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## Synthesis and Characterization of Multiferroic BFO Nanoparticles by Auto-combustion Route with Various Complexing Agents

Sanjay Godara<sup>1</sup>, Nidhi Sinha<sup>1,2</sup> and Binay Kumar<sup>1\*</sup>

<sup>1</sup>Crystal Lab, Department of Physics & Astrophysics, University of Delhi, Delhi-07, India

<sup>2</sup>Department of Electronics, SGTB Khalsa College, University of Delhi, Delhi-07, India

\*Corres.author: b3kumar69@yahoo.co.in, Phone: +91- 9818168001.

**Abstract:** BFO nanoparticles (NPs) were synthesized by low temperature auto-combustion route using various complexing agents like glycine, oxalic acid, citric acid, succinic acid and maleic acid. Phase purity, structural characterization and thermal properties of as-obtained BiFeO<sub>3</sub> NPs were carried out with TG/DTA, XRD, TEM and FT-IR techniques. Thermal analysis revealed that optimum calcination temperature is the lowest for the sample prepared with citric acid (450 °C). Powder X-ray diffraction confirmed the single phase of samples prepared with citric acid, glycine and oxalic acids. TEM images show the spherical morphology of particles with average size of 50 nm. Citric acid was found to be a better fuel for synthesising bismuth ferrite NPs by this method.

**Keywords:** BFO nanoparticles; Chemical synthesis; Multiferroic; Thermo-gravimetric analysis.

### Introduction and Experimental:

Bismuth ferrite (BFO), as being the representative multiferroic material with rhombohedrally distorted perovskite structure (ABO<sub>3</sub> type) and simultaneously exhibiting ferroelectric ( $T_C=825^\circ\text{C}$ ) and antiferromagnetic ( $T_N=370^\circ\text{C}$ ) ordering well above the room temperature, finds tremendous applications in the field of spintronics, low energy consuming and highly dense non-volatile memory devices[1,2]. BFO have spin spiral of period 62 nm and it exhibits net residual magnetization for the nano-sized particles which is enhanced with decreasing particles size[3]. BFO is an excellent ferroelectric material with high remnant polarization ( $E_r$ ) up to  $90 \mu\text{C}/\text{cm}^2$  in thin films [1]. However, saturated polarization at bulk is restricted on account of low resistivity [2]. Even if BFO is mostly investigated multiferroic, its practical applications are limited on account of its compositional instability and stoichiometric phase-pure synthesis is a challenging task. Conventionally, BFO ceramics has been synthesized by high temperature solid state reaction method, which leads to secondary phases like Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and Bi<sub>25</sub>FeO<sub>39</sub>[4]. Nano-sized BFO is synthesized by other low temperature processes like Hydrothermal, Sol-Gel and Pechini's methods [5-7].

In this work, BFO NPs were synthesized by low temperature auto-combustion route using various complexing agent like citric, succinic, maleic, oxalic acid and glycine (labelled as CBFO,SBFO, MBFO, OBFO

and GBFO respectively). Bismuth and Iron nitrate (Sigma Aldrich) in equal stoichiometry were taken as sources of metal ions and dissolved in 1N nitric acid with vigorous stirring. Complexing agents, in ratio to metal ions 2:1, were mixed with heating at 80 °C and obtained light brownish solutions and kept on hot plate for drying. As-synthesized samples were characterized with TG-DTA (Netzsch-409STA), XRD (Bruker, D8;Cu,  $\lambda = 1.5405 \text{ \AA}$ ), TEM and FT-IR (Perkin Elmer BX, KBr pellet).

## Results and Discussion:

Auto-combustion process is based on the principals of propellant chemistry and is accompanied by a high energy redox reaction between metal nitrates as oxidant and organic fuels as reducing agent and released energy is used for oxide formation[6].

Thermal analysis (TG/DTA) are the useful tool to get optimum calcination temperature of chemically synthesized precursors. Fig. 1 depicts the variations in weight loss and heat flows through precursors prepared with various complexing agents during temperature treatment in N<sub>2</sub> environment. In TGA, there are step like weight loss of about 40% up to 400 °C for all precursors and then become flat region, which is the suitable range of temperature for calcination to obtain phase pure BFO. Largest weight loss (20%) in temperature range 150-300 °C is due to release of large amount of gases on combustion of fuel which are simultaneously confirmed by exothermic peaks in DTA plots and released energies are used for oxides formation[7]. Ignition temperature is different for each complexing agent and this is lowest for citric acid, 148 °C. Largest and narrow DTA peak for CBFO implies release of large energies comparison to other complexing agents, which turns into it superior fuel for auto-combustion process to synthesize BFO NPs.

