Room-temperature saturated ferroelectric polarization in BiFeO$_3$ ceramics synthesized by rapid liquid phase sintering

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Single-phased ferroelectromagnet BiFeO$_3$ ceramics with high resistivity were synthesized by a rapid liquid phase sintering technique. Saturated ferroelectric hysteresis loops were observed at room temperature in the ceramics sintered at 880 °C for 450 s. The spontaneous polarization, remnant polarization, and the coercive field are 8.9 μC/cm^2, 4.0 μC/cm^2, and 39 kV/cm, respectively, under an applied field of 100 kV/cm. It is proposed that the formation of Fe^{2+} and an oxygen deficiency leading to the higher leakage can be greatly suppressed by the very high heating rate, short sintering period, and liquid phase sintering technique. The latter was also found effective in increasing the density of the ceramics. The sintering technique developed in this work is expected to be useful in synthesizing other ceramics from multivalent or volatile starting materials. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1667612]

Ferroelectromagnets are a family of materials having coupled ferroelectric and magnetic order parameters that result in simultaneous ferroelectricity and ferromagnetism.[1] These materials, therefore, not only have potential applications in magnetic and ferroelectric devices, but also the ability to couple the electric and the magnetic polarization in these materials, providing an additional degree of freedom in device design. Besides the potential applications, the fundamental physics of ferroelectromagnet materials is also interesting and fascinating.

Perovskite BiFeO$_3$ is ferroelectric (T_C: 1103 K) and antiferromagnetic (T_N: 643 K). It exhibits weak magnetism at room temperature due to a residual moment from a canted spin structure.[2] Though BiFeO$_3$ was discovered in the 1960's and its structure and properties have been extensively studied,[3,4] transport measurements have been hampered by leakage problems. Low resistivity of the sample at room temperature makes the observation of the ferroelectric loop very difficult. This seriously limited the application of this material. In order to enhance the resistivity and observe a hysteresis loop, measurements were done at 80 K by Teague, Gerson, and James.[5] They obtained a ferroelectric hysteresis loop from a single crystal, with a spontaneous polarization of 3.5 μC/cm^2 in the (100) direction, but the saturation of the loop was not observed even at fields as high as 55 kV/cm.

Recently, observation of saturated ferroelectric hysteresis loops in BiFeO$_3$ thin films at room temperature has been reported.[6,7] As for the BiFeO$_3$ bulk ceramic, recent work was focused on solid solutions of BiFeO$_3$ with other ABO$_3$ perovskite materials, such as BaTiO$_3$, which can prevent second phase formation and increase sample resistivity.[8,9] This enables the study of physical properties of BiFeO$_3$ rich phases and extrapolates it to the pure BiFeO$_3$ compound. Other research work on BiFeO$_3$ ceramic involved synthesizing pure phase BiFeO$_3$ by leaching the impurity phase with dilute nitric acid,[10] but the saturated loop was not obtained in this pure phase BiFeO$_3$ ceramic due to its lower density and high conductivity. For the investigation of electric properties and actual applications of BiFeO$_3$ ceramics, it is necessary and still a challenge to synthesize high resistivity samples. In this letter, we report a technique for synthesizing pure phase BiFeO$_3$ ceramics with high resistivity by rapid liquid phase sintering. Saturated ferroelectric loops have been observed at room temperature in these BiFeO$_3$ ceramic samples.

Samples of BiFeO$_3$ were prepared by the solid state reaction method. High purity Bi$_2$O$_3$ (99.99%) and Fe$_2$O$_3$ (99.99%) powders were carefully weighed in stoichiometric proportions (1:1 mole ratio) and thoroughly mixed in an agate mortar for about 10 h using high purity isopropyl alcohol as a medium. The average size of the obtained mixture particles is about 0.5–1 μm. The mixture was then dried and pressed into a 10×5×2 mm^3 bar at 10 MPa pressure. Then the prepared bars were sintered for 450 s in air at different temperatures using a rapid thermal processor (RTP) with which a high heating rate up to 100 °C/s could be obtained. For electric properties measurements, the bar was cut into a slice with a thickness of 0.2–0.3 mm and Ag top electrodes with a 1.2 mm diameter were pasted on. Ferroelectric properties of the synthesized BiFeO$_3$ ceramics were measured using a RT6000 ferroelectric tester under virtual ground conditions and all measurements were carried out at room temperature.

