Solid State Science and Technology, Vol. 22, No 1 & 2 (2014) 120-125
ISSN 0128-7389 | *http://journal.masshp.net*

STRUCTIRE AND MAGNETIC PROPERTIES OF $BiFeO_3$ AND $Bi_{0.9}Sm_{0.1}FeO_3$

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ABSTRACT

In this work, we have reported that Sm doping can contribute a good effect on magnetic properties of $BiFeO_3$ (BFO) ceramics. The effect of substitution of Sm^{3+} ion on Bi^{3+} site were investigated based on the structure and magnetic properties. Multiferroic BFO and $Bi_{0.9}Sm_{0.1}FeO_3$ samples were prepared by conventional solid state reaction. The phase exists and the crystal structure was confirmed by X-Ray Diffraction and has showed that the both samples were polycrystalline with rhombohedral R3C structure. By using Scanning Electron Microscope (SEM), the average grain size obtained for $Bi_{0.9}Sm_{0.1}FeO_3$ is smaller (0.5-1.5 µm) than pure BFO (1-3 µm). Vibrating Sample Magnetometer (VSM) measurement at room temperature showed that $Bi_{0.9}Sm_{0.1}FeO_3$ have higher magnetization saturation of 11.181 x 10^{-2} emu/g remnant magnetization (1.84x 10^{-2}) and coercivity field (1541.9 Oe) than pure $BiFeO_3$.

Keywords: multiferroic; structure; magnetism; $BiFeO_3$

INTRODUCTION

Multiferroic materials are defined as a single phase material that can exhibit both antiferro/ferromagnet and ferroelectric properties simultaneously. The phenomenon of multiferroic materials has large potential applications in memory storage due to their ability for magnetoelectric response to control and tuning of magnetism using electric field and control the electricity by changing the magnetic field. Whenever in a system that are required both an inductor and a capacitor, the single component multiferroic can be replaced. However, the magnetoelectric coupling must be large and have high transition temperature to become effectively use for the application at room temperature. Ferromagnetic and ferroelectric polarization both decrease with increasing temperature, with a phase transition to an unpolarized (paramagnetic or paraelectric) state which often occurring beyond the transition temperature, Tc. Bismuth Iron Oxide (BFO) is the most common type of multiferroic material that can exhibit multiferroic properties at room temperature which are T_N ~ 370°C for antiferromagnetic and T_c ~ 810°C for ferroelectric [1]. Ferrolectricity is generated by the existence of 6s lone pair of Bi^{3+} cation that cause off centering from the centrosymmetric position of the cation structure whereas magnetic properties is contributed by Fe^{3+}. Preparation of BFO by conventional solid state reaction always be challenging due to the critical temperature range stabilities because of low melting temperature of Bi_2O_3 and usually the secondary phases were not completely eliminated. There are various advanced preparation methods that have been reported for synthesizing single phase BFO for example hydrothermal, combustion, sol-gel technique [2- 4]. However these known synthesis techniques required complex procedures and take a longer reaction time. According to previous reports [5-9], partial substation of Bi site by lanthanide elements is the way to stabilize the required single phase and can give relatively higher ferroelectric and magnetization values. In this study, the comparative between $BiFeO_3$ and $Bi_{0.9}Sm_{0.1}FeO_3$ based on the structure and magnetic properties had been investigated.

METHOD

$BiFeO_3$ and Sm doped BFO samples were synthesized by the solid state reaction method. Stoichiometric amounts of high purity (~99.9%) of Bi_2O_3, Fe_2O_3, and Sm_2O_3 were carefully weighed and were mixed in mortar for 2 hours. The mixture was calcined at 825ºC for 10 h in air followed by furnace cooling and it was reported [10] that 825°C can give maximum amount of BFO phase by conventional solid state method. Pellets from the synthesized powders wire prepared using pressing machine at a pressure of 5 tones and sintered at 825ºC with heating rate of 2^oC/ min and cool inside the furnace. Phase identification, crystallographic structure and quantification of the samples after sintering were performed by X-Ray diffractometer (XRD) using Cu Kα radiation with wavelength of 1.54056 Å in the 2θ range of 20-70° at room temperature. The data were refined by using the Rietveld analysis program. The phase, microstructure and grain size of the sample were observed using Field Emission Scanning Electron Microscope (FESEM) with attachment of Energy Dispersive X-ray (EDX). EDX were used for compositional analysis of the sample for both of pure $BiFeO_3$ and $Bi_{0.9}Sm_{0.1}FeO_3$. Vibrating sample magnetometer (VSM, Lakeshore 7407) was used for magnetization characterization at room temperature with applied field up to 1T.

