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Fabrication of Ferroelectric Lead Iron Tungstate Ceramics Via a Two-Stage Solid-State Reaction

Chung-Hsin Lu* & Yeak-Chong Wong

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

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Abstract: Ferroelectric $Pb(Fe_{2/3}W_{1/3})O_3$ was synthesized via a new two-stage solid-state reaction discussed in the present study. This method utilized Fe_2WO_6 prepared at the first-stage which subsequently reacted with a stoichiometric amount of PbO at the second stage. This process efficiently suppressed the formation of lead tungstates and liquid phases; in addition, pyrochlore phase was formed as the only intermediate compound. A substantial amount of pyrochlore phase was converted to $Pb(Fe_{2/3}W_{1/3})O_3$ at around 710°C associated with an endothermic reaction. On heating up to 750°C over 99% perovskite $Pb(Fe_{2/3}W_{1/3})O_3$ was formed, and this formation became complete at 840°C. Compared with the conventional solid-state reaction, this process not only simplified the formation process, but also reduced the formation temperature of $Pb(Fe_{2/3}W_{1/3})O_3$. The crystal structure of Fe_2WO_6 did not significantly influence the formation mechanism; whereas, the morphology of $Pb(Fe_{2/3}W_{1/3})O_3$ was markedly affected by the grain size of Fe_2WO_6. By using this process, pure $Pb(Fe_{2/3}W_{1/3})O_3$ with a submicron microstructure was successfully fabricated.

INTRODUCTION

Lead iron tungstate $Pb(Fe_{2/3}W_{1/3})O_3$, a relaxor ferroelectric compound with a perovskite structure, has been widely utilized in the fabrication of multilayer capacitors with Ag/Pd internal electrodes due to its characteristics of a high dielectric permittivity and low-temperature sinterability.[1] For the sake of controlling calcination conditions, the conventional solid-state reaction of $Pb(Fe_{2/3}W_{1/3})O_3$ has been thoroughly investigated.[2–6] In the reaction process, a substantial amount of lead tungstates and pyrochlore phase are produced; in addition, two liquid phases are formulated at 690 and 860°C, respectively.[5,6] The formation of these liquid phases is involved with the reaction between several unknown phases.[5,6] The progression of the formation of these intermediate compounds causes the complexity in the reaction process, hence resulting in the difficulty in fabricating pure $Pb(Fe_{2/3}W_{1/3})O_3$ compound.

Various kinds of solution methods have been used for alternating the reaction routes so as to yield pure $Pb(Fe_{2/3}W_{1/3})O_3$ without parasite lead tungstates. Using a two-stage precipitation process[7] or sol–gel process[8] can fabricate pure $Pb(Fe_{2/3}W_{1/3})O_3$ because both the homogeneity and reactivity of reactants are significantly improved in the starting materials. Despite the fact that the goal of obtaining pure $Pb(Fe_{2/3}W_{1/3})O_3$ has been achieved, considering the complicated and severe operation conditions demanded by the above solution processes, an alternative method excluding the handling of solution and of moisture-sensitive materials such as alkoxides is still required. This needed to be developed considering economical factors in mass production for industry.

The two-stage solid-state reaction is a synthesis process first used by Swartz and Shrout[9] in fabricating perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$. In this process,

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*To whom correspondence should be addressed.

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MgO is first reacted with Nb_2O_5 to produce columbite $MgNb_2O_6$, followed by the second reaction between the $MgNb_2O_6$ and PbO. Adding 2% excess PbO can eliminate the presence of pyrochlore phase and produce pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ phase.

It is considered that the two-stage solid-state reaction can bypass the formation of intermediate compounds, e.g. lead tungstates and liquid phases formed in the conventional solid-state reaction, thereby simplifying the reaction process. Therefore, the difficulty in synthesizing a pure compound will be reduced. In this study, the following two-stage solid-reaction sequence is designed for synthesizing $Pb(Fe_{2/3}W_{1/3})O_3$:

the first stage: $Fe_2O_3 + WO_3 \rightarrow Fe_2WO_6$
and the second stage:

$$Fe_2WO_6 + 3PbO \rightarrow Pb(Fe_{2/3}W_{1/3})O_3$$

In the above process only oxides of solid-powder form are utilized and no solution is required to be treated. The reaction mechanism and microstructural evolution in the obtained powders are investigated in this work.

