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Tailoring Combustion Method Synthesized Bismuth Ferrite Nanomaterials by varying Fuel and Fuel to Oxidizer Ratio

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ABSTRACT: The effect of fuel and 'fuel/oxidant' ratio on the characteristic properties of combustion synthesized Bismuth Ferrite ($BiFeO_3$) nanomaterials was investigated. The effects of different fuels keeping stoichiometric 'fuel/oxidant' ratio and then choosing a fuel with different 'fuel/oxidant' ratio on features of $BiFeO_3$ nanocrystallites were explored. The XRD investigation confirms formation of nanocrystalline $BiFeO_3$ and the crystalline size of $BiFeO_3$ changes with varying fuels and 'fuel/oxidant' ratio. The crystalline size of $BiFeO_3$ increases remarkably with increase of φ from 0.8 to 2.9 and well supported by reaction parameters. Also relation of parameters of unit cell and shift in diffraction peaks has been investigated in context with varying characteristics of fuels used.

Keywords: Combustion method, 'Fuel/oxidizer' ratio**,** multiferroicity, nanocrystalline, stoichiometric ratio.

I. INTRODUCTION

Combustion Method has emerged as an encouraging route, for synthesizing transition metal oxides in nanocrystalline form. The technologically useful magnetic, mechanical, optical, electrical, catalytic properties of metal oxides and ferroelectric, piezoelectric, ferromagnetic, ferrimagnetic, and multiferroic properties of complex oxides in particular have engrossed the attention of material scientists [1, 2]. Tailoring materials with desired configuration, and properties for accurate uses is the foremost task faced by researchers. A number of research studies confirmed the appearance of the metastable phases of material in their nanostate [3]. Many prevalent preparation techniques viz; hydrothermal synthesis, chemical vapour deposition, sol gel method, sputtering are being used for synthesizing nanocrystalline materials. The capability of combustion method lies in producing nano sized crystalline especially of oxides at a lesser temperatures in surprisingly small time make it peculiar amid the prevailing solution chemistry methods [3].

A fuel is a substance that can burn and the oxidant is a material that offers oxygen for burning. A significant amount of heat can be created by mixing oxidizer and fuel in suitable proportion due to exothermic chemical reaction. The properties of fuel and the fuel/oxidizer ratio affects the reaction parameters like heat of combustion and gas evolution and these parameters play decisive role in shaping characteristic properties of products [4]. The surface area, morphology and particle size of the products of combustion synthesis are affected by the amount of gases escaping. Larger release of gases hampers particle growth. Mainly metal nitrates and appropriate fuel are used for combustion synthesis of oxides. The 'fuel/oxidizer' ratio is among the most significant factors influencing the attributes of synthesized powders obtained via combustion. Thermodynamic modelling shows that with increase of the 'fuel/oxidant' ratio increases gas generation.

The materials exhibiting two or more of the ferroic orders, viz; ferromagnetic, ferroelectric, ferroelastic along with mutual coupling among them belongs to a class of multiferroics [5]. Bismuth Ferrite ($BiFeO_3$) is taken as the model multiferroic having rhombohedral perovskite structure. Bismuth Ferrite displays multiferroicity at room temperature with Neel temperature and Curie temperature ~ 820°C and 370°C respectively and also have capability to be tailored in regard to different structures and properties [6, 7]. The undertaken study comprises of synthesis of Bismuth ferrite using combustion method without using solvent. The nitrates of metal act as oxidizers and in first set different fuels were taken in stoichiometric ratio, in other set one fuel having different fuel to oxidizer ratio were taken. The mathematical calculations for fuel to oxidizer ratio were done based on method evolved [8]. The simplicity, cost effectiveness and the wide applicability range of combustion method technique make it economically attractive. The possibility to attain products in the desired size and shape along with self-purifying attribute involved are advantages of this method.

