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Synthesis and properties of multiferroic $BiFeO_3$ ceramics

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Abstract $BiFeO_3$ was synthesized using a modified sol–gel process, i.e., so-called Pechini method, as evidenced by X-ray diffraction pattern. Optimal conditions for the synthesis of single-phase BiFeO3 ceramics were obtained. This Pechini technique developed in this work is expected to be useful in synthesis of doped $BiFeO_3$ or $BiFeO_3$-based solid solution. Conventional sintering and spark plasma sintering processes were used to fabricate $BiFeO_3$ ceramics. Ferroelectric and magnetic loops were measured at room temperature. The ceramic sample shows a stable dielectric constant and low loss tangent between 100 Hz and 10 MHz.

Keywords $BiFeO_3$ · Multiferroic · Sol–gel process · Spark plasma sintering

1 Introduction

Multiferroic materials have more than one order parameters, such as ferroelectric and magnetic order. At first, magnetoelectrics exhibit the coexistence of ferroelectric and magnetic orders. Therefore, these materials have potential applications in magnetic and ferroelectric devices. At the same time, the coupling between two order parameters provides an addition degree of freedom in device design. $BiFeO_3$ is one of the very few magnetoelectrics with high phase transition temperatures (Curie temperature ~1083 K, and Néel temperature ~657 K). Since its discovery in 1960s, difficult synthesis of $BiFeO_3$ and its current leakage have hampered its practical applications. There is a revival of $BiFeO_3$ because of its possible novel applications [1]. Nowadays, several techniques have been successful in synthesis of pure $BiFeO_3$ ceramics. In the solid state route [2], Bi_2O_3 and Fe_2O_3 are reacted at temperature of 800–830 °C and impure $Bi_2Fe_4O_9$ phases are removed by washing in HNO_3. The disadvantage of this process lies in the necessary of leaching the unwanted phases using an acid and the impurity appears again in the sintering process. A modified method is rapid liquid phase sintering [3, 4] described by following: Bi_2O_3 and Fe_2O_3 were thoroughly mixed in an agate mortar and the mixture was dried and pressed into the pellets and sintered in air at 860 °C with a high heating rate up to 100 °C/s. This method can result in a high resistivity and polarization value of $BiFeO_3$, but also leads to high dielectric loss and more defects. Another technique for synthesis of $BiFeO_3$ is precipitation/coprecipitation method [5]. Recently Sushmita [6] successfully synthesized nanosized $BiFeO_3$ via soft chemical route using tartaric acid as a complexing agent.

In this work, we report the synthesis of a pure BiFeO3 by modified Pechini method. The technique is more simple, energy saving and cost effective than other methods. $BiFeO_3$ ceramics fabricated via using two sintering processes, i.e., conventional sintering and spark-plasma-sintering (SPS) illustrate a stable frequency dependence of the dielectric constant and a low dielectric loss at room temperature, unlike $BiFeO_3$ ceramic samples reported elsewhere [4].

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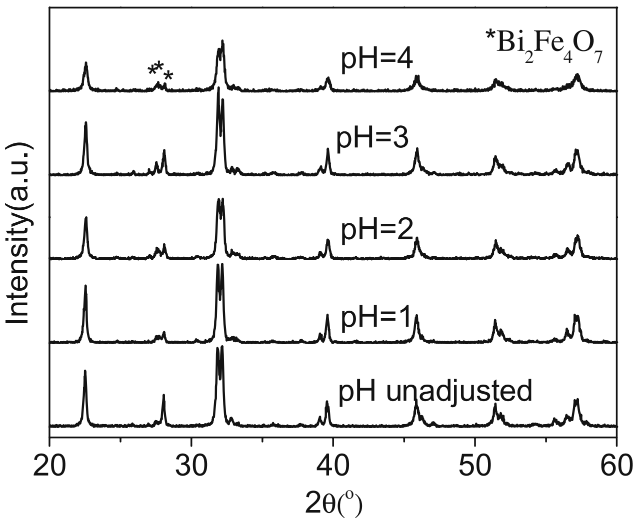

