



A promising sol–gel route to suppress pyrochlore phase during the synthesis of multiferroic $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ using inorganic salts

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ABSTRACT

This paper reports a promising route to synthesize multiferroic $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ by sol–gel method with inorganic salts of $(\text{CH}_3\text{COO})_2\text{Pb}\cdot\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, and $(\text{NH}_4)_5\text{H}_5[\text{H}_2(\text{WO}_4)_6]\cdot\text{H}_2\text{O}$. The pyrochlore phase was largely suppressed by increasing the calcination temperature, and high purity of perovskite phase was obtained at 725 °C which is much lower than the temperature used in other synthesizing processes. Microstructural investigations revealed that the synthesized $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ particles have cubic morphology and superlattice crystal structure. The formation of $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ was not sensitive to the pH value of the solution, which is another advantage of this sol–gel method.

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1. Introduction

Lead iron tungstate, $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ (PFW), is an important Pb-based relaxor ferroelectric showing antiferromagnetic characters [1–3]. As the first discovered multiferroic material with relaxor properties, its physicochemical properties have been fully investigated by various researchers [4–6]. Since its electric and magnetic performance can be easily regulated by the formation of solid solution with other ferroelectrics, such as $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3\text{–PbTiO}_3$, $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3\text{–Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$, and $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3\text{–BiFeO}_3$ [7–10], it is also an attractive candidate for future information storage, low-temperature sintering multilayer capacitors, the emerging field of spintronics, piezoelectric transducers, as well as sensors [3,11,12].

In order to prepare PFW without detrimental pyrochlore phase ($\text{Pb}_2\text{FeWO}_{6.5}$), which reduces the dielectric capability of the product, many synthesizing techniques have been proposed and investigated. Conventional solid reaction is widely used for ceramic fabrication. The sintering of PbO , WO_3 , and Fe_2O_3 with 5% excess Fe_2O_3 can depress the formation of pyrochlore phase [13], whereas residual iron ions can decrease the dielectric constant [14]. The columbite method invented by Swartz and Shrouf is mostly adopted in the synthesis of lead-based relaxor ferroelectrics, like $\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ and $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ [15]. In this method PbO

was allowed to mix with Wolframite Fe_2WO_6 , which was formed by pre-reacting Fe_2O_3 and WO_3 at 1000 °C, and then the mixture was heated up to 890 °C for the formation of PFW. But the purity of the product is difficult to reach a high value because of repeated mixing steps of the components. Mechanical activation, well established for synthesizing alloys and intermetallic, is a novel technology to produce complex ferroelectrics [16]. Recently, Ang et al. [17] and Khim et al. [18] have fabricated several PbO -based electroceramics by this method. However, iron contamination by the loss of stainless-steel cylindrical vial and stainless-steel ball and the high energy cost involved make it difficult to conduct it outside labs.

According to our knowledge, in all these solid reaction methods mentioned above, the precursors need to be heated up to over 850 °C and the formation of impurities (especially that of pyrochlore) is still an important problem in the final product. The sol–gel process is a versatile solution to fabricate ceramics with more homogenous ultra-fine powders. Sol–gel processed with alkoxide has been developed to prepare PFW according to the study by Lu et al. [19]. Unfortunately, alkoxide precursors are not only expensive but also volatile [20]. In this paper, inorganic salts were used as precursors to synthesize PFW by sol–gel method. Due to molecular homogeneity, pure PFW was successfully synthesized without pyrochlore at a relatively lower sintering temperature.

