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

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(Received 26 September 1994; accepted 16 January 1995)

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 FeWO_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 FeWO_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 FeWO_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. 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. 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. The formation of these liquid phases is involved with the reaction between several unknown phases. 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 or sol-gel process 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 in fabricating perovskite Pb(Mg_{0.33}Nb_{0.67})O_3. In this process,
MgO is first reacted with Nb₂O₅ to produce columbite MgNb₂O₆, followed by the second reaction between the MgNb₂O₆ and PbO. Adding 2% excess PbO can eliminate the presence of pyrochlore phase and produce pure Pb(Mg₁ₓNb₂₋ₓ)O₃ 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(Feₓ₃W₁₋ₓ)O₃:

- First stage: Fe₂O₃ + WO₃ → Fe₂WO₆
- Second stage: Fe₂WO₆ + 3PbO → Pb(Feₓ₃W₁₋ₓ)O₃

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, Fe₂O₃ (99.9%, Aldrich Chem. Co. Inc., USA) and WO₃ (99.9%, Aldrich Chem. Co. Inc., USA) were used as starting materials for synthesizing Fe₂WO₆. 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 WO₃ powder-bed to prevent the volatilization of WO₃. After calcination, the surface of pellets was stripped off to eliminate the attached WO₃ 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 Fe₂WO₆ to fabricate Pb(Feₓ₃W₁₋ₓ)O₃ perovskite. The mixing, drying, and pressing procedures were the same as described above. The mixed Fe₂WO₆ and Pb(Feₓ₃W₁₋ₓ)O₃ precursors were analyzed by differential thermal analysis (DTA) and thermogravimetry (TGA) using Al₂O₃ as standard. DTA was carried out in flowing air at a rate of 80 °C/min with heating and cooling rates of 5°C/min. The mixed Pb(Feₓ₃W₁₋ₓ)O₃ 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 Fe₂WO₆

Figure 1 (a) and (b) depicts the DTA and TGA curves of the thermal and weight variation for the mixed materials of Fe₂WO₆. 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 Fe₂WO₆ 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 Fe₂O₃ and WO₃.](image)

![Fig. 2. Weight loss of the mixture of Fe₂O₃ and WO₃ heated at various temperatures for 2 h.](image)
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Fig. 3. X-ray diffraction patterns of (a) form 2-Fe$_2$WO$_6$ with residual Fe$_3$O$_4$ formed via being calcined at 1100°C for 6 h, (b) form 2-Fe$_2$WO$_6$ formed via being heated at 1100°C for 6 h with a WO$_3$ powder-bed, (c) form 1-Fe$_2$WO$_6$ 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$_3$O$_4$ in the final products which directly influences the stoichiometric ratio of cations in Fe$_2$WO$_6$. 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$_2$WO$_6$ can be fabricated by means of introducing WO$_3$ powder-bed (Fig. 3(b) and (c)); on the other hand, residual Fe$_3$O$_4$ was present in products when no powder-bed was utilized (see Fig. 3(a)).

Two different forms of Fe$_2$WO$_6$ 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$_2$WO$_6$. The variation of the crystal structure of Fe$_2$WO$_6$ 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$_2$WO$_6$ will undergo a monotropic phase-transformation at higher temperatures to produce form 2 Fe$_2$WO$_6$, and to alter the structure from columbite to α-PbO type. As shown in Fig. 4, no reaction occurred between Fe$_3$O$_4$ and WO$_3$ at 700°C. Form 1 of Fe$_2$WO$_6$ 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$_2$WO$_6$. 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$_2$WO$_6$. It seems that the phase transformation

Fig. 4. Formation diagram of form 1 and form 2 of Fe$_2$WO$_6$. 
of Fe$_2$WO$_6$ 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$_{1/3}$)$_3$O$_9$, prepared via form 1 and form 2 of Fe$_2$WO$_6$, are denoted as PFW1 and PFW2, respectively. The microstructures of the two forms of Fe$_2$WO$_6$ used in the Pb(Fe$_{2/3}$W$_{1/3}$)$_3$O$_9$ 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$_{1/3}$)$_3$O$_9$**

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. 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.