Figure 1 presents the x-ray diffraction (XRD) patterns of BiFeO$_3$ samples calcined for 450 s at 750, 800, 820, and 880 °C, respectively. None of the patterns show any Bi$_2$O$_3$ and Fe$_2$O$_3$ diffraction peaks. This means that the solid state reaction between Bi$_2$O$_3$ and Fe$_2$O$_3$ powder in the sintered samples was full and completely finished in the short sintering time. Diffraction peaks that come from the ceramic sample RTP sintered at 880 °C for 450 s can be indexed only as BiFeO$_3$, indicating that a pure phase BiFeO$_3$ was synthesized. On the other hand, for the samples sintered at lower temperatures, in addition to the major BiFeO$_3$ phase, the presence of the Bi$_{36}$Fe$_2$O$_{57}$ impurity phase was detected in an XRD pattern. This impurity phase also may be indexed as
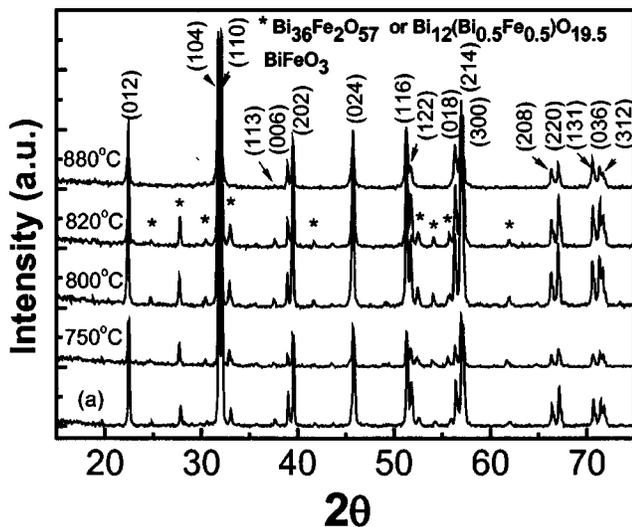

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FIG. 1. X-ray θ–2θ scans from the BiFeO$_3$ ceramic samples synthesized by the rapid sintering processing at different sintering temperatures. Pure phase BiFeO$_3$ with high resistivity was synthesized at 880 °C. Curve (a) shows the XRD pattern of BiFeO$_3$ ceramic sintered at 880 °C for 3 h by conventional solid state reaction sintering technique.
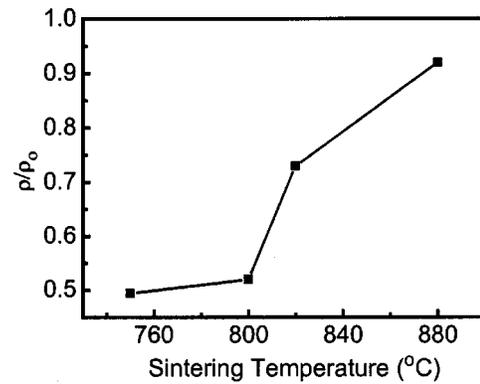

FIG. 2. Relative density of BiFeO$_3$ ceramics sintered at different temperatures by the rapid liquid phase sintering technique. At 880 °C, a compact bulk with 92% relative density was obtained.

Bi$_{12}$(Bi$_{0.5}$Fe$_{0.5}$)O$_{19.5}$, because its diffraction pattern is very similar to Bi$_{36}$Fe$_2$O$_{57}$. Although the detailed process of this rapid sintering technique is being further researched, the results presented by the XRD patterns showed that higher sintering temperatures would benefit to avoid the formation of impurity phase and to obtain pure phase BiFeO$_3$. As the melting point of Bi$_2$O$_3$ is 817 °C, the appearance of the liquid phase seems to play an important role during the synthesizing reaction. The liquid phase will accelerate the synthesizing reaction and probably prevent the formation of the second phase. As a contrast, the XRD θ–2θ scan from BiFeO$_3$ ceramic sintered at 880 °C for 3 h by a conventional solid state reaction sintering technique was also shown in Fig. 1(a). This XRD pattern is very similar to those from the ceramic samples sintered by RTP at lower temperatures. The impurity phase always appeared during the synthesis of BiFeO$_3$ by conventional sintering process, as reported by other authors.[11,12] As for the samples sintered at 820 °C by the RTP, the existence of an impurity phase can be attributed to the fact that this sintering temperature is very close to the melting point of Bi$_2$O$_3$. Considering the high heating rate and short sintering period, the melting of Bi$_2$O$_3$ in this temperature was probably not in full.

