Enhanced ferromagnetism and weak polarization of multiferroic $BiFeO_3$ synthesized by sol-gel auto-combustion method

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ABSTRACT

$BiFeO_3$ powders and ceramics were prepared by sol-gel auto-combustion method. Optimal conditions for the synthesis of pure $BiFeO_3$ powders were experimentally obtained by X-ray diffraction patterns analysis. Enhanced room magnetic property with saturated magnetization (m_s) of 2.5emu/g and 0.02emu/g was observed respectively both in powders calcined at 500ºC (3h) and in ceramics sintered at 830ºC (3h). The latter also exhibited distinct ferroelectricity features with a considerable spontaneous polarization ($2P_s$=13.2μC/cm^2) at a low electric field of 6KV/cm, but failed to saturate due to its large leakage current.

Key words: ferroelectrics, magnetic property, sol-gel auto-combustion method; X-ray techniques

1.INTRODUCTION

Multiferroic materials which exhibit a coexistence of (anti)ferromagnetism, (anti)ferroelectricity, or (anti)ferroelasticity, has become the focus of research due to both their fascinating fundamental physics and great potential of multifunctional application.But multiferroic materials are rare as natural resources. As an interesting candidate of the few multiferroic materials, single-phase $BiFeO_3$ (BFO) is a rhombohedrally distorted perovskite crystallized in space group *R*3*C*, possessing ferroelectricity order (T_C=1083K) coupled with antiferromagnetism order (T_N=643K) at room temperature [1]. Recent, work on density functional calculations predicated that BFO would represent a macroscopic magnetization of about 0.9emu/g owing to a residual moment from a canted spin structure [2], as proved in the observation about BFO single-crystal and thin films [3-4]. However for bulk BFO, M-H loops are only observed at very low temperature. On the other hand, a relatively large leakage current density in BFO ceramics may also make it difficult to obtain a well-saturated hysteresis loop [4].

In our present work, we investigated Sol-gel auto-combustion method and obtained the optimal technical parameters to manufacture pure BFO. The structure, magnetic and ferroelectricity of BFO at room temperature will be discussed.

2.EXPERIMENTAL

BFO powders and ceramics were prepared via sol-gel auto-combustion method. The phase identification was examined by using X-ray diffractometer (XRD, Philips X'pert PW3373/10). Microstructure of ceramics was investigated by Scanning electric microscope (SEM, FEI Quanta 2000). Magnetic hysteresis (M-H) measurements were carried out at room temperature by using vibrating sample magnetometer with the maximum magnetic field of 12kOe (VSM, Nanjing Univeristy, BHV-55). Ceramics were polished to ~0.3mm and pasted by silver on both surfaces as electrodes, and then Ferroelectric hysteresis (P-E) measurements at room temperature were measured by using ferroelectric loop trace at a frequency of 50Hz(Huazhong University of Science and Technology, ZT-1).

3. RESULTS AND DISCUSSION

Fig.1 shows the influence of precursor's pH values on BFO powders' structure.

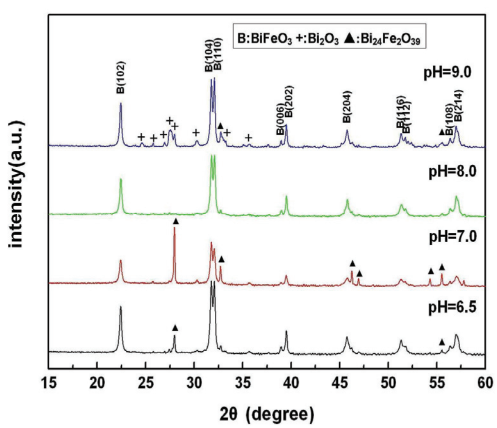

Fig.1: XRD patterns of BFO powders obtained by different precursor solution's pH

It is found that all the samples have single-phase BFO pervoskite crystal structure. For pH=9.0, it is observed that powders exist a few impurities peaks corresponding to $Bi_{24}Fe_2O_{39}$ (JCPDS NO.42-0201) and Bi_2O_3 (JCPDS No: 50-1088). The onset of Bi_2O_3 may be contributed to high pH value to make Bi_2O_3 separate from sol-gel during heating and calcining process. For pH=8.0, pure BFO phase is found and the powders' average size is 112nm (measured by zeta potential & particle sizing device, Macvern 2S90), indicating that it is viable to fabricate the pure and smaller BFO powders when pH value is 8.0.

