Electrical and Magnetic Properties of BiFeO$_3$ Multiferroic Ceramics

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The multiferroic BiFeO$_3$ has been investigated extensively in both thin film and ceramic form. However, the synthesis of a perfect sample with high resistivity is a prerequisite for examining its properties. This paper reports the synthesis of multiferroic BiFeO$_3$ along with its structural, electrical and magnetic properties in ceramic form. Polycrystalline ceramic samples of BiFeO$_3$ were synthesized by solid-state reaction using high purity oxides and carbonates. The formation of a single-phase compound was confirmed by x-ray diffraction and its lattice parameters were determined using a standard computer program. The microstructural studies and density measurement confirmed that the prepared samples were sufficiently dense for an examination of its electrical and magnetic properties. The dc electrical conductivity studies show that the sample was resistive with an activation energy of ~0.81 eV. The magnetization measurement showed a linear (M~H) curve indicating antiferromagnetic characteristics.

Keywords : multiferroic, X-ray diffraction, conductivity, SEM

1. Introduction

Recently, there has been considerable interest in the development of a single material with different physical properties and a range of functionality. In some insulating materials, an external magnetic field can induce electric polarization and an external electric field can induce changes in magnetization. This type of material exhibits simultaneously ferroelectric, ferroelastic and magnetic ordering in the same phase and is hence called magneto-electric or multiferroic [1-7]. These materials have potential applications in magnetic and ferroelectric devices. In addition, they have the ability to couple the electric and magnetic polarization and provide an extra degree of freedom in device design. In view of this, these materials allow conversion between the energies stored in magnetic and electric fields for a wide range of applications in sensors, actuators, transducers and magneto-optical devices [4, 7, 8]. Apart from its potential application, the fundamental physics of magnetoelectric materials is also fascinating [9-11]. Although pure multiferroic materials are relatively rare in nature due to their simultaneous ferroelectric and ferromagnetic behavior, still there are some quite promising materials. BiFeO$_3$ (BFO) is one such

material with a rhombohedral distorted perovskite structure of space group R3c or C^{3V}_6 with both ferroelectric (Tc = 1103 K) and anti ferromagnetic (T$_N$ = 643 K) characteristics [12]. A single crystal of BFO shows a hysteresis loop at liquid nitrogen temperatures [13]. A large number of studies on BFO single crystals, ceramics and thin films were reported but there are very few reports on its ferroelectric properties due to the high electrical conductivity (owing to the presence of impurity phases, such as Bi$_{36}$Fe$_2$O$_{57}$, Bi$_2$Fe$_4$O$_9$, Bi$_{25}$FeO$_{40}$, Bi$_{12}$(Bi$_{0.5}$Fe$_{0.5}$)O$_{19.5}$ [9, 14]), high defect concentration, poor sample quality and inhomogeneous magnetic spin structure [12]. The presence of an impurity phase, high defect concentration and inhomogeneous magnetic spin structure results in a high leakage current, which makes this material unsuitable for practical applications. In addition, the formation mechanism is complex and its temperature stabilizing limit is narrow. Therefore, the primary requirement is to prepare a phase pure, defect free and homogeneous compound that can be exploited for practical applications. In view of the above mentioned practical difficulty, this study modified the synthesis conditions of time and temperature to obtain a phase pure compound with enhanced physical properties, particularly high resistivity. This paper reports the synthesis of a phase pure BFO compound along with its microstructural, transport and magnetic properties.

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2. Experimental

A polycrystalline ceramic sample of BiFeO$_3$ was prepared by a solid state reaction method under controlled time and temperature conditions. A high purity (99.99%) stoichiometric mixture of Bi$_2$O$_3$ and Fe$_2$O$_3$ was mixed thoroughly in a liquid medium and calcined at 600 °C-800 °C for 2 hours. The process of firing and mixing was repeated a number of times. Finally, cylindrical pellets were prepared by applying a pressure of 5 tonnes/cm^2 using a hydraulic press. The pellets were sintered at approximately 880 °C in an electric furnace under controlled conditions of time and temperature. Some pellets were also sintered at 860 °C-870 °C for different times. The sintered pellets were coated with silver paint as electrodes for the electrical measurements. Structural analysis was performed by X-ray diffraction (XRD) using CuK$_\alpha$ radiation with a nickel filter over a wide scanning range of 2θ from 10° to 90° at a scanning rate of 2° 2θ/minute. The instrument was calibrated using pure silicon provided with the instrument.

The microstructural investigations were carried out by scanning electron microscopy (SEM, JEOL, JSM-5600) with different magnifications in back scattered mode. The dc electrical conductivity measurements were performed using a laboratory made setup from room temperature (RT) to 455 K in air. The dc magnetization measurements were obtained using a Lakeshore 7300 vibrating sample magnetometer (VSM) at room temperature (RT) and low temperature (20 K).