II. MATERIALS AND METHOD

A. Materials Used

(i) Using different fuels: In preparation of $BiFeO_3$, the suitable quantities of Bismuth nitrate ($Bi(NO_3)_3.5H_2O$), ferric nitrate ($Fe(NO_3)_3.9H_2O$), and fuel citric acid ($C_6H_8O_7$), glycine (NH_2CH_2COOH) and polyvinyl alcohol (C_2H_4O–) one fuel at a time were used. The synthesis was performed at stoichiometric oxidants to fuel ratio.

(ii) Using different oxidant/fuel ratio: In this case for preparing $BiFeO_3$, the appropriate amounts of Bismuth nitrate, ferric nitrate, and glycine (NH_2CH_2COOH) were used. Three samples of $BiFeO_3$ were synthesized having 'oxidant/fuel' ratio values as fuel lean (1: 0.8), the stoichiometric (1:1) and fuel rich (1: 2.9). Under equilibrium condition the combustion reaction can be put as given by equation (1):

$$3Bi(NO_3)_3.5H_2O + 3Fe(NO_3)_3.9H_2O + (10\varphi)\ NH_2CH_2COOH + 22.5(\varphi-1)\ O_2\ (g) \rightarrow 3BiFeO_3 + (20\ \varphi)\ CO_2\ (g) + (42+25\ \varphi)\ H_2O\ (g) + (9+5\varphi)\ N_2(g) \quad (1)$$

Where φ is the multiplication factor and have values φ < 1 for fuel lean, φ =1 for stoichiometric and φ > 1 for fuel rich state.

B. Synthesis Method

The reactants comprising of the oxidants and the fuel were taken in the requisite molar ratios and mixed while heating at ≈ 80 °C on a hot plate. The water of crystallization of the nitrates act as solvent and a clear solution gets formed which on further heating results in viscous liquid. At this stage the temperature was raised to 150°C resulting into formation of a gel. This temperature slowly eliminates the water from gel. During this process we observed boiling, frothing, fumes, smoldering, flaming and auto-ignition takes place resulting in the fast evolution of huge volume of gases and powders in the form of voluminous foam are obtained. The powders were grinded in pestle mortar and calcination was done at 600°C for 2 hours to attain fine crystalline form of powders.

C. Characterization

The X-ray diffractometer of Panalytical X'Pert Pro having copper source ($K_{\alpha 1}$ =1.5406Å) was used to determine the product phase compositions. Scherrer formula [9] as given by Eqn. (2) was used to calculate the average crystalline size from XRD patterns by means of the three highest peaks

$$d = \frac{0.9\,\lambda}{b(\cos\theta)} \quad (2)$$

where d is the crystalline size in nm, b is the full width at half maxima in radian, λ is the wavelength = 0.15406 nm, θ is the Bragg angle in degree.

The unit cell of the perovskite cube can also be designated in a hexagonal frame of reference, where the c-axis of hexagonal system lies parallel to the diagonal of cube of perovskite system [6]. The hexagonal unit cell Eqn. (3) was used to determine cell parameters and Eqn. (4) was used to calculate the volume V of the unit cell

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (3)$$

$$V = \frac{\sqrt{3}}{2}a^2c \quad (4)$$

where (h k l) represents miller indices of a plane, a, c represents unit cell's lattice parameters, d is interplanar spacing.

Propellant chemistry has been used to calculate the parameters related with the combustion reaction like number of moles of fuel used per mole of Bismuth Ferrite, Number of moles of gases released per unit mole of Bismuth Ferrite [8].

The Fourier Transform Infrared (FTIR) spectrum for $BiFeO_3$ with stoichiometric 'oxidant/fuel' ratio was obtained.

III. RESULTS AND DISCUSSION

A. X-Ray Diffraction

The X-Ray Diffraction patterns of synthesized Bismuth Ferrite are as shown in Fig. 1 and 2.

