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Magnetic and electrical properties of single-phase multiferroic BiFeO₃

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We have reported the structural, thermal, microscopic, magnetization, polarization, and dielectric properties of BiFeO₃ ceramics synthesized by a rapid liquid-phase sintering technique. Optimum conditions for the synthesis of single-phase BiFeO₃ ceramics were obtained. Temperature-dependent magnetization and hysteresis loops indicate antiferromagnetic behavior in BiFeO₃ at room temperature. Although saturated ferroelectric hysteresis loops were observed in single-phase BiFeO₃ ceramic synthesized at 880 °C, the reduced polarization is found to be due to the high loss and low dielectric permittivity of the ceramic, which is caused by higher leakage current. © 2005 American Institute of Physics. [DOI: 10.1063/1.1881775]

I. INTRODUCTION

Multiferroics are a class of materials with coupled electric, magnetic, and structural order parameters that yield simultaneous effects of ferroelectricity, ferromagnetism, and ferroelasticity in the same material.¹ These materials offer a wide opportunity for potential applications in information storage, such as spintronic devices and sensors, where both electric and magnetic polarizations can be coupled, giving enough opportunity for manipulating devices. The perovskite BiFeO₃ (BFO) belongs to this class of multiferroic materials with ferroelectric transition temperature $T_c \sim 1103$ K and antiferromagnetic transition $T_N \sim 643$ K. BFO belongs to other magnetic ferroelectrics, such as YMnO₃ and BiMnO₃. Bulk BFO, especially synthesized through solid solution, exhibits weak ferromagnetic properties at room temperature due to residual moment from a canted spin structure,² which is believed to be generated from the impurity phase related to Fe phase separation. In addition, a major problem generally encountered in transport measurements is the high leakage current due to the low resistivity of the sample, which creates difficulties in the observation of the ferroelectric hysteresis loops. The high leakage current in bulk is attributed to defects and nonstoichiometry. Therefore, this material becomes unsuitable for applications. However, there is tremendous success in the fabrication of heteroepitaxially constrained thin films of BFO which shows enhanced polarization with saturated hysteresis loop and ferromagnetic behavior at room temperature.^{3,4}

There are several reports^{5,6} on the fabrication of BFO dispersed in BaTiO₃ matrix to restrict the second phase, leak-

age current, and low resistivity in the sample. Recently, single-phase BFO ceramic samples have been synthesized by rapid liquid-phase sintering technique.⁷ These ceramic samples show relatively high resistivity and saturated ferroelectric hysteresis loops at room temperature and could be useful for potential applications. This is a dramatic improvement over past techniques used for the fabrication of BFO ceramics in which very often canted ferromagnetic spin structures were observed due to the impurity phase. However, detailed studies on microscopic grains, thermal, magnetic, and electrical properties related to frequency-dependent dielectric loss are still lacking in this potentially important ceramic sample. In this paper, we report on the development of various microstructures of liquid-phase-sintered samples processed at various temperatures, thermal properties, temperature-dependent magnetic behavior, and electrical properties including ferroelectric loops and related dielectric loss up to $f=1$ MHz. Our results suggest that pure BFO samples exhibit antiferromagnetic behavior over the whole temperature region, 5–300 K, and saturated ferroelectric loops at room temperature. However, the ceramic sample shows high dielectric loss, especially at higher frequency range, which may be one of the major challenges for applications.

II. EXPERIMENT

BiFeO₃ samples were synthesized by the solid-state reaction method. Stoichiometric amounts of Bi₂O₃ (99.99%) and Fe₂O₃ (99.99%) powders were thoroughly mixed using isopropyl alcohol and ground. The mixtures were dried, pressed, and sintered at different temperatures for 400–450 s, as described in Ref. 7 for rapid liquid-phase sintering. Phase identification was performed by the x-ray powder diffraction

