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# Synthesis of bismuth titanate with urea as fuel by solution combustion route and its dielectric and ferroelectric properties

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#### 1. Introduction

The increasing demand for environmentally benign materials directs the material scientists toward producing lead free ceramic materials to be used in non-volatile random access memories (NVRAM), actuators, sensors and piezoelectric components [1]. It is well known that bismuth titanate (Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, BIT) belongs to the family of ferroelectric materials with layered structures and also can be expressed as  $(Bi_2O_2)^{2+}(Bi_2Ti_3O_{10})^{2-}$ . The layered structure is constructed by alternative stacking of TiO<sub>6</sub> octahedra (perovskite slab) and a monolayer of  $(Bi_2O_2)^{2+}$  along the *c*-axis [2].

BIT has low dielectric permittivity and high Curie temperature ( $T_c = 670 \,^{\circ}$ C) and hence is useful for applications in wide temperature range [3]. Above  $T_c$ , it possesses paraelectric tetragonal structure proposed by Aurivillius [4] and below  $T_c$ , this structure becomes orthorhombic exhibiting ferroelectric properties. However, it possesses high electrical conductivity and makes the poling process difficult [5]. Work is being carried out in our laboratory to decrease the electrical conductivity of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>. Low temperature synthesis and densification of randomly oriented grains are desirable to control the conductivity path along the layers [6].

BIT has been prepared by a number of methods to reduce the sintering temperature and hence the grain growth. These methods include conventional solid state reaction [7], sol-gel [8–10], hydrothermal [1,11], metal organic decomposition [2], and

### ABSTRACT

Preparation of ferroelectric bismuth titanate ( $Bi_4Ti_3O_{12}$ ) is carried out by solution combustion route with urea as fuel at much lower calcinations temperatures. The single phase bismuth titanate was obtained after calcinations at 800 °C. SEM micrographs of the calcined powders show agglomerated, flaky and foamy morphology, which is typical of combustion synthesis and that of sintered ceramics shows the grain formation. Behavior of dielectric constant and dielectric loss as a function of temperature of asprepared sample are reported in this communication. Ferroelectric to paraelectric phase transition occurs at the temperature  $T_c \sim 660$  °C. Its remnant polarization ( $2P_r$ ) is very less of the order of 0.012 µC/cm<sup>2</sup>. © 2013 Elsevier GmbH. All rights reserved.

> coprecipitation [12]. The reports regarding solution combustion synthesis of bismuth titanate using urea as fuel are rare and ferroelectric and dielectric properties of this material synthesized by SC route with urea as fuel have not been reported so far hence it is extensively studied in this paper. Urea is chosen as fuel as it occupies the center stage among all fuels used in combustion synthesis due to its easy availability and high exothermicity [13]. Urea has low reducing power of +6 and generates less number of moles of gases [14].

> The solution combustion technique is the quasi-atomic dispersion of the component cations in the liquid precursors, which facilitates the synthesis of crystallized powder with low particle size and high purity at low temperatures [15,16].

In this paper, the structural and chemical characterization and also dielectric ad ferroelectric properties of BIT synthesized by solution combustion synthesis with urea as fuel are reported.

#### 2. Experimental

Bismuth titanate  $(Bi_4Ti_3O_{12})$  powders were synthesized using the solution combustion technique. Bismuth(III) nitrate pentahydrate (Merck) and titanium(IV) isopropoxide (Sigma Aldrich) were used as starting materials with the mole ratio of 4:3. Bismuth nitrate pentahydrate was dissolved in 2-methoxyethanol at room temperature, and urea was added to aid in the combustion process. Titanium isopropoxide solution along with acetyl acetone, which is used as chelating agent, was added to Bi solution while being continuously stirred. The final mixture was then stirred for 1 h, and was heated on a hot plate at 200 °C leading to evaporation



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Fig. 1. XRD pattern of as-prepared bismuth titanate, after combustion without calcinations, after calcination at 800 °C and after sintering.

