Ceramic synthesis of $0.08BiGaO_3$–$0.90BaTiO_3$–$0.02LiNbO_3$ under high pressure and high temperature*

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(Received 27 January 2016; revised manuscript received 7 March 2016; published online 31 May 2016)

In this paper, the preparation of $0.08BiGaO_3$-$0.90BaTiO_3$-$0.02LiNbO_3$ is investigated at pressure 3.8 GPa and temperature 1100–1200 °C. Experimental results indicate that not only is the sintered rate more effective, but also the sintered temperature is lower under high pressure and high temperature than those of under normal pressure. It is thought that the adscititious pressure plays the key role in this process, which is discussed in detail. The composition and the structure of the as-prepared samples are recorded by XRD patterns. The result shows that the phases of $BaTiO_3$, $BaBiO_{2.77}$, and $Ba_2Bi_4Ti_5O_{18}$ with piezoelectric ceramic performance generate in the sintered samples. Furthermore, the surface morphology characteristics of the typical samples are also investigated using a scanning electron microscope. It indicates that the grain size and surface structure of the samples are closely related to the sintering temperature and sintering time. It is hoped that this study can provide a new train of thought for the preparation of lead-free piezoelectric ceramics with excellent performance.

Keywords: lead-free piezoelectric ceramics, high pressure and high temperature, morphology

PACS: 82.45.Aa, 07.35.+k, 81.10.–h **DOI:** 10.1088/1674-1056/25/7/078202

1. Introduction

As a kind of polycrystalline materials of mechanical energy and electrical energy transformation function, piezoelectric ceramic are extensively applied in medical, industrial, aerospace and other fields.[1–3] However, different application devices need the corresponding piezoelectric ceramics with different performance parameters in the practical application, which requires researchers to improve the performances of the piezoelectric ceramic materials accordingly. Presently, changing preparation technology and the modification of the piezoelectric ceramic by doping ions are commonly used to improve the performance of the piezoelectric ceramic.[4–6] However, the crystallinity, mechanical and electrical properties of piezoelectric ceramic would be affected seriously when the piezoelectric ceramic is heavily doped by ions.[7]

In recent years, to meet the demand of environmental protection, lead-free piezoelectric ceramics have been paid more and more attention by researchers.[8–14] However, there are some deficiencies of the thermostability and repeatability of the preparation technology of the lead-free piezoelectric ceramics sintered under normal pressure conditions. As we all known, the primary effect of high pressure is volume contraction and shortening of the interatomic and intermolecular distances. Along with the structural modifications are various changes in physical properties such as electric/thermal conductivity, viscosity, melting and magnetic properties. Exploring and understanding the new physical phenomenon under high pressure would open a new avenue for designing and synthesizing materials with unique properties. Furthermore, reports about the synthesis of lead-free piezoelectric ceramics sintered under high-pressure and high-temperature (HPHT) conditions are rarely published.

In this paper, we discuss the synthesis and characteristics of lead-free piezoelectric ceramics sintered under HPHT conditions. It is believed that it would provide a new way and shine a light on lead-free piezoelectric ceramics synthesis.

2. Experimental

Powders of $BiGaO_3$ (99.99% purity), $BaTiO_3$ (99.5 % purity), and $LiNbO_3$ (99.9 % purity) are mixed at a molar ratio of 0.08:0.90:0.02 and milled in the distilled water using a zirconia ball mill in a polyethylene pot for 1.5 h. After drying, the well mixed powders were pressed into a disk (the diameter of 10 mm and the height of 3 mm) without any binder to avoid the samples being contaminated. Then, the samples were treated under HPHT conditions and the synthesis processes of lead-free piezoelectric ceramics at a fixed pressure 3.8 GPa, shown in Fig. 1.

*Project supported by the National Natural Science Foundation of China (Grant No. 51172089), the Natural Science Foundation of Education Department of Guizhou Province, China (Grant Nos. KY [2013]183 and LH [2015]7232), and the Research Fund for the Doctoral Program of Tongren University, China (Grant No. DS1302).