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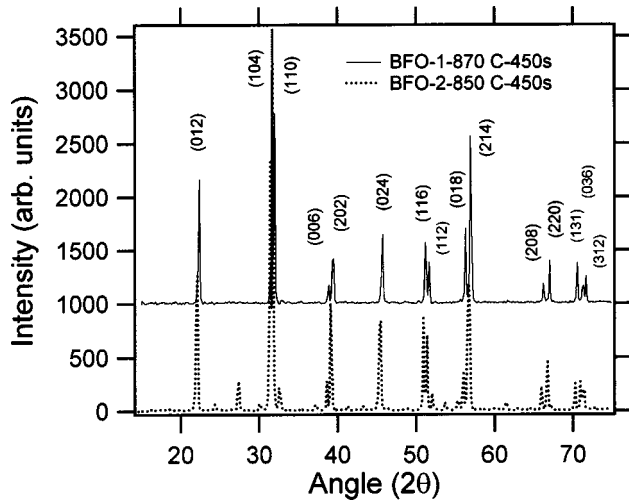


FIG. 1. X-ray diffraction pattern of BiFeO_3 ceramics synthesized at 820 and 880 °C by liquid-phase sintering. The asterisks represent the undesired second phase.

(XRD) method on a Rigaku x-ray diffractometer using $\text{Cu } K\alpha$ radiation. The magnetization was measured using Quantum Design superconducting quantum interference device [SQUID magnetic property measurement system (MPMS)]. RT6000 ferroelectric tester and Agilent dielectric bridge measured the ferroelectric and dielectric properties of the sintered ceramics at room temperature, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the BFO samples sintered at 850–880 °C, respectively, prepared by liquid-phase sintering for ~ 450 s. The sample sintered at 880 °C shows a single phase, whereas the sample sintered at 850 °C shows evidence for the presence of a second phase, probably arising from $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$ and related phases. Hence the rapid sintering at 880 °C for a short time shows a completion of reaction to form a single-phase BiFeO_3 . It is noted that the sintering temperature higher than that of 880 °C, such as at 890 °C, forms many undesirable phases. In order to investigate the thermal behavior related to phase changes and melting phenomena in BFO, differential scanning calorimetry (DSC) results are presented in Fig. 2. A distinct endothermic transition at 825 °C in heat flow versus temperature curve is observed. This transition is very consistent with the change in curvature in heat-flow curve, as shown in Fig. 2 as dashed lines. The melting point of Bi_2O_3 is about 825 °C and this transition can be certainly assigned due to the melting of Bi_2O_3 . Therefore, it remains very important at what temperature the liquid phase of Bi_2O_3 forms a single-phase material with Fe_2O_3 . It turns out that 880 °C becomes the exact temperature for rapid sintering where single-phase BFO is formed. On the other hand, there is a remarkable weight loss after the second transition at 960 °C, indicating loss of Bi_2O_3 through sublimation process. Hence rapid heating rate and short-time sintering of BiFeO_3 at 880 °C remains a clue to avoid loss of Bi, segregation of Fe_2O_3 , and formation of other undesired phases, as indicated by the XRD. Lower-

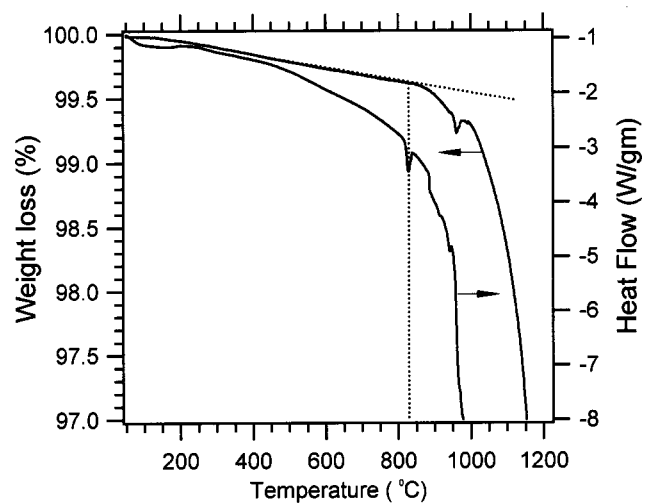


FIG. 2. Temperature dependence of weight loss and heat flow of BFO measured by differential scanning calorimetry.

temperature rapid sintering is also unfavorable due to the incomplete melting of Bi_2O_3 and the formation of intermediate phases.