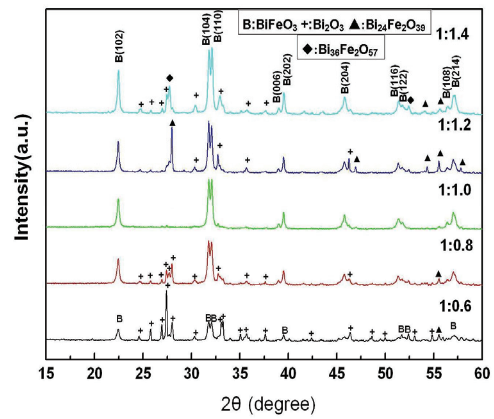

Fig.2: XRD patterns of BFO powders obtained by different metal cations/ citrate acid

Fig.2 demonstrates the effect of the proportion of iron cation to citrate acid on BFO powders' structure. For the proportion of 1:0.6 and 1:0.8, the powders can be defined as the mixture of Bi_2O_3 and BFO. Until up to 1:1, all the XRD patterns were indexed with BFO structure. However with further increasing in the proportion (1:1.2, 1:1.4), impurities such as $Bi_{24}Fe_2O_{39}$, Bi_2O_3 or $Bi_{36}Fe_2O_{57}$ occurred.

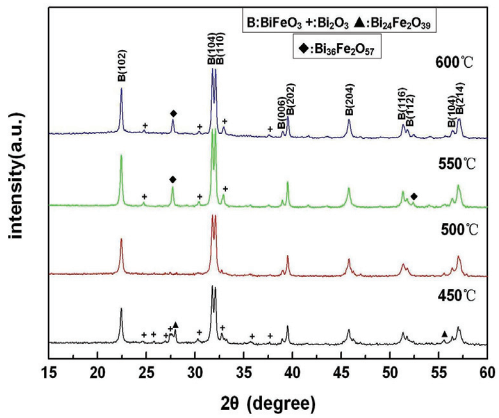

Fig.3: XRD patterns of BFO powders calcined at different temperature for 3h

Fig. 3 represents XRD patterns of powders calcined at different temperatures. It can be seen that BFO was obtained above 450ºC. While for powders calcined at 450ºC, 550ºC and 600ºC, there were impurity phases of Bi_2O_3, $Bi_{24}Fe_2O_{39}$ and $Bi_{36}Fe_2O_{57}$.

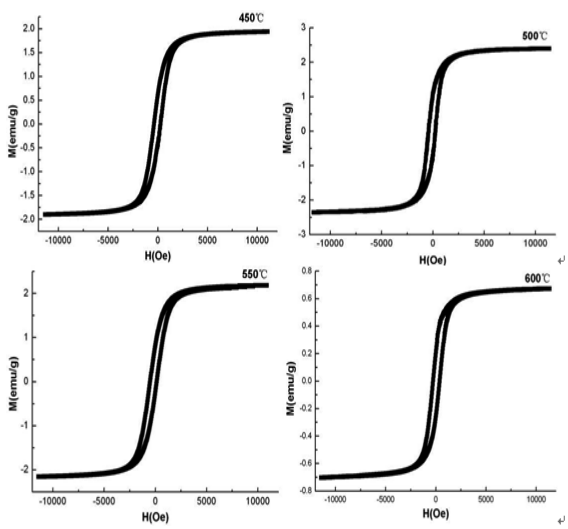

Fig.4: Room temperature magnetic hysteresis loops of BFO powders calcined at different temperature (3h).

Fig.4 shows the magnetic hysteresis loops of BFO powders calcined at different temperatures, measured by vibrating sample magnetometer at room temperature. All the calcined powders show weak ferromagnetic ordering at room temperature, similar to thin films[3]. The values of the saturated magnetization (m_s) are respectively 2.0, 2.5, 2.1 and 0.7 emu/g for 450ºC, 500ºC, 550ºC and 600ºC. The corresponding values of the coercive field (H_c) are almost the same (≈400Oe).

Fig.5 shows the magnetic M versus applied fields H of BFO ceramic calcined at 830ºC (3h) at room temperature by vibrating sample magnetometer.A weak net magnetization of 0.02emu/g is much better than previous work [4] and comparable to some lanthanum-modified BFO ceramics.

