International Journal of Advance Research in Science and Engineering
Vol. No. 5, Special Issue No. 01 , May 2016
www.ijarse.com
IJARSE
ISSN 2319 - 8354

STRUCTURAL AND MORPHOLOGICAL STUDIES OF $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$ MULTIFERROIC CERAMICS

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ABSTRACT

Lead free multiferroic samples of $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$ (x=0.0, 0.3) have been synthesized by conventional solid state reaction method using high purity starting materials, including Bi_2O_3, Nd_2O_3, TiO_2, Fe_2O_3 and NiO. The ground and well mixed powders were firstly calcined and then pressed into pellets under a uniaxial pressure of 5 ton and then sintered at 1000 ºC in a muffle furnace. X-ray diffraction studies confirm the formation of single phase with orthorhombic unit cell for both the samples. The orthorhombic distortion was found to increase with substitution. Local distortions in the crystal structure were confirmed by Raman spectroscopy with the suppression of Raman modes at 267, 850 and 537 cm^{-1}. Scanning electron microscopy reveals the plate-like growth of grains for x=0.0, whereas plate like morphology was hindered with substitution. These lead-free ceramic samples may show multiferroic behaviour which may found useful application in designing multiple state memory elements, data storage devices and sensors.

Keywords: X-Ray Diffraction, Ferroelectricity, Multiferroic, Scanning Electron Microscopy.

I. INTRODUCTION

The multiferroic materials in which ferroelectricity and ferromagnetism co-exist have been of a great interest for modern electronics and functional devices. A single phase multiferroic material is one that possesses two or all the three of ferroic orders i.e. ferroelectricity, ferromagnetism, ferroelasticity [1-4]. These materials can be used as non volatile memories, sensors, transducers and data storage devices. Many of the oxide materials, demonstrating miscellaneous behavior such as dielectric, ferroelectric, magnetic and multiferroic properties have been investigated by scientific community during the last few years [1-3]. Recently there has been upsurge in search of multiferroic systems due to the observation of good magnetoelectric coupling in bulk and thin films of some of the transition metal oxides [5]. The coupling between co-existing ferroic order parameters sure it feasible to write data binary bit by an electric field and interpret it by magnetic field, and vice versa. This gives an additional freedom in electronics device designing. However this is a rare phenomenon since ferroelectricity and ferromagnetism are mutually exclusive groups. Various attempts have been made to synthesize room temperature multiferroic materials, among which doping of magnetic species into ferroelectric materials is probably one of the most effective ways [5, 6].

Many multiferroic compounds have been studied during the past decades but most of these materials possess small magneto-electric coupling at room temperature. Ferromagnetism is successfully introduced into $BaTiO_3$ and $PbTiO_3$, by substituting magnetic ions at the Ti-sites [1-3]. Recently, a studies on the iron (Fe) and Nickel (Ni) doped $PbTiO_3$ ceramics have been reported [7-9]. But the lead (Pb) based compounds are extremely toxic and non-eco-friendly. So, lead is restricted for vastly used in large applications. As an alternate, bismuth titanate have attracted great attention because of its high-performance, large polarization, and lead and fatigue-free characters [3]. $Bi_4Ti_3O_{12}$ (BIT) is a layered structured compound belonging to the Aurivillius family having general formula $[Bi_2O_2]^{2+}[A_{n-1}B_nO_{3n+1}]^{2-}$ with n=3. The multiferroic behaviour in BIT is observed by partial substitution of Fe, Co, Ni, and Zn ions at Ti-site and observed as best doping elements for improving the ferromagnetic properties. But the system encountered a problem of high losses due to conduction [10]. The volatile nature of bismuth ions (Bi^{3+}) creates the Bi-vacancies accompanied by oxygen vacancies which are responsible for high conduction related losses in BIT. It has been reported that substitution at the Bi-site by either La^{3+} or Nd^{3+} ions, lead to improved ferroelectric properties [4]. As in present research scenario, synthesis and investigation of single-phase multiferroic with high magnetoelectric properties is a hot topic for research.

According to our knowledge, no report has been yet so far published on co-substitution of Fe and Ni at the Ti-site in the BIT system. In the present work, we have synthesized ceramic samples by conventional solid state reaction method. The structural and morphological studies were carried out using X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM) respectively.

