A novel approach to synthesize, studies of structural and electrical characteristic of \( \text{Bi(Ni}_{0.30}\text{Ti}_{0.30}\text{Fe}_{0.40})\text{O}_3 \) nanoceramics

Nitin Kumar, Alok Shukla*

Department of Physics, National Institute of Technology Mizoram, Aizawl-796012, India

*Corresponding author Email: alops.nitmz@gmail.com

Abstract. In this study, we report a novel approach to synthesize the \( \text{Bi(Ni}_{0.30}\text{Ti}_{0.30}\text{Fe}_{0.40})\text{O}_3 \) [arbitration BNTF30/40] nanoceramics by standard ceramic method at an ambient temperature of 1013 K. Carbonates and oxides powder were utilised as a raw materials in an appropriate stoichiometric amounts. X-ray diffraction pattern assigned that the BNTF30/40 sample presents a single phase of orthorhombic symmetry. The crystallite size obtain from X-ray data suggests the formation of BNTF30/40 nanoceramics in the range between 20 to 45 nm. Bulk density of the prepared pallets were measured and found to be more than 94 percent. The basic characterization tools have been used respectively with Field Emission Scanning Electron Microscope and Spectroscopy based techniques to obtain the correlation between surface morphology and electrical characteristic of specimen sample. Electrical characteristic of the as-synthesized material was studied in the experimental temperature range between RT to 623 K at different operated frequency (25 kHz - 500 kHz).

1. Introduction
Recently, perovskite based nanoceramics have been attracted broad attention because of its better unique properties and a wide range of applications in scientific and technological interests [1-2]. Also, nanoceramic materials contain various regardful features with bulk materials due to their morphological and particle size characteristics [3]. Multiferroic materials shows a simultaneous existence of ferroelectric and anti-ferromagnetic nature in the same phase. Among all multiferroics family, bismuth ferrite is an inorganic chemical compound having perovskite structure with unusual compound of bismuth, iron and oxygen. Bismuth ferrite belongs to a rhombohedrally distorted perovskite phase with physical characteristic of ferroelectric (Curie temperature ~1093K) and anti-ferromagnetic (Neel temperature ~643K) nature with R3c space group [4]. It’s also exhibits most promising lead-free piezoelectric and having multiferroic properties at room temperature. This studied compound is extremely active and having a pair of spectacular consequences due to its new kind of applications such as liquid crystal display, television, microwave, digital recording and satellite communications [5]. So far, pure bismuth ferrite nanoceramics powders have been synthesized by various techniques, such as spark plasma sintering [6], co-precipitation [7] hydrothermal [8], sol-gel methods [9]. Based on detailed literature survey and various successful endeavours has already been focused to synthesize the bismuth ferrite based novel compounds were reported recently, including lead free multiferroics and electronic materials obtained via solid-state route [10-13].

In this views, the unavailability of information and requirement, novel sample of nickel and titanium co-doped \( \text{Bi(Ni}_{0.30}\text{Ti}_{0.30}\text{Fe}_{0.40})\text{O}_3 \) [BNTF30/40] nanoceramics has been synthesized by standard ceramic method at an ambient temperature of 1013 K. However, in this study, structural, morphological and electrical features (dielectric constant and loss) of as-synthesized nanoceramics have been thoroughly investigated and the corresponding characteristic were reported.
2. Materials and experimental methods

In this study, all high-purity of chemical components (carbonate and oxide) and reagent materials were obtained from commercially available Sigma-Aldrich and Merck. These raw materials were used without any further purification. In this work, the (BiO)₂CO₃·H₂O, NiO, TiO₂, and Fe₂O₃ were used to prepare the specimen samples. The synthesis technique has performed by applying various steps; such as mechanical mixing (both dry and wet medium), high-temperature calcinations (1003 K for 6 h) in an air atmosphere and high-temperature sintering (1013 K for 8 h). For wet mixing methanol (Merck Ltd., India) was used as a solvent. The formation and structural phase of BNTF30/40 as-synthesized compound were analysed by using powder X-ray Diffractometer in Bragg angles between (20° ≤ 2θ ≤ 60°) ranges at a slow scan speed with the presence of CuKα₁ radiation. The surface morphology (grains distribution and grain size) of sintered pellets were recorded by Field Emission Scanning Electron Microscope (Carl Zeiss) at room temperature (298 K). For the electrical measurements of BNTF30/40 pellets were recorded with a function of frequency (wide range) at selected temperature variation by utilizing computer-interfaced Phase Sensitive Meter (PSM/1735).