2. Experimental procedure

The sol was prepared from the reagents of $(\text{CH}_3\text{COO})_2\text{Pb}\cdot\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, and $(\text{NH}_4)_5\text{H}_5[\text{H}_2(\text{WO}_4)_6]\cdot\text{H}_2\text{O}$ and the procedure of the preparation was as illustrated in Fig. 1. Citric acid was dissolved in de-ionized water with ultrasonic vibration, while ethylene diamine tetraacetic acid (EDTA) was dissolved by adding

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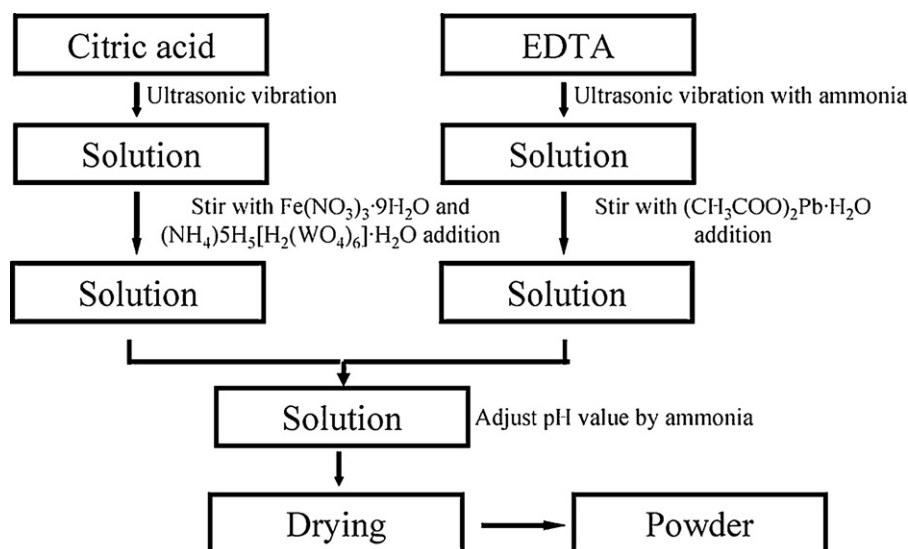


Fig. 1. Flow chart showing the preparation of PFW by the sol-gel process using inorganic salts.

aqueous ammonia. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_5\text{H}_5[\text{H}_2(\text{WO}_4)_6] \cdot \text{H}_2\text{O}$ were mixed in citric acid solution at a ratio of $\text{Fe}:\text{W}=2:1$. $(\text{CH}_3\text{COO})_2\text{Pb} \cdot \text{H}_2\text{O}$ was added to the EDTA solution and stirred until it dissolved completely. Then the two solutions were blended together at an atomic ratio of 1:1 and stirred for 1 h at different pH values (pH 6, 7, 8, 9) modulated by aqueous ammonia. The powders derived from the solution dried at 400°C for 4 h were pressed into pellets under 10 MPa, which were subsequently heated at temperatures ranging from 600 to 800°C for 2 h.

Thermal analysis was carried out by thermal gravity and differential scanning calorimetry (TG/DSC, Setsys Evolution 18) from room temperature to 815°C in air at a rate of $5^\circ\text{C}/\text{min}$ during heating and quenching. The resultant phase from the sintering treatment was examined by X-ray diffraction (XRD, D/max 2400), scanning electron microscope (SEM, LEO, SUPRA 35), and transmission electron microscope (TEM, JEOL 2010).

3. Results and discussion

3.1. Thermal analysis on the sintering process

The results of the TG/DSC analyses on the dried gel are illustrated in Fig. 2. According to the TG profile, a total weight loss of 5.5% occurred below 400°C , which should have been caused by burning of organics. This is also verified by two exothermic peaks at 136 and 383°C in the DSC profile, which indicate the disappearance of residual organics during heating. When the temperature was increased above 500°C , there was one exothermic peak at 537°C and two