Figure 3 shows the scanning electron microscopy (SEM) results of BFO synthesized by rapid thermal sintering at 850, 880, and 890 °C. The SEM micrographs elucidate the grain growth phenomena in sintered BFO at various temperatures. The grain size increases enormously with increasing temperature. The average grain of 1–2 μm increases to 5–10 μm in size when sintering temperature increases from 850 to 880 °C. However, the density and number of bright spots that probably correspond to segregated Fe_2O_3 particles decreases dramatically when sintering temperature increases from 850 to 880 °C. In fact, several red-colored spots embedded in a black matrix were noticed when examined in an optical microscope. This suggests that the bright spots observed in SEM are due to Fe_2O_3 particles. On the other hand, the SEM micrograph of the sample sintered at 890 °C shows a uniform surface displaying very large grains ($> 50 \mu\text{m}$). However, this sample is multiphase due to partial loss of Bi_2O_3 from its melt, as discussed in x-ray and DSC studies. This suggests that although large grains are produced by melting, the grains contain many undesired phases.

In order to illustrate the magnetic ordering in BFO, the temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves are presented in Fig. 4(a). In these measurements, the sample was cooled in either ZFC to a desired temperature and then a magnetic field was applied or FC. The measurements were done while warming the sample in the magnetic field for both cases. For $H = 0.2$ T, the FC and ZFC curves separate at around 160 K and $M_{\text{FC}} - M_{\text{ZFC}}$ increases as temperature decreases. However, the FC and ZFC curves again merged at very low temperatures. There is a distinct irreversibility at ~ 160 K accompanied by a remarkable thermomagnetic hysteresis (or irreversibility) with $M_{\text{ZFC}} \neq M_{\text{FC}}$ at the irreversibility temperature T_{irr} . This type of irreversibility in magnetization is generally indicative of antiferromagnetic (AF) ordering;⁸ however, for a simple AF no thermomagnetic hysteresis is expected. This latter effect is traditionally accepted as a hall-

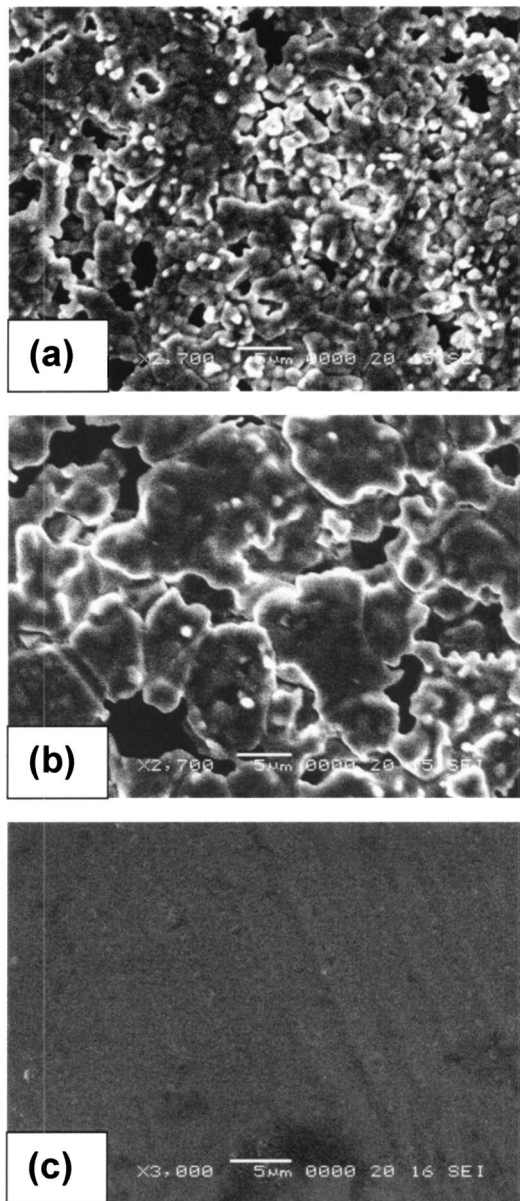


FIG. 3. Scanning electron microscopic images of BFO ceramics synthesized at (a) 820, (b) 880, and (c) 890 °C by rapid liquid-phase sintering. The indicated scale in all images is 5 μm.

mark of a spin-glass system⁹ with a characteristic spin-glass transition temperature T_g . The most interesting phenomenon is the observation of an anomalous temperature dependence of magnetization, such as a decrease in magnetization down to 150 K accompanied by a small jump at about 265 K, and then a sharp increase of magnetization, as the temperature is further lowered. Although the latter temperature-dependent magnetization behavior is understood in the framework of antiferromagnetic correlation, the decrease of magnetization with temperature in the temperature range of from 265 to about 150 K remains puzzling and could not be explained.