3. Results and discussions

3.1. X-ray powder diffraction

Fig. 1 display X-ray powder diffraction pattern of Bi(Ni₀.₃/Ti₀.₇0Fe₀.₄0)O₃ nanoceramics sample at room temperature. The crystalline and structural phase were analyzed by using ‘POWDMULT’ software of XRD data. All major diffraction peaks were indexed and properly assigned (least-squares refinement) corresponding to the orthorhombic symmetry phase rather than rhombohedral symmetry of pure bismuth ferrite. The sub-refined observed and calculated inter planar spacing distance d [(Σd = d(observed) – d(calculated) = minimum deviation)] as well as its structural parameters are found to be as; a=19.8657Å, b=4.2715Å, c=7.2716Å with minimum standard deviation (SD = ±0.002). From the strong reflection peak (6 0 1) of XRD pattern, the crystallite size is found 38 nm by the broadening of reflection peaks. Additionally, the average crystallite size is found to be 31 nm of the said studied compound. The perovskite type BNTF 30/40 compound, tolerance factor (F₁) is defined in general by relation, F₁ = (〈R_{Bismuth}〉 + 〈R_{Oxygen}〉)/√2 〈(〈R_{Nickel + Titanium + Iron}〉 + 〈R_{Oxygen}〉); where, 〈R_{Bismuth}〉, 〈R_{Nickel + Titanium + Iron}〉 and 〈R_{Oxygen}〉 shows the ionic radii (average) of X, Y and Oxygen-site compounds respectively. The calculated value of tolerance factor is found 0.82 for as-synthesized compound, it’s clearly suggests the distortion from ideal perovskite symmetry.

3.2. Morphological studies

In order to confirm the chemical composition and stoichiometric proportion of as-synthesize BNTF 30/40 sintered pellets have been analysed by using Energy Dispersive X-ray spectroscopy (EDX) and recorded data is summarized in Fig.2 (a). The EDX analysis were performed in both (by selecting single particles and as well as an average mode), the experimental atomic balance confirms the existence of used elements of bismuth, nickel, titanium, iron and oxygen in the ratios of 14.04 %, 2.43 %, 2.64 %, 6.17 % and 74.73 %, respectively. In addition, Fig.2(b) shows the surface morphological investigations and elemental analysis of the BNTF30/40 nanoceramics, which has been carried out by utilizing the scanning electron microscope with field emission detector. The micrograph image clearly shows most of the grains are very dense, un-uniformly distributed and having submicron size throughout the surface of the sample. The dense structure along with small size of grains (nickel and titanium co-substituted) depicts much smaller grains as compared to the pure bismuth ferrite. The different shape and size of grain behaviour clearly indicates the presence of polycrystalline nature.
3.3. Electrical characteristic of Bi(Ni$_{0.30}$Ti$_{0.30}$Fe$_{0.40}$)O$_3$ nanoceramics

Electrical characteristic is one of the important role of ceramics. This analysis provides a vital info of the quantity and nature of polarizations, origin of defects and relaxation process. In this analysis, the experimental data has been recorded by the combination of phase sensitive meter setup, computer, and automatic furnace along with sample holder. The dielectric parameters (relative dielectric permittivity as well as tangent loss) of as-synthesized material were estimated using the general relation at a particular operated temperature with selected frequency [14]. Fig.3a and 3b (inset) illustrates the temperature versus frequency dependence (at some selected frequencies) of permittivity and tangent loss (tan δ) plots for BNTF30/40 nanoceramics. These dispersion curves (dielectric permittivity versus temperature at selected frequency) shows increasing trend on rising temperature for all frequency range (25 to 500 kHz). This increasing trend of dielectric permittivity for BNTF30/40 on increasing temperature may be explained with the electron–phonon interaction [15]. The observed numeric values of dielectric permittivity were 237 (25 kHz), 232 (500 kHz) at 298K, whereas at 623K the
values were 267 (25 kHz) and 244 (500 kHz). In addition, Fig. 3b (inset) exhibits, temperature dependence versus tangent loss spectrum at different operated frequency. The rate of dielectric loss factor is increases continuously at rising all operated temperatures with all respective frequencies. This nature (increasing trend of loss factor) arises may be due to the presence of scattering induced charge carriers and defects. Furthermore, the tangent loss factor values at 25 kHz and 500 kHz at 298 K and 623K were found to be 0.01, 0.005, 0.11 and 0.04 respectively. These observed results are much consistent with our earlier reported one [12].