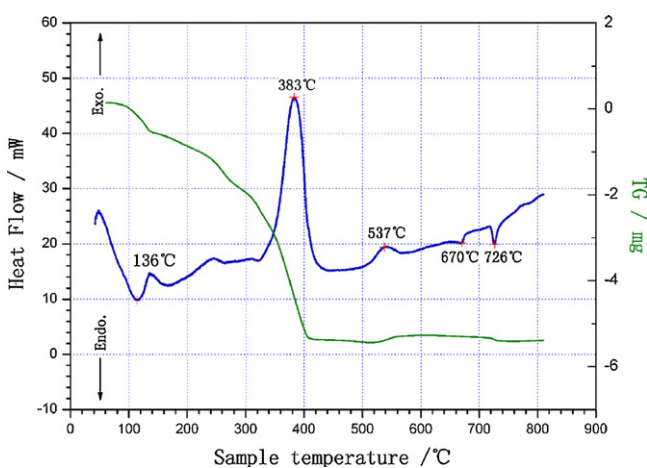


Fig. 2. TG/DSC results of the dried precursors ranging from room temperature to 815°C .

endothermic peaks at 670 and 726°C . As no changes were recorded in the cooling run (not shown here), the formation of liquid phases could be excluded. Thus all the three peaks were generated from solid-state reactions during heating. The exothermic peak of 537°C appeared to result from the formation of the pyrochlore phase – $\text{Pb}_2\text{FeWO}_{6.5}$, while the endothermic peaks at 670 and 726°C should have resulted from the formation of the perovskite PFW phase. The details of these reactions will be discussed in the following sections.

3.2. Phase identification and purity calculation

The phases of the pellets developed at different sintering temperatures were identified by XRD as shown in Fig. 3. It was found that below or at 600°C the major product was pyrochlore, which is verified by peaks appearing at a 2θ of 29.5° , 34.2° , 49.1° , and 58.4° . As the temperature increased from 650 to 725°C , the peaks of PFW at 2θ of 31.8° , 45.5° , and 56.6° became stronger and stronger, indicating the formation of PFW. When the temperature was over 750°C or 800°C , PbWO_4 and PbW_2O_5 were detected. It was obvious that before the formation of PFW, the pyrochlore phase was

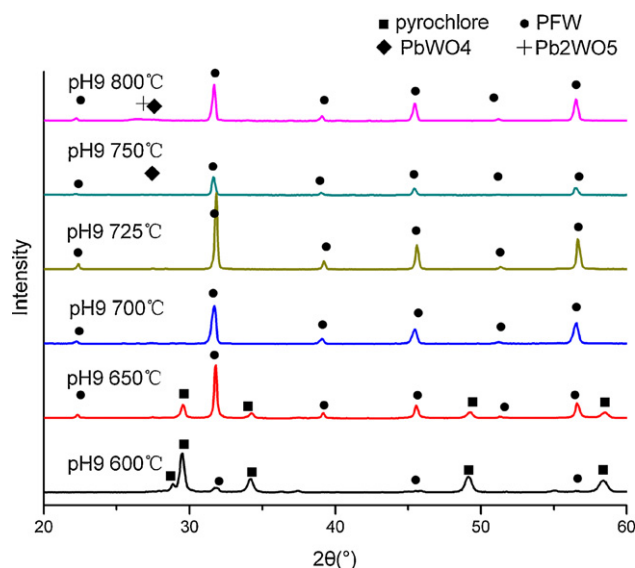


Fig. 3. XRD patterns of the final products sintered at different temperatures.

the main impurity and its proportion was effectively reduced by the increase of temperature. The relative amount of the perovskite phase can be calculated approximately by the following equation [21]:

$$\text{Perovskite intensity(\%)} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{pyro}} + I_{\text{PbO}} + I_{\text{PbWO}_4}} \right) \times 100,$$

where I_{perov} , I_{pyro} , I_{PbO} , and I_{PbWO_4} refer to the intensities of the (1 1 0) perovskite peak, (2 2 2) pyrochlore peak, the highest lead oxide peak, and the highest lead tungsten oxide peak, respectively. The calculated results are shown in Fig. 4. As the sintering temperature increased from 600 °C, the purity of PFW also increased and reached 98.5% at 725 °C. After that, the value decreased a little to 97.0% due to the formation of PbWO_4 and PbW_2O_5 impurities at higher temperatures.