Furthermore, the existence of a liquid phase in the sintering process will also be beneficial to increase the density of the sintered ceramics. Figure 2 shows the relative density of these samples sintered at different temperatures. A rapid increase in the density from 52% to 73% was observed when the sintering temperature increased to 820 °C from 800 °C, and this change in sintering temperature was just across the melting point of Bi$_2$O$_3$. A relative density value of 92% was obtained when the samples were sintered at 880 °C, indicating that compact ceramic could be synthesized using this sintering technique.

Polarization hysteresis loops of these samples were measured and shown in Fig. 3. For the sample with pure phase BiFeO$_3$ sintered by RTP at 880 °C, a saturated polarization hysteresis loop was observed at room temperature under an

applied field of 100 kV/cm. The spontaneous polarization (P_s), remnant polarization (P_r), and the coercive field (E_c) are 8.9 μC/cm^2, 4.0 μC/cm^2, and 39 kV/cm, respectively. As to the samples with an impurity phase synthesized at lower temperature, the measurements for the electric properties indicate that these samples are still highly resistive. Even in the sample synthesized at 750 °C with poor relative density of 49%, polarization hysteresis loops can also be observed in Fig. 2, though the loops are not saturated. This implies that the impurity phase in the samples does not increase the leakage remarkably in BiFeO$_3$ ceramic. It is known that the deviation from oxygen stoichiometry leads to valence fluctuation of Fe ions ($+3$ to $+2$ state) in BiFeO$_3$, resulting in high conductivity.[7] Our explanation for the high resistivity of the BiFeO$_3$ ceramic samples synthesized by the rapid sintering techniques is as follows: In the conventional sintering processing for BiFeO$_3$, the slow heating rate and long sintering time will enable the equilibrium concentration of oxygen vacancies at high temperatures to be reached and will result in the high oxygen vacancy concentration in the synthesized products. Eventually, the frozen oxygen vacancy leads to a deviation from oxygen stoichiometry in the synthesized products.
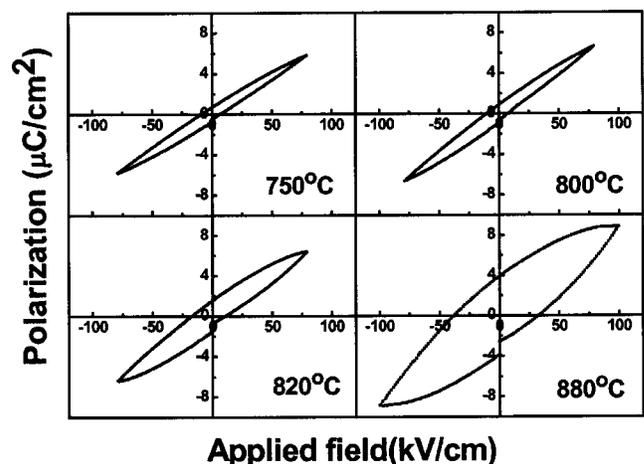

FIG. 3. Polarization hysteresis loops of BiFeO$_3$ ceramics sintered by the rapid liquid phase sintering process at different temperatures. A room temperature saturated polarization with P_s of 8.9 μC/cm^2 was observed in the pure phase BiFeO$_3$ ceramic synthesized at 880 °C, under an applied field of 100 kV/cm.

