Rietveld refinement of barium substituted bismuth ferrite synthesized using sol-gel technique

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Abstract

Barium substituted bismuth ferrite ($Bi_{0.8}Ba_{0.2}FeO_3$) was synthesized using ethylene glycol based sol-gel method followed by heat treatment at 800°C for 15 min. In order to study the effect of barium substitution on structural parameters the rietveld refinement of the sample was performed. Structural transition from the rhombohedral perovskite (ABO_3) crystal structure to pseudo-cubic has been confirmed. Ba substitution at Bi site suppresses the secondary phases of $BiFeO_3$ such as $Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$ etc. The crystallite size of the prepared barium substituted $BiFeO_3$ (BBFO) nano-multiferroic calcined at 800°C is found to be ~ 20 nm. The functional groups in the calcined sample were identified by FTIR analysis. TG-DSC analysis of the sample has also been performed. It is expected that structural changes made by barium in $BiFeO_3$ would also affect its magnetic behavior. Copyright © 2017 VBRI Press.

Keywords: Structural, rhombohedral, perovskite, nano-multiferroic, rietveld analysis.

Introduction

Multiferroic materials have attracted a lot of attention because of their potential practical applications. Among large number of available multiferroics, $BiFeO_3$ (BFO) with a distorted rhombohedral structure (R3c) is a fascinating multiferroic material because of its ferroelectric transition temperature (T_c) and antiferromagnetic Neel temperature (T_N) well above the room temperature [**1, 2**]. BFO exhibits distorted rhombohedral structure with space group R3c. The study of BFO is now tremendously active and has already given a lot of stunning results. BFO have applications in the field of radio, television, microwave and satellite communications, audio-video and digital recording [**3, 4**]. However, BFO has some inherent problems such as preparation of the phase pure compound, a high leakage current, lower magneto-electric coupling coefficient and wide difference in ferroic transition temperatures (T_c and T_N), which limits its applications. So far, bismuth ferrite powders have been prepared by the solid-state method, spark plasma sintering, co-precipitation, sol-gel and hydrothermal etc. [**5-7**]. It has been demonstrated that synthesis of pure bismuth ferrite using solid state reaction method is very difficult task. During the preparation impurity phases such as $Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$ etc. appear very often [**8**]. But BFO ceramic nanoparticles synthesized using sol-gel technique results a pure phase material.

Further, the alkaline earth ion substitution at Bi site has proved helpful in suppressing the formation of impurity phases and supports the formation of single-phase material. Also, it has been reported that substituting alkaline earth ions at Bi site in particular concentration can effectively modulate the crystal structural parameters of bismuth ferrite [**9, 10**]. But structural symmetry of the Ba substituted bismuth ferrite is not clear yet. In the present study, Ba substituted bismuth ferrite (BBFO) has been synthesized using sol-gel method followed by heat treatment at 800°C for 15 min. In order to confirm the structural symmetry in BBFO, Rietveld refinement was performed. It has been shown that substitution of 20% Ba ions at Bi site results structural transition from rhombohedral (R3c) to pseudo-cubic (Pm3m) structure. Fourier Transform Infrared (FTIR) analysis also supports this structural change. Further, TG-DSC analysis demonstrates the effect of Ba on ferromagnetic transition temperature.

Experimental

Materials

Nanoparticles of $Bi_{0.8}Ba_{0.2}FeO_3$ were synthesized using ethylene glycol based solgel method. The starting materials were $Bi(NO_3)_3{\cdot}5H_2O$ (purity 99%), $Fe(NO_3)3{\cdot}9H_2O$ (purity 98%), and $Ba(NO_3)_2$ (purity 99%)

of sigma-aldrich (india) and used without further purification.

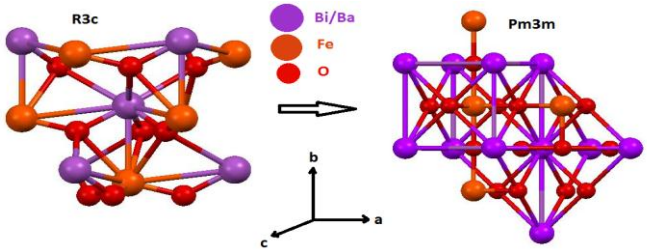

Fig. Structural Transition in Barium substituted $BiFeO_3$(BFO).

Synthesis

$Bi(NO_3)_3{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $Ba(NO_3)_2$ were dissolved in ethylene glycol in proper stoichiometric proportions. Mixture was stirred continuously until a clear solution was observed. The solution was placed for gel formation and allowed to dry overnight. The dried gel was calcined to obtain as-prepared sample. As-prepared samples were sintered at 800°C for 15min.

