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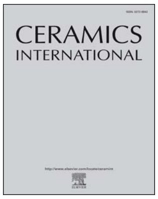

# Effects of $Nd^{3+}$ and high-valence $Nb^{5+}$ co-doping on the structural, dielectric and magnetic properties of $BiFeO_3$ multiferroics

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## ABSTRACT

$Bi_{0.90}Nd_{0.10}Fe_{1-x}Nb_xO_3$ ($0 \le x \le 0.05$) multiferroics have been studied to reveal the effect of Nb doping on the physical properties of the neodymium modified $BiFeO_3$. These samples have been synthesized via conventional solid state reaction method. The structural characterization was performed by XRD technique and Rietveld refinement. Rietveld refinement results confirmed that all samples crystallized in rhombohedral symmetry. In the vicinity of anti-ferromagnetic Neel-temperature ($T_N$), an anomaly was observed in dielectric constant ($\varepsilon'$) and loss tangent ($\tan \delta$) which indicates the existence of magnetoelectric coupling. It is observed that with Nb doping dielectric constant was reduced and Neel temperature shifted towards higher temperature. The impedance (Nyquist plots) and modulus spectroscopy revealed that materials possess non-Debye type of relaxation. The doping of donor ion is able to suppress the existence of oxygen vacancies which results in increase in resistivity. The B-site doping by higher valence ion suppresses the existing modulated spin structure by structural distortion, results in released net magnetization. The room temperature remanent magnetization increased with Nb doping and all powder samples possess weak ferromagnetism. The possible reasons for the notable magnetic and dielectric performance of prepared samples were discussed.

## 1. Introduction

Multiferroics materials have fascinated ever-increasing attention in current years due to the potential applications in actuators, sensors, data storage devices, transducers and spintronic devices for intensive research [1–3]. The coexistence of at least two ferroic orders (ferromagnetic, ferroelasticity, ferroelectric and ferrotoroidicity) is essential condition for multiferroics materials [4]. These have evidence of spontaneous polarization, magnetization and strain, which are additionally controlled by applied field (electric, magnetic and strain etc.) [3]. $BiFeO_3$ (BFO) is still a highly popular candidate in multiferroics category, at room temperature the compound belongs to rhombohedral symmetry with $R3c$ space group. It is highly investigated from the research point of view as it exists in a stable phase with ferroic orders (antiferromagnetic order with $T_N = 640\,K$ and ferroelectric order with $T_C = 1140\,K$) well above the room temperature [5,6]. Apart from the co-existence of these ferroic orders, coupling between these two is also necessary for its use in device fabrication [6]. BFO possesses G-type antiferromagnetic ordering, with the incommensurate spiral spin structure of long-range order around 62 nm [5]. The magnetic behaviour of BFO is preferentially controlled by Fe-ion as its magnetic moment coupled anti-ferromagnetically with adjacent planes and ferromagnetically with pseudo-cubic planes. The spiral spins modulated spin structure and canting of spin results in the cancellation of net magnetization and exhibit the linear magnetoelectric effect [7]. The recent experimental survey on BFO outlines its crucial inherent issues, which limits its use for practical applications. The limitations of BFO are addressed as (1) preparation of stoichiometric $BiFeO_3$ is a challenging task due to phase stabilization in a narrow temperature range and frequent occurrence of impurity phases, such as $Bi_{25}FeO_{39}$ and $Bi_2Fe_4O_9$ leads to high leakage current (2) The volatile nature of Bi ion is responsible for generation and accumulation of oxygen vacancies resulting valance fluctuation of Fe (+2 and +3), and (3) low value of magnetization is attributed to the existence of incommensurate antiferromagnetic spiral spin structure, which cancels net magnetization (4) weak magnetoelectric coupling [8–10]. These defects in turn consequences unsaturated P-E loop (polarization hysteresis) and low resistivity in prepared samples [6,11]. The high leakage current and net zero macroscopic magnetization restrict bismuth ferrite in multifunctional device fabrication. Therefore, various strategies are being designed to improve multiferroics properties of BFO which include: (1) A site substitution by divalent ion ($Ca^{2+}$, $Sr^{2+}$, $Pb^{2+}$ and $Ba^{2+}$) [7,12], rare earth ions ($La^{3+}$, $Nd^{3+}$, $Eu^{3+}$ and $Ho^{3+}$) [13–15] and B-site substitution by higher valance ion ( $Nb^{5+}$, $Ti^{4+}$ and $V^{5+}$) [2,16–18] for