EXPERIMENTAL

At the first stage, Fe_2O_3 (99+%, Aldrich Chem. Co. Inc., USA) and WO_3 (99+%, Aldrich Chem. Co. Inc., USA) were used as starting materials for synthesizing Fe_2WO_6. Oxides were ball-milled in a plastic jar with ethanol for 48 h using zirconium oxide balls. Then the mixed slurry was dried at about 70°C by using a rotary evaporator. The dried powder was uniaxially cold-pressed into pellets by applying pressure of 196 MPa and heated at 700–1100°C for 2–48 h. The pressed pellets were placed in an alumina crucible and buried in a WO_3 powder-bed to prevent the volatilization of WO_3. After calcination, the surface of pellets was stripped off to eliminate the attached WO_3 powder which would influence the stoichiometric ratio of products.

At the second stage, PbO (99·9%, Aldrich Chem. Co. Inc., USA) was mixed with prepared Fe_2WO_6 so as to fabricate $Pb(Fe_{2/3}W_{1/3})O_3$ perovskite. The mixing, drying, and pressing procedures were the same as described above. The mixed Fe_2WO_6 and $Pb(Fe_{2/3}W_{1/3})O_3$ precursors were analyzed by differential thermal analysis (DTA) and thermogravimetry (TGA) using Al_2O_3 as standard. DTA was carried out in flowing air at a rate of 80 cc/min with heating and cooling rates of 5°C/min. The mixed $Pb(Fe_{2/3}W_{1/3})O_3$ precursor was heated to specific temperatures in a furnace and quenched in air to examine the reaction mechanism and microstructure variation. X-ray powder diffraction (XRD) was performed in order to analyze the formation of resultant compounds. The applied voltage and current were 40 kV and 30 mA, respectively, using a Cu tube with a Ni filter. Scanning electron microscopy (SEM) was utilized for observing microstructural variation in heated specimens.

RESULTS AND DISCUSSION

Fabrication of Fe_2WO_6

Figure 1 (a) and (b) depicts the DTA and TGA curves of the thermal and weight variation for the mixed materials of Fe_2WO_6. No exothermic or endothermic peaks in DTA can be observed over the whole measured temperature range; however, the base-line of DTA was gradually shifted to the exothermic side from above 800°C. This result implies that the formation of Fe_2WO_6 was sluggish and may initiate from around 800°C. Notably, two stages of weight loss occurred in the TGA curve. The weight loss at the first stage was about 2%, at a temperature lower than 400°C. It

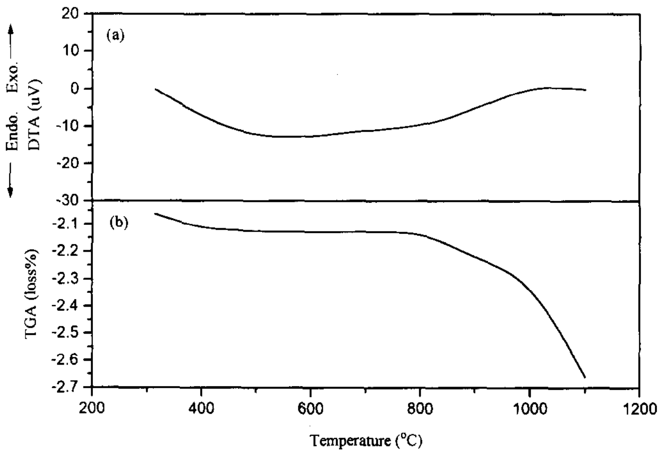


Fig. 1. (a) Differential thermal analysis, and (b) thermogravimetric analysis of the mixture of Fe_2O_3 and WO_3.

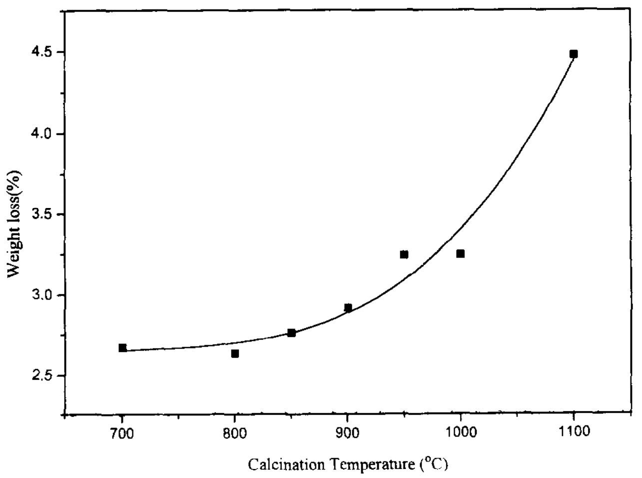


Fig. 2. Weight loss of the mixture of Fe_2O_3 and WO_3 heated at various temperatures for 2 h.