3. Results and Discussion

Fig. 1a shows the XRD pattern of BiFeO$_3$ calcined at 600 °C-800 °C and sintered at 880 °C for 5-10 minutes (300-600 seconds). The diffraction pattern does not show any of the impurity phases reported previously [9] and there is no indication of any Bi$_2$O$_3$ or Fe$_2$O$_3$ peaks. This suggests that the solid state reaction between Bi$_2$O$_3$ and Fe$_2$O$_3$ is complete under the controlled sintering conditions. The diffraction pattern of the sample sintered at 880 °C was indexed to the perovskite type phase pure BFO. On the other hand, the sample sintered for a longer time and at temperatures other than 880 °C showed impurity phases in addition to the BiFeO$_3$ phase (Fig. 1b). The XRD pattern always showed impurity phases during the conventional sintering process. A moderate heating rate and small sintering time of ~5-10 minutes at 880 °C resulted in liquid phase sintering as the melting point of Bi$_2$O$_3$ is 817 °C and hence a phase pure BiFeO$_3$. On the other hand, the high heating rate and lower sintering
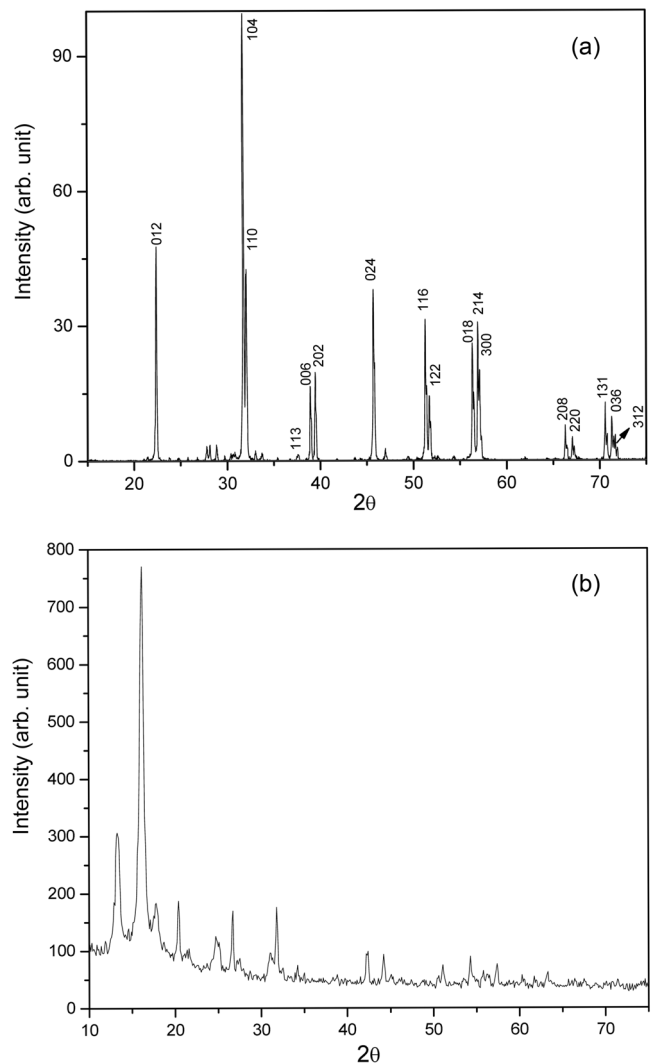

Fig. 1. (a) XRD patterns of BiFeO$_3$ sintered at 880 °C. (b) XRD patterns of BiFeO$_3$ sintered at 860 °C.

temperature probably results in the formation of impurity phases. The density measurement of the sample sintered at 880 °C indicates that compact ceramics could be synthesized under controlled conditions of time and temperature. XRD confirmed that the prepared specimens were a single phase with a perovskite type distorted rhombohedral cell and cell parameters of a = 3.96 A, α = 89.5° in the space group R3c, which is consistent with the reported value [15].

SEM image of the pure compound showed a homogeneous microstructure with an average grain size of ~10-14 μm (Fig. 2), which is much smaller than the grain size of the pure BFO compound (~100 μm) reported by Jun et al. [16] despite using the same method of preparation. Furthermore, the grain size of Nb doped BFO reported by the same author was comparable to the present result. This shows that under controlled conditions of time and
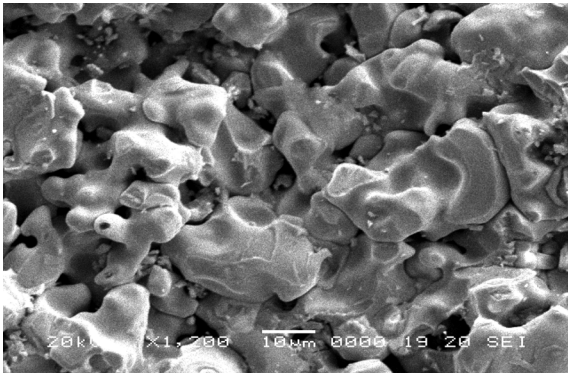
Fig. 2. SEM image of Bi FeO$_3$.