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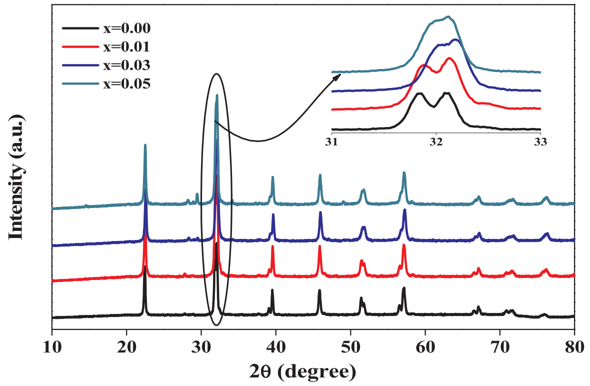

**Fig. 1.** X-ray diffraction pattern $Bi_{.90}Nd_{.10}Fe_{1-x}Nb_xO_3$ ($0 \le x \le 0.05$); magnified view of XRD pattern in diffraction angle range of 31–33° (in inset).

**Table 1**
Rietveld refined structural parameters for all prepared samples.

| Sample | Cell parameters | Atoms | Position coordinates x | y | z | Profile R-Factors (%) |
|---|---|---|---|---|---|---|
| **x = 0.00** | a = 5.572 Å | Bi/Nd | 0 | 0 | 0.2823 | $R_P = 5.51$ |
| | c = 13.829 Å | Fe/Nb | 0 | 0 | 0.0055 | $R_{WP} = 7.17$ |
| | V = 371.99 Å$^3$ | O | 0.8866 | 0.6252 | 0.4901 | $\chi^2 = 3.78$ |
| **x = 0.01** | a = 5.574 Å | Bi/Nd | 0 | 0 | 0.3332 | $R_W = 4.71$ |
| | c = 13.822 Å | Fe/Nb | 0 | 0 | 0.1068 | $R_{WP} = 6.08$ |
| | V = 371.97 Å$^3$ | O | 0.8841 | 0.6441 | 0.5399 | $\chi^2 = 3.97$ |
| **x = 0.03** | a = 5.575 Å | Bi/Nd | 0 | 0 | 0.3379 | $R_W = 4.47$ |
| | c = 13.792 Å | Fe/Nb | 0 | 0 | 0.1091 | $R_{WP} = 5.84$ |
| | V = 371.239 Å$^3$ | O | 0.8933 | 0.6544 | 0.5431 | $\chi^2 = 3.42$ |
| **x = 0.05** | a = 5.571 Å | Bi/Nd | 0 | 0 | 0.2764 | $R_W = 4.39$ |
| | c = 13.777 Å | Fe/Nb | 0 | 0 | 0.0062 | $R_{WP} = 6.41$ |
| | V = 370.375 Å$^3$ | O | 0.8906 | 0.6444 | 0.4811 | $\chi^2 = 4.41$ |

enhanced multiferroics properties. The Nd substitution at A site is known to transform structural, dielectric and magnetic properties [3,8,19]. $Nb^{5+}$ due to higher valence suppresses the charge defect such as oxygen vacancies and increased resistivity in doped BFO [20,21]. The previous study indicated that substitution at A and B site or simultaneously affect magnetic properties and increases resistivity (reduced leakage current). So, in this work, we have investigated the effect of $Nd^{3+}$ and $Nb^{5+}$ substitution on BFO system, with special emphasis on corelation between structural, electrical and magnetic properties.