II. EXPERIMENTAL DETAILS

Polycrystalline single phase samples of $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$ (x=0.0, 0.3) were synthesized by conventional solid state reaction method. Stoichiometric amounts of Bi_2O_3, Nd_2O_3, TiO_2, Fe_2O_3 and NiO with purity >99.95% (Sigma Aldrich) were used as the starting material. The weighed powders of each composition with 3 wt. % excess of Bi_2O_3 were continuously ground in mortar pestle with acetone for 6 hrs for homogeneous mixing. The ground powders were then poured into silica crucible and calcined at 700 ^oC in a programmable furnace. The calcined powders of each composition were then pressed into pellets of diameter 11 mm and thickness of 1 mm using hydraulic press at a pressure of 5 Tones. Finally, the pallets were sintered at 1000^oC for 4 hrs with 5 ^oC per minute heating rate and cooled in furnace atmosphere.

To study the crystallographic structures, X- ray diffraction pattern of the ceramic samples was recorded with X'Pert PRO PANalytical Diffractometer using Cu-Kα radiation (λ=1.54 Å) over a 2θ range between $20^o \le 2\theta \le 60^o$ at scanning rate of 2^o/minute. Local structural distortions within the samples were studied using Raman spectroscopy (Reinshaw invia Raman microscope) equipped with Argon laser (λ=514.5 nm) operated at 20 mW. The microstructures and elemental composition were investigated by using scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

3.1 X-ray diffraction studies

Fig. 1 shows the room temperature X-ray diffraction patterns of $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$ (x=0.0, 0.3) ceramic samples sintered at 1000 °C.

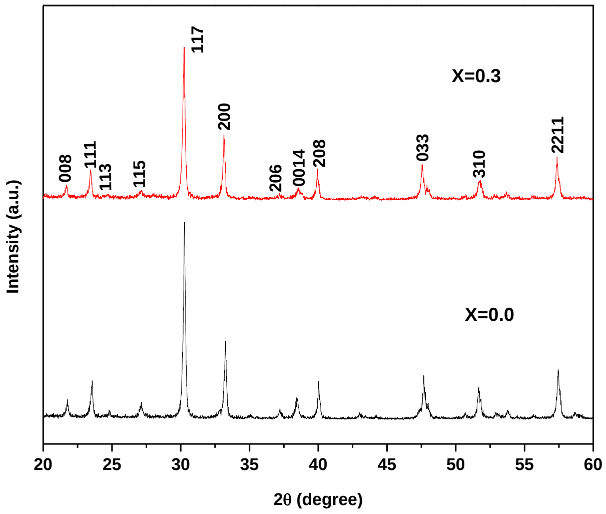

Fig. 1 X-ray diffraction pattern for $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$ with x=0.0, 0.3

For both the samples all the diffraction peaks correspond to the pure phase of $Bi_4Ti_3O_{12}$ having orthorhombic unit cell (JCPDS card No. 89-7500). The lattice parameters and unit cell volume computed for both the samples are listed in Table 1, which clearly reveal that the lattice parameters and unit cell volume change upon substitution. The orthorombocity $\delta = 2(a - b)/(a + b)$ was also calculated from the lattice parameters. The orthorombocity was found to increase from 2.5×10^{-3} to 4.7×10^{-3} with the increasing content of Fe^{+3} and Ni^{+2} ions from x = 0.0 to 0.3 in BIT, implying a relaxation of the structural distortions in the system. The observed relaxation in structural distortions may be attributed to different ionic radii of Ti^{+4} and Ni^{+2} or Fe^{+3}.

Table 1 Lattice parameters, unit cell volume and orthorombocity for $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$, x=0.0, 0.3

Parameters	x=0.0	x=0.3
Lattice parameters (Å)	a=5.3876	a=5.4041
	b=5.3737	b=5.3783
	c=32.7919	c=32.7675
Unit cell volume $(Å)^3$	949.36	952.38
Orthorombocity (δ)	2.5×10^{-3}	4.7×10^{-3}

3.2 Raman spectroscopy studies

The Raman spectrum of $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$ with x=0.0, 0.3 ceramic samples at room temperature is shown in Fig. 2. Theoretically, there are 24 Raman active modes for orthorhombic BIT [11, 12]. However, as shown in Fig. 2, only the Raman modes at about 116, 147, 225, 269, 327, 353, 536, 560, 610 and 850 cm^{-1} were observed in the present system. The modes above 200 cm^{-1} have been assigned as the internal modes of TiO_6 octahedra of BIT [12]. The mode at around 225 cm^{-1} is Raman inactive and it is often observed because of the distortion of octahedron. It is observed that the mode at 225 cm^{-1} disappears and intensity of 269 cm^{-1} mode decreases with increasing substitution from x=0.0 to x=0.3 can be attributed to the distortion of TiO_6 octahedra and hence the increase of orthorhombicity [13]. The modes at 536, 560 cm^{-1} and at 327 and 353 cm^{-1} tend to merge with each other upon substitution, which corresponds to the distortion in TiO_6 octahedra caused by A-site substitution in terms of change in the strength of Bi-O bond. Hence, the results obtained from Raman spectra correlate well with the XRD patterns.

