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Impact of Fe on structural modification and room temperature magnetic ordering in BaTiO₃



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ABSTRACT

Ba_{1-x}Fe_xTiO₃ ($x = 0, 0.005, 0.01$) polycrystalline ceramics are prepared using solid state reaction method. Structural studies through XRD, Raman and XPS confirm single tetragonal phase for BaTiO₃ whereas a structural disorder tends to intervene with the introduction of smaller Fe ions which reduces the tolerance factor and tetragonality ratio. Grain size of the samples is estimated using SEM micrographs with ImageJ software and chemical composition is confirmed using EDX spectra. Raman spectra measured in the temperature range of 303 K to 573 K shows light on the structural phase transition exploiting a significant disappearance of the 306 cm⁻¹ mode. Further, structural analyses suggest the entry of Fe into the B-site upon increasing its concentration in BaTiO₃. The dopant sensitive modes lying at around 640 cm⁻¹ and 650 cm⁻¹ are assigned to lattice strain. A reduction in ferroelectric to paraelectric transition temperature is observed with a transformation from diffused type to normal ferroelectric upon the increased Fe content. The oxidation state of Fe in the BaTiO₃ lattice has been decided using EPR Spectra precisely. Room temperature magnetic ordering is observed in Fe substituted BaTiO₃ using PPMS. The coexistence of ferroelectric and magnetic ordering is established in the present study for optimized Fe substituted BaTiO₃.

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1. Introduction

The multiferroic perovskites house electric and magnetic phases predominantly. They have widened the miniaturization of many conventional devices and their applications as they form passive components. The multifunctional characteristics of perovskites are modified with the structural distortions induced by the nature of substituent cations to suit to a variety of applications. However it is really challenging to retain suitably the different ferroic phases at room temperature. The most preferred candidate is BaTiO₃ (BTO) which efficiently supports development of multiferroic platform with ferroelectric transition temperature (T_c) above 400 K. The coexistence of ferroic conditions is realizable as it allows substitution of various cations in its Ba (A) and Ti (B)-sites. The transition metal (TM) cations doping in BTO have provided a series of polymorphic forms like rhombohedral, orthorhombic, tetragonal cubic phases and hexagonal structures [1,2]. The different phases are achieved due to the choice of dopants, their concentration, and sintering temperature [3–5]. A large variety of potentially useful theoretical and experimental details about electrical and magnetic properties of BTO with different substitutions have been reported from time to time [6–23].

Since the theoretical prediction of magnetic ordering in transition element doped BTO by Nakayama and Yoshida [24], in order to orchestrate the multiferroicity the research on BaTiO₃ has grown at a

stupendous pace. Subsequently one of the extensively studied dopants in A and b sites of BTO is Fe, but for higher concentration of it [25–35].

It is understood from the literature that a viable solution lies in the optimization of the doping concentration of Fe in A-site of BTO to achieve electrical and magnetic order without much mutual loss [36–45]. Ultimately a clear strategy is deduced by the incorporation of a smaller or dilute quantity of cation (Fe) in A-site in the BTO matrix. The present proposal of us is to have a controlled lower concentration of Fe fairly within the limit of solubility in Ba site. It is of further interest to create a strain as a result of ionic differences between Fe and parent elements in BTO matrix which would build magnetic interaction with electric ordering [46].

2. Materials and methods

For the synthesis of Ba_{1-x}Fe_xTiO₃ ($x = 0$ (BTO), $x = 0.005$ (BFTO-1), $x = 0.01$ (BFTO-2)), required quantities of barium carbonate, titanium dioxide and ferric oxide are taken as reactants. The pre-ground powders of the reactants are calcined at 1173 K followed by the stages of pre-sintering in steps of 50 K till 1323 K each for 12 h. The intermittent and final grinding are done using agate mortar and pestle. The thermal treatments for the samples are carried out using high purity alumina crucibles in the air atmosphere with heating and cooling rate of 5 K/min and 100 K/h respectively. The pellets of dimension 13 mm diameter and 1.3 mm thickness are prepared using KBr Hand Press applying 5 Tons pressure for 5 min. Further, sintering of the samples is