Combining XRD results with those of DSC, it was deduced that the pyrochlore phase formed below 600 °C (around 537 °C in Fig. 2). As the sintering temperature increased, the large reduction of pyrochlore should be due to the transformation from $\text{Pb}_2\text{FeWO}_{6.5}$ to $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ by the reaction, $2\text{Pb}_2\text{FeWO}_{6.5} + \text{Fe}_2\text{O}_3 + \text{PbO} \rightarrow \text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$, which resulted in an endothermic peak of 670 °C as shown in Fig. 2 and a rapid growth of the perovskite phase [22]. At a higher temperature of over 750 °C, the formation of PbWO_4 and PbW_2O_5 impurities seemed to result from the decomposition of $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$. However, there were no obvious DSC peaks at this temperature range. It was concluded that pure PFW perovskite product could be synthesized at 725 °C using this sol–gel method whose optimal temperature is much

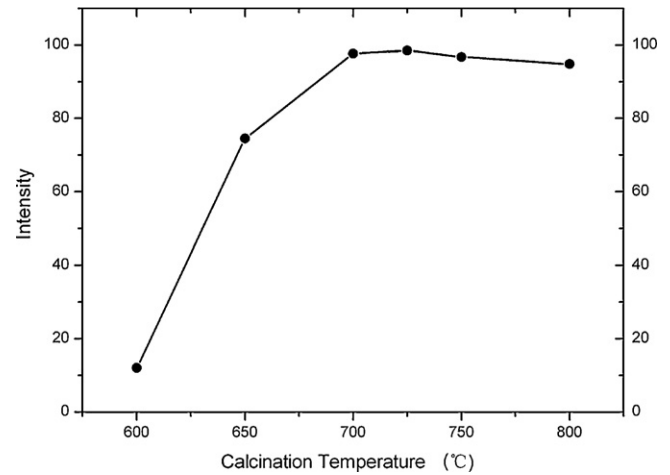


Fig. 4. The purity of PFW in the final products as a function of sintering temperature, which reached 98.5% at 725 °C and decreased a little to 97.0% at 800 °C.

lower than other solid reaction methods with a sintering temperature as high as 870 °C [17,23].

3.3. Microstructural investigation on the final product

The microstructures of the pellets sintered at different temperatures were first examined by SEM, as shown in Fig. 5. At 600 °C (see Fig. 5a), the fine particles agglomerated together with