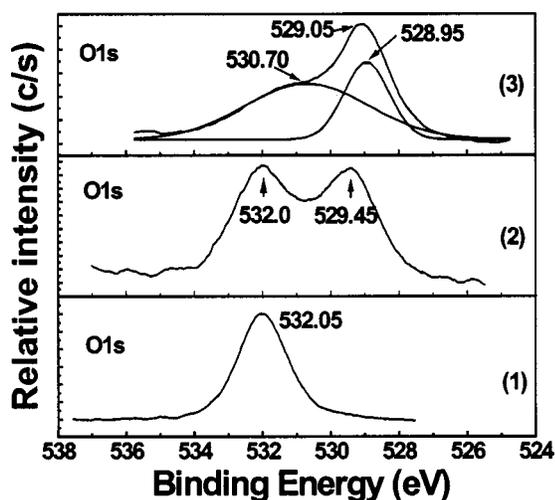Appl. Phys. Lett., Vol. 84, No. 10, 8 March 2004

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FIG. 4. XPS results for O $1s$ from BiFeO$_3$ ceramics. Curves (1) and (2): From BiFeO$_3$ samples prepared by the rapid liquid phase sintering technique at 880 °C and 820 °C, respectively. Curve (3): From a BiFeO$_3$ sample prepared at 880 °C by the conventional solid state reaction sintering process.

Thus, both the BiFeO$_3$ phase and the impurity phase are highly conductive due to the existence of Fe^{2+} and oxygen deficiency. In rapid sintering processing, the formation of Fe^{2+} and oxygen deficiency is greatly suppressed because there are only several seconds of preheating time and several hundred seconds of sintering time. Therefore, the synthesized samples are highly resistive even though there is a second impurity phase. Despite the difficulty in determining Fe^{2+} in these ceramic samples, x-ray photoelectron spectroscopy (XPS) analysis of oxygen in these samples gives some evidence for our argument. Curves (1) and (2) in Fig. 4 show the XPS results of O $1s$ from the BiFeO$_3$ sample sintered at 880 °C and 820 °C, respectively, by the rapid sintering technique. Only one peak was observed in curve (1). It is understandable because there is only a single pure BiFeO$_3$ phase in the sample synthesized at 880 °C by rapid sintering technique. Then the peak value of 532.05 eV should correspond to the O $1s$ binding energy of the BiFeO$_3$ phase. In curve (2), besides the peak at 532.0 eV from the O $1s$ binding energy of the BiFeO$_3$ phase, another peak at 529.45 eV was also observed. This additional peak value then corresponds to the O $1s$ binding energy of the Bi$_{36}$Fe$_2$O$_{57}$ impurity phase. Obviously, the O $1s$ binding energy of the BiFeO$_3$ phase in these two samples prepared by the same sintering technique is very close. Curve (3) in Fig. 4 shows the XPS results of O $1s$ from the BiFeO$_3$ sample sintered by conventional solid state reaction sintering. From the XRD patterns, we know that there are also two phases including the BiFeO$_3$ phase and the Bi$_{36}$Fe$_2$O$_{57}$ impurity phase in this sample, so two

peaks ought to be detected, as in curve (2). In fact, the asymmetric broad band at 529.05 eV shown in curve (3) can be Gaussian divided into two subbands at 530.70 and 528.95 eV, corresponding to the O $1s$ binding energy of the BiFeO$_3$ phase and the impurity phase in this sample. These two values of O $1s$ binding energy shifted 1.35 and 0.5 eV, respectively, to the smaller values from the O $1s$ binding energy in these samples fabricated by rapid sintering technique. This smaller O $1s$ binding energy indicates there is more negative charge for each oxygen ion in the sample synthesized by the conventional sintering process. It is probably due to more oxygen deficiency in this sample; then the negative charge induced by oxygen deficiency will redistribute in the residual oxygen ions, leading to a smaller O $1s$ binding energy.

In conclusion, a pure phase BiFeO$_3$ ceramic with a high resistivity was synthesized using a rapid liquid phase sintering technique. Saturated polarization hysteresis loops were observed at room temperature in the BiFeO$_3$ ceramic sample. It is proposed that less Fe^{2+} and an oxygen deficiency in the RTP sintered samples are responsible for the lower leakage in these samples. The highly resistive materials synthesized in this work will provide a possibility for the study of electric properties and the practical applications of BiFeO$_3$ ceramic. The sintering technique developed in this work will also be useful in synthesizing other materials from volatile or multivalent components.

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