RESULTS AND DISCUSSIONS

Figure 1 shows XRD pattern for both BFO and BSFO samples after being sintered at 825°C for 10 hours. The major peak was identified as a polycrystalline $BiFeO_3$ with rhombohedral distorted perovskite structure, R*3C* space group (ICDD code: 006-6143). For pure BFO, the diffraction peaks were clear and sharp indicating good crystallization of the sample but small amount of secondary phases $Bi_{25}FeO_{40}$ (ICDD code: 002-2156) and $Bi_2Fe_4O_9$ (ICDD code: 000-9807) were existed. This is because of lower sintering temperature used due to the low melting point of Bi element. In order to investigate the effect of Sm doping on the Bi site, the graphs shows secondary phases were eliminated.

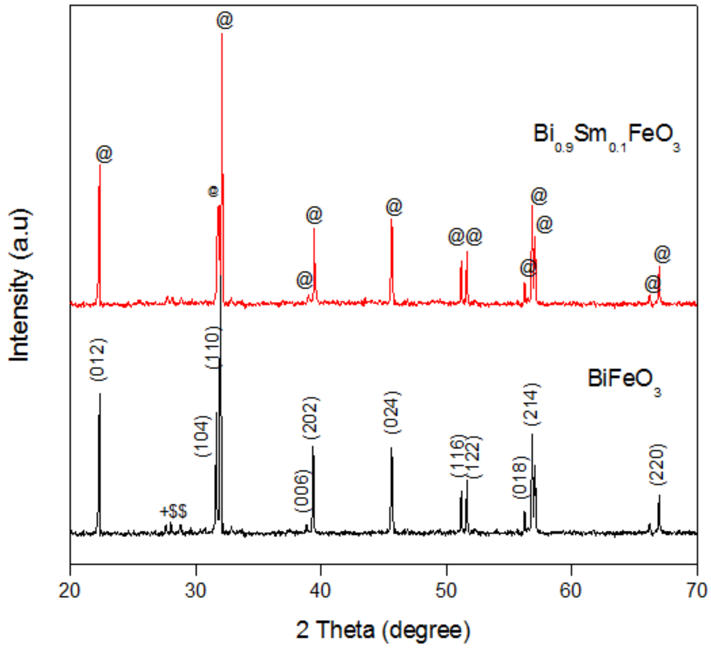

Figure 1: XRD graph of BFO and BSFO sample

Table 1: Structural Parameters of BFO and BSFO

Name of Sample	$BiFeO_3$(BFO)	$Bi_{0.9}Sm_{0.1}FeO_3$(BSFO)
Purity Fraction (%)	88%	98.5%
Lattice Parameter a=b (Å)	5.5788 (2)	5.5685 (5)
Lattice Parameter c (Å)	13.8691 (5)	13.8145 (1)
Volume of Cell (Å^3)	373.8122	370.9863
Good of Fitness	5.100	4.439

It can be clearly seen the diffraction peak (110) at angle 2θ 31.96 for pure sample gradually shifted to high diffraction angle 2θ 32.08 which originated from the decrease of lattice constant of the BSFO samples. The structural parameters were refined by using the Rietveld analysis program. The lattice parameters estimated by Rietveld were listed in the Table 1. Rietveld formulated a method of assigning each peak a Gaussian shape and then allowing the Gaussians to overlap so that an overall line profile could be calculated. The method was originally developed by neutron diffraction and in favorable cases, the Rieltveld method can be used to solve a structure from the diffraction data. Substitutions of Bi^{3+} (1.31Å) cation by Sm^{3+} (1.22Å) ion that have smaller ionic radii cause a significant structural distortion that can improve the magnetic properties of the sample.