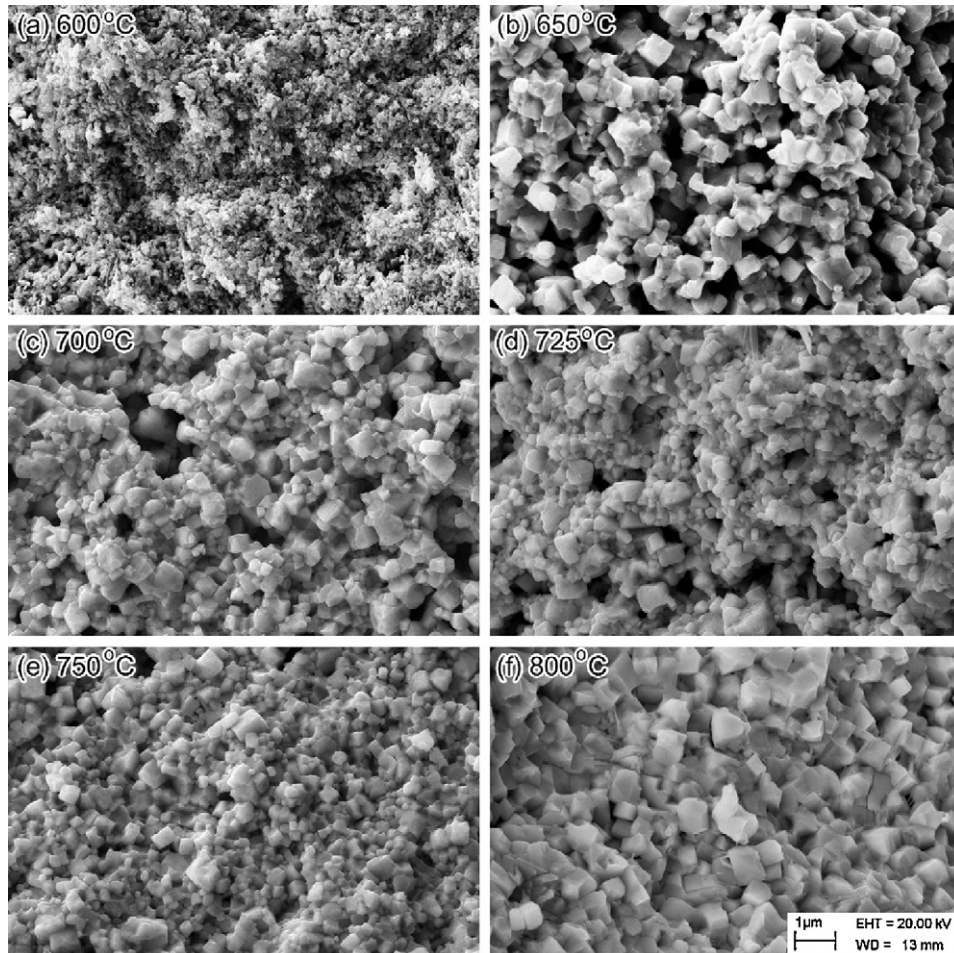


Fig. 5. Fresh fractured cross-section images of the samples sintered at (a) 600 °C, (b) 650 °C, (c) 700 °C, (d) 725 °C, (e) 750 °C, and (f) 800 °C.

