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Structural, magnetic and electrical properties of $BiFeO_3$ co-substituted with Pr–Mn

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ABSTRACT

Samples of stoichiometry $Bi_{1-x}Pr_xFe_{1-x}Mn_xO_3$ ($x = 0$, 0.10, 0.15, 0.20) have been synthesized by solid-state reaction method. Fe is found to be in the mixed and single oxidation states for pure and substituted samples, respectively. Mn is in +3 state, as inferred from XPS. XRD analysis indicates the formation of stoichiometric phase with control over the Bi and Fe rich secondary phases. The $x = 0.10$ sample shows thermal stability and characteristic ferroelectric–paraelectric transitions are observed in all the samples, from the thermal studies. Effect of substitution on the grain size distribution is not observed in the SEM picture. Magnetization values from the hysteresis curves obtained at the maximum applied field, increases with substitution indicating the effect of Pr–Mn in $BiFeO_3$. The substituted samples show different response in resistivity and dielectric behaviour than the pure sample, as understood from impedance spectroscopy data. Defects, and charge carriers resulting from Pr–Mn substitution are responsible for this change in conductivity.

1. Introduction

One of the most studied single phase multiferroic materials is $BiFeO_3$ with G-type antiferromagnetic ordering ($T_N \sim 643$ K) and ferroelectric transition temperature of ~1103 K [1]. This wide difference between the magnetic and electrical transition temperatures leads to a weak magneto-electric (ME) behaviour [2]. In the absence of strong ME behaviour, its potential for application in the field of spintronics and low field magnetic sensors is remote. Hence it becomes necessary to improve and understand the ME coupling in $BiFeO_3$ employing different approaches for the purpose of device application. The methodology for research has been towards favourable modification of properties by the substitution in either Bi-site or Fe-site separately in $BiFeO_3$ [2]. Structural distortion, phase transition, reduced grain size, decrease in concentration of Fe^{2+} ions, and control over oxygen vacancies are some of the important aspects dealt with in the literature reports on A- or B-site substituted $BiFeO_3$ [3,4]. The Bi sites have been substituted with alkaline earth (AE) or rare earth (RE) elements. The AE ions like Ba^{2+} and Sr^{2+} have bigger ionic radius than Bi^{3+} ions [5]. In the case of RE ions like Tb^{3+}, Pr^{3+}, Gd^{3+} and Dy^{3+}, the ionic radius is smaller to that of Bi^{3+} [5]. The transition metal (TM) elements are substituted at the Fe-sites. The ionic radius of TM ions like Mn, Cr, and Ti depends on their valency, which is smaller or similar to that of Fe^{3+} ions [5]. This difference in ionic radius, valency and individual properties of substitutional elements creates structural distortion resulting in modified properties.

Recently there has been an increase in the number of reports on A–B site co-substituted $BiFeO_3$. The co-substituted $BiFeO_3$ exhibits interesting properties due to the effect of both the A-B substituents, thereby providing a new facet for research [4,6–10]. The charge state, ionic radius and individual properties are the criteria for selecting the A–B co-substituents. Interesting phenomena have been reported for the combination of either, TM (Mn, Co) and RE (Dy, Pr, Nd, Tb) elements [6,7,11] or TM (Mn, Co, Ti) and AE (Sr, Ba) [9,10,12] elements.

A structural phase transition from rhombohedral to tetragonal or orthorhombic is reported with increasing Pr concentration in $BiFeO_3$ [13,14]. The crystal structure is stabilized with control over the Fe^{2+} concentration (created as a result of charge compensation) and the oxygen vacancies due to Pr substitution in $BiFeO_3$ [4]. The change in lattice parameters established by Pr substitution induces a weak ferromagnetic behaviour resulting from the modification of the spiral spin antiferromagnetic structure [13]. This leads to an increase in the global magnetization behaviour with applied fields. The Pr substituted $BiFeO_3$ exhibits better electrical properties than pure $BiFeO_3$ [15].

The Pr–Mn co-substitution in $BiFeO_3$ also leads to a phase transition from rhombohedral to tetragonal or orthorhombic above ~15% concentration [16,17]. An increase in magnetization with

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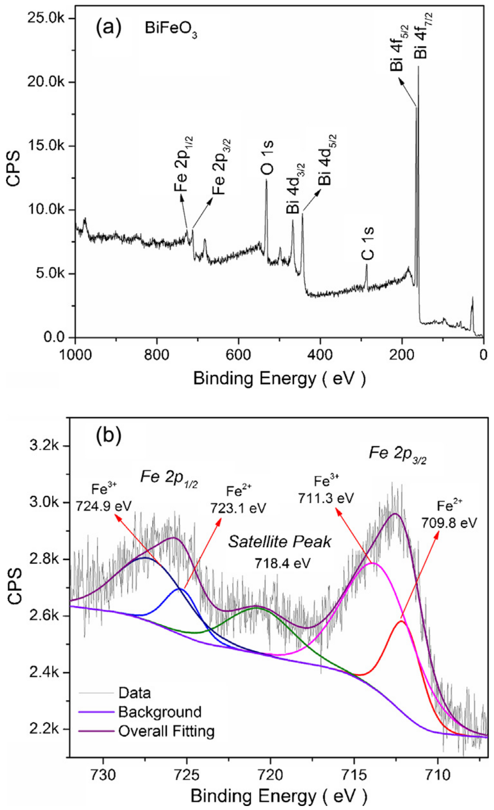

Fig. 1. (a) XPS survey spectrum of $BiFeO_3$. (b) Narrow energy-window scan of Fe.

