Structural and Magnetic Properties of Nano Multiferroic BiCo_xFe_{1-x}O₃ Ceramics

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ABSTRACT

BiCo_xFe_{1-x}O₃ nano multiferroic ceramics with x = 0.0, 0.05, 0.10, 0.15, 0.20and 0.25 were synthesized by solution combustion technique. The resulting products were characterized by X–ray diffraction (XRD), vibrating sample magnetometer and by Mössbauer spectroscopy. Magnetic hysteresis loops were clearly observed in Co substituted samples and magnetization was increased. Saturation magnetization (M_s) increases with increasing Co concentration. At doping level upto 5 % Co, the improvement in the magnetic behavior appears to arise from a combination of the partial destruction of spin cycloids and increased interaction between magnetic ions. Increase in saturation magnetization beyond 5 % Co content can be explained on the basis of magnetic impurity phases formed with BiFeO₃ structure. Using Mössbauer spectroscopy it is observed that Fe exists in the +3 oxidation state.

Keywords: Ceramics; Characterization methods; Magnetic properties; Mössbauer spectroscopy; Spin cycloids; Solution combustion technique

1. Introduction

Multiferroic materials exhibit ferroelectric and ferromagnetic/antiferromagnetic properties in same phase, have been widely studied in recent years, due to their abundant physics and potential application in the sensors, data storage, and spintronics [1,2]. Among the rare multiferroic materials, bismuth ferrite (BiFeO₃) has become an extremely popular multiferroic material these days because of its unique properties of having room-temperature ferroelectric and magnetic orders. BiFeO₃ has a rhombohedrally distort perovskite structure assigned to the space group R3c at room temperature and shows ferroelectric order up to $845\pm5^{\circ}$ C according to the straumanis method and coefficients of thermal expansion by Bucci et al [3]. At the same time, it

shows G-type canted antiferromagnetism below 370° C [4], in which all neighboring magnetic spins are oriented antiparallel to each other [5]. Inducing lattice distortion is one way to enhance the magnetic properties of BiFeO₃ by enhancing the canting of the antiferromagnetic arranged neighboring spins. Cation doping is one of most promising and popular approache to modify the magnetic properties of BiFeO₃ either Bi with Tb, Nd, Sm, Gd, Ca, Sr [6-11] or Fe with Co, Mn, Sc [12-17]. Therefore, in the present work, we intend to report the effect of Co substitution (5–25 mole% at the Fe site) on structural and magnetic properties of BiFeO₃ ceramics [BiCo_xFe_{1-x}O₃] prepared by solution combustion technique.

2. Experimental

Nano multiferroic BiCo_xFe_{1-x}O₃ (BCFO) ceramics were synthesized by the solution combustion technique with a weighted amount of Fe (NO₃)₃· 9H₂O, Bi (NO₃)₃· 5H₂O, Co (NO₃)₂· 6H₂O and L–alanine were first dissolved in 2– methoxyethanol for 45 min by means of ultrasonic cleaner. Bismuth nitrate was taken 5 mol % excess to compensate Bi loss during sintering process. A clear solution was obtained by constant stirring for 3h. Solution was then heated at magnetic stirrer heater at 80°C with constant stirring till autocombustion took place. The prepared powder was grounded and calcined at 400°C for 2h, at 600°C for 1h, at 700°C for 1h and finally at 800°C for 30 min.

Phase identification of the powder samples were carried out by X-ray powder diffraction (XRD), using a XPERT-PRO diffractometer with Cu K α radiation at step of 0.02 in the range $2\theta = 20^{\circ}$ to 60° . A vibrating sample magnetometer (VSM Lakeshore7400series) was used for measuring the field dependent magnetization of powder samples. Mössbauer effect measurements were carried out using a standard PC-based spectrometer equipped with a Weissel velocity drive operating in the constant acceleration mode. The Mössbauer spectra are fitted with NORMOS–SITE program and the obtained hyperfine parameters are with respect to natural iron.

3. Results and discussion

X-ray diffraction pattern of BiCo_xFe_{1-x}O₃ ceramics are shown in Fig.1. The XRD patterns for the calcined samples reveal the well crystallized pattern as that of pure BiFeO₃ along with some impurity phases which are always obtained along with BiFeO₃ as the minor phase due to chemical kinetics of formation [18]. XRD study for x = 0.0 composition shows that the powder crystallizes in rhombohederal distorted perovskite R3c phase and minor impurity phase Bi₂Fe₄O₉, Bi₂₅FeO₃₉ ($2\theta \sim 27^{\circ}$ - 28°) is detected [19–21]. Impurity peaks corresponding to Bi₁₂(Bi_{0.5}Fe_{0.5})O_{19.5}, Bi₂O₃ were observed with Co substitution at the 2 θ around 30° and around 24° [22,23]. With increase in Co substitution we found that peak corresponds at 2 θ around 27.8° become more dominant than BiFeO₃ structure. This makes us to conclude that cobalt substitution leads to extra phase Bi₁₂Co_{0.8}O_{18.8} with BiFeO₃ structure [24]. From the XRD pattern shown in Fig. 1, it can be concluded that a small amount of Co (x>0.05) substitution changes the microstructure of BiFeO₃, probably much more stable

structure of Bi₁₂Co_{0.8}O_{18.8}.