followed by combustion process, which is an exothermic chemical reaction that resulted in the production of flame. The reaction lasted for about 5 min producing dry foam like flakes. These flakes were then crushed in an agate mortar and then calcined at 800 °C for 3 h. After calcinations, the powder was pressed at a pressure of 8 tons into pellets of 10 mm diameter. Finally, the pellets were sintered at 1050 °C in covered alumina crucible for 5 h. The calcined powders were analyzed for the presence of phases using X-ray diffractometer (Rigaku – Miniflex II) equipped with Cu  $K_{\alpha}$ radiation. The surface morphology of the powders and the pellets was observed using scanning electron microscope (IEOL-ISM6390). The thermal analysis of the precursor mixture was performed on DTA equipment Simultaneous Thermal Analyzer (Melter Toledo). The dielectric measurements were performed on Alpha High Resolution Dielectric Impedance Analyzer using Nova Controls in the frequency range from 1 Hz to 1 MHz from room temperature to 750 °C. Platinum coating was done on both surfaces of the pellets for ohmic contacts. P-E Loop measurements were performed on *P–E* Loop tracer (Marine, India).

#### 3. Results and discussion

#### 3.1. X-ray diffraction studies

X-ray diffraction studies conducted on the sample after combustion, after calcinations and sintering are presented in Fig. 1. It is observed that in the as-combusted powder along with main peak (corresponds to BIT), secondary intermediate phases are also seen. The X-ray diffraction pattern also exhibits amorphous nature in the powder before calcinations. The secondary phases were eliminated and the crystallinity of the as-prepared sample increased only after calcinations at 800 °C for 3 h. In the XRD pattern of the sintered ceramics it is noticed that the intensity corresponding to planes (008) and (0014) increased indicating growth along *c*-axis. This suggests that large number of phases are parallel to the crystallographic planes (00*l*). The XRD patterns of  $Bi_4Ti_3O_{12}$  crystals were indexed based on those given in JCPDS data cards file no. 72-1019. It is observed that, the as-prepared sample has orthorhombic symmetry and it is end-centered lattice with lattice constants a = 5.448 Å, *b* = 5.411 Å and *c* = 32.83 Å.

#### 3.2. TG-DTA analysis

The relative weight loss and the differential thermal analysis of the precursors are presented in Fig. 2. It is noticed that the first weight loss of 37% occurred from  $100 \,^{\circ}$ C to  $200 \,^{\circ}$ C, which is accompanied by an exothermic peak indicating combustion reaction. This weight loss is due to the decomposition and



Fig. 2. TG-DTA curves of the as-synthesized bismuth titanate powders.

decarbonization of organic fuel that is urea used in the reaction and hence the combustion reaction initiated by decomposition of urea and it also corresponds to the first nucleation events [17] that can be conformed from XRD results. The observed second weight loss at around 550 °C can be attributed to vaporization of carbon content left after the combustion process. We noticed that after 600 °C there is no weight loss. As such, 800 °C was chosen as calcinations temperature.

#### 3.3. SEM analysis

The SEM micrographs of the prepared powders are presented in Fig. 3(a). It is seen that the particles do not show any definite shape. A great number of agglomerates with a flaky morphology can be seen in the powder, which is typical of combustion synthesis products [18]. The milling in agate mortar before compacting and sintering was adopted in order to break the agglomerates. Fig. 3(b) shows the SEM micrographs of sintered pellets at 1050 °C for5 h. Here grain formation can be seen clearly.

#### 3.4. Dielectric properties

Fig. 4 shows the variation of dielectric constant with temperature. It is observed that the ferroelectric to paraelectric phase transition temperature is 660 °C. Apart from the peak at  $T_c$ , a hump in the dielectric versus temperature curve is seen around 500 °C. This has also been reported by earlier researchers and is attributed to the phenomenon such as structural distortions [19], space charge relaxation [20], and oxygen vacancy movement [21]. The temperature corresponding to the peak in the low temperature range is denoted as 'depolarization temperature' ( $T_d$ ), which is suggested to be the indication of stability of ferroelectric domains [22]. The depolarization temperature also corresponds to the ferroelectric to anti-ferroelectric transition as the specimen is depolarized and loses its piezoelectric activity over this temperature [3]. Also, the dielectric constant decreases as the frequency increases.

Fig. 5 presents the variation of dielectric loss with temperature. Dielectric loss remains constant and is very less of the order of 0.2 below  $T_c$  and a sudden rise in loss factor is observed around



Fig. 3. (a and b) SEM micrographs of calcined BIT powders and of BIT ceramics, respectively.

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