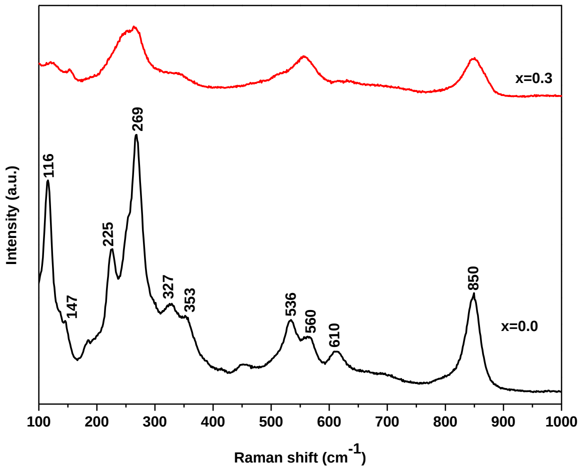

Fig. 2 Raman spectra for $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$ with x=0.0, 0.3

3.3 Morphological studies

The SEM micrographs of $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$, x=0.0, 0.3 are shown in Fig. 3. It is clearly visible that both the samples are composed of plate like grains. This peculiar plate like morphology of the grains is a distinctive feature of bismuth based layered structure compounds. Figure 3a, shows the relatively larger plate like structure for pure BIT sample in comparison to the substituted sample. It is evident from the Fig. 3b, that, with increasing Fe and Ni concentration the grain morphology becomes more anisotropic and the alignment of the grains gets hindered. There is no additional phase segregation has been observed in the system.

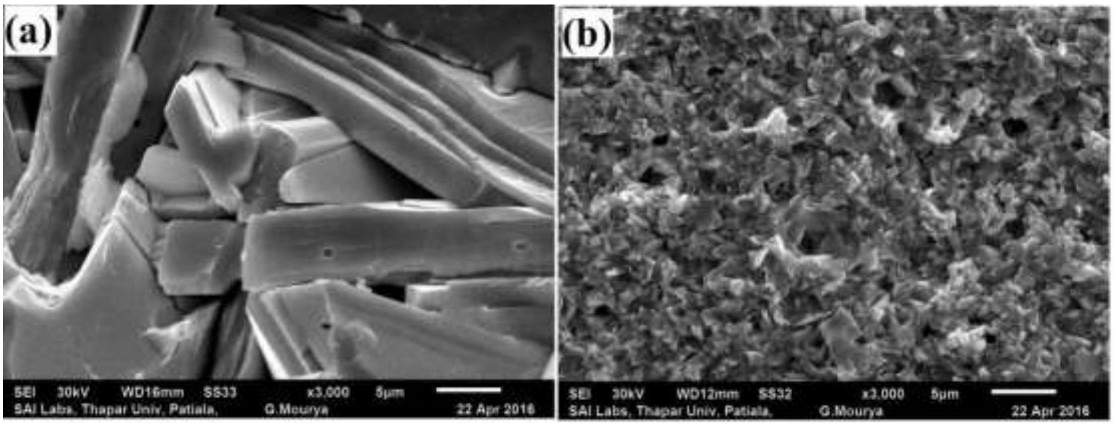

Fig. 3 SEM micrographs of $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$ with x=0.0, 0.3

IV. CONCLUSIONS

Polycrystalline ceramic samples of $Bi_{3.15}Nd_{0.85}(Ti_{3-x}Fe_{x/2}Ni_{x/2})O_{12}$ with x=0.0, 0.3 has been prepared by conventional solid state reaction method. X-ray diffraction pattern confirms the single phase formation for both the samples with orthorhombic unit cell. Partial substitutions by Fe and Ni ions increase the orthorombocity. The same results are confirmed by Raman spectroscopy which shows the suppression in Raman mode intensities. Morphological studies confirm the reduction in grain size with the evaluation of more randomly oriented grains. These ceramic samples may show enhanced multiferroic properties which are under investigation. These multiferroic materials may found useful application in designing cost-effective electromagnetic devices such as multiple state memories and data storage devices.

V. ACKNOWLEDGEMENTS

We would like to acknowledge Dr. Vishal Singh, Centre for Materials Science and Engineering for Raman spectroscopy measurements.

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