Fig. 1 X-ray diffraction pattern of $BiFeO_3$ fabricated at 700 °C for 1 h from the sol obtained at different pH values by a normal Pechini method

2 Experimental

The powders of $BiFeO_3$ were prepared with the Pechini method as described below. $Fe(NO_3)_3$•$9H_2O$ and citric acid ($C_6H_8O_7$) were taken in a suitable stoichiometry and dissolved in a required amount of distilled water. The solution was stirred and heated at 70 °C for 3 h to form a sol. Aqueous ammonia was used to adjust the pH value. Bi $(NO_3)_3$•$5H_2O$ was then slowly added to the Fe–sol in order to avoid the precipitation of bismuth salts. The sol was dried at 130 °C in an oven for 12 h to form a gel. The gel was slowly heated to 700 °C and then kept for 1 h to obtain $BiFeO_3$ powder. In order to avoid the impurity, the Pechini method was modified as following. The gel was kept in an oven at 200 °C and then decomposed into nanosized metal oxides, which was rapidly heated to a high temperature e.g.,

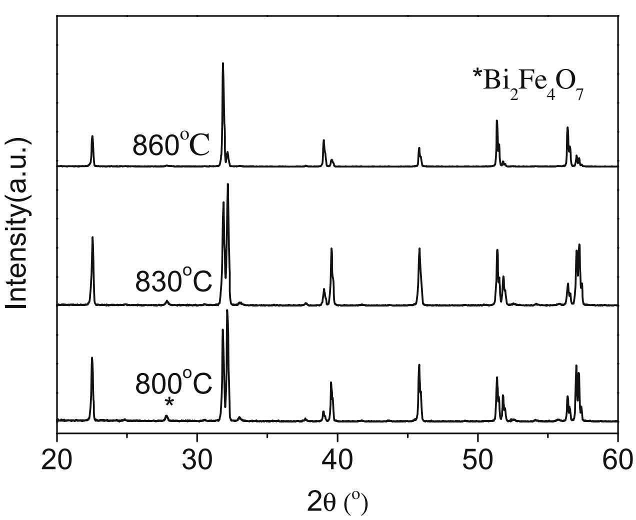

Fig. 2 X-ray diffraction pattern of $BiFeO_3$ calcined at different temperature for 3 min by the modified Pechini method

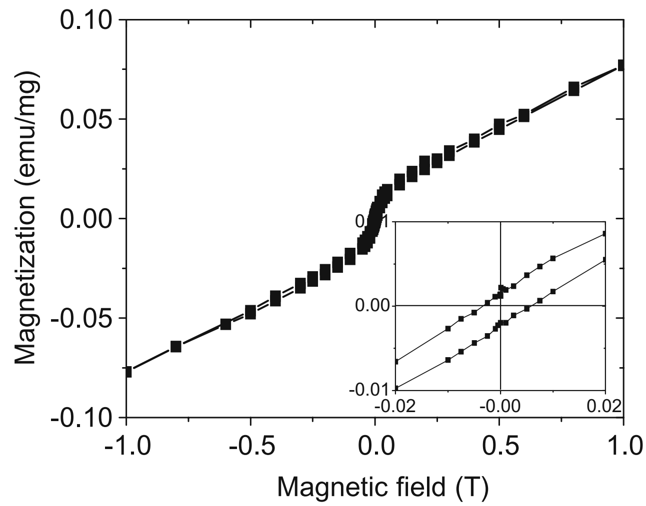

Fig. 3 The M–H curve at room temperature for $BiFeO_3$ calcined at 860 °C for 3 min by the modified Pechini method