The average grain/ particle size for $BiCo_xFe_{1-x}O_3$ ceramic powder was calculated from XRD peak broadening using Deby–Scherrer formula [25] and was found to be 20.6 nm, 16.0 nm, 16.5 nm, 17.0 nm, 17.5 nm, 18.0 nm, respectively. Fig 2 shows the TEM image of BiFeO₃ powder sample with size distribution in the range of 16-20 nm. The particle size calculated from XRD is well supported by TEM measurement.

Fig. 3, shows the room temperature magnetization-magnetic field (M-H) hysteresis loops of BiCo_xFe_{1-x}O₃ ceramic powder samples for the maximum magnetic field of 20000 Oe. In pure BiFeO₃, the magnetization varies nearly linearly with the applied magnetic field, confirming that sample is antiferromagnetic G-type magnetic structure [26] and having a residual magnetic moment due to a canted spin structure (weak ferromagnetic). The magnetic field dependent magnetization for $BiCo_xFe_{1-x}O_3$ (x = 0.05, 0.10, 0.15, 0.20, 0.25) exhibits a clear hysteresis loop at room temperature. The magnetic hysteresis loops in co-substituted BiFeO₃ were still observed at room temperature suggesting that the Neel temperature of the co-substituted specimens was higher than room temperature. The saturation magnetization, remanent magnetization and coercivity [Table 1] for x = 0.05, 0.10, 0.15, 0.20 and 0.25 are much greater than those of $BiFeO_3$ prepared under similar conditions. The plausible explanations for the appearance of ferromagnetism has been suggested : the canting of the antiferromagnetically ordered spins by a structural distortion [27,28]. It appears that the modification of the anti-parallel spin structure by Co cooperatively contribute to the higher remanent magnetization in co-substituted BiFeO₃ [17].

We can envisage the following reasons [29] for the enhancement of the magnetization resulting from Co substitution in nanoscale particles in BFO sample: (i) reduction in particle size of the range of the modulation length of the spin cycloid (~62 nm), (ii) variation in the oxygen stoichiometry or Fe^{2+} ion (iii) change in the structure (iv) magnetism of dopant ions. As calculated above, grain size of our samples are less than the long range cycloid order. Thus, one of the important contributions for the enhancement of the magnetization of doped BFO is the uncompensated surface spins induced by the size effect of the nanoparticles. With the decrease in particle size, the uncompensated surface spins are more significant because of the increase in specific surface area. According to the report by Park et al [30], the presence of oxygen stoichiometry or Fe^{2+} ion can also lead to the enhancement of magnetization. In order to explore the effect of oxygen stoichiometry or Fe^{2+} ion on the ferromagnetism in different samples, it is essential to investigate the Fe local environment. For this reason Mossbauer spectra were recorded to determine the Fe valence and occupation site.

The RT Mossbauer spectra of the nanoparticles are shown in Fig. 4. The spectra of BFO were fitted to be two sextets and one doublet. For doublet, I.S. (isomer shift) = 0.12 mm/s and Q.S. (quadrupole splitting) = 0.72 mm/s suggest the existence of a paramagnetic impurity (Bi₂Fe₄O₉) [31], in agreement with those of XRD. The two sextets correspond to the Fe³⁺ ions of BFO in two different crystallographic environments [32,33]. The same synthesis procedure with Co substitution gives a perfect sextet. This supports our assertion that the increased magnetization in BCFO is due to changes in magnetic interaction caused by Co substitution in the BFO lattice.

The hyperfine parameters of sextet 1 are characteristics of high-spin Fe^{3+} . Their small QS value shows that this site corresponds to a typical octahedral site. In comparison with the typical octahedral site, the H_{hf} value of sextet 2 is reduced and corresponds to a distorted octahedral site. The appearance of distorted octahedral site is closely correlated with the doped ions. From table 1, we can find that the area of the distorted octahedral sites increases with decreasing average ionic radius. This further supports that the reduction in the average ionic radius of the Bi site leads to a larger distortion of BiFeO₃. The lattice distortion brings about the enhancement of the DM interaction [21]. The enhancement of the DM interaction results in stronger canting spins. This makes the antiferromagnet to be of a lager net magnetization parallel to the easy axis. So the structural change of the samples is another factor which results in the enhancements of magnetization.