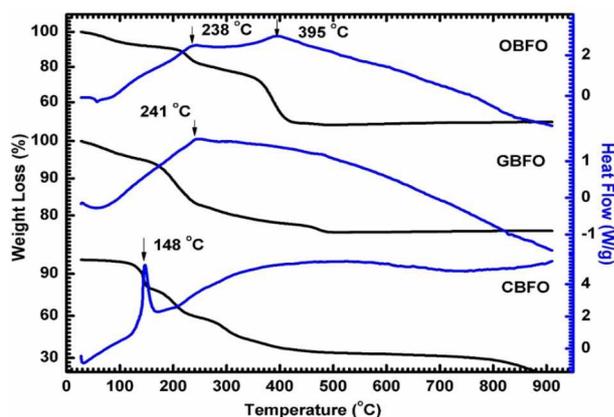


Fig. 1. TG-DTA of BFO precursors, synthesized with various complexing agents.

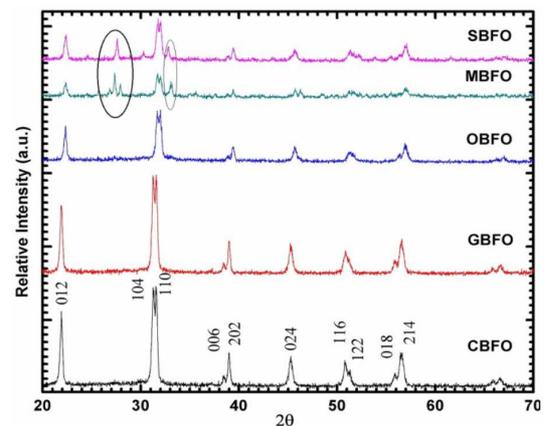


Fig. 2. XRD patterns of various BFO NPs.

Fig. 2 shows the XRD patterns of as-synthesized BFO NPs with various complexing agents and calcined at 500 °C which are fairly matched to JCPDS card 86-1518 and confirms the formation of rhombohedral structure with space group R3c (No.161)[1]. It can be seen that relative high intensity and no trace of impurity peaks were obtained for CBFO and GBFO, which reveals the glycine and citric acid are appropriate complexing agents for preparation of BFO NPs. Also, SBFO and MBFO have prominent peaks for undesired phases like Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> etc. The crystallite size of NPs were calculated using Scherrer formula and average size found to be approximately 45 and 50 nm for GBFO and CBFO, respectively, which were also confirmed by TEM micrograph shown in Fig.3. CBFO NPs were spherical shaped and uniformly distributed but GBFO particles were highly agglomerated.

Fourier transformed infrared (FT-IR) spectra of thermally treated at various temperatures of CBFO precursor and variation in absorption for transformation of dried gel to BFO NPs, are shown in Fig. 4. In curve for 500 °C, two intense peaks at 466 and 560 cm<sup>-1</sup> are due to stretching and bending vibrations of Fe-O bond, respectively and are fundamental absorptions of FeO<sub>6</sub> octahedral in perovskite[6,8]. Other absorption band at lower temperature may be due organic molecules like OH, H<sub>2</sub>O and trapped nitrate ions [6].

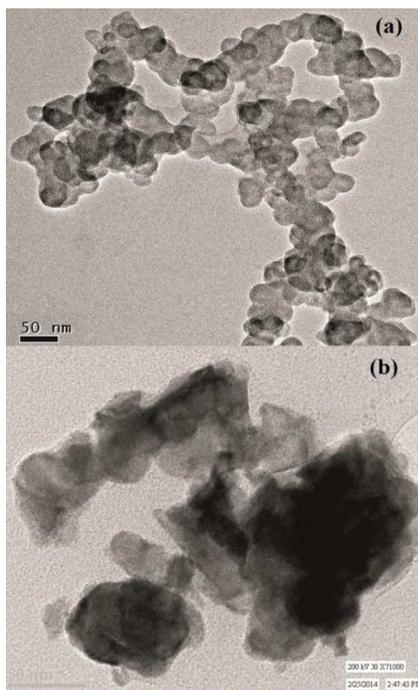


Fig. 3. TEM images of (a) CBFO  
(b) GBFO

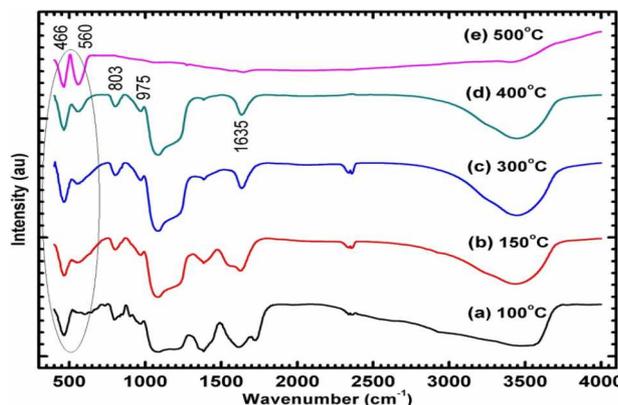


Fig. 4. FT-IR spectrum of the powder CBFO and calcined at different temperatures.

In summary, we have synthesized BFO NPs by Auto-combustion process using different complexing agents. Glycine and citric acid are found to be better fuels, as compare to others which dominant in secondary phases. Powder XRD and FT-IR confirms the phase purity and TEM micrograph shows spherical shape of BFO NPs synthesized with citric acid. Hence, synthesized single phase BFO NPs with this method can be used for various multiferroic applications of technological importance.

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