## 2. Experimental

$BiFeO_3$, Nd (10%) doped $Bi_{0.90}Nd_{0.10}FeO_3$ and co-doped with Nb, i.e., $Bi_{0.90}Nd_{0.10}Fe_{1-x}Nb_xO_3$ (x = 0.01, 0.03, 0.05) were prepared by solid state reaction method. All modified bismuth ferrites were prepared using $Bi_2O_3$, $Nd_2O_3$, $Fe_2O_3$ and $Nb_2O_5$ oxides (99% purity) ingredients. These oxides were mixed mechanically in an agate mortar and pestle for 2 h. Then calcination was performed for this homogenous mixture at 673 K for 2 h. Now calcined powder was reground for 30 min followed by final heat

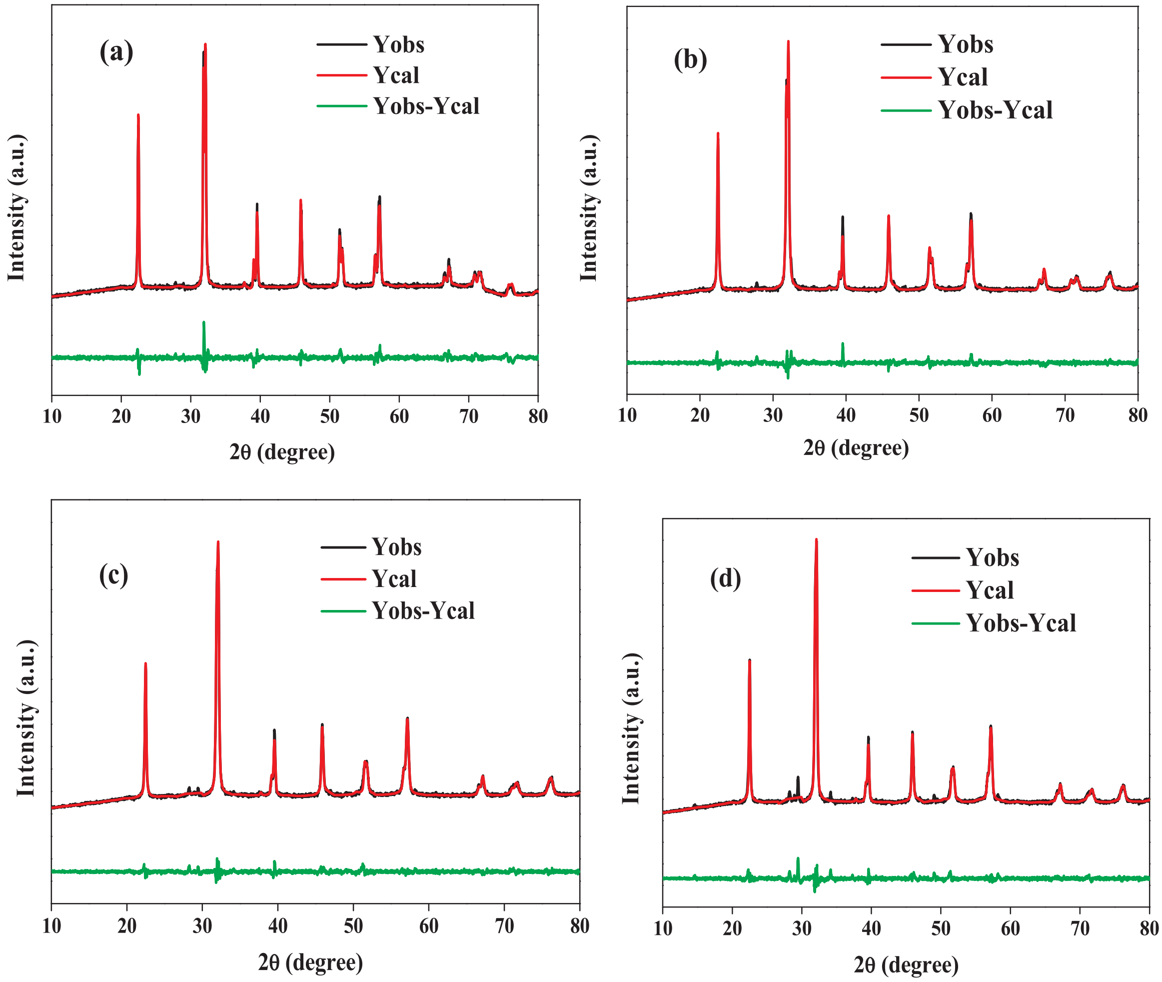

**Fig. 2.** Observed, calculated, and difference of XRD patterns obtained for the $Bi_{0.90}Nd_{0.10}Fe_{1-x}Nb_xO_3$; (a) x = 0.00, (b) x = 0.01, (c) x = 0.03 and (d) x = 0.05 compounds at room temperature.