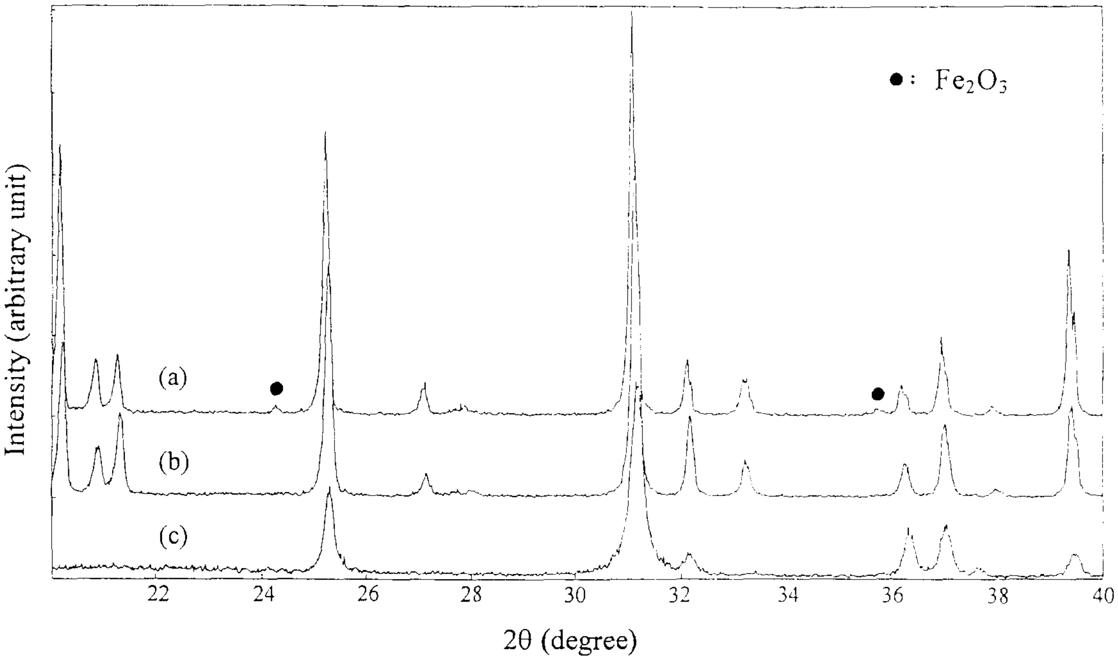


Fig. 3. X-ray diffraction patterns of (a) form 2-Fe_2WO_6 with residual Fe_2O_3 formed via being calcined at 1100°C for 6 h, (b) form 2-Fe_2WO_6 formed via being heated at 1100°C for 6 h with a WO_3 powder-bed, (c) form 1-Fe_2WO_6 formed via being heated at 800°C for 6 h and 850°C for 8 h with a WO_3 powder-bed.

was caused by the combustion of residual resin introduced during ball-milling. Above 800°C, the weight loss markedly increased with the increase in temperature. The volatilization of WO_3 is believed to be responsible for the weight loss at the second stage. Prepared pellets were calcined from 700 to 1100°C for 2 h so as to further examine the behavior of weight loss at elevated temperatures. Similar results can be seen in Fig. 2. From this figure, it is evident that the weight loss was substantially increased from about 800°C.

The volatilization of WO_3 during heating will leave residual Fe_2O_3 in the final products which directly influences the stoichiometric ratio of cations in Fe_2WO_6. For the sake of preventing volatilization of WO_3, in the following experiments, pellets were buried in a WO_3 powder-bed during the heating process so as to suppress the loss of WO_3. The effect of the WO_3 powder-bed on resultant products is shown in Fig. 3. Pure Fe_2WO_6 can be fabricated by means of introducing WO_3 powder-bed (Fig. 3(b) and (c)); on the other hand, residual Fe_2O_3 was present in products when no powder-bed was utilized (see Fig. 3(a)).

Two different forms of Fe_2WO_6 can be synthesized by varying the calcination temperature and dwelling time. Figure 3(b) and (c) illustrates the XRD patterns for form 2 and form 1 of Fe_2WO_6. The variation of the crystal structure of Fe_2WO_6 in terms of calcination temperature and time is depicted in Fig. 4. Form 1 was formed at low temperatures with a columbite structure. Form 1 of Fe_2WO_6 will undergo a monotropic phase-transformation at higher temperatures to produce form 2 Fe_2WO_6, and to alter the structure from columbite to α-PbO type.[10,11] As shown in Fig. 4, no reaction occurred between Fe_2O_3 and WO_3 at 700°C. Form 1 of Fe_2WO_6 began to generate at 800°C but not completely. Prolonging the dwelling time to 8 h at 800°C still could not yield pure form 1. However, when the temperature was raised to 850°C even only for 2 h, all reactants became form 1 of Fe_2WO_6. Heating at 900°C for 8 h can also obtain form 1; meanwhile, prolonging the dwelling time to 48 h at the same temperature can yield form 2. On heating at 950°C over 2 h, the final product turned out to be form 2 of Fe_2WO_6. It seems that the phase transformation