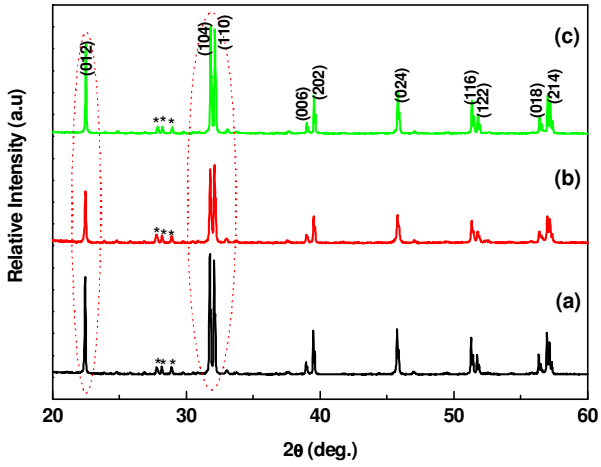


Fig. 1. X-Ray Diffraction pattern of Bismuth Ferrite ($BiFeO_3$) with stoichiometric 'fuel/oxidizer' ratio and varying fuel (a) Glycine, (b) Polyvinyl alcohol (c) Citric Acid.

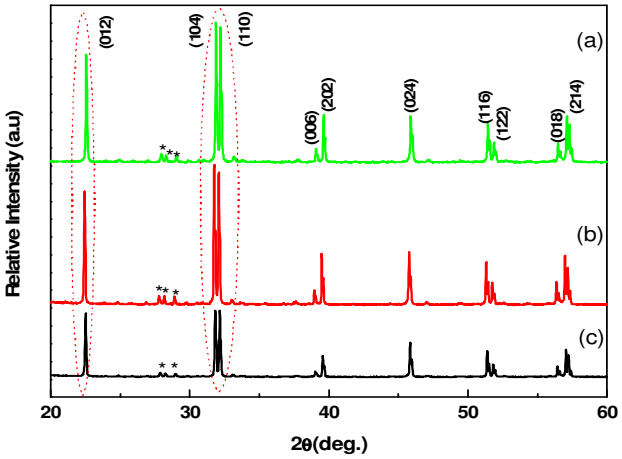
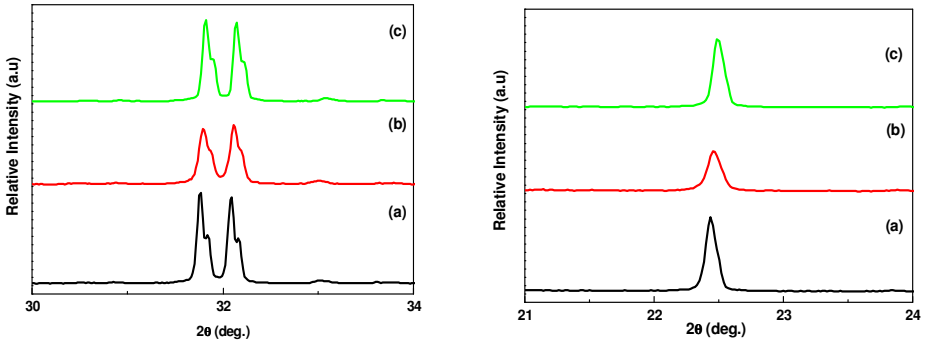
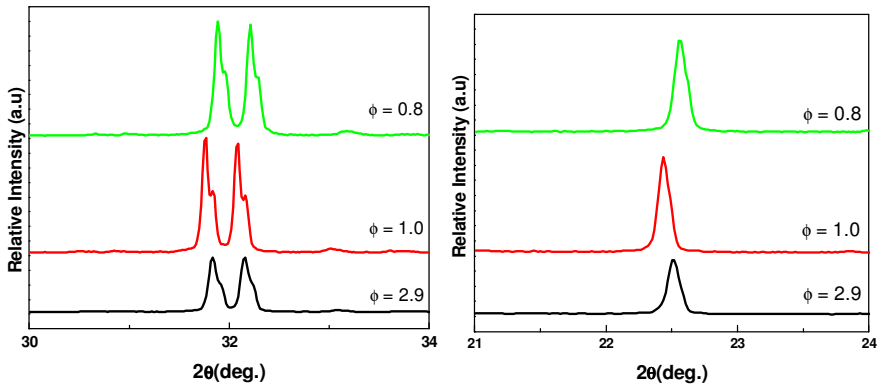