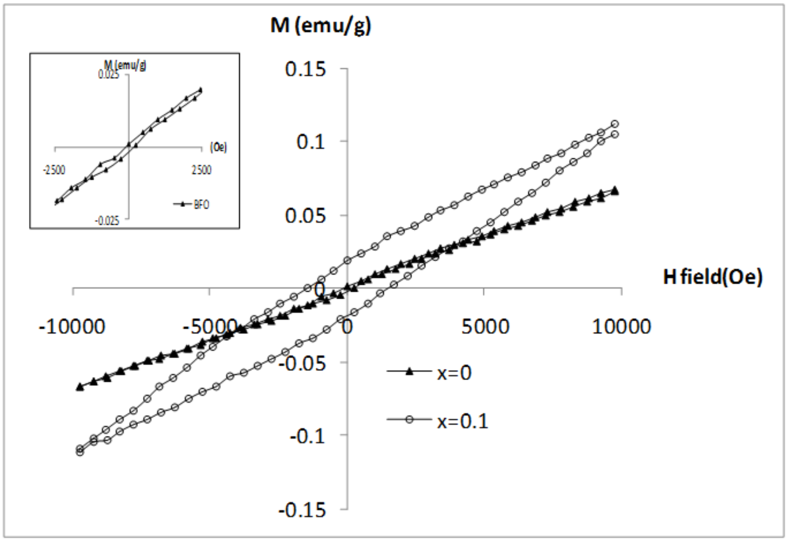

Figure 2: Hysteresis VSM of BFO and BSFO sample

Table 2: Magnetic Properties of BFO and BSFO

Name of Sample	$BiFeO_3$	$Bi_{0.9}Sm_{0.1}FeO_3$
Hc (Oe)	191	1541.9
Ms (emu/g)	6.85×10^{-2}	11.18×10^{-2}
Mr (emu/g)	1.81×10^{-3}	18.4×10^{-3}

The results of the magnetic measurement on the samples are presented in Figure 2 and the value details are listed in Table 2. The hysteresis graph of BFO and BSFO ceramics were recorded at room temperature as a function of magnetization value (M) versus applied magnetic field (H) with 1Tesla maximum applied field. The result clearly showed a different pattern of hysteresis graph which exhibit different magnetic properties. The large applied field is required to cause rather small changes in magnetization and only small value is retained when applied field is removed. For BFO sample, a very narrow loop was observed indicating weak ferromagnetic behavior with magnetization saturation (Ms) $\approx 6.85 \times 10^{-2}$ emu/g and Hc ≈ 191Oe whereas for Sm-doped sample, it shows a larger hysteresis loop with higher Ms $\approx 11.181 \times 10^{-2}$ emu/g and Hc ≈ 1541.9 Oe. The result shows the same trend in the reports [11] which stated that Sm doping leads to the collapse of space modulated spin structure giving rise to long range canted antiferromagnetic order. The improvement in magnetization of Sm-doped BFO is because of the successful eliminations of the secondary phases that affected the magnetism value in the sample.