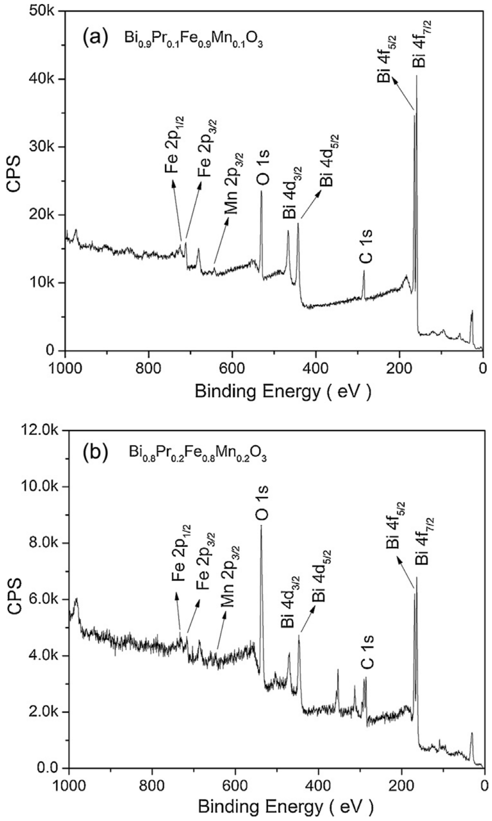

Fig. 2. (a) XPS survey spectrum of $Bi_{0.9}Pr_{0.1}Fe_{0.9}Mn_{0.1}O_3$. (b) XPS survey spectrum of $Bi_{0.8}Pr_{0.2}Fe_{0.8}Mn_{0.2}O_3$.

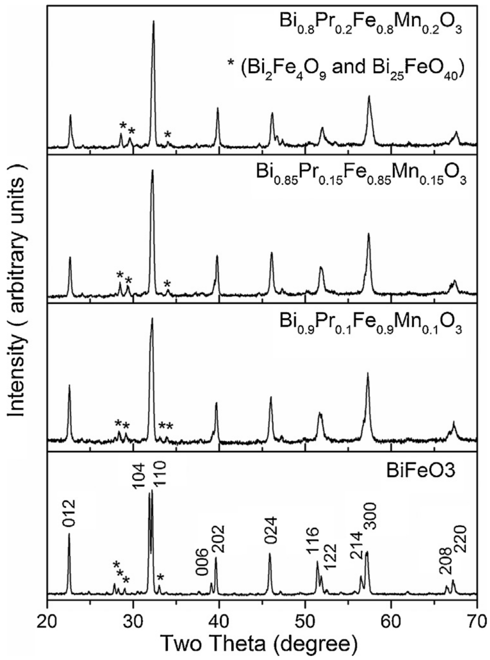

Fig. 3. X-Ray diffraction plots of $Bi_{1-x}Pr_xFe_{1-x}Mn_xO_3$ ($x = 0$, 0.1, 0.15, 0.2) samples. *Indicates secondary peaks.

Pr–Mn substitution is observed with a suppression of the leakage current. The formation of oxygen vacancies with a decrease in grain size is also reported. On the whole, only a few reports are available on Pr–Mn co-substitution in $BiFeO_3$ and those too discuss only a few physical aspects [11,18–20]. Therefore an in-depth study of the properties of Pr–Mn co-substituted $BiFeO_3$ is of interest for interesting outcomes. Hence, this report gives an insight into the effect of Pr–Mn co-substitution on $BiFeO_3$ prepared using the solid state reaction method, based on their oxidation states, resulting in the modified structural, magnetic and electrical properties.

2. Experimental

$BiFeO_3$ ($x = 0$): powders of $(BiO)_2CO_3$ and Fe_2O_3 were taken in stoichiometric proportion and ground in mortar for an hour. Ground powders were sintered initially at 750 °C for 6 h, 790 °C for 4 h and finally at 800 °C for 2 h with intermediate grinding for 10 min before each sintering.

$Bi_{1-x}Pr_xFe_{1-x}Mn_xO_3$ ($x = 0.10$, 0.15, 0.20): Stoichiometric proportion of $(BiO)_2CO_3$, Fe_2O_3, Pr_6O_7 and Mn_2O_3 were taken and ground in mortar for 1 h. Initially the powders were sintered at 750 °C for 6 h, 830 °C for 4 h and finally at 850 °C for 2 h with intermediate grinding for 10 min before each sintering.

The Cu-Kα radiation was used to obtain X-ray diffraction (XRD) data at room temperature. X-ray photoelectron spectroscopy (XPS) measurement was done in a DAR400-XM1000 (OMICRON Nanotechnologies, Germany) instrument equipped with dual Al/Mg anodes as the X-ray source. Al anode was used to obtain the survey and elemental spectrums. The peak of C 1*s* at 284.5 eV was

Table 1
Cell parameters of $Bi_{1-x}Pr_xFe_{1-x}Mn_xO_3$ ($x = 0$, 0.10, 0.15, 0.20) samples.

Composition	*a* (Å)	*c* (Å)	*c*/*a*	Volume (Å^3)
$BiFeO_3$	5.5779(2)	13.865(4)	2.48	373.5
$Bi_{0.9}Pr_{0.1}Fe_{0.9}Mn_{0.1}O_3$	5.5764(4)	13.810(9)	2.46	370.4
$Bi_{0.85}Pr_{0.15}Fe_{0.85}Mn_{0.15}O_3$	5.5670(4)	13.756(9)	2.47	369.1
$Bi_{0.8}Pr_{0.2}Fe_{0.8}Mn_{0.2}O_3$	5.5582(4)	13.682(9)	2.46	367.1