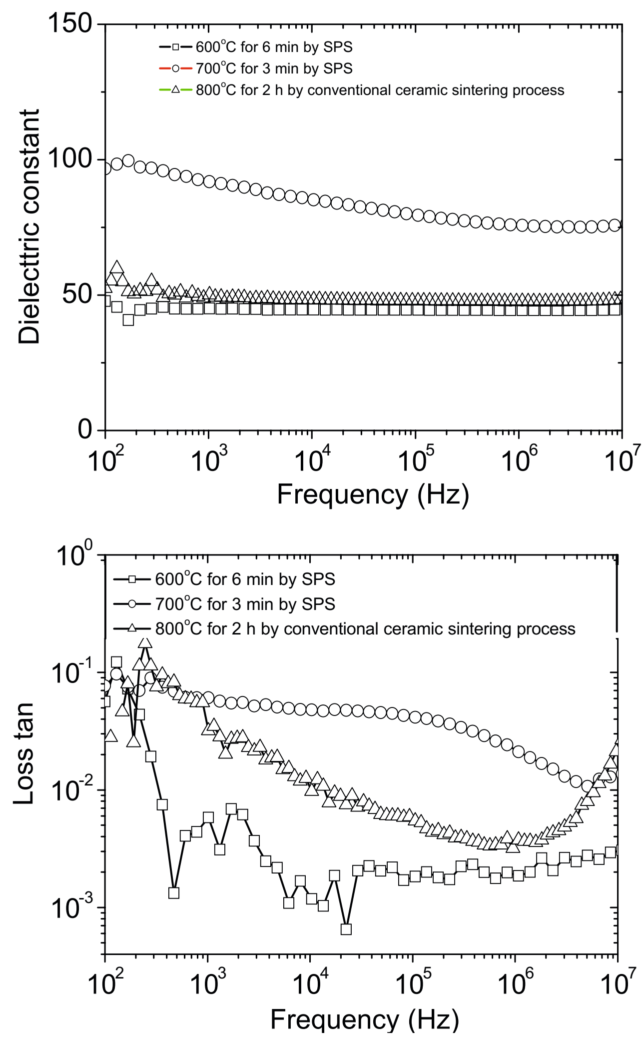

Fig. 4 Frequency dependence of the dielectric constant and loss of the $BiFeO_3$ ceramics fabricated via different sintering processes

800, 830, or 860 °C in a minute and calcined for 3 min to form $BiFeO_3$ powder. The pellet samples were prepared using a cold isostatic press at a pressure of 250 MPa, and then were sintered at 800 °C for 2 h. In order to minimize loss of bismuth oxide during high-temperature sintering, an equilibrium Bi_2O_3 vapor pressure was established using $BiFeO_3$ powder and placing the samples in a covered alumina crucible. For comparison, SPS process was also used to fabricate $BiFeO_3$ ceramics.

Phase identification was performed by the x-ray powder diffraction (XRD) method on a Rigaku D/max-rB x-ray diffractometer. The magnetization was measured using a vibrating sample magnetometer (VSM). Dielectric measurements were performed at room temperature using Aglient dielectric bridge in the range from 100 Hz to 10 MHz, and ferroelectric loop measurements were done using RT6000VHS ferroelectric tester (Radiant Co.).

