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# Stoichiometric control in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ synthesis by novel hybrid solid state reaction

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Key words: Bismuth titanate, synthesis, sol-gel, colloids, dielectric

## Abstract

The synthesis of bismuth titanate  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT) is performed via a novel solid state reaction. The reaction is designed to control the stoichiometric content of the highly volatile element, *i.e.* Bi. The chemical route consists in trapping bismuth oxide colloids in a stabilized titanium based sol gel solution. The resulting colloidal-solution hybrid ink can be processed via various ceramic processes. After gelation of  $\text{TiO}_2$  in the sol-gel component the mixture reacts at high temperature (850 °C) to yield the BiT phase. The obtained material is *c*-axis oriented, and its lattice parameters, shrinkage and density matches the pure  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  phase. The sintered material exhibits enhanced higher dielectric constant (232) than usually reported for this phase.

## 1. Introduction

Bismuth titanate  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT) is considered one of the most promising high temperature lead-free piezoelectric materials [1,2]. BiT is a member of the Aurivilius family and its structure consists of a triple perovskite unit  $[\text{Bi}_2\text{Ti}_3\text{O}_{10}]^{2-}$  sandwiched between  $(\text{BiO}_2\text{O}_2)^{2+}$  layers [3,4]. It exhibits a high Curie temperature ( $T_c = 675^\circ\text{C}$ ) [5], very low fatigue and high dielectric constants [1], which makes it a potential candidate for applications in piezoelectric devices, memory storage (FERAM) in a wide range of high temperature environment, and electro optics devices [3,6].

BiT powder is usually prepared via solid state reaction (SSR) [7,8] by milling stoichiometric amount of bismuth oxide  $\text{Bi}_2\text{O}_3$  and titania  $\text{TiO}_2$ . Bismuth is, however, a highly volatile element and high temperature treatments in SSR can easily lead to bismuth evaporation, resulting in a poor control on composition, phases and properties [9,10]. Furthermore, the SSR technique yields generally agglomerated and coarsened particles, with limitations on microstructural control and processing flexibility [11]. Several wet-chemical techniques such as sol-gel [12], co-precipitation [13], hydrothermal [14] or polymeric precursor synthesis [15] can be alternatives to SSR to produce BiT powder. These techniques allow a better control of powder microstructure, stoichiometry and particle size and lead to enhanced properties. However, bismuth salts or alkoxides can be difficult to handle, while bismuth oxide powders are readily available, cheap and harmless. In this work, bismuth titanate is prepared via a novel wet route by mixing bismuth oxide powder and a stable titanium based sol gel solution, called reactive ink, previously developed for inkjet printing [16]. The resulting suspension, here called “hybrid ink”, can potentially be deposited by various ceramic processes such as tape casting, inkjet or 3D printing after viscosity and particle size adjustments. By this method, BiT is formed during heat treatment of the suspension via solid state reaction, while the bismuth powder is covered by  $\text{TiO}_2$  and not directly exposed to air, as in SSR. In this communication, we describe the experimental protocol used to produce pure BiT, and characterize the material obtained at high temperature as well as a measurement of its dielectric properties.

## **2. Experimental**

Experimental details such as preparation and characterization methods are reported in the supplementary information document.

## **3. Results and Discussion**

The crystallization behavior of BiT was studied by X-ray diffraction on the milled gel powders calcined in air at different temperatures. Figure 1 shows the XRD pattern of the powders calcined at different temperatures between 500 °C and 850 °C. The powder calcined at 500 °C exhibits a yellow color due to the presence of  $\text{Bi}_2\text{O}_3$ , which is confirmed by the XRD pattern. As the temperature increases the powders become whiter due to  $\text{Bi}_2\text{O}_3$  loss and appearance of the BiT phase. The XRD patterns show the onset of the crystalline BiT in agreement with literature [17]. BiT has a Curie

temperature ( $T_c$ ) of 675 °C; hence the crystal belongs to a pseudo-tetragonal phase below  $T_c$  and pseudo-orthorhombic phase above. The splitting of the reflection at  $2\theta \approx 33^\circ$  in the XRD patterns recorded at 700, 800 and 850 °C suggests indeed that these crystals have a pseudo-orthorhombic structure [17] at these temperatures. To verify this theory, Rietveld refinements were performed on the XRD pattern of the powder calcined at 850°C. The Rietveld analysis (detailed in the supplementary information) shows that all the peaks can be attributed to orthorhombic BiT (Fmmm). Finally the pattern recorded 850 °C exhibits a well-defined BiT crystalline structure. Diffraction peaks observed on this pattern were indexed according to literature [18]. Moreover no signal from the  $\text{Bi}_2\text{O}_3$  crystalline phase can be detected. As the temperature increases, the peak width decreases, corresponding to crystallite size increase. This suggests that the particles agglomerate and probably sinter during the heat treatment, leading to grain growth. The lattice parameters of the BiT phase in the sample calcined at 850 °C were refined with Rietveld analysis and were  $a = 5.40255 \text{ \AA}$ ,  $b = 5.44174 \text{ \AA}$ , and  $c = 32.7370 \text{