Characterization techniques

The crystal structure was studied by X-ray diffraction (XRD) performed at room temperature in a Rigaku Multiflex-II instrument using CuKα radiation (λ = 1.5406 Å), generated at 30 kV and a current of 15 mA with step of 2°. X-ray patterns were analyzed by the Rietveld refinement using FULLPROF program. In order to investigate, structural evolution of the prepared samples TG-DSC measurement was conducted on a TG-DSC instrument (SDT Q600) under nitrogen protection at a heating rate of 10°C/min with experimental precision of ± 1°C. To study the compositional characteristics from optical excitation of vibrational modes, infrared spectra were recorded in the range 4000-400cm^{-1} using FTIR spectrometer.

Results and discussion

X-Ray diffraction

XRD profile pattern of Bi0.8Ba0.2FeO3 ceramic (sintered at 800°C) are presented in **Fig. 1**. In the literature it has been reported that bismuth ferrite (BFO) exhibits a distorted rhombohedral structure having space group R3c [JCPDS No. 86-1518] with a most intense peak doublet in diffraction pattern around 2θ = 32°, which is the characteristic doublet of distorted R3c crystal structure [**11**]. This peak doublet merged in a sharp and intense single peak for BBFO **(see Fig.1(a)),** indicating the structural transition from the rhombohedral (R3c) to pseudocubic (Pm3m) crystal symmetry [**12**]. Further, XRD pattern of BBFO shows minor impurity/secondary phases of $BiFeO_3$ such as $Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$ etc. In order to confirm the structural transition, rietveld refinement of BBFO was carried out using Fullprof program **(Fig. 1(b)).** The refinement of BBFO was performed using Pm3m space group having cubic symmetry. The reliability parameter (χ^2, R_{Bragg}, R_F) values suggest that simulated data is well matched with experimental XRD data. The crystallite size of the prepared samples has been calculated using Scherrer's formula and listed in **Table1**.

Table 1. Space group, crystallite size, position co-ordinates of atoms and reliability factors for the sintered sample.

Sample	Space group	Crystallite size (nm)	Atom	Position	X	Y	z	R-factors (%)
BBFO	Pm3m	19.8	Bi/Ba	1*b*	0.5	0.5	0.5	χ^2 = 3.27
			Fe	1*a*	0	0	0.0	R_F = 4.47
			O	3*d*	0	0	0.5	R_{Bragg}=5.93

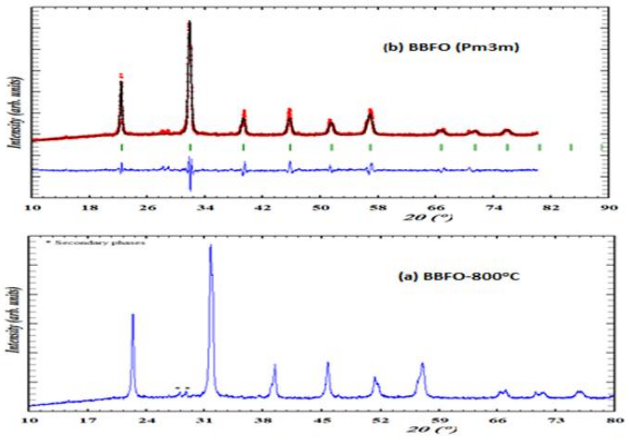

Fig. 1. (a) XRD profile pattern of $Bi_{0.8}Ba_{0.2}FeO_3$ ceramic sintered at 800°C (b) profile fitting using FULLPROF program.

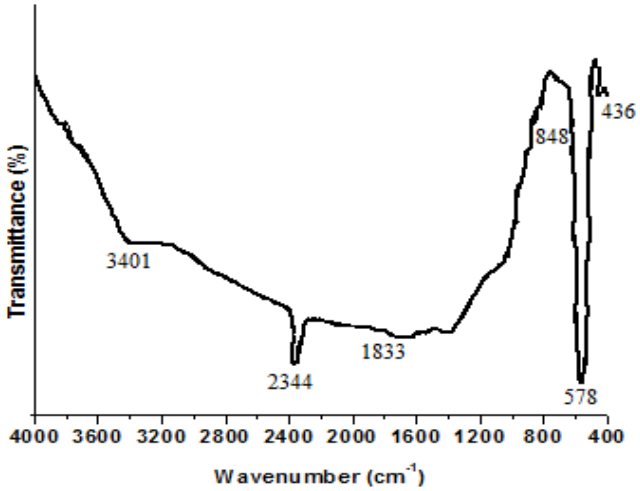

Fig.2: FTIR spectra of $Bi_{0.8}Ba_{0.2}FeO_3$ ceramic sintered at 800°C.

