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Structural transition, magnetic and optical properties of Pr and Ti co-doped $BiFeO_3$ ceramics

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ABSTRACT

$Bi_{1-x}Pr_xFe_{1-x}Ti_xO_3$ ceramics with $x=0.00$, 0.10 and 0.20 were synthesized by a solid state reaction method. Rietveld fitting of the diffraction data reveals structural transition from rhombohedral phase (R3c) for $x \le 0.10$ to orthorhombic phase (Pnma) for $x=0.20$. Room temperature M–H hysteresis measurements reveal that magnetization increases due to the structural distortion and partial destruction of spin cycloid caused by co-doping in $BiFeO_3$ ceramics. FT-IR spectra exhibit broad absorption bands, which may be due to the overlapping of Fe–O and Bi–O vibrations in FeO_6 octahedra of these ceramics. UV–visible spectroscopy results show strong absorption of light in the spectral range of 480–640 nm, indicating optical band gap in the visible region for these samples.

1. Introduction

Multiferroic materials exhibit two or more than two ferroic properties in the same phase. In these materials, magnetization is controlled by dielectric polarization and vice-versa. Due to the coupling between ferroelectric and magnetic domains, the multiferroic materials offer a new class of applications in multistage information storage devices like FeRAM, MRAM, etc. [1,2]. $BiFeO_3$ (BFO), with a rhombohedrally distorted perovskite structure, having R3c space group symmetry, is one of the few multiferroics that shows both ferroelectricity and G-type anti-ferromagnetism with Curie temperature (T_C) ~1103 K and Néel temperature (T_N) ~643 K respectively [3]. In addition to magnetoelectric applications, BFO might find applications in femtosecond laser pulses [4], solar cell [5], photocatalytic materials and optoelectronic devices [6], due to its small band gap, which enhances its visible region absorbance. Small band gap allows carrier excitation in BFO with commercially available femtosecond laser pulses, and hence enables scientists community to develop ferroelectric ultrafast optoelectronic devices as widely demonstrated in semiconductors [6]. Although, these properties are very useful in terms of applications, BFO has some inherent problems, e.g. preparation of the phase pure compound, high leakage current, wide difference in ferroic transition temperatures, and low magnetoelectric coupling coefficients.

In order to overcome all these problems, partial substitutions of rare-earth ions (Y^{3+}, La^{3+}, Nd^{3+}, Sm^{3+}, $Pr^{3+/4+}$, Gd^{3+}, Dy^{3+}, etc) at A site for Bi^{3+}ions or transition metal ions (Zr^{4+}, Mn^{4+}, Ti^{4+}, Cr^{3+}, Co^{2+}, Sc^{3+}, etc.) at B site for Fe^{3+}ions have been carried out [7–12]. These substitutions have been found effective for improving the ferroelectric or/and the magnetic properties since the ferroelectricity and magnetism in BFO are caused by the lone pair electrons of Bi^{3+} ions at A sites and partially filled "*d*" orbital electrons of Fe^{3+} ions at B sites respectively. A and B sites co-substitution is reported to further enhance the multiferroic properties of BFO, both in the thin films as well as in bulk ceramics [13]. Further, A site and B site doping with off valent ions separately or simultaneously will be helpful to understand the defect chemistry in these materials. Since the valence of Ti^{4+} ion is higher than that of Fe^{3+} ion, the Ti^{4+} ions substitution for Fe^{3+} ions at B-site may help in reducing the oxygen vacancies without changing ionic state of Fe^{3+} locally. Another possibility is the change in the ionic state of Fe^{3+} to Fe^{2+} without affecting the oxygen vacancies which may lead to distortion in FeO_6 octahedra and suppress the inhomogeneous magnetic spin structure. It has been reported that Pr substitution is an efficient way to improve the multiferroic properties of BFO [11,12]. The strength of Pr–O bond (753 ± 17 kJ/mol) is higher than that of Bi–O bond (343 ± 6 kJ/mol) [14,15]; therefore, substitution of Pr^{3+} ion for Bi^{3+} will prevent the creation of defects, i.e. volatilization of Bi atoms and hence the oxygen vacancies. Ti substitution at *B* site is found to decrease the leakage current significantly and induce a remanent magnetization in BFO [16]. Therefore, it is fascinating to study the effect of co-substitution of Pr and Ti on BFO in order to have the combined advantages of the two. Recently, enhanced multiferroic properties of co-substituted BFO

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ceramics with Pr, Sr, La, Ce at A-site and Zr, Ti, Nb at B-site have been studied [7–9]. However, no reports are available about Pr^{3+} (1.126 Å) at Bi^{3+} (1.31 Å) site and Ti^{4+} (0.604 Å) at Fe^{3+} (0.645 Å) site [17] co-substituted BFO ceramics to date. In view of the above, we have synthesized Pr and Ti co-substituted BFO ceramics to study the influence of simultaneous doping on the structural, magnetic and optical properties of these materials.

2. Experimental details

Pr and Ti co-doped BFO ceramics with $x=0.00$, 0.10, and 0.20 were synthesized by a solid state reaction method. The mixed powders for each composition in stoichiometric proportion were calcined at 750 °C for 2 h. Diffraction patterns of sintered samples have been recorded at room temperature using an X-ray Powder Diffractometer (XRD 6000, Shimadzu analytical, Japan) with Cu Kα radiation ($\lambda \sim 1.5418$ Å). Magnetization (M–H hysteresis loop) measurements were made using a vibrating sample magnetometer (VSM-7305, Lakeshore). Optical band gap of these materials was calculated using spectra taken from a UV spectrometer (Perkin-Elmer, Lambda-35). Infrared spectroscopy (IR) was done at room temperature by a Perkin-Elmer BXII.