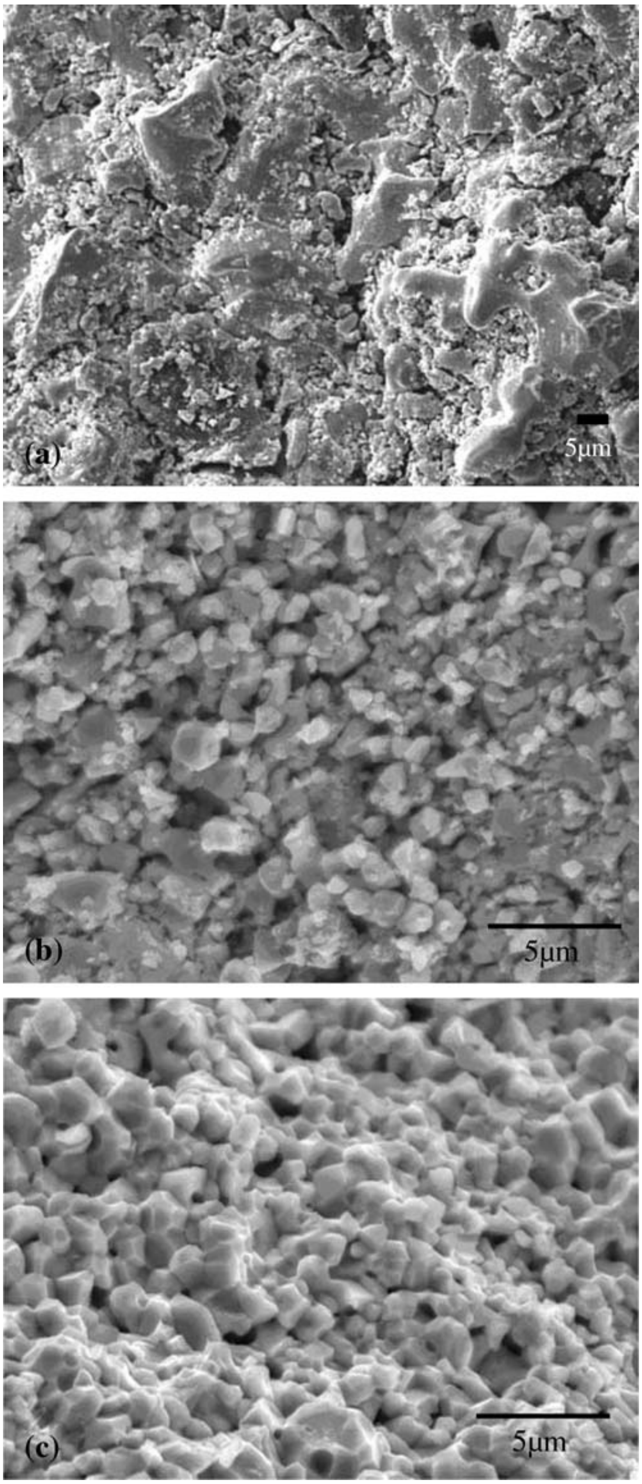

Fig. 5 Scanning electron microscopic image of $BiFeO_3$ ceramics sintered at (**a**) 800 °C for 2 h via conventional ceramic sintering, (**b**) 600 °C for 6 min via SPS, and (**c**) 700 °C for 3 min via SPS process

3 Results and discussion

Figure 1 shows the XRD patterns of the $BiFeO_3$ samples obtained in different pH values by the normal Pechini method. It is noted that this method leads to a lot of impurity phases $Bi_2Fe_4O_7$, which is also described by others [6]. It is found that the pH value has an effect on the purity of $BiFeO_3$ and purer $BiFeO_3$ powder can be obtained at pH=1.

In order to eliminate the impurity in the samples, we modify the Pechini method. The gel was kept in an oven at 200 °C and then rapidly heated to a high temperature. As shown in Fig. 2, the diffraction peaks for the sample sintered at 860 °C can be indexed only as $BiFeO_3$, indicating that a pure phase $BiFeO_3$ was synthesized. The presence of $Bi_2Fe_4O_7$ was detected in addition to major $BiFeO_3$ phase, as the samples were sintered at lower temperatures.