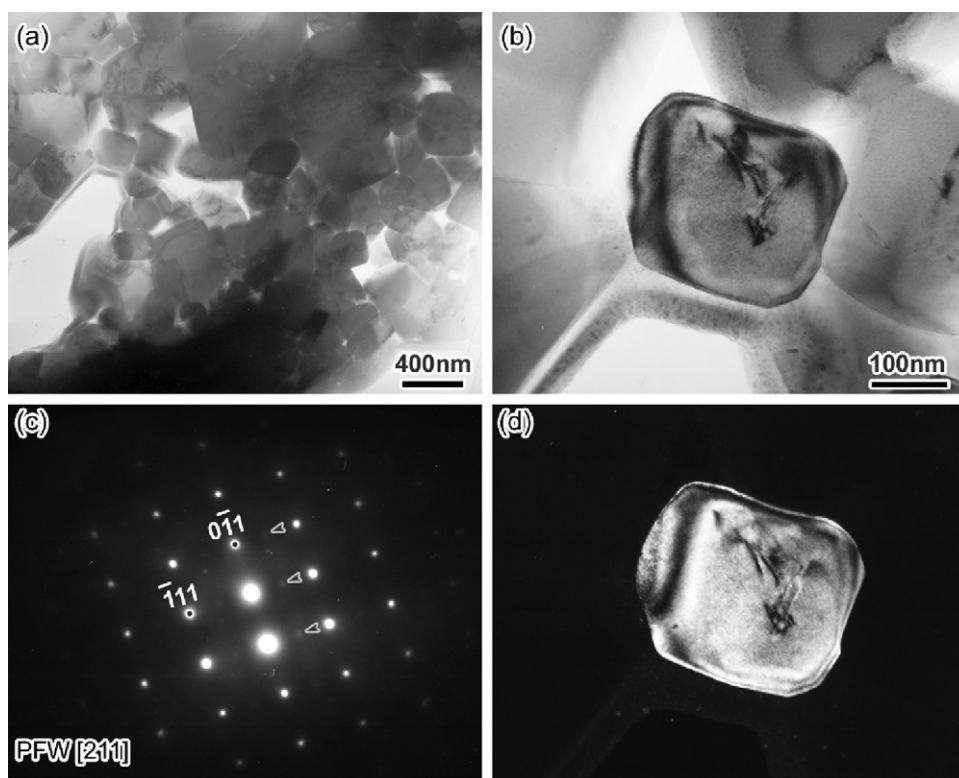


Fig. 6. TEM images of the PFW sintered at 725 °C with pH9. (a) and (b) Bright-field images and (d) corresponding dark-field image showing the cubic morphology of PFW particles; (c) the selected-area electron diffraction pattern indicating the suppressspots of $1/2(1-1-1)$ as marked by arrowheads.

spherical/angular morphology, which are pyrochlore ($\text{Pb}_2\text{FeWO}_{6.5}$) as verified by XRD. When the sintering temperature increased to 650 °C (see Fig. 5b), big cubical particles were formed, which were identified as PFW ($\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$). Among the big PFW particles, small spherical/angular pyrochlore particles were still remaining. At a temperature of 700 and 725 °C, the small particles also appeared to have a cubic morphology, indicating the complete formation of PFW. Considering the size of the PFW particles, it was found that variation decreased as the sintering temperature increased from 600 to 700 °C and 725 °C. The PFW synthesized at 725 °C is the most homogeneous one with a narrow size distribution (see Fig. 5d). As the sintering temperature was further increased, the product became inhomogeneous again and only big particles were left at 800 °C (see Fig. 5f). It was believed that at this high temperature small PFW particles decomposed to form PbWO_4 and PbW_2O_5 . Thus only big particles were left with a homogeneous size distribution.

The synthesized products, especially the small particles, were further investigated using TEM. Fig. 6 shows TEM images of the sample sintered at 725 °C. In the bright-field image (see Fig. 6a), not only big particles but also small ones were studied. Small particles also have a cubic morphology, as verified by corresponding bright-field and dark-field observations as shown in Fig. 6b and d, respectively. Also, it was confirmed by selected-area electron diffraction that both big and small particles have a perovskite crystal structure (see Fig. 6c). It is necessary to point out that weak superlattice spots of $1/2(1-1-1)$ were observed in our sample, as indicated with arrowheads in Fig. 7c. These spots represent the existence of the nanoscale cation-ordered domains in the perovskite structure [24]. The above TEM observations agree well with XRD and SEM results, confirming the formation of homogeneous PFW at 725 °C with a high purity.

3.4. Effect of pH value on the synthesis of PFW

In sol–gel method, the final product is generally affected by the pH value of the mixed solution. This effect was also studied in our work by varying the pH value from 6 to 9 using aqueous ammonia. The dried powders were sintered at the same temperature of 725 °C. XRD examination reveals that regardless of pH variation, PFW is the main phase with few (almost no) impurities in the final product as shown in Fig. 7. The intensity of the diffraction peak became stronger as the pH value increased from 6 to 9,

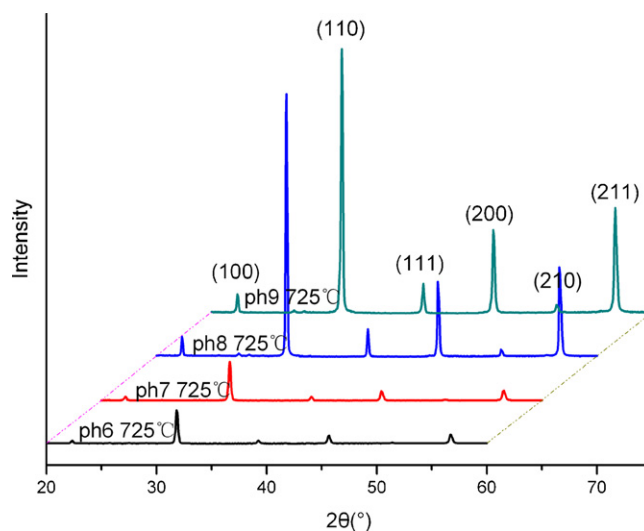


Fig. 7. XRD patterns of the samples sintered at 725 °C from the mixed solution with different pH values.