Fig. 2. X-Ray Diffraction pattern of $BiFeO_3$ with fuel glycine and 'fuel/oxidizer' ratio (φ) (a) φ =0.8, (b) φ =1.0, (c) φ = 2.9



(a) (b)

Fig. 3. Magnified view of the XRD peaks around 3(a) 2θ = 32°; 3(b) 2θ = 22.5° by varying fuel (a) Glycine (b) Polyvinyl Alcohol (c) Citric Acid.



(a) (b)

Fig. 4. Magnified view of the XRD peaks around 4(a) 2θ=32°; 4(b) 2θ = 22.5° with fuel to oxidizer ratio (φ) (a) φ = 0.8, (b) φ =1.0, (c) φ = 2.9.

The observed peaks of the powders matches well with the values of miller indices (h k l) of the representative peaks in File No. 86-1518 of JCPDS data (1998). It discloses that at room temperature the synthesized bismuth ferrite powders own rhombohedral perovskite structure with space group R3c [10].

The asterisks (*) represents traces of secondary phase Mullite bismuth ferrite ($Bi_2Fe_4O_9$).

The characteristic peaks of $BiFeO_3$ become sharper and stronger for φ= 0.8 and 1.0 in comparison with φ = 2.9, indicating that $BiFeO_3$ powders are better crystallized for fuel to oxidizer ratio around stoichiometric composition.

Enlarged view of the diffraction peaks for (012) and (104), (110) reflections around 2θ = 22.5° and 32° is shown in Fig. 3 and 4. Yu *et al.,* [11] reported that shifting of XRD peaks towards lower angles correspond to an increase in lattice parameters. The trend in slight shift of diffraction peaks signposts change in parameters of lattice which in turn creates distortion in the rhombohedral structure [12] without transforming the structure of $BiFeO_3$.

Furthermore the maxima of diffraction angles for different fuels descend in the order from citric acid, polyvinyl alcohol to glycine. It shows that parameters of the unit cell witness the decrease in same order.

B. Fuel Parameters

Decomposition Temperature (°C), Total moles of gases released per unit mole of Bismuth Ferrite and physical appearance of chemical reaction taking place by varying fuels has been summarized in Table 1.

The studies has shown that vigorous combustion reaction results due to fuel containing amine ($–NH_2$) ligand with iron nitrate [13]. The dynamic highly flaming type reaction for fuel glycine might be due to presence of amine ligand.

C. Crystallite Size and Cell Parameters

The formulation of hexagonal unit cell were used to calculate various parameters of unit cell for all $BiFeO_3$ samples and summarized in Table 2 and 3.

Table 1: The reaction parameters of fuels for synthesis of Bismuth Ferrite samples.

Name of Fuel	Decomposition Temperature (°C)	Total moles of gases released per unit mole of Bismuth Ferrite	Physical appearance of chemical reaction
Polyvinyl alcohol ($C_2H_4O–$)	231	29	Smouldering
Citric Acid ($C_6H_8O_7$)	175	33.7	Flaming
Glycine (NH_2CH_2COOH)	262	34.3	Highly Flaming

Table 2: The parameters of unit cell for $BiFeO_3$ samples.

Fuel	Lattice Parameter a (Å)	Lattice Parameter c (Å)	Volume of unit cell V $(Å)^3$	Crystallite Size (nm)
Polyvinyl alcohol	5.57082	13.8503	372.2	91
Citric Acid	5.56642	13.8394	371.4	105
Glycine	5.57776	13.8608	373.4	43

Table 3: The parameters of unit cell for all $BiFeO_3$ samples (Fuel Glycine).