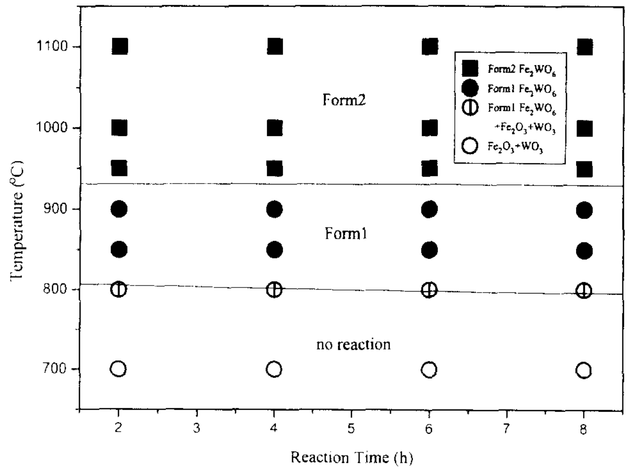


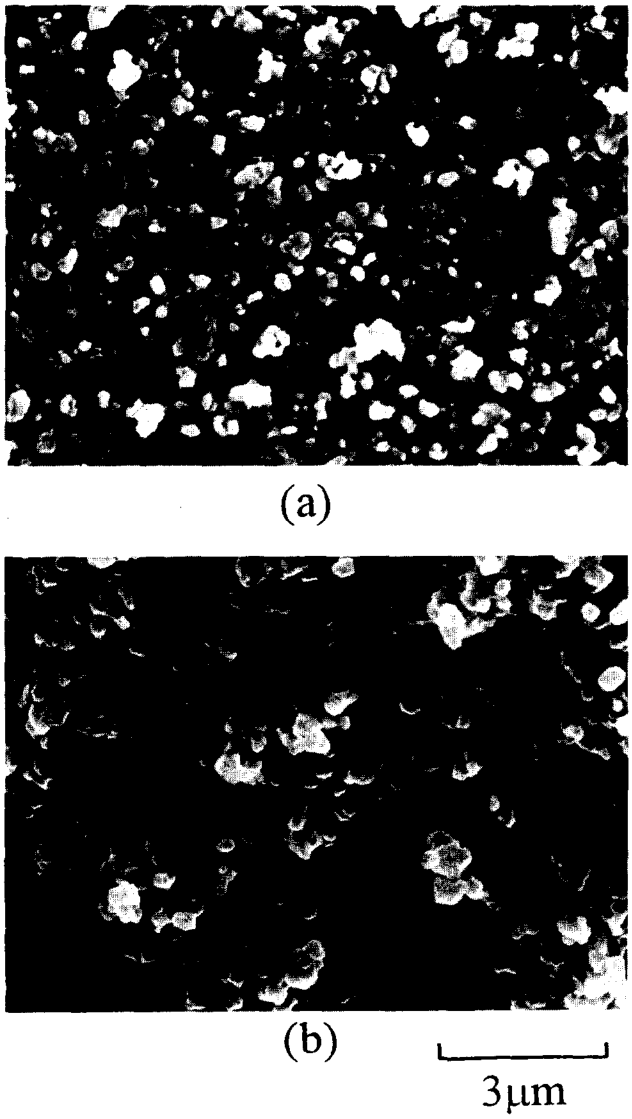
Fig. 4. Formation diagram of form 1 and form 2 of Fe_2WO_6.

of Fe_2WO_6 from form 1 to form 2 took place at temperatures between 900 and 950°C.

In the following experiments, form 1 synthesized via 800°C–2 h and subsequent 850°C–8 h heating, and form 2 synthesized at 900°C for 48 h, were utilized as the starting materials to react with a stoichiometric amount of PbO at the second stage of reaction. The raw materials of $Pb(Fe_{2/3}W_{1/3})O_3$, prepared via form 1 and form 2 of Fe_2WO_6, are denoted as PFW1 and PFW2, respectively. The microstructures of the two forms of Fe_2WO_6 used in the $Pb(Fe_{2/3}W_{1/3})O_3$ synthesis are shown in Fig. 5. No obvious difference between them can be distinguished except that form 2 had a slightly larger grain size than form 1.