One of the suspects for such anomalous magnetization may be the oxygen vacancy concentration and also the existence of Fe^{2+} ions. It was proposed⁴ that the oxygen deficiency may lead to valence fluctuation of Fe ions (3+ to 2+ states) in BFO resulting in high conductivity. However, such

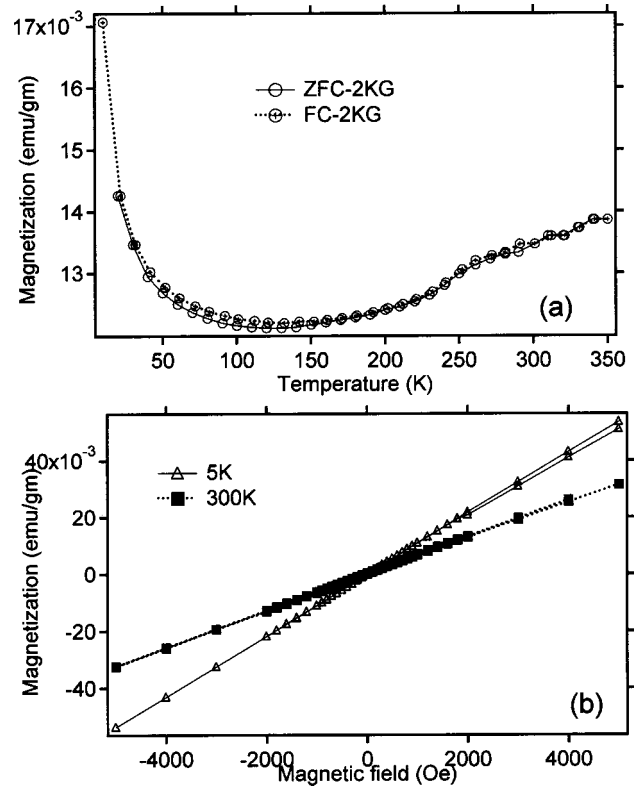


FIG. 4. (a) The temperature-dependent FC and ZFC magnetizations of BFO ceramic synthesized by liquid-phase sintering at 880 °C. (b) The magnetization hysteresis loops of BFO at 5 and 300 K.

a possibility was recently ruled out in samples synthesized by liquid-phase sintering⁷ where sintering time for the heating, sintering, and cooling times were limited to seconds only. We argue that even though the sintering time is considerably small, there may exist small concentrations of oxygen vacancies resulting in Fe^{2+} and Fe^{3+} valence fluctuations which may influence significantly both magnetic and electrical properties. Hence, the observed anomalous magnetization behavior may be related to such valence fluctuations, although further experiments are necessary to reveal the complete fact. However, the magnetic hysteresis loops, as shown in Fig. 4(b), illustrate a linear field dependence, indicating that BFO shows antiferromagnetic behavior both at 5 and 300 K. On the other hand, the magnetization and magnetic hysteresis results confirm the absence of canted ferromagnetic behavior in this sample. This suggests the absence of Fe-related clusters or impurities in the sample.

The ferroelectric polarization hysteresis loops are presented in Fig. 5 for the BFO sample sintered at 880 °C. According to previous reports,^{2,10} the spontaneous polarization in BFO ceramics and single crystals is significantly lower than the expected value for other ferroelectric materials having comparable T_c , such as PbTiO_3 with $T_c \sim 763$ K, and spontaneous polarization of 80–100 $\mu\text{C}/\text{cm}^2$. The spontaneous polarization (P_s), remnant polarization (R_s), and the coercive field (E_c) are about 3.5 $\mu\text{C}/\text{cm}^2$, 2.5 $\mu\text{C}/\text{cm}^2$, and 40 kV/cm, respectively. Although these values are very comparable to the values reported in the single crystal,¹⁰ they are almost half of the reported values for BFO ceramics synthesized using the same technique. However, a saturated polar-