3. Results and discussion

Fig. 1(a) shows the diffraction patterns of the compositions with $x=0.00$, 0.10 and 0.20 in the $Bi_{1-x}Pr_xFe_{1-x}Ti_xO_3$ (BPFTO) system. The expanded patterns clearly show the peak reflections (104) at 31.89°, (110) at 32.13° and (006) at 39.14°, (202) at 39.54° for $x=0.00$ and 0.10 samples (Fig. 1b). It has been observed from XRD patterns that the sample with $x=0.20$ shows only one broad peak at $2\theta \sim 32.13°$ and $\sim 39.57°$ that correspond to the reflections (121) and (220) respectively. The distinct peaks for (104), (110) and (006), (202) planes for $x=0.0$ samples are found to be nearly merged into a single broad peak of (121) and (220) for $x=0.20$. This clearly indicates the structural transformation from rhombohedral (R3c) to orthorhombic (Pnma). The structural transition may be due to the distortion of FeO_6 octahedron by the substitution of Ti doping, which changes both Fe–O and Fe–O–Fe bond angles. Bi–O bond length is also changed due to the substitution of Pr in Bi site. Interestingly, the peak splitting behavior was found to decrease with increasing Pr and Ti concentrations. Unit cell volume has decreased with increasing concentrations. This decrease in volume is expected because of small ionic size of Pr^{3+} and Ti^{4+}. The observed, calculated and difference profiles of the XRD data have been obtained by Rietveld analysis for all these samples. Lattice parameters, unit cell volume, weighted pattern R_{wp}, the expected pattern R_{exp} and the goodness of fitting parameter χ^2 are also listed in Table 1. The fit between observed and calculated profile has been found to be relatively good for $0 \leq x \leq 0.20$ which confirms the structural transition from rhombohedral (R3c) phase ($x \leq 0.10$) to the orthorhombic (Pnma) phase ($x=0.20$).

Fig. 2 shows the room temperature magnetic hysteresis (M–H) loops for $x=0.00$, 0.10 and 0.20 samples in the BPFTO system. Magnetization has been found to be increased with applied magnetic field for all these compositions. As seen from the figure, no hysteresis behavior is observed for pure BFO; however the magnified figure shows a very poor hysteresis. Compositions with $x=0.10$ and $x=0.20$ show strong hysteresis behavior. Pure BFO is known to have a G-type anti-ferromagnetic (AFM) order with a residual magnetic moment very low due to the canted spin structure [1]. The appearance of a poor hysteresis loop (see inset of Fig. 2) for the pure sample indicates a very weak ferromagnetism at room temperature because cycloid spin structure could be suppressed and the net magnetization will be enhanced by the uncompensated spins. On the other hand, oxygen defects could also enhance the magnetization by introducing Fe^{2+} into the ferromagnetic order across Fe^{3+}–O^{2-}–Fe^{2+} [18]. For $x=0.10$ and 0.20 the loops are not saturated and magnetization increases with dopant concentration; values are listed in Table 1. The average remanent magnetization is calculated as $M_r = (M_r^+ + M_r^-)/2$. Thus, a significant increase in net magnetization suggests the addition of non-magnetically active Ti^{4+} ions at magnetically active Fe sublattice sites in AFM lattice which breaks the Fe–O–Fe network. The appearance of weak ferromagnetism for $x \geq 0.10$ may be attributed to the following reasons: the breakdown of the balance between the antiparallel sublattice of Fe^{3+} due to substitution of different valance, or the canting of the antiferromagnetically ordered spin by a structural distortion. Structural distortion might be associated with structural transformation [19,20] (change in space group) or partial modification or change in bond length between Bi–O and Fe–O metal ions. In the present case, Pr and Ti substitutions in BFO ceramics support structural transformation from rhombohedral (R3c) to orthorhombic (Pnma). This structural change, i.e. change in bond length and bond angle caused by co-substitution, may affect the magnetic properties.

FT-IR spectra of all samples are shown in Fig. 3 in the wave number range of 380–800 cm^{-1}. The broad absorption bands, around 440 cm^{-1} and 570 cm^{-1} for all samples, are due to overlapping of bismuth oxide and iron oxide in bending and stretching modes of vibrations. Absorption peaks at 570 cm^{-1} and 440 cm^{-1} are characteristics of O–Fe–O stretching and bending vibrations of FeO_6

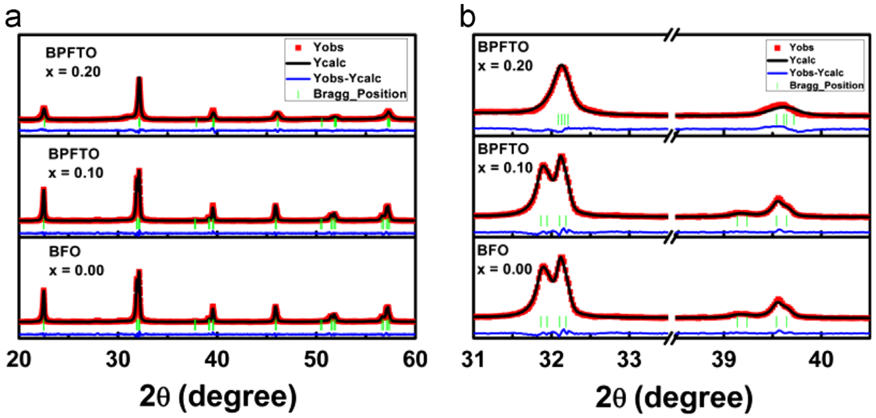

Fig. 1. (a) Diffraction patterns and (b) magnified view of the peak positions for 2θ at $\sim 32°$ and $\sim 39°$ for $x \leq 0.20$ in the system $Bi_{1-x}Pr_xFe_{1-x}Ti_xO_3$.