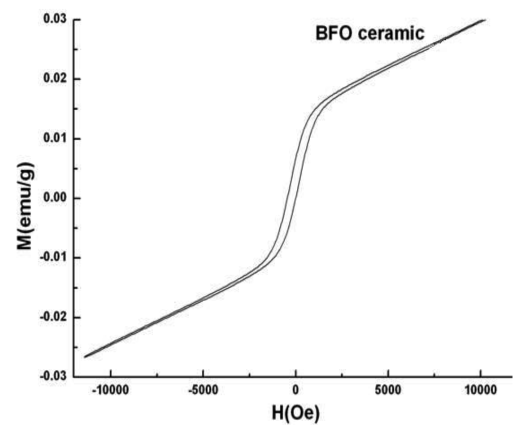

Fig.5 Room temperature magnetic hysteresis loops of multiferroic properties of BFO ceramic sintered at 830ºC

The hysteresis loops together with a small remnant magnetization and coercive field are achieved in our samples which confirmed that BFO is antiferromagnet and weak intrinsic ferromagnetism. The powders (500ºC) arecorresponding to pure phase (from fig.3) and smaller average size (112nm) and hence the largest M_s. At 600ºC, the M_s decreased largely, indicating higher calcined temperature hampers the release of potential ferromagnetism. Magnetic properties of our samples both powders and ceramic are much better than those in other reports and theory prediction [2]. The oxygen vacancies and valence fluctuation (the coexistence of Fe^{2+} and Fe^{3+}) may lead to the structure distortion in the pervoskite with the canting of antiferromagnetically ordered Fe-O-Fe chains of spin, resulting in suppressing the spin spiral and hence releasing potential weak ferromagnetic.

The ferroelectricity polarization hysteresis loops are presented in Fig.6.for BFO sample sintered at 830 ºC for 3h.The spontaneous polarization (P_s), remnant polarization (P_r) and the coercive field (E_c) are about 6.6μC/cm^2, 2.4μC/cm^2,and 2.0KV/cm, respectively. The P-E curve of our samples shows distinct ferroelectricity features and

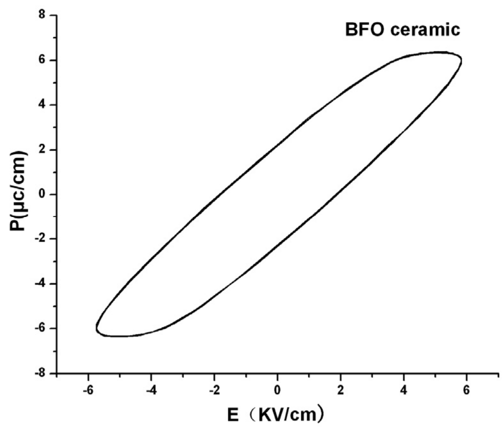

Fig.6: Room temperature P-E curves of multiferroic properties of BFO ceramic sintered at 830ºC

exhibits a considerable Ps even under a low applied electric field (less than 6KV/cm) but without saturation. However, as the electric field increased to 7KV/cm, breakdown occurred, which may be mainly due to the ceramics' large leakage current and relatively low resistivity which restrains ferroelectricity property.

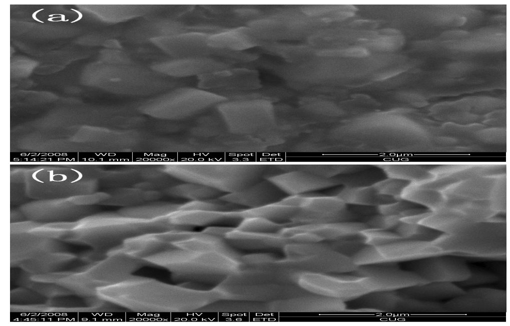

Fig.7: Scanning electron micrographs of BFO ceramics sintered at 830ºC (a) natural surface (b)

SEM photograph (Fig.7) reveals that the grain size in ceramics is submicronmeter with approximately less than 1μm and randomly oriented, and the grain growth is homogeneous.

4.CONCLUSIONS

In summary, sol-gel auto-combustion method was an effective way to prepare high quality BFO powders and ceramics. Optimal conditions for synthesizing pure BFO powders with average size of ~112nm are as follows: precursor solution's pH 8.0, mental cations/ citrate acid ratio 1:1 and calcined temperature 500ºC (3h). Enhanced room ferromagnetic with M_s of 2.5emu/g and 0.02emu/g was observed in BFO powders and ceramics. Meanwhile, The P-E curve of ceramic shows distinct ferroelectricity features with 2P_s of 13.2μC/cm^2, 2P_r of 4.8μC/cm^2, *H*c of 2.0KV/cm under a low restricted applied electric 6KV/cm.

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