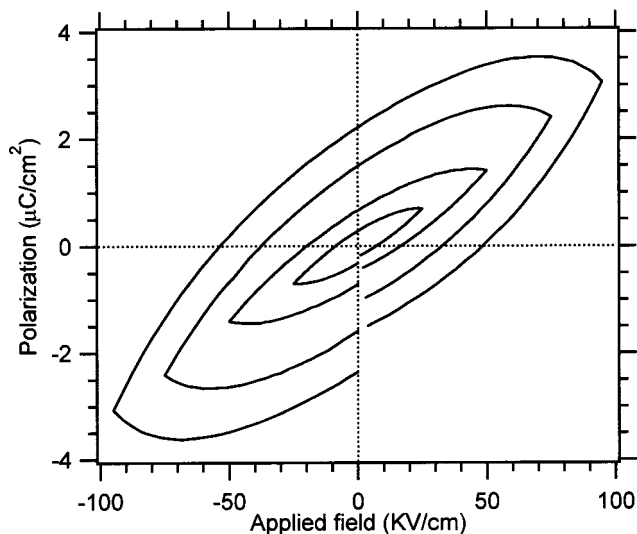


FIG. 5. Polarization hysteresis loops of BFO ceramic synthesized by liquid-phase sintering at 880 °C for different field cyclings.

ization hysteresis loop was observed at room temperature under an applied field of 95 kV/cm. In order to understand the origin of such low values for P_s , R_s , and E_c , the dielectric constant and the loss as a function of frequency are presented in Fig. 6. It is clear from Fig. 6 that the dielectric constant is a strong function of frequency and it decreases significantly with increasing frequency. However, a reverse trend is obtained for the dielectric loss factor, $\tan \delta$. The high loss in this material generally originated from the higher conductiv-

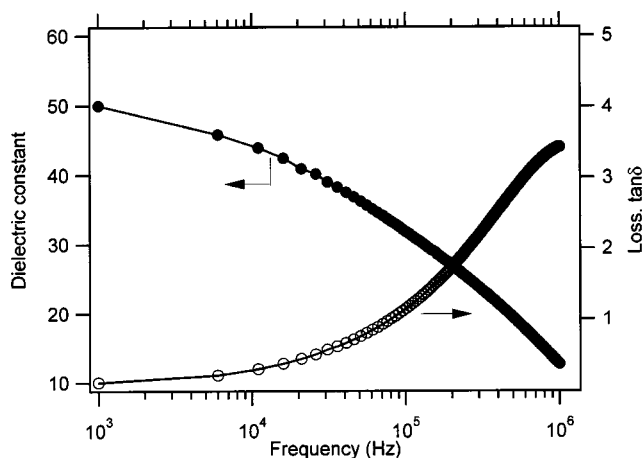


FIG. 6. Frequency dependence of the dielectric constant and loss of the BFO ceramic synthesized by liquid-phase sintering at 880 °C.

ity causing higher leakage current. This is one of the major reasons for obtaining lower values for P_s , R_s , and E_c in BFO pure materials. Therefore, it is necessary to synthesize BFO in other dielectric matrix to enhance its dielectric and loss properties in order to realize its practical applications.

IV. CONCLUSION

We have reported the x-ray, thermal, microscopic, magnetization, polarization, and dielectric properties of BiFeO₃ ceramics synthesized by a rapid liquid-phase sintering technique. Temperature-dependent magnetization and hysteresis loops indicate antiferromagnetic behavior in BiFeO₃ at room temperature. Anomalous temperature-dependent magnetization behavior predicts the presence of a small concentration of oxygen-related defects due to Fe valence fluctuations. Although saturated ferroelectric hysteresis loops were observed in single-phase BiFeO₃ ceramic synthesized at 880 °C, the reduced polarization is found to be due to the high loss and low dielectric permittivity of the ceramic. In the present paper, we have exclusively demonstrated the multiphase–single-phase–multiphase transition in BiFeO₃ ceramics with increasing sintering temperature and their structural, thermal, and microscopic evolutions. The persisting leakage current problem in optimally sintered ceramics needs to be solved for better applications.

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