Fuel to oxidizer ratio (φ)	Lattice Parameter a (Å)	Lattice Parameter c (Å)	Volume of unit cell V $(Å)^3$	Crystallite Size (nm)
0.8	5.56426	13.8297	370.8	38.6
1.0	5.57776	13.8608	373.4	40.6
2.9	5.56560	13.7963	370.1	64.2

The unit cell volume and parameters of bismuth ferrite changes by varying fuel. Maximum values of parameters of unit cell were observed for glycine fuel then for polyvinyl alcohol and least for citric acid and this trend corroborates with X-Ray Diffraction studies. The decrease in decomposition temperature of fuel and observed decrease in cell parameters follows same trend. The tendency of decrease in parameters of unit cell might owe to decrease in decomposition temperature by varying fuel which in turn can tailor the characteristics of the material. The crystallite size of $BiFeO_3$ with polyvinyl alcohol, citric acid and Glycine (stoichiometric 'fuel/oxidizer' ratio) was found to be ~ 91 nm, 105 nm and 43 nm respectively. This observation can be attributed to the fact that due to more moles of gases released per unit mole of $BiFeO_3$ for glycine the growth of crystallites gets hindered.

The crystallite size of $BiFeO_3$ (φ = 0.8, 1.0, 2.9) was found to be ~ 38.6 nm, 40.6 nm and 64.2 nm for φ = 0.8, 1.0, 2.9 respectively. This observation can be endorsed to the fact that by increasing 'fuel/oxidizer ratio' (φ), more fuel is available so the flame temperature increases which in turn increases crystallite size [14].

It was observed that with increase or decrease of fuel to oxidizer ratio (φ) than stoichiometric ratio, cell parameters and unit cell volume decreases which indicates contraction of unit cell and hence causes distortion in structure.

D. Fourier Transform Infra-red (FTIR) Spectra

FTIR spectra with wave number ranges from 400–1600 cm^{-1} for $BiFeO_3$ (φ = 1.0) nanopowder is as shown in Fig. 5.

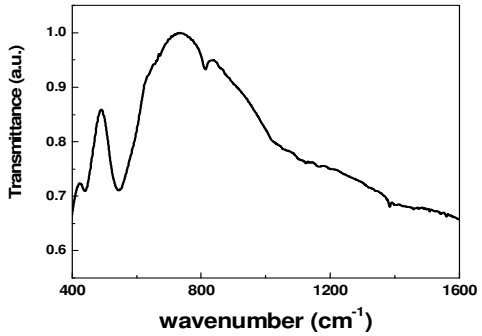


Fig. 5. FTIR spectra of $BiFeO_3$ with stoichiometric 'fuel/oxidizer' ratio.

The bands between 700 cm^{-1} and 400 cm^{-1} were mainly ascribed to the characteristic metal oxide bonds of perovskite structure of $BiFeO_3$ which indicates the presence of a highly crystalline BFO phase [15]. The band at around 1380 cm^{-1} owes to the presence of trapped nitrates whereas the band at 1630 cm^{-1} indicates the vibrations due to bending of H_2O [16].

IV. CONCLUSION

Bismuth Ferrite $BiFeO_3$ nanopowders were successfully synthesized via combustion process by varying 'fuel/oxidizer' ratio and fuels. By varying 'oxidant to fuel ratio' and type of fuel $BiFeO_3$ powders of changeable crystallite size can be accomplished at lower temperatures by combustion synthesis. Also parameters of unit cell for $BiFeO_3$ samples shows high dependence on the characteristic parameters of the fuel and the type of chemical reaction. In addition, the XRD nanocrystalline size of the $BiFeO_3$ powders is remarkably increased as φ rises from 0.8 to 2.9. Also unit cell parameters decreases and structure of $BiFeO_3$ gets distorted for fuel rich and fuel deficient sample. Thus, the synthesis and tailoring of nano-crystalline materials with cost effective combustion method using different fuels and varying 'fuel/oxidizer' ratio generates a huge range of curiosity to promote research.

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