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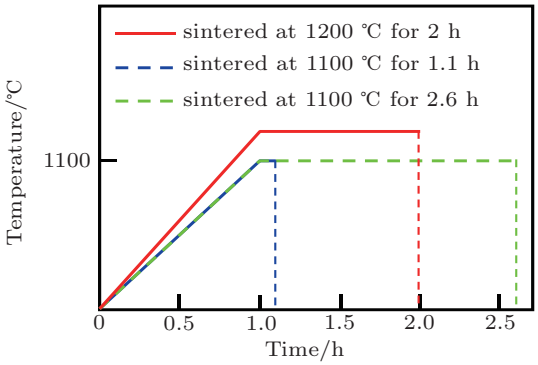


Fig. 1. (color online) Synthesis processes of lead-free piezoelectric ceramics at pressure of 3.8 GPa.

After that, the surfaces of the obtained samples were polished and investigated using a scanning electron microscope (SEM) to analyze the microstructure. Furthermore, the samples were studied using x-ray diffraction (XRD) with Cu-$K\alpha$ ($\lambda = 1.5418$ Å) radiation performed on an x-ray diffractometer (D/MAX-RA).

During the experiment process, temperature was calibrated using a Pt6%Rh–Pt30%Rh thermocouple, whose junction was placed near the crystallization sample. Pressure was measured at room temperature by the change in resistance of standard substances (thallium and barium) and at high temperature by the graphite–diamond equilibrium.

3. Results and discussion

Lead-free piezoelectric ceramics sintering experiments were carried out using a China-type large volume cubic high-pressure apparatus (CHPA) (SPD-6×1200) at temperatures of 1100–1200 °C and a fixed pressure of 3.8 GPa. A schematic diagram of the growth cell is shown in Fig. 2.

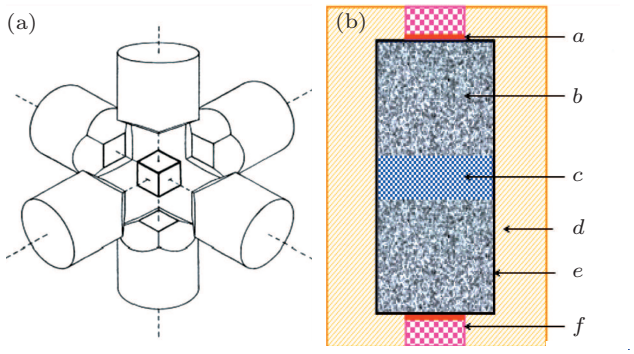


Fig. 2. (color online) (a) Schematic diagram of high pressure cell. (b) Schematic diagram of growth cell. Here, *a*: metal sheet; *b*: ZrO_2; *c*: sample; *d*: pyrophyllite; *e*: graphite heating tube; *f*: steel ring.

Figure 3 shows the optical images of the sample before and after HPHT treatment. It is clearly seen that the sample transforms from white to black after HPHT treatment, according to Figs. 3(a) and 3(b). Figure 3(c) describes the SEM of the sample before HPHT treatment and the size of the raw materials is about 1–2 μm.

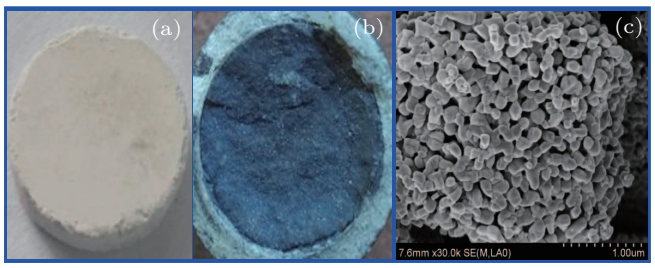


Fig. 3. (color online) Optical images of the sample before and after HPHT treatment: (a) the sample before HPHT treatment; (b) the sample after HPHT treatment; (c) SEM of the sample before HPHT treatment.