Formation process of $Pb(Fe_{2/3}W_{1/3})O_3$

The DTA results for PFW1 and PFW2 were similar. The representative curves for PFW1 are illustrated in Fig. 6. During heating, only an endothermic peak can be observed near 710°C. In the two cooling runs from 730 and 870°C, respectively, no thermal variation could be found. For conventional solid-state reaction, two endothermic peaks occurred near 690 and 860°C, respectively, corresponding to the formation of liquid phases.[6,7] In contrast to the conventional solid-state reaction, the fact that no endothermic reactions occurred at 690 and 860°C during heating and no exothermic reactions took place in cooling indicates that no liquid phases were formed in the two-stage solid-state reaction.


(a)

(b)

Fig. 5. Scanning electron micrographs of (a) form 1-Fe_2WO_6 and (b) form 2-Fe_2WO_6.

The PFW1 and PFW2 samples were heated and quenched at temperatures from 400 to 870°C, and then analyzed via XRD. The relative amount of each resultant compound present in PFW1 and PFW2 was semi-quantitatively calculated as follows:

$$\text{Relative intensity of compound } i\ (\%) = \frac{I_i}{\Sigma(I_i)} \times 100\%$$

where I_i is the intensity of the strongest diffraction peak for compound i. As shown in Fig. 7, the formation process of PFW1 was similar to that of PFW2. No lead tungstates and other unknown phases were present during reaction except pyrochlore phase appearing as the only intermediate compound. In both PFW1 and PFW2, PbO and Fe_2WO_6 concentration decreased with rising temperature and completely disappeared at 600°C. Pyrochlore phase began to form at 400°C and its amount increased up to 600°C. The formation of $Pb(Fe_{2/3}W_{1/3})O_3$ initiated from 500°C; in addition, its content significantly increased from above 700°C accompanied by a corresponding reduction in pyrochlore phase. Up to 750°C, over 99% perovskite $Pb(Fe_{2/3}W_{1/3})O_3$ can be obtained. When the temperature was raised to 840°C, pure $Pb(Fe_{2/3}W_{1/3})O_3$ was entirely yielded. According to the DTA (Fig. 6) and XRD (Fig. 7) results, it was

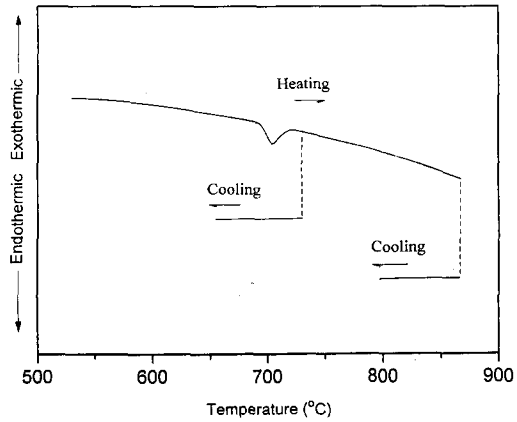


Fig. 6. Differential thermal analysis of the mixture of PbO and Fe_2WO_6.

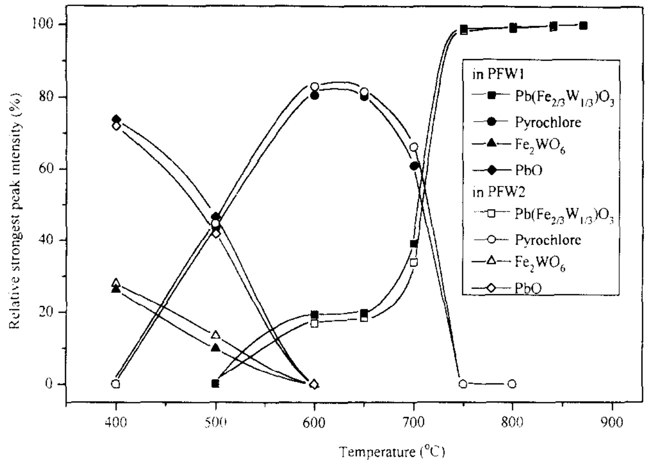


Fig. 7. Content of resultant compounds in PFWl and PFW2 specimens.

evident that the endothermic reaction at around 710°C could be ascribed to the reaction of pyrochlore phase converting to $Pb(Fe_{2/3}W_{1/3})O_3$.

Comparing the formation process of PFWl to that of PFW2, it is noted that the amount of pyrochlore phase in PFWl was slightly less than that in PFW2 at a low temperature range; nevertheless, the amount of $Pb(Fe_{2/3}W_{1/3})O_3$ in PFWl was slightly greater than that in PFW2 at elevated temperatures. These results imply that when the amount of pyrochlore phase is reduced at low temperatures, the formation of $Pb(Fe_{2/3}W_{1/3})O_3$ would be facilitated at high temperatures. On the other hand, the crystal structure of Fe_2WO_6 did not seem to obviously influence the formation process of $Pb(Fe_{2/3}W_{1/3})O_3$.