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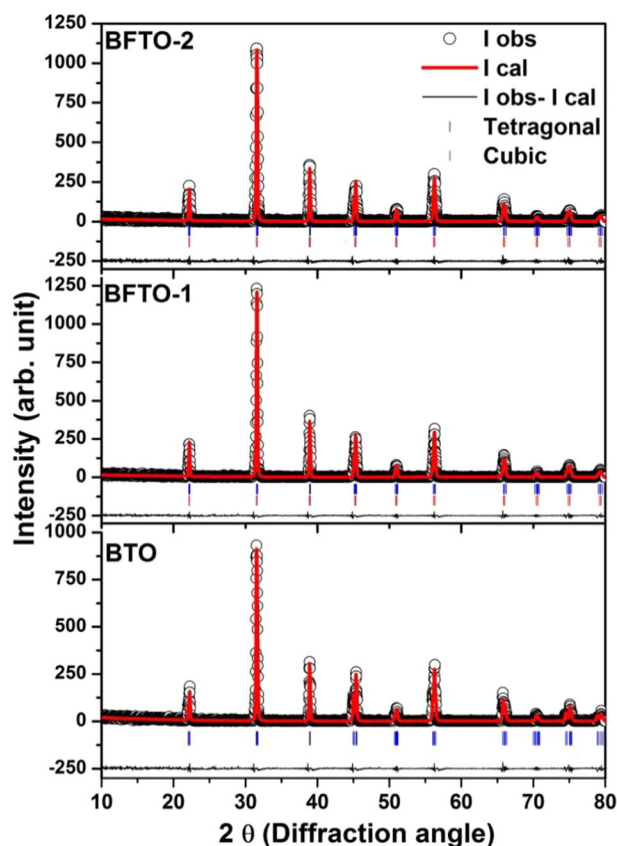


Fig. 1. Profile fit XRD patterns of Fe doped BTO.

carried out at 1373 K for 24 h. The pellets thus obtained are crushed, ground for an hour and made available for further characterizations.

The phase purity and crystallinity are determined using PANalytical X-ray Diffractometer (Model: X'Pert PRO) with an X-ray radiation source of $\text{Cu-K}\alpha$ ($\lambda_{\text{K}\alpha 1} = 1.54056 \text{ \AA}$; $\lambda_{\text{K}\alpha 2} = 1.54439 \text{ \AA}$). The samples are mounted on flat aluminium holder and data is obtained in a conventional Bragg Brentano (BB) parafocusing geometry. X-ray diffraction data are collected in the range $10\text{--}80^\circ$ with step size of 0.02° with a scan rate of 0.70 s and subjected to profile refinement. Diffraction patterns of samples each of mass 450 mg are analyzed to determine the lattice parameters, c/a ratio and tetragonal (or cubic) nature. FullProf software package is used for refinement of lattice parameters. A Scanning electron Microscope (SEM) (HITACHI Model: S-3400N) with an accelerating voltage of 15 kV is used to study surface morphology of the prepared samples in secondary electron detection mode. The elemental distribution analyses of the samples are carried out using a fully automated quantitative Energy Dispersive X-ray Spectroscopy EDX (Thermo S-3400N) attached with the SEM. Phase formation is studied using Differential Scanning Calorimeter (TA – Q20 DSC). Raman scattering spectra are recorded using Confocal micro-Raman spectrometer (Renishaw inVia Reflex) having a liquid-nitrogen cooled charge-coupled device multichannel detector ($256 \text{ pixels} \times 1024 \text{ pixels}$). The measurements are carried out with an excitation wavelength of 488 nm in the