FTIR analysis

Structural changes in formation of the BBFO have been investigated by FTIR spectroscopy. **Fig. 2** shows FTIR spectra of BBFO sintered at 800°C. The presence of O-H stretching vibrations (around 3500-3000cm^{-1}), C-H vibrations (around 2345 cm^{-1}) C=O symmetric vibrations (around 1420-1310 cm^{-1}) along with metal-oxygen vibrations around 600-400cm^{-1}, is clearly evident from the

FTIR spectra. The characteristic peaks of Fe-O bending vibrations and Fe-O stretching vibrations in FeO_6 octahedral unit of bismuth ferrite has been reported around 440cm^{-1} and 575cm^{-1}, respectively. BiO_6 octahedral structural unit also possess characteristic peaks at 540cm^{-1} and 450cm^{-1}. The peak at 578cm^{-1} in BBFO reveals a shift toward higher wave number, which supports the structural transition from low symmetry (R3c) to higher symmetry (Pm3m) for BBFO [**13**].

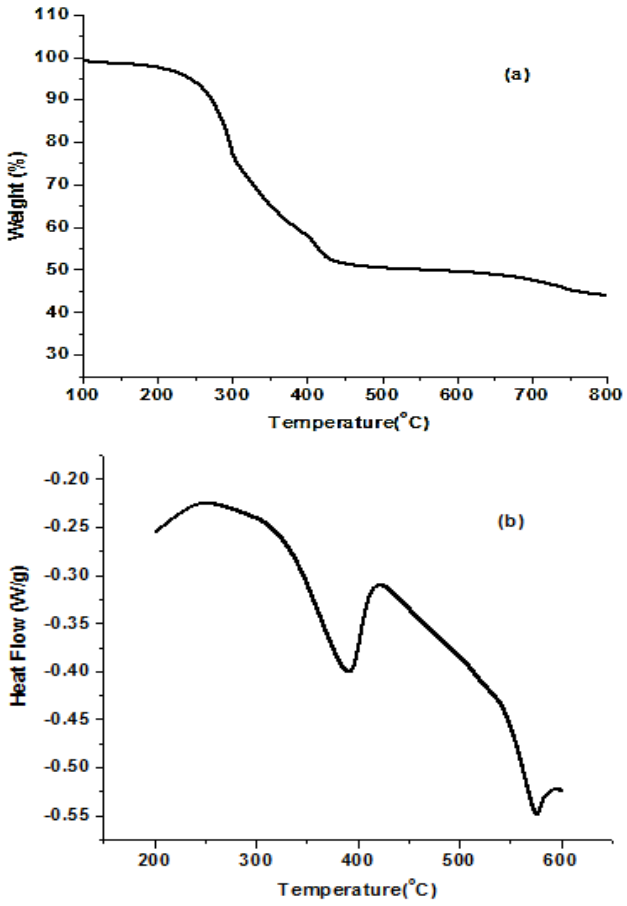

Fig.3:(a) TG curve of dried gel $Bi_{0.8}Ba_{0.2}FeO_3$ ceramic (b) DSC curve of $Bi_{0.8}Ba_{0.2}FeO_3$ ceramic.

TG-DSC analysis

The TG curve of the BBFO ceramic dried gel in the temperature range 100-800°C is shown in **Fig. 3(a).** The total weight loss in the sample is nearly 55%. The major weight loss in the temperature range 200-300°C occurs due to the decomposition of hydroxides. Further, weight loss in the region 301-450°C is due to the volatilization of tartaric acid. The DSC curve in the temperature range 200-600°C is shown in **Fig. 3 (b).** Endothermic peaks in the DSC curve represent first order phase transition. The ferromagnetic transition temperature of the bismuth ferrite has been reported to 347°C [**14**] but DSC curve of BBFO shows a endothermic peak at higher temperature. Thus, Ba substitution at Bi site increases the ferromagnetic transition temperature.

Conclusion

Barium(Ba) substituted bismuth ferrite was synthesized using ethylene glycol based sol-gel method followed by heat treatment at 800°C for 15 min. Rietveld analysis confirmed a structural transition from the rhombohedral perovskite (ABO_3) crystal structure to pseudo-cubic Pm3m structure. Ba substitution at Bi site also proved helpful to suppress the secondary phases of $BiFeO_3$ such as $Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$ etc. The crystallite size of the prepared barium substituted $BiFeO_3$ (BBFO) nano-multiferroic calcined at 800°C was found ~20 nm. FTIR and TG-DSC analysis also support structural changes made by the Ba substitution in BFO.

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