Microstructural evolution

Figures 8 and 9 show the microstructure of PFWl and PFW2 specimens quenched at 600, 750 and 870°C, respectively. Comparable microstructure evolution was observed in PFWl and PFW2. At 600°C, the major compound present in specimens was pyrochlore phase which had a grain size around 0·1–0·2 μm. When the temperature was raised to 750°C, most of the pyrochlore phase converted to perovskite $Pb(Fe_{2/3}W_{1/3})O_3$. At this temperature the grain size of $Pb(Fe_{2/3}W_{1/3})O_3$ was approximately 0·2–0·3 μm. Up to 870°C, the grain-size of $Pb(Fe_{2/3}W_{1/3})O_3$ still lay in the submicron range of 0·5–0·6 μm. The grain of $Pb(Fe_{2/3}W_{1/3})O_3$ prepared by the two-stage solid-state reaction turned out to be the finest among all other synthesis processes.[6–8]

The grain-size effect of form 2-Fe_2WO_6 on the formation of $Pb(Fe_{2/3}W_{1/3})O_3$ was also examined. The calcination condition for Fe_2WO_6 was increased to 950°C for 8 h. The microstructures of Fe_2WO_6 and derived $Pb(Fe_{2/3}W_{1/3})O_3$ are shown in Fig. 10(a) and (b). It was found that both Fe_2WO_6 and $Pb(Fe_{2/3}W_{1/3})O_3$ had larger grain size than those shown in Figs 5(b) and 9(c). This indicates that controlling the grain size of Fe_2WO_6 can effectively alter the grain size of $Pb(Fe_{2/3}W_{1/3})O_3$.

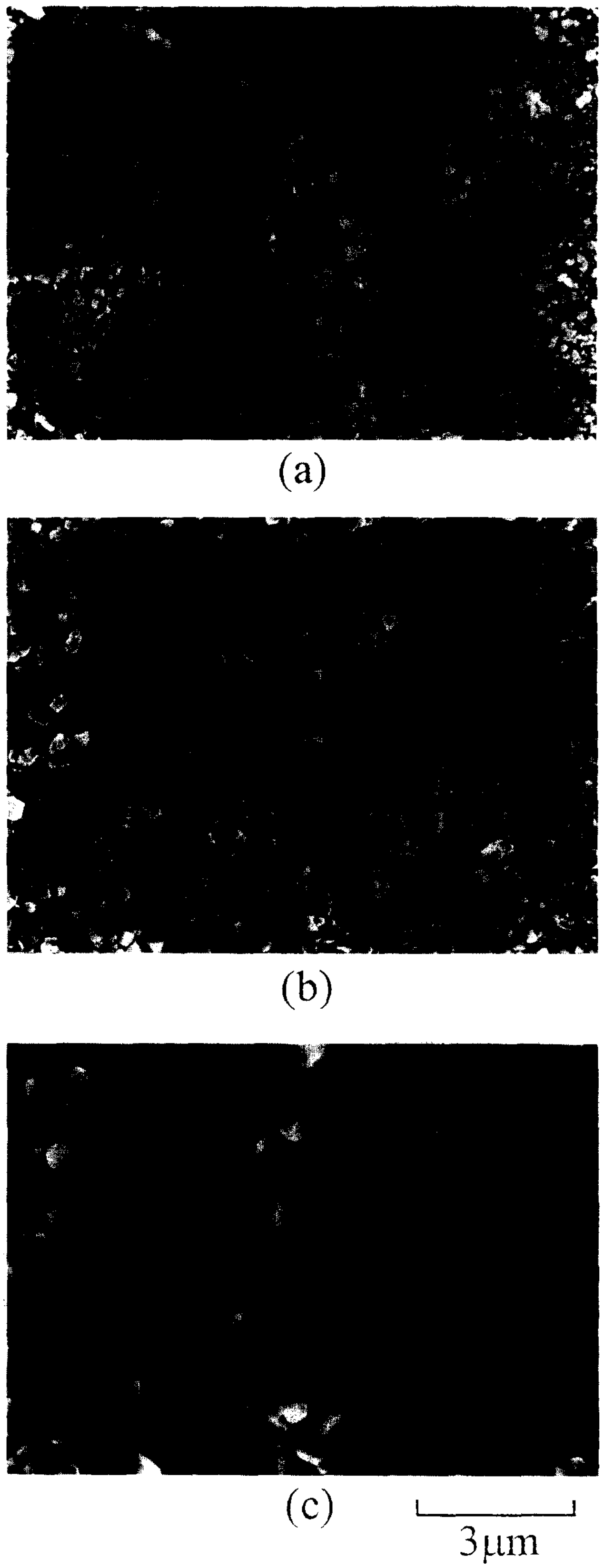


Fig. 8. Scanning electron micrographs for PFWl quenched at (a) 600°C, (b) 750°C and (c) 870°C.

