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# Effect of secondary phases on the structure, morphology and dielectric properties of BiFeO<sub>3</sub> synthesized through solution combustion technique

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In the present work, pure phase Bismuth Ferrite (BiFeO<sub>3</sub>) was synthesized through the solution combustion technique using acetylacetone as chelating agent and urea as fuel. The samples calcined at various temperatures were studied to understand the formation of secondary phases along with pure BiFeO<sub>3</sub> and the effect of these secondary phases on the structure, morphology and dielectric properties of BiFeO<sub>3</sub>. Further, the crystallographic parameters were calculated using Rietveld refinement. XRD and SEM analysis reveals that at higher calcinations temperatures the secondary phases disappear (12.53% to 0.07%) and the grains become uniformly distributed over the large area. While FTIR spectra reveals that highly crystalline BiFeO<sub>3</sub> obtained at higher temperature. Dielectric properties were found to improve in pure bismuth ferrite as compared to the samples with secondary phases.

Key words: Combustion synthesis, X-ray diffraction, Secondary phase, Dielectric properties.

#### Introduction

Multiferroics is a new class of materials which exhibit more than one of ferroelastic, ferromagnetic and ferroelectric properties simultaneously in a specific temperature range [1]. According to the literature, the single as well as double perovskite based multiferroics are rarely present in the nature [2]. Much attention has been focused on the bismuth ferrite (BiFeO<sub>3</sub>) because it represents the correlation between spin of (anti) ferromagnetic material and charge of (ferro) electric material at room temperature. This is one of the unique concepts that provide fruitful applications in the development of multiple state memory, spintronics and sensor devices [3].

BiFeO<sub>3</sub> shows rhombohedral distorted perovskite structure (a = b = 5.578 Å, c = 13.868 Å) and R3c space group at room temperature [4].It possesses high Curie temperature T<sub>C</sub> = 1103 K and G type spin ordering Neel temperature T<sub>N</sub> = 643 K [5]. The precise control of temperature and stoichiometry are the key parameters in the synthesis of pure BiFeO<sub>3</sub> [6]. The Bi rich and/or Fe rich contents lead to the formation of Bi<sub>25</sub>FeO<sub>3</sub> and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>3</sub> along with pure BiFeO<sub>3</sub>, respectively. The best results would be obtained by selecting the proper ratio of these contents. In addition to that, the BiFeO<sub>3</sub> is metastable between 447 °C to 767 °C and above this temperature pure BiFeO<sub>3</sub> phase come into the existence, which means that the temperature stability range is very narrow. Presence of these secondary phases result in the high leakage current due to electrical instability and exaggerated grain growth, which causes detrimental effects on dielectric properties of the ceramics [7].

To overcome this problem, some alternate approaches are desired. Various techniques have been proposed by many researchers to remove unwanted phases, such as leaching with diluted HNO<sub>3</sub> [8], use of effective doping [9], microwave-hydrothermal process [10], specific stoichiometry e.g. addition of Bi excess or Bi rich flux [11] and make a solid solution of BiFeO<sub>3</sub>-ABO<sub>3</sub> which helps to even improve the resistivity [12]. However, the solution combustion technique provides an easy and convenient route for the preparation of multiferroics. It provides quasi atomic dispersion of the cationic component in the liquid precursors facilitates the synthesis of crystallized powder with small particle size and with high purity at low temperatures [13]. The study of BiFeO<sub>3</sub> synthesized using solution based combustion with urea as fuel is very rare in the literature. Urea has low reducing power of +6 and evolved a lesser number of moles of gases [14]. It is chosen as fuel because it occupies the center stage among all fuels used in combustion synthesis due to its easy availability and high exothermicity [15]. Hence, in this paper, we report, the structural and chemical analysis of BiFeO<sub>3</sub> synthesized by solution based combustion synthesis using urea and also discuss the impact of secondary phases on the structure, morphology and dielectric properties of the as synthesized material i.e. BiFeO<sub>3</sub>.