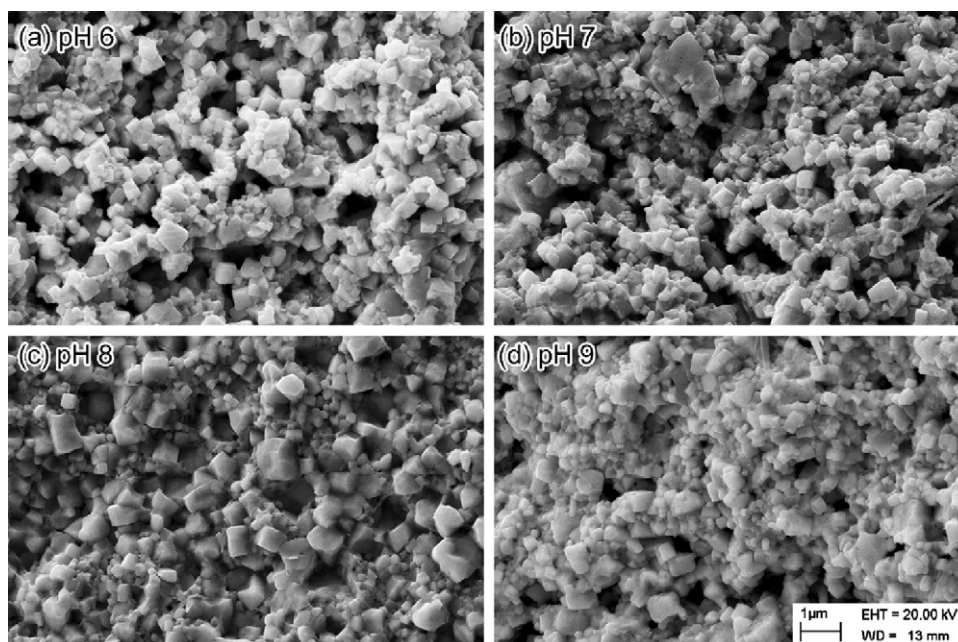


Fig. 8. Fresh fractured cross-section images of the samples sintered at 725 °C with a mixed solution of (a) pH 6, (b) pH 7, (c) pH 8, and (d) pH 9.

which indicates a better crystallization of the sintered PFW. The corresponding microstructures are shown in Fig. 8, in which the morphology of the particles is similar and the size variation is small.

Although the pH value of the mixed solution has some effects on the crystallization and homogeneity of the particles, it does not affect the purity of the PFW. From this point of view, our method is better than other sol–gel methods that make use of alkoxide which is sensitive to pH value to fabricate perovskite [25]. Therefore, the advantage of our method is that it makes the synthesis of PFW easy to handle.

4. Conclusions

Pure PFW with perovskite structure, $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$, was successfully fabricated by a new sol–gel method using inorganic salts. The optimal sintering temperature was 725 °C, and the formation of pyrochlore was effectively suppressed. This sintering temperature is much lower than the temperatures used in other methods like conventional solid reaction and columbite method, which are usually over 850 °C. The usage of inorganic precursors not only reduces the cost involved in buying expensive alkoxide salts as in other sol–gel methods, but also makes the synthesis easy to be manipulated due to its nonsensitivity to pH value. The obtained PFW particles have a cubic morphology and superlattice crystal structure, with a better homogeneity when sintered at 725 °C and pH9.

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