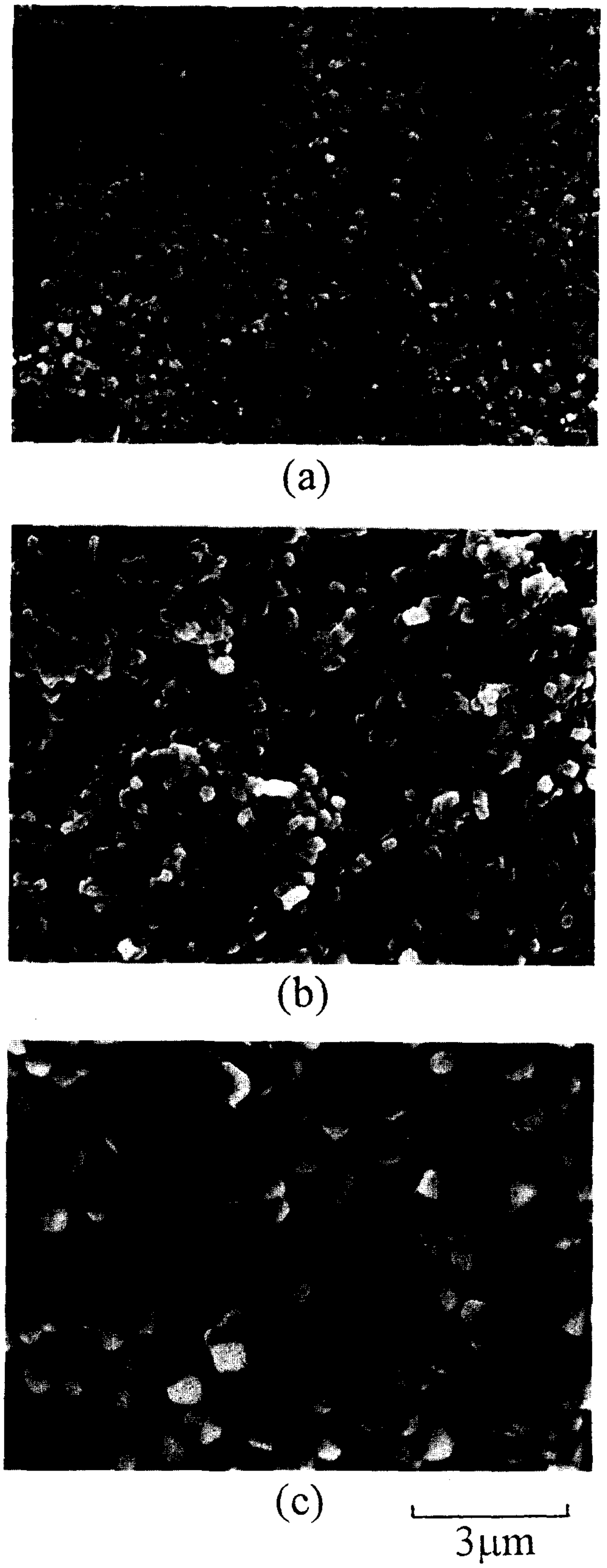


Fig. 9. Scanning electron micrographs for PFW2 quenched at (a) 600°C, (b) 750°C and (c) 870°C.

In the reaction between PbO and Fe_2WO_6, PbO is considered to unidirectionally diffuse into Fe_2WO_6 in generating the pyrochlore phase. Hence Fe_2WO_6 determines the morphology of the pyrochlore phase, and the pyrochlore phase will subsequently influence the morphology of $Pb(Fe_{2/3}W_{1/3})O_3$.