The observed isomer shift values from Mössbauer data (Table 2) clearly shows that the spectra correspond to high spin Fe^{3+} ions. No signal of Fe^{2+} is detected for all samples. So the enhancement of magnetization of the nanoparticles cannot result from Fe^{2+} or the variation of oxygen stoichiometry.

Apart from above factor discussed, the occupation and the magnetic moment of the substituted ions are other important factors influencing the magnetism of the samples. If the added cobalt substituted with B sites of iron of BiFeO3, the antiferromagnetic spin configuration of BiFeO3 cannot persist locally due to the differences of the magnetic moment between Fe³⁺ (5 μ B) and Co³⁺ (4 μ B) at the B– site. A local collapse of the antiferromagnetic spin structure leads to an increase in the total spontaneous magnetization. It is therefore possible that local ferrimagnetic spin structures were formed around the B-site, where an iron atom was substituted by a cobalt atom, and that the total mass value of the magnetic moment increased by increasing the cobalt content. In case of 5 % substituted Co-BiFeO3 the wt % of secondary magnetic phase is less; therefore, it can be considered that the increment of the saturation magnetization might be attributed to cobalt addition. Further, magnetization observed for x = 0.05 is in good agreement to earlier reported value [11], which clearly suggest that the wt % of secondary magnetic phase is very less and not contributing to the enhancement of magnetization. The saturation magnetization increased drastically with increasing cobalt contents beyond 5 %, which can be explained on the basis of magnetic impurity phases (Bi12Co0.8O18.8) formed with $BiFeO_3$ structure. The magnetic behavior is in consistent with earlier report on $BiCo_xFe_{1-x}O_3$ ceramics prepared by hydrothermal method [11].

Sample	H _c (Oe)	M _r (emu/g)	M _s (emu/g)
x = 0.0	40	0.003	0.03
x = 0.05	558	0.739	1.978
x = 0.10	555	1.839	5.730
x = 0.15	466	2.472	9.496
x = 0.20	533	4.460	13.524
x = 0.25	577	5.798	20.767

Table 1. Magnetic parameters obtained from M-H curve.

Sample	Subspectrum	I.S(mm/s)	Q.S(mm/s)	H(T)	Width(mm/s)	Area(%)
x = 0.0	sextet 1	0.25	0.33	49.38	0.38	49.39
	sextet 2	0.23	-0.11	48.90	0.33	39.51
	doublet	0.12	0.72	-	0.60	11.10
x = 0.05	sextet 1	0.27	0.152	50.40	0.32	18.26
	sextet 2	0.25	0.068	48.20	0.50	81.74
x = 0.10	sextet 1	0.27	0.109	50.02	0.30	32.63
	sextet 2	0.23	0.066	48.02	0.46	67.37
x = 0.15	sextet 1	0.26	0.117	50.26	0.36	33.64
	sextet 2	0.22	0.034	48.04	0.47	66.36
x = 0.20	sextet 1	0.25	0.09	50.19	0.36	37.74
	sextet 2	0.19	0.039	48.04	0.40	62.26
x = 0.25	sextet 1	0.24	0.080	50.24	0.54	53.33
	sextet 2	0.17	0.005	48.04	0.45	46.67

Table 2. Mössbauer parameters obtained after fitting the room temperature spectra.



Fig. 1 XRD pattern of $BiCo_xFe_{1-x}O_3$ ($0 \le x \le 0.25$) ceramic samples (*, # indicates the presence of impurity phases).



Fig 2. TEM image of BiFeO₃ powder sample calcined at 800°C for 30 min.



Fig. 3 Magnetization-magnetic field (M-H) hysteresis loops of $BiCo_xFe_{1-x}O_3$ ($0 \le x \le 0.25$) ceramic samples at room temperature.



Fig. 4 Mössbauer spectra of $BiCo_xFe_{1-x}O_3$ ($0 \le x \le 0.25$) ceramic samples at room temperature.

4. Conclusions

Nano multiferroic $BiCo_xFe_{1-x}O_3$ ceramic samples were synthesized by solution combustion method. The saturation magnetization was enhanced with cobalt contents. For small concentration of Co upto 5 %, we attribute this to the formation of a local ferrimagnetic spin structure due to the substitution of an iron atom at the B–site by cobalt. At higher concentration of Co doping the drastic increase in magnetization is

attributed to the formation of magnetic phase impurity with $BiFeO_3$ structure. The improvement in the magnetic properties at x = 0.05 are likely to be caused by a combination of factors such as the partial destruction of spin cycloids, and magnetic interaction between magnetic ions, namely Fe and Co.

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