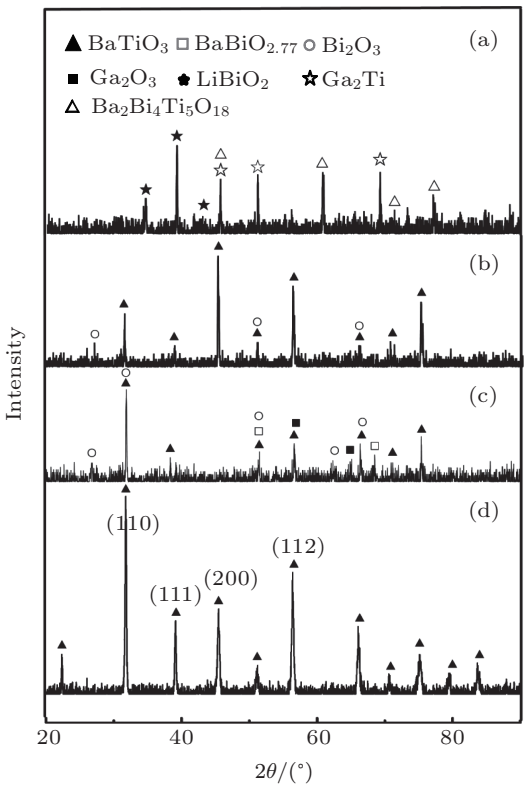


Fig. 4. The x-ray diffraction patterns of lead-free piezoelectric ceramics: (a) sintered at 1200 °C for 2 h; (b) sintered at 1100 °C for 1.1 h; (c) sintered at 1100 °C for 2.6 h, and (d) before HPHT treatment.

In order to understand the composition and the structure of the as-prepared samples, figure 4 shows the XRD patterns of $0.08BiGaO_3$–$0.90BaTiO_3$–$0.02LiNbO_3$ ceramics. Figure 4(a) indicates that the synthesized sample is mainly composed by $LiBiO_2$, Ga_2Ti, and $Ba_2Bi_4Ti_5O_{15}$. Displayed in Figs. 4(b) and 4(c), it manifests that the sintered samples are principally constituted by $BaTiO_3$ and Bi_2O_3. Furthermore, Ga_2O_3 and $BaBiO_{2.77}$ structures are observed in Fig. 4(c). Figure 4(d) shows the characteristic peaks of the raw materials before HPHT treatment as a reference. The structure difference of three samples probably attributes to the different synthesis processes. In these phases, $BaTiO_3$, $BaBiO_{2.77}$, and $Ba_2Bi_4Ti_5O_{18}$ can show the piezoelectric ceramic performance. While the left phases do not display the piezoelectric ceramic performance and these phases will partly weaken the piezoelectric ceramic performance of the sintered samples.

Additionally, it was noticed that the diffraction peak responding to the (200) orientation of $BaTiO_3$ disappears. Considering the crystal growth habit, the growth rate of the (200) surface is larger at 1100 °C and 3.8 GPa, which probably leads to the (200) surfaces disappearing in the final crystals. Hence, the diffraction peak responding to (200) orientation of $BaTiO_3$ is not detected.

To investigate the surfaces morphology of the synthesized samples, figure 5 shows the SEM configurations of three typical samples obtained according to the synthesis processes in Fig. 1. It is clearly seen that the grain size of the sample in Fig. 5(a) is about 1–3 μm. Furthermore, it is noticed that the space around the grains is filled up with filler. It probably attributes to that the raw materials is not completely sintered. Figure 5(b) indicates the SEM morphology, which corresponds to the sample sintered at 1100 °C for 1.1 h. Based on Fig. 5(b), the obvious grains are not noticed. However, the distinct cracks on the sample surface are observed. We can see from Fig. 5(c) that the grain size of the sintered sample is 3–10 μm and obviously larger than that of sample Fig. 5(a), which is responsible for the grain growth with the sintering time increasing. Additionally, it is noticed that grains are connected to each other and there is no crack on the sample surface. As for the non-uniformity of the grains belonging to the sample sintered at 1100 °C for 2.6 h, it could be explained by grain nucleation time. Obviously, the size of grains nucleating early was larger than that of grains nucleating later.

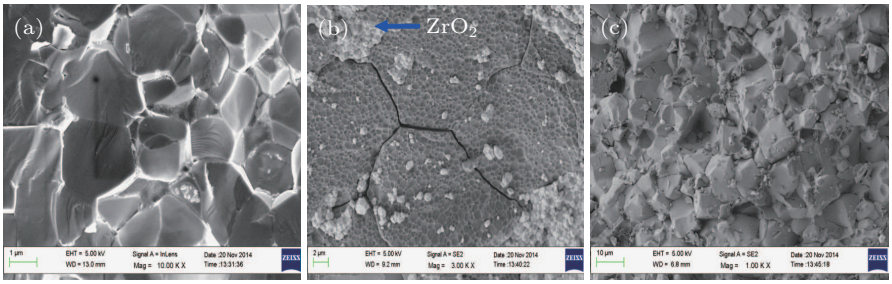


Fig. 5. (color online) SEM of the typical samples synthesized at pressure 3.8 GPa: (a) sintered at 1200 °C for 2 h; (b) sintered at 1100 °C for 1.1 h; (c) sintered at 1100 °C for 2.6 h.