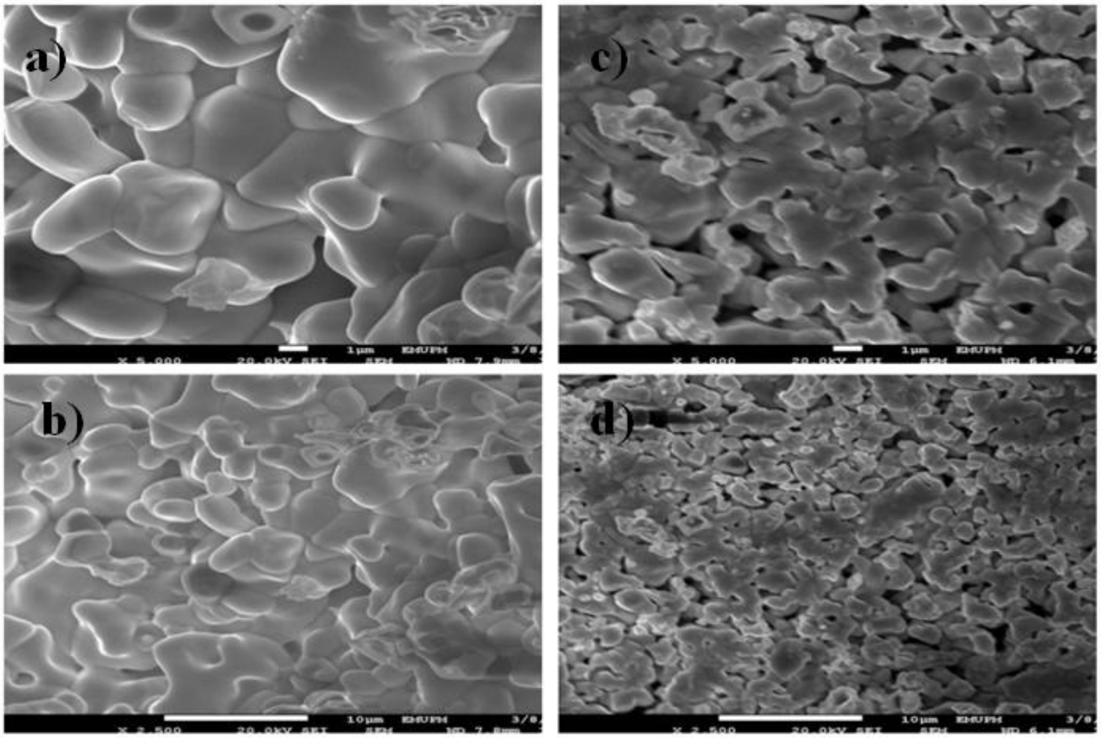

Figure 3: SEM micrograph: a) $BiFeO_3$ (5000X magnification) b) $BiFeO_3$ (2500X magnification) c) $Bi_{0.9}Sm_{0.1}FeO_3$ (5000X magnification) d) $Bi_{0.9}Sm_{0.1}FeO_3$ (2500X magnification)

Figure 3 shows the SEM micrograph for both BFO and BSFO compound. For both conditions, the grains structures are not uniformly distributed throughout the sample but clear grain boundaries can be observed. The range of grain size for BFO is 1-3 µm. By introducing Sm element in BFO compound, the range of grain size was significantly reduced into 0.5-1.5 µm. The magnetization process is attributed by moving of domain wall and the spinning of electron. By introducing Sm element into the sample, the larger loop suggests that the magnetic domain wall movements are easier and hence more magnetic moment is aligned. In addition, in decreased grain size in BSFO and relatively higher degree of disorder in the materials. Increase in the spin canting can also be a contributor to the magnetism [12].

CONCLUSION

Polycrystalline distorted perovskite structure of BFO and $Bi_{0.9}Sm_{0.1}FeO_3$ have been prepared by conventional solid state reaction. Sm substitution at Bi site eliminated the secondary phases in $BiFeO_3$ phase and can stabilize the crystal structure. XRD diffraction pattern, for BSFO(x=0.1) showed that there were high $BiFeO_3$ phase without the existence of secondary phases. Substitutions of Bi^{3+} (1.31Å) cation by Sm^{3+} (1.22 Å) ion cause structural distortion that can be improve the magnetic properties of the sample. The improvement in the magnetization for BSFO may be attributed to the smaller grain size of the material and due to the high degree of crystalline

ACKNOWLEDGMENTS

The researcher is grateful to University Putra Malaysia and MOSTI for the scholarship under National Science Fellowship (NSF) and Research University Grant Scheme (RUGs) for the financial support of this research.

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