Fig.3: Temperature dependent dielectric parameters: (a) Dielectric permittivity versus temperature (b) Dielectric loss versus temperature at several frequencies between 25 kHz and 500 kHz for Bi(Ni$_{0.30}$Ti$_{0.30}$Fe$_{0.40}$)O$_3$ nanoceramics

4. Conclusion
In this summary, multi-doped (nickel and titanium co-substituted) Bi(Ni$_{0.30}$Ti$_{0.30}$Fe$_{0.40}$)O$_3$ nanoceramics has been synthesized by the standard ceramic method at an ambient temperature of 1013 K. Its structural, morphological and electrical characteristics were analysed with the X-ray powder diffraction (XRPD), field emission scanning electron microscopy (FESEM) and phase sensitive meter (PSM) techniques respectively. The XRPD analysis suggests single-phase formation of orthorhombic phase symmetry. The crystallite size of some major peaks were obtained in the range of 20 to 45 nm. The measured bulk density of the prepared pallets was found to be 94 percent of theoretical one. The dielectric parameters (dielectric permittivity as well as dielectric loss) are strongly temperature and frequency dependent, and found to be decreasing order with rising frequencies. Thus, the study is the signature of to detect the structural phase transition in the material. Further work on these lines are in progress.

References
[1] Binner J and Vaidhyanathan B 2008 Processing of bulk nanostructured ceramics J. Eur. Ceram. Soc. 28 pp 1329–1339
[2] Mazaheri M, Valefi M, Hesabi Z R and Sadrezaaad S K 2009 Two-step sintering of nanocrystalline 8Y$_2$O$_3$ stabilized ZrO$_2$ synthesized by glycine nitrate process Ceram. Int. 35 pp 13–20
[3] Sobhani A and Niasari M S 2014 A new simple route for the preparation of nanosized copper selenides under different conditions Ceram. Int. 40 pp 8173–8182
[4] Wang J, Neaton J B, Zheng H, Nagarajan V, Ogale S B, Liu B, Viehland D, Vaithyanathan V, Schlom D G, Waghmare U V, Spaldin N A, Rabe K M, Wuttig M and Ramesh R 2003 Epitaxial BiFeO₃ multiferroic thin film heterostructures Science 299 pp 1719-1722

[5] Johari A 2011 Synthesis and characterization of bismuth ferrite Nnanoparticles, AKGEC International Journal of Technology 2 pp 17-20

[6] Dai Z and Akishige Y 2010 Electrical properties of multiferroic BiFeO₃ ceramics synthesized by spark plasma sintering Journal of Physics D: Applied Physics 43 pp 445403-445407

[7] Selbach S M, Tybell T, Einarsrud M A and Grande T 2007 Size- dependent properties of multiferroic BiFeO₃ nanoparticles Chemistry of Materials. 19 pp 6478-84

[8] Ha S H, Kim K S, Kim H G, Lee H G, Kang H W, Kim J S and Cheon Ch I 2010 Synthesis and characterization of multiferroic BiFeO₃ powders fabricated by hydrothermal method, Ceram. Int 36 pp 1365-1372

[9] Jiang Q, Nan C, Wang Y, Liu Y and Shen Z 2008 Synthesis and properties of multiferroic BiFeO₃ ceramics, Journal of Electroceramics 21 pp 690-693

[10] Kumar N, Shukla A, Behera C and Choudhary R N P 2016 Structural, Electrical and Magnetic Properties of Bi(Ni₀.₄₅Ti₀.₄₅Fe₀.₁)O₃ J. Alloys Comp. 688 pp 858-869

[11] Shukla A, Kumar N, Behera C and Choudhary R N P 2016 Structural and Electrical characteristics of (Co, Ti) modified BiFeO₃ J. Mater. Sci. Mater. Electron. 27 pp 7115-7123

[12] Shukla A, Kumar N, Behera C and Choudhary R N P 2016 Structural, Dielectric and Magnetic Characteristics of Bi(Ni₀.₂₅Ti₀.₂₅Fe₀.₅₀)O₃ Ceramics J. Mater. Sci. Mater. Electron. 27 pp 1209–1216

[13] Kumar N, Shukla A and Choudhary R N P 2017, Structural, electrical and magnetic characteristics of Ni/Ti modified BiFeO₃ lead free multiferroic material, J Mater Sci: Mater Electron. 27 pp 6673–6684

[14] Moulson A J and Herbert J M 2003 Electroceramics: Materials, Properties, Applications (USA: Wiley- Hoboken NJ)

[15] Kityk I V and Janusikat M M 2001 Nonstoichiometric defects and optical properties in LiNbO₃ J. Phys. Chem. B 105 (49) pp 12242-12248

Acknowledgment
The financial assistance received from SERB-DST under EMR Project (No. EMR/2015/002420) to one of the author AS is highly acknowledged.