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:

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

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$_2$WO$_6$ 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$_{1/3}$)$_3$O$_9$ 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$_{1/3}$)$_3$O$_9$ can be obtained. When the temperature was raised to 840°C, pure Pb(Fe$_{2/3}$W$_{1/3}$)$_3$O$_9$ was entirely yielded. According to the DTA (Fig. 6) and XRD (Fig. 7) results, it was
evident that the endothermic reaction at around 710°C could be ascribed to the reaction of pyrochlore phase converting to Pb(Fe₂W₁₋₃)O₃.

Comparing the formation process of PFW₁ to that of PFW₂, it is noted that the amount of pyrochlore phase in PFW₁ was slightly less than that in PFW₂ at a low temperature range; nevertheless, the amount of Pb(Fe₂W₁₋₃)O₃ in PFW₁ 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(Fe₂W₁₋₃)O₃ would be facilitated at high temperatures. On the other hand, the crystal structure of Fe₂WO₆ did not seem to obviously influence the formation process of Pb(Fe₂W₁₋₃)O₃.

**Microstructural evolution**

Figures 8 and 9 show the microstructure of PFW₁ and PFW₂ specimens quenched at 600, 750 and 870°C, respectively. Comparable microstructure evolution was observed in PFW₁ 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(Fe₂W₁₋₃)O₃. At this temperature the grain size of Pb(Fe₂W₁₋₃)O₃ was approximately 0.2–0.3 μm. Up to 870°C, the grain-size of Pb(Fe₂W₁₋₃)O₃ still lay in the submicron range of 0.5–0.6 μm. The grain of Pb(Fe₂W₁₋₃)O₃ 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-Fe₂WO₆ on the formation of Pb(Fe₂W₁₋₃)O₃ was also examined. The calcination condition for Fe₂WO₆ was increased to 950°C for 8 h. The microstructures of Fe₂WO₆ and derived Pb(Fe₂W₁₋₃)O₃ are shown in Fig. 10(a) and (b). It was found that both Fe₂WO₆ and Pb(Fe₂W₁₋₃)O₃ had larger grain size than those shown in Figs 5(b) and 9(c). This indicates that controlling the grain size of Fe₂WO₆ can effectively alter the grain size of Pb(Fe₂W₁₋₃)O₃.

**Fig. 8.** Scanning electron micrographs for PFW₁ quenched at (a) 600°C, (b) 750°C and (c) 870°C.
In the reaction between PbO and Fe$_2$WO$_6$, PbO is considered to unidirectionally diffuse into Fe$_2$WO$_6$ in generating the pyrochlore phase. Hence Fe$_2$WO$_6$ 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$_3$.

In the conventional solid-state reaction, PbO, Fe$_2$O$_3$ and WO$_3$ are used as starting materials. Lead tungstates PbWO$_4$ and Pb$_2$WO$_5$ are very easily formed during reaction. In the two-stage solid-state reaction, tungsten species react with Fe$_2$O$_3$ and are bound in Fe$_2$WO$_6$, 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
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powder-shape (see Figs 8(c) and 9(c)) instead of a facet-shape. 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. This inhomogeneity results in the formation of the 860°C liquid phase and the formation of parasite Pb2WO6 with Pb(Fe1,3W0.3)O3. 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(Fe2.3W0.3)O3 ceramics. Fe2WO6 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(Fe2.3W0.3)O3 accelerated at around 710°C, accompanied by an endothermic reaction. At 840°C, pure Pb(Fe2.3W0.3)O3 perovskite was yielded. The crystal structure of Fe2WO6 did not significantly affect the formation process; however, the grain size of Fe2WO6 directly influenced that of Pb(Fe2.3W0.3)O3. Through controlling the grain size of Fe2WO6, Pb(Fe2.3W0.3)O3 with a submicron microstructure was yielded.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial assistance by the National Science Council, Taiwan, under Grant NSC 82-0405-E002-399.

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