temperature, the homogeneity of the compound is improved, giving a uniform microstructure and improved properties. To obtain the insulating behavior of BFO, its dc electrical conductivity was measured from RT to 455 K (Fig. 3). The resistivity did not change from RT to 356 K. However, a further increase in temperature to 455 K resulted in a decrease in resistivity. The activation energy was calculated by plotting the log σ vs 1/T curve using the relation $\sigma = \sigma_o \exp (-E_a/kT)$. The activation energy calculated from Fig. 3 was 0.81 eV, which is much higher than that obtained by Jun *et al.* [16]. This suggests better insulation properties than an earlier report by Jun *et al.*, where activation energy was only 0.58 eV. This result is similar to the result obtained in the case of Nb doped BiFeO$_3$ and a BiFeO$_3$-BaTiO$_3$ solid solution [17]. This increase in resistance might be explained by the increase in grain boundary resistance, which contributes mainly to the total resistance. This result is also supported by the homogeneous and spherical grain size, which is much smaller than that obtained previously [16].

Fig. 4 shows the magnetization as a function of the magnetic field (hysteresis loop) for BFO at RT. Magneti-
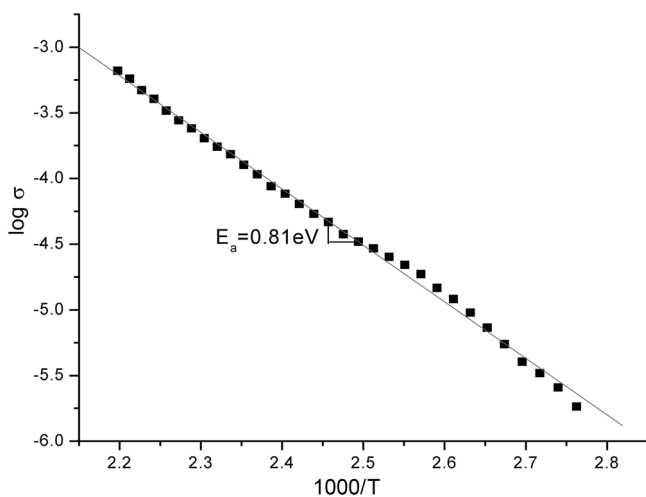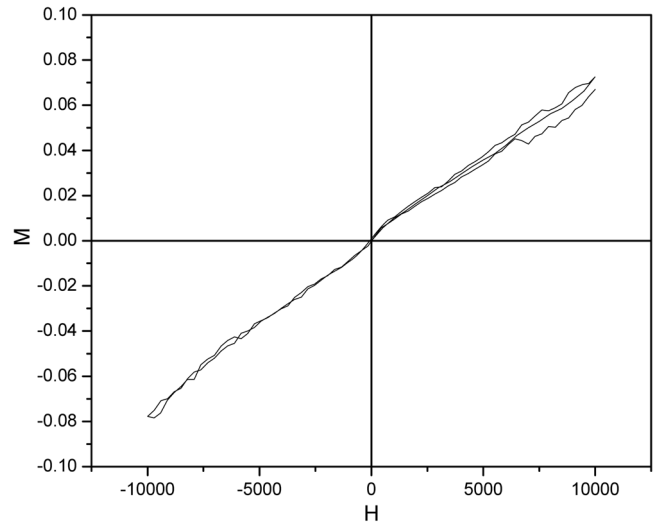

Fig. 4. M~H curve for BiFeO$_3$ measured at 300 K.

zation varied linearly with the applied magnetic field up to a measured field of 10 kOe, which is consistent with the reported value [16]. Indeed, BiFeO$_3$ is antiferromagnetic with a G-type magnetic structure [18] but has a residual magnetic moment due to a canted spin structure (weak ferromagnetic) [19]. The M~H curve was also measured at 20 K and produced a similar result to that observed at RT. The M~T curve at 44 Oe from 20 to 300 K showed similar behavior to that reported by Jun *et al.* [16]. The magnetization value was almost constant over temperature range of 20 to 300 K.

4. Conclusion

Highly resistive BFO ceramic samples were prepared by a slight variation in the sintering conditions. The dc conductivity measurements and SEM confirmed its highly resistive nature. The improved resistance allows measurements of the dielectric constant at RT. However, the coupling between the electric and magnetic dipole requires more work and further explanation.

Acknowledgement

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Fig. 3. log σ vs 1000/T curve for BiFeO$_3$.

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