Figure 3 shows the variation of magnetization (M) with an applied field (H) of $BiFeO_3$ calcined at 860 °C for 3 min at room temperature. A magnetic hysteresis loop in the M–

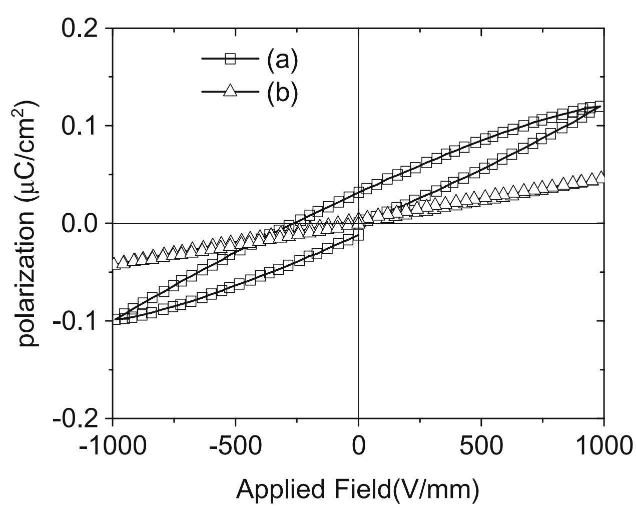

Fig. 6 Polarization hysteresis loops of $BiFeO_3$ ceramic sintered (*a*) at 700 °C for 3 min and (*b*) 600 °C for 6 min via SPS process

H curve is observed, which indicates that the sample shows ferro- or ferrimagnetic behavior at room temperature.

The frequency dependent dielectric constant and loss of the samples fabricated via different sintering processes are presented in Fig. 4. It is clear from Fig. 4 that the dielectric constant is a stable value in the measured frequency range. But the dielectric loss has a distinct change with the frequency. The loss tangent of the samples fabricated via SPS at 600 °C is much lower than the value by 10–300% for $BiFeO_3$ ceramics via the rapid liquid phase sintering process [4]. The sintering process plays a key role in the dielectric properties. The sample via the conventional sintering process has higher conductivity and cannot be polarized at room temperature, but has a low loss tangent 1%. This phenomenon is inconsistent with the viewpoint that the high loss is generally originated from the higher conductivity causing higher leakage current and it is one of the major reasons for lower values for spontaneous polarization and coercive electric field in $BiFeO_3$ pure materials [4]. When sintered at 600 °C for 6 min via SPS, the sample has a dielectric constant of 45 and loss of 0.1–1% which is the lowest as reported so far. When the sintering temperature reaches 700 °C, the dielectric constant of the sample increases to 80–100 and the loss tangent is also up by 1–10%.

Because the low resistivity and low loss simultaneously appear at the sample via conventional sintering process, we conclude, resistivity is not only key factor that affects the loss tangent, which mainly affects the feasibility of polarization. The samples via the SPS process can get enough high resistivity ($10^{8–9}$ Ωcm) to be polarized. The relationship between the dielectric, loss and sintering conditions needs a further research.

Figure 5 shows the scanning electron micrograph of $BiFeO_3$ ceramics. The sample via conventional sintering has an abnormal sintering with the grain size of 10–30 μm. When the SPS technique is used, the grain growth can be well controlled. $BiFeO_3$ ceramics via SPS at 600 °C for 6 min has grains in diameter of 0.4–1 μm but not dense enough. When sintered at 700 °C for 3 min, the sample has a grain size of about 1 μm and high density.

We have also measured ferroelectric hysteresis loops of the ceramics at room temperature (Fig. 6). $BiFeO_3$ via SPS at 600 °C has no obvious ferroelectric hysteresis. The polarization increases when the sintering temperature increases to 700 °C. The spontaneous polarization, remnant polarization, and the coercive field are about 0.12 μC/cm^2, 0.031 μC/cm^2, and 3.5 kV/cm, respectively, under an applied field of 10 kV/cm. In a word, ferroelectric and magnetic orders coexist in this compound at room temperature.

4 Conclusion

In summary, a pure phase BiFeO3 has been synthesized by modified Pechini method. The conventional sintering and spark plasma sintering process has been used to fabricate $BiFeO_3$ ceramics. Ferroelectric and magnetic loops have been observed in the $BiFeO_3$ ceramics at room temperature. Dielectric constant is stable between 100 Hz and 10 MHz, and the loss could decrease to 0.1%. Polarization and magnetization should be improved for practical applications.

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