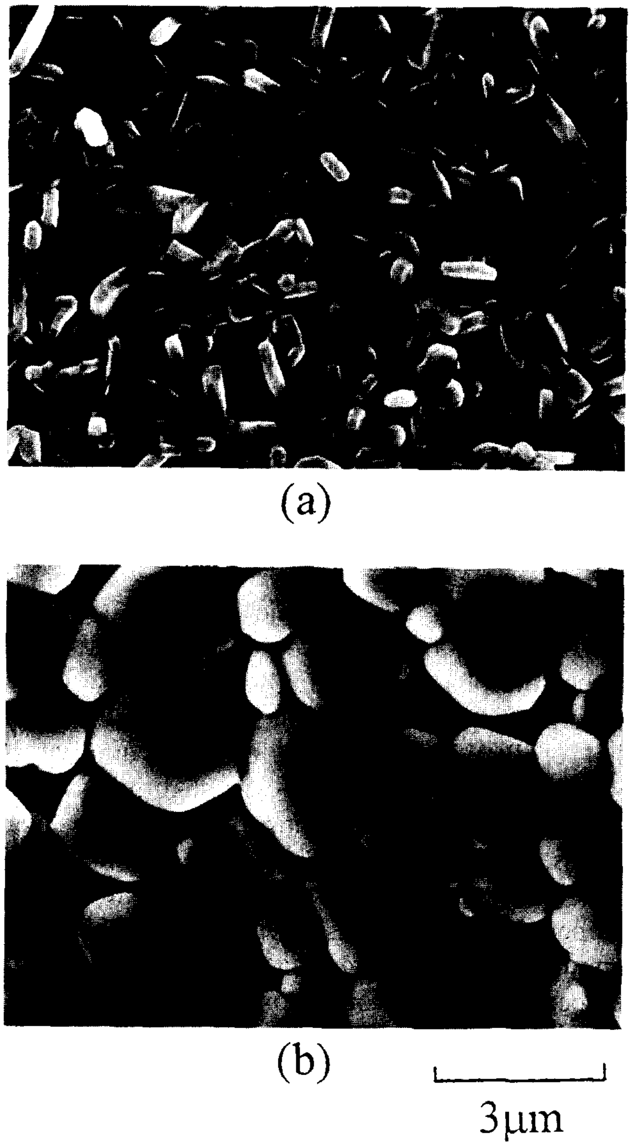


Fig. 10. Scanning electron micrographs of (a) form 2-Fe_2WO_6 calcined at 950°C for 48 h, and (b) the 870°C-quenched specimen of the mixture of PbO and form 2-Fe_2WO_6 obtained at 950°C.

Therefore, Fe_2WO_6 with a large grain-size induces $Pb(Fe_{2/3}W_{1/3})O_3$ to grow to a large grain-size.

Comparison with conventional solid-state reaction

In the conventional solid-state reaction, PbO, Fe_2O_3 and WO_3 are used as starting materials. Lead tungstates $PbWO_4$ and Pb_2WO_5 are very easily formed during reaction.[5] In the two-stage solid-state reaction, tungsten species react with Fe_2O_3 and are bound in Fe_2WO_6, therefore, no lead tungstates can be formed. The absence of lead tungstates eliminates the formation of other intermediate compounds derived from them. As a result, no 690°C liquid phase can be generated in the new process. The absence of the liquid phase causes pyrochlore phase to be formed as a powder-shape (see Figs 8(c) and 9(c)) instead of a facet-shape.[5] Furthermore, the formation temperature of pyrochlore phase is reduced from 650 to 400°C. This is attributed to the decrease in the number of intermediate compounds as well as to the simplification of the reaction process.

In conventional solid-state reaction, insufficient mixing will result in inhomogeneous distribution of Fe species in mixed materials.[12] This inhomogeneity results in the formation of the 860°C liquid phase and the formation of parasite Pb_2WO_5 with $Pb(Fe_{2/3}W_{1/3})O_3$.[6] In the two-stage solid-state reaction, the mixing efficiency can be enhanced because of the decrease in the number of mixed materials. This enhancement will solve the problem in distributing Fe species. Consequently, the high temperature liquid phase is not formed, and pure perovskite compound can be successfully obtained.

CONCLUSIONS

A new two-stage solid-state reaction was developed for fabricating pure perovskite $Pb(Fe_{2/3}W_{1/3})O_3$ ceramics. Fe_2WO_6 was formulated at the first stage, followed by the second reaction with a stoichiometric amount of PbO. Compared with conventional solid state reaction, this process significantly simplified the reaction mechanism and suppressed the formation of lead tungstates and liquid phases. Pyrochlore phase was formed as the only intermediate compound at low temperatures. The conversion of pyrochlore phase to $Pb(Fe_{2/3}W_{1/3})O_3$ accelerated at around 710°C, accompanied by an endothermic reaction. At 840°C, pure $Pb(Fe_{2/3}W_{1/3})O_3$ perovskite was yielded. The crystal structure of Fe_2WO_6 did not significantly affect the formation process; however, the grain size of Fe_2WO_6 directly influenced that of $Pb(Fe_{2/3}W_{1/3})O_3$. Through controlling the grain size of Fe_2WO_6, $Pb(Fe_{2/3}W_{1/3})O_3$ with a submicron microstructure was yielded.

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