temperatures range of 303 K–503 K. The acquisition time and illumination power of the laser used for the present study are 20 s and 1 mW respectively. Dielectric parameters are measured at some selected frequencies (1 Hz, 100 Hz, 1 kHz, 100 kHz and 1 MHz) using Broad band Dielectric Spectrometer (NOVOCONTROL Technologies GmbH & Co. Germany Model: Concept 80). Pellets of dimension $10 \text{ mm} \times 1 \text{ mm}$ are prepared for electrical study purpose by mixing the powders with a few drops of polyvinyl alcohol (PVA) solution which serves as binder. The pellets are post-heated at 1373 K for 12 h for densification and elimination of the organic binder (PVA). Further, these sintered pellets are gold sputtered on both sides for better contact and then sandwiched between gold coated bronze electrodes. Dielectric study is performed at different selected frequencies and its temperature dependence is done in the temperature range of 303 K–423 K at 1 kHz frequency. X-ray Photoelectron spectroscopy (Omicron nanotechnology) has been used for surface characterization of the investigated samples. Electron spin resonance studies were performed in X-band, 9.5 GHz (Varian E-112 ESR Spectrometer) at ambient condition. Room temperature magnetic properties (M-H loop) are performed using Physical Property Measurement System (PPMS-Quantum Design model E-2) with the applied field of 12 kOe.

3. Results and discussion

3.1. Structural study

XRD pattern of the samples with profile fit is shown in Fig. 1. The diffraction patterns of BTO fit perfectly with the standard pattern of tetragonal BaTiO_3 of space group $P4mm$ (JCPDS: 00-005-0626). However, an appreciable disparity is observed for Fe doped BTO when fit with tetragonal phase only whereas it fits well with the combination of tetragonal and cubic phases. Therefore dual phase fit is carried out with the assumption of coexisting tetragonal and cubic phases. The lattice parameters calculated from the FullProf profile fit are listed in Table 1. The modification of BTO lattice with Fe doping is evidenced from the variation of lattice constants (a and c). The pictorial representation of atoms in the unit cell as shown in Fig. 2 is demonstrated to estimate the bond length between Ti–O and Ba–O in the pristine and doped samples and it is given in Table 1. A small change in lattice constant upon doping is noticed. It is attributed to the appropriate site occupancy of the solute cations. The observed c/a ratio of the tetragonal lattice decreases from 1.0091 (BTO) to 1.0045 (BFTO-1). But, for BFTO-2, it slightly increases to 1.0049. In both samples Ti atom is bereft of any distraction in the form of doping. Therefore, the only change in the bond length of Ti–O is due to the advent of Fe–O sub-lattice. The bond length of Ti–O in a and c direction is 1.997 Å and 2.015 Å respectively. The bond length is varied to 2 Å and 2.009 Å with the presence of 0.5% of Fe ions in the respective directions. It can be attributed to the incorporation of Fe in A-site of BTO that has resulted in a reduction of Ti displacement with respect to Oxygen anions. An increased doping of Fe does not alter the bond length along c -direction i.e., it remains 2.009 Å. However the bond is stretched along a axis compared to the pure BTO while compressed along a -axis compared to BFTO-1. It is due to the replacement of some of the Ti ions by Fe atoms as there is no change in Ba–O bond length upon doping (refer Table 1). Thus the site occupation of Fe takes place in the A and B sites for higher doping concentration. It is

Table 1

The observed lattice parameters and strain values of pure and doped BTO.

Sample	Tetragonal phase			Cubic phase	Ti–O bond length (Å)	Ba–O bond length (Å)	Strain (ϵ)
	a (Å)	c (Å)	c/a	a (Å)			
BTO	3.9944	4.0308	1.0091	–	1.997	2.837	0.00071
BFTO-1	3.9993	4.0173	1.0045	4.0084	2.000	2.834	0.00160
BFTO-2	3.9985	4.0181	1.0049	4.0086	1.999	2.834	0.00146

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