550°C, and by calcined the two-stage precipitation PZT precursor at 500°C for 2 h, respectively. The weight losses of all the three PZT powders occurred at the temperature lower than 550°C are very smaller than 3 wt %, which may be brought about from the release of adsorbed water. Over 550°C, there is no weight loss occurrence from the powder obtained by two-stage precipitation route, but there is a large weight loss occurrence from the powder obtained by coprecipitation route. From 550 to 1000°C, the weight loss of the powder obtained by coprecipitation route calcined at 500 or 550°C is about 6.15 wt% and 6.51, respectively. The change of the chemical composition verified with ICP demonstrated that the weight loss of the PZT powder prepared by coprecipitation route is brought about from the evaporation of lead oxide. This implies that the powder synthesized via coprecipitation route is of poor thermal stability because of the evaporation of lead oxide at high temperature, and

that synthesized via two-stage precipitation route is of good thermal stability.

Due to the presence of zirconium and titanium hydroxides, the agglomeration of lead hydroxide is inhibited and the precursor prepared by precipitation route is of high reactive ability, making the synthesis of PZT powder realized at considerable low temperature. In the coprecipitation route, some lead oxide forms accompanying the perovskite PZT phase formation because the well mixture of Pb^{2+} , Zr^{4+} and Ti^{4+} ions in the precursor facilitates the combination of Pb^{2+} ions. Since the specific surface of the prepared PZT powder is very bigger, the PbO evaporation occurs easily, resulting in the PZT powders obtained via coprecipitation route calcined at the temperature lower than 600°C of poor thermal stability and the PZT powders obtained by calcined at high temperature of Pb-poor chemical composition. In the two-stage precipitation route, the $(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}(\text{OH})_2$ were firstly prepared by coprecipitation route and then mixed with the precipitate of $\text{Pb}(\text{OH})_2$ forming the PZT precursor, which enhanced the combination of Zr^{4+} and Ti^{4+} ions that occupy a same structure point in perovskite PZT structure and made the $\text{Pb}(\text{OH})_2$ encapsulated with $(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}(\text{OH})_2$. This special combination and structure of the particle of the PZT precursor hinder the combination of Pb^{2+} ions preventing the PbO formation and evaporation, and facilitate the pyrochlore formation as well as the transformation to perovskite PZT phase. So the PZT powders obtained by two-stage precipitation route are not only of stoichiometric composition and pure perovskite PZT phase but also of good thermal stability in the temperature range of RT to 1000°C, only the powders calcined at low temperature contain a few nanocrystal pyrochlore.

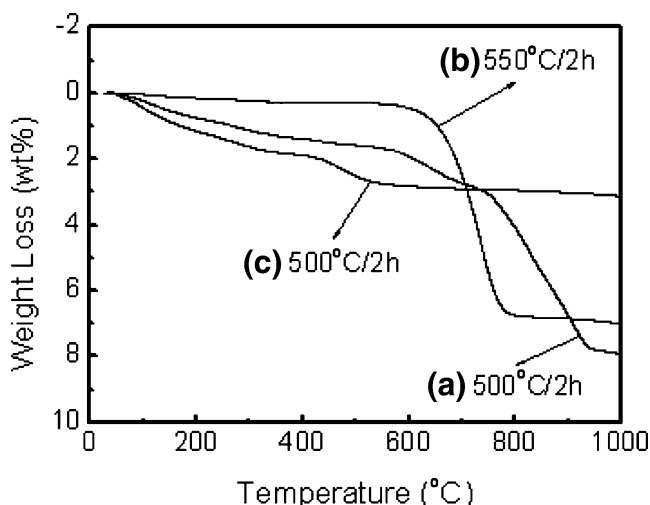


Fig. 3 TG curves of the PZT powders by calcined the precursor prepared via coprecipitation route at (a) 500°C, (b) 550°C or via (c) two-stage precipitation route at 500°C for 2 h, respectively

4 Conclusion

Although the synthesis of perovskite PZT powder can be realized via coprecipitation route at low temperature, the synthesized PZT powder easily occurs the evaporation of PbO and of poor thermal stability. By modifying the coprecipitation route, a two-stage precipitation route was proposed. By this route, not only is the synthesis of pure perovskite PZT powder realized at low temperature but also the powder obtained is of good thermal stability below the temperature of 1000°C. The enhancement on the combination of Zr^{4+} and Ti^{4+} ions and encapsulation of the particle of $\text{Pb}(\text{OH})_2$ by $(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}(\text{OH})_2$ hinder the formation of PbO and avoid the large weight loss occurrence, improving the thermal stability of the synthesized PZT powder.

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