The occurrence of the cracks on the sample surface showing in Fig. 4(b) could be explained by the following. A rapid cooling method is usually adopted when ceramic sintering is completed under HPHT conditions. In the initial stage of cooling, the cooling rate of the sintered sample surface is larger than that of the sample center. It would result in that surface shrinkage degree is larger than that of the sample center. Hence, it makes the sample surface give rise to tensile stress and the sample center generate compressive stress, respectively. Afterwards, the cooling rate of sample surface decreases gradually and the temperature gradient between the sample surface and sample center also decrease with the continuous cooling of the whole sample. In the last stage of cooling, the sample core area begins to shrink more strongly, but it is hampered by the cooled surface. It would lead to that the thermal stresses of the sample surface and center tends to reverse. Namely, the sample center gives rise to tensile stress and the sample surface generates compressive stress until the temperature of both the sample surface and the sample center tends to be uniform. Therefore, it is believed that the cracks emergence may be attributed to the reversal of the thermal stress in the sample. Additionally, it may be another reason for the occurrence of cracks that the crystallization of the sample does not carry out completely, which leads to the binding force being weaker. Furthermore, the synthesis pressure acted on the sample is not completely consistent, owing to its own characteristics of high-pressure apparatus. A certain pressure gradient exists when the synthesis pressure transports from the external to the internal. Hence, the pressure of the sample center is higher than that of the sample edge, which has the potential to cause the occurrence of cracks.

Furthermore, it is noticed that the sintering rate is larger under HPHT conditions than that of the sample sintered under normal pressure condition.[15] In fact, there are many pores in the sample before being sintered. The pores pressure would be enhanced during the sintering process under normal pressure. It would counteract the interfacial energy function to a certain degree, which plays a role of the driving force of the ceramic crystallization. On the other hand, material filling in the closed pores could be achieved only by volume diffusion, which is slower than the interfacial diffusion. However, the adscititious high pressure would make the contact areas of grains produce the plastic when the ceramic sample is sintered under HPHT conditions. It could result in increasing the contact areas of grains. Meanwhile, the adscititious high pressure could make the interatomic distance shorten. Then, atoms or vacancies would generate the volume diffusion and the interfacial diffusion. Additionally, the grain boundary dislocations may also climb along the grain boundary, leading to grain boundary sliding. Furthermore, the adscititious high pressure could play the key role as the driving force of the ceramic crystallization beside the surface energy. Hence, the sintering efficiency un-

der high pressure is higher than that of under normal pressure condition.

Additionally, the difference of the sintering temperature under different pressure conditions is noticed. Previously, it was published that high-performance Pb-free piezoelectric ceramics could be synthesized at 1200–1250 °C for 3 h under normal pressure.[15] However, our experimental results indicate that it could be prepared at 1100 °C under high pressure. It is an interest of the sharp decline of synthesis temperature under different pressure conditions. As is well known, the specific surface area of the powders would increase with the powder particle size decreasing. It results that the total surface energy and chemical activity of the original powders are enhanced accompanied with the increase of the sintering driving force. Theoretical calculation showed that the sintering rate could increase 64 times when the initial particle size decreased from 2 μm down to 0.5 μm. Even, the sintering rate could increase 640000 times when the initial particle size decreased from 2 μm down to 0.05 μm. In this study, it is the adscititious high pressure that probably forces the size of the raw materials to become smaller. Hence, the sintering temperature is lower under HPHT conditions.

4. Conclusions

In this study, Pb-free piezoelectric ceramics is sintered successfully at pressure 3.8 GPa and temperature 1100–1200 °C. Both the sintered rate and sintered temperature of ceramics samples are significantly affected by the adscititious high pressure, which could accelerate the ceramic process of raw materials. Based on the SEM results, we discussed the surface morphology characteristics of the typical samples synthesized at HPHT. Additionally, the XRD result shows that the phases of $BaTiO_3$, $BaBiO_{2.77}$, and $Ba_2Bi_4Ti_5O_{18}$ with piezoelectric ceramic performance are generated in the sintered samples.

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