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# Experimental

#### **Synthesis**

BiFeO<sub>3</sub> was synthesized by solution based combustion method. High purity metal nitrates, 2-methoxyethanol, acetylacetone and urea were used as a starting material. To avoid precipitation by the reaction of bismuth nitrate and water, it was first dissolved in 2-methoxyethanol to form bismuth complex, while iron (III) nitrate was dissolved in 2-methoxyethanol and small amount of acetylacetone. The experimental utilization of acetylacetone was explained in our previous studies [16]. For the bismuth precursor solution, an excess of Bi and small amount of La nitrate were taken in the fabrication of BiFeO3 to compensate the evaporation of bismuth oxide during the thermal treatment. Appropriate quantities of Fe and Bi precursor taken together with the addition of urea were mixed thoroughly and homogenized by constant stirring. The final mixture was stirred for 1 hour and then, it was kept in a muffle furnace at 500 °C leading to evaporation followed by combustion process which resulted in the emission of flame. The reaction lasted for 5 min producing brown flakes and finally converted into the volcano-ash. These flakes were then crushed and calcined at different temperature ranging from 650 °C to 800 °C. Then all the calcined powders was pressed into pellets of 10 mm diameter and sintered at 820 °C for 3 hrs.

 $Bi(NO_3)_3 + Fe(NO_3)_3 + 5CH_4N_2O = BiFeO_3 + 5CO_2 + 10H_2O + 8N_2$ 

## Characterization

The DTA/TGA analysis of the starting precursor mixture was performed on the Simultaneous Thermal Analyzer (Melter Toledo). The calcined sample was characterized for the identification of the different phases in BFO by using X-ray diffractometer (Bruker D8 Advance) equipped with CuK $\alpha$  ( $\lambda = 1.54$  Å) radiation. FTIR Spectroscopy (380 Thermo Fisher Scientific) was used to confirm the formation of the BiFeO<sub>3</sub> by the solution combustion methods. The surface morphology of the samples was studied through scanning electron microscopy (JEOL-JSM 6390). For developing the electrical contact, gold was coated on the surfaces of the pellets by sputtering technique. The dielectric constant and the dissipation factor of the samples were measured using an Alpha high resolution dielectric impedance analyzer using Novo control in the frequency range from 1Hz to 1MHz at room temperature.

# **Results and Discussion**

# Thermal analysis (DTA-TGA)

The differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) curves were used to investigate the mechanistic approach for the phase



Fig. 1. The DTA/TGA curve with temperature.

formation during thermal decomposition. Figure 1 depicts TGA/DTA curve of Fe  $(NO_3)_3 \cdot 9H_2O$  : Bi  $(NO_3)_3 \cdot 5H_2O$  of 1 : 1 ratio mixed with solvents and urea as fuel. The mass variation was observed between 150°C to 600°C. The sharp exothermic peak is observed at 210 °C which was accompanied by weight loss of around 71% due to the decomposition of urea between 150 °C-300 °C and the vaporization of water between 25 °C-150 °C. The urea decomposes into carbon-dioxides and N<sub>2</sub>. In the combustion process, a large amount of heat is evolved and this is utilized for carrying out for further reaction. The very small weight loss between 400 °C-500 °C is observed due to the decomposition of the metal nitrate by the following reaction:

$$2M(NO_3)_3 \rightarrow M_2O_3 + 6NO_3 + 1.5O_2$$

No further thermal events were observed after 500  $^{\circ}$ C to 1000  $^{\circ}$ C, indicating that the reaction between the precursors is completed up to 500  $^{\circ}$ C. The powder was chosen for thermal treatment at temperatures above 650  $^{\circ}$ C for minimization of the secondary phases.

#### **XRD** analysis

XRD patterns of BiFeO<sub>3</sub> powders calcined at different temperatures for 3 hrs are presented in Figure 2(a). As shown in XRD Figure 2(b), the traces of secondary phases such as  $Bi_2Fe_4O_9$  (JCPDS file no. 01-074-1098) and  $Bi_{25}FeO_{39}$  (JCPDS file no. 01-078-1543) apart from the pure BFO phase were observed at lower temperature. Bernado *et al* [17] have also reported that, the presence of these phases at the lower calcinations temperature. Moreover, pure BiFeO<sub>3</sub> is not stable and decomposes into  $Bi_2Fe_4O_9$  and  $Bi_{25}FeO_{39}$  phase according to reaction:

 $49BiFeO_3 \rightarrow 12Bi2Fe_4O_9 + Bi_{25}FeO_{39}$ 

Thus, the pure  $BiFeO_3$  is stable at temperatures above 767 °C. Due to small differences in Gibbs free energy



**Fig. 2.** (a). X-ray diffraction patterns of  $BiFeO_3$  at different Calcined temperature. (b) Magnified XRD peaks with secondary phases.

between the BiFeO<sub>3</sub> and the decomposition products, even minor variation in temperature may shift the equilibrium of the BiFeO<sub>3</sub> formation/ decomposition according to reactions:

 $12Bi_{2}Fe_{4}O_{9} + Bi_{25}FeO_{39} \leftrightarrow 49BiFeO_{3}$ 

As the calcined temperature was increased, the intensity of all the peaks corresponds to these secondary phases decreases. At calcination temperature 800 °C, the sample displayed reflection from the planes corresponding to the rhombohedral structure of BiFeO3 (JCPDS file no. 01-086-1518). All the peaks could be indexed in the rhombohedral distorted perovskite structure with the space group R3C. Only very weak peaks (negligible) corresponding to Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> phase are observed and the major phase becomes more prominent with the increase in calcination temperature. The Rietveld refinement technique was used to investigate the crystal structure of BiFeO<sub>3</sub> powder obtained by SC route and calcined at 800 °C as shown in Figure 3. The Figure 4 represents the unit cell of BiFeO3. The crystallite size and lattice strain of the samples was estimated by using Williamson-Hall



Fig. 3. The Rietveld refinement using Fullprof suit program (2.05) for  $BiFeO_3$  calcined at 800 °C.



**Fig. 4.** Unit cell of BiFeO<sub>3</sub>.

method [18]. According to this method, the total broadening  $\beta_t$  is a sum of broadening due to crystalline size ( $\beta_{size}$ ) and that due to lattice strain ( $\beta_{strain}$ ) present in the material.

$$\beta_{t} = \beta_{size} + \beta_{starin} \tag{1}$$

Where,  $\beta_{\text{size}} = \frac{k\lambda}{D\cos\theta}$  (from Debye-Sherrer's formula) and strain ( $\epsilon$ ). Therefore the modified equation is

$$\beta_t = \frac{k\lambda}{D\cos\theta} + 4\varepsilon \tan\theta \tag{2}$$

After the rearrangement, the equation (2) has been plotted between  $\beta_t^*\cos\theta$  and  $4\sin\theta$ . The crystallite size was estimated by intercept on the y axis and the strain



Fig. 5. Williamson-Hall plots of  $BiFeO_3$  calcined at various temperatures.

through slope line as shown in the Figure 5. All the parameters obtained by using XRD peaks data are tabulated in the Table I.

# **FTIR** analysis

FTIR spectra of BiFeO<sub>3</sub> derived from a solution combustion synthesis are shown in Figure 6. The strong absorption peaks between 400-600 cm<sup>-1</sup> are attributed to the presence of Fe-O stretching and bending vibration which is characteristic of octahedral FeO groups that confirmed the formation of perovskite structure. The peak (indicated by \*) at 810 cm<sup>-1</sup> of Fe-O can be attributed to the formation of highly crystalline BiFeO<sub>3</sub> phase, which becomes stronger with increase in calcination temperature [19]. The bands between 1350-1410 cm<sup>-1</sup> are due to the presence of traces of trapped nitrates in the BiFeO<sub>3</sub> [20]. It is clearly evident from the

Table 1. XRD parameters.



Fig. 6. FTIR of BiFeO<sub>3</sub> calcined at various temperatures.

Figure 6 that the intensity of these bands decreases with increase in calcinations temperature indicating the evaporation of nitrates. The bands between 3000-3600 cm<sup>-1</sup> corresponds to the antisymmetric and symmetric stretching of H<sub>2</sub>O and OH bond groups while the peak at 1630 cm<sup>-1</sup> corresponds to the bending vibrations of H<sub>2</sub>O molecule, which could be attributed to the absortion of water from the environment [10], [21]. Residual water and hydroxyl groups are usually detected in the prepared samples, so the further heat treatment is necessary for their elimination.

# SEM analysis

Figure 7(a) to (d) shows the SEM images of the pure and secondary phases influenced BiFeO<sub>3</sub> pellets sintered at 820 °C. The obtained image in the Figure 7(a) show that the sample exists predominantly plate like structure which confirms the presence of impurities/secondary phases like Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> [22]. The secondary phase is irregular plate like and distributed thoroughly. This suggests that the growth of the secondary phase is mostly at the lower temperature which is also confirmed by the XRD and TGA/DTA results. Also the secondary phase contribution in BFO could affect the porosity. The grain

$a = b = 5.5782$ Å, $c = 13.869$ Å, $V = 373.788$ Å, GOF = 2.740, $R_{Bragg} = 3.492$ , $R_{profile} = 7.035$					
Atomic positions					
		Х	Y	Z	Bond Length (Å)
6	Bi	0.0000	0.0000	-0.01035	B-O 2.4764
6	Fe	0.0000	0.0000	0.20823	Fe-O 2.0447
18	0	0.44280	0.01870	0.95200	O-O 3.0151
Crystalline size (D) and Strain ( $\varepsilon \times 10-5$ )				Phase percentage of BFO	
700 °C		97.293		8.9841	87.41%
750 °C		105.109		4.655	92%
800 °C		141.769		3.41393	99.93%



**Fig. 7.** The SEM images of BiFeO<sub>3</sub> with secondary phase  $Bi_2Fe_4O_9$  (plate like structure) and (b)-(d) Calcined samples at various temperatures and sintered at 820 °C with their respective particle size distribution curve.

size was found to be inhomogeneous. The sample sintered at 820 °C was found to posses higher density with homogeneous grains size distribution and well define shape. Also triplet junctions are observed. The grains become enlarged (1.06  $\mu$ m, 1.49  $\mu$ m and 1.84  $\mu$ m) with the increase in the calcination temperature, as shown in Figure 7(b) to (d).

#### **Dielectric properties**

Figure 8 shows the frequency dependence of dielectric constant at room temperature for sintered pellets at 820 °C of as synthesized bismuth ferrite. Four types of polarizations the interfacial (P<sub>int</sub>), dipolar (P<sub>d</sub>), ionic (P<sub>i</sub>) and an electronic (Pel) polarization contributes to the dielectric constant of material. At low frequencies, it is the dipolar (P<sub>d</sub>) and interfacial (P<sub>int</sub>) polarizations that contribute to the dielectric constant and it is impossible for dipolar polarization  $(P_d)$  to follow the electric field in the high frequency region. However, at higher frequencies the electronic polarization (Pel) is effective and contribution due to dipolar (P<sub>d</sub>) becomes insignificant [23]. Therefore, the dielectric constant is smaller at higher frequencies as all polarizations do not contribute at higher frequencies. From the Figure 8, it is clearly observed that the presence of secondary phases also contributes to the dielectric constant. The materials possessing secondary phases contributed materials show no dispersion characteristic as compared to materials with pure phase. Also the



**Fig. 8.** Room temperature dielectric constant vs frequencies of pure and secondary phases influnced BiFeO<sub>3</sub>.



**Fig. 9.** Room temperature dielectric losses vs frequencies of pure and secondary phases influenced BiFeO<sub>3</sub>.

value of dielectric constant is found to be lower for BFO with secondary phases than that of pure BFO. The obtained higher value of the dielectric constant for pure BFO at 1 KHz is 68, which is higher as compare to that reported previously [24]. The recent results are suggested that the secondary phases play a crucial role in altering dielectric properties. Mainly, their incorporation results in charge imbalance which is directly related to the defects in the sample. Therefore, large number of oxygen vacancies will be formed that lead to increase the conductivity of the material. The similar results were observed by Cheng *et al* [25] and also, which are the cause of high leakage current in the sample [26].

Figure 9 shows the variation of dielectric loss  $tan(\delta)$ as a function of frequency (Hz) at room temperature. It is observed that  $tan(\delta)$  decreases with increase in frequency in pure BFO. The low losses at higher frequencies are generally due to the higher resistivity which indicates low leakage current. It is also observed that the secondary phases influenced materials the value of  $tan(\delta)$  increases monotonically at higher frequency. This may be due to the consequences of inductance component in the measurement system [27] The shape and density of secondary phases could be the causes behind the high dielectric loss in these materials.

# Conclusions

Multiferroic bismuth ferrite is synthesized successfully using solution based combustion synthesis with urea as fuel. It was found that urea decomposes at low temperatures and the synthesis is completed at 200 °C and the secondary phases are eliminated by calcination at 800 °C for 3 hours. The FTIR peak at 810 cm<sup>-1</sup> confirms the formation of highly crystalline BFO phase. SEM images show that the as prepared BiFeO<sub>3</sub> has uniform grain size distribution. The traces of secondary phases and density alter the dielectric properties. The as-synthesized pure ceramics exhibit good dielectric properties and have great potential for device applications.

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# References

- 1. Y.A. Chaudhari, C.M. Mahajan, et al., Ceramics–Silikáty 58 [1] (2014) 65-69.
- 2. A. Sharan, J. Lettieri, et al., Physical Review B 69 [21] (2004) 214109.
- 3. S. Srivastava and P. Athe, International Journal of Material Science Innovations (6) [1] (2013) 330-355.
- 4. F. Kubel and H. Schmid, Acta Crystallographica Section B: Structural Science 46 [6] (1990) 698-702.

- 5. G. Smolenski and I. Chupis, Soviet Physics Uspekhi 25 [7] (1982) 475.
- 6. R. Palai, R. Katiyar, et al., Physical Review B 77 [1] (2008) 014110.
- 7. K.-W. Tay, Y.-P. Fu, et al., Ceramics International 36 [4] (2010) 1239-1244.
- 8. S. Shetty, V. Palkar, et al., Pramana 58 [5-6] (2002) 1027-1030.
- 9. C. Chen, C. YU, et al., Journal of Ceramic Processing Research 15 [6] (2014) 424-427.
- G. Biasotto, A. Simoes, et al., Materials Research Bulletin 46 [12] (2011) 2543-2547.
- A. Lahmar, K. Zhao, et al., Solid State Ionics 202 [1] (2011) 1-5.
- R. Pandu, K. Yadav, et al., Indian Journal of Engineering and Materials Sciences 17 [6] (2010) 481-485.
- O. Subohi, G. Kumar, et al., Optik-International Journal for Light and Electron Optics 125 [2] (2014) 820-823.
- 14. R. Lenka, T. Mahata, et al., Journal of Alloys and Compounds 466 [1] (2008) 326-329.
- O. Subohi, G. Kumar, et al., Physica B: Condensed Matter 407 [18] (2012) 3813-3817.
- P. Jain and S. Srivastava, Digest Journal of Nanomaterials and Biostructures 10 [1] 141-147.
- M. Bernardo, Boletín de la Sociedad Española de Cerámica y Vidrio 53 [1] (2014) 1-14.
- 18. V. Mote, Y. Purushotham, et al., Journal of Theoretical and Applied Physics 6 [1] (2012) 1-8.
- 19. V. Annapu Reddy, N. Pathak, et al., Journal of Alloys and Compounds 543 (2012) 206-212.
- 20. A. Zalesskii, A. Frolov, et al., Physics of the Solid State 45 [1] (2003) 141-145.
- 21. Z. Gabbasova, M. Kuz'min, et al., Physics Letters A 158 [9] (1991) 491-498.
- 22. J.-T. Han, Y.-H. Huang, et al., Journal of crystal growth 294 [2] (2006) 469-473.
- 23. S. Barbar, S. Jangid, et al., Ceramics International 39 [5] (2013) 5359-5363.
- 24. A. Srivastava, H. Singh, et al., Journal of Alloys and Compounds 552 (2013) 336-344.
- C. Chen, Z. Tang, et al., Journal of Ceramic Processing Research 13 [2] (2012) 184-187.
- 26. Z. Cheng, A. Li, et al., Journal of Applied Physics 103 [7] (2008) 07E507-507E507-503.
- 27. T. Tohma, H. Masumoto, et al., Materials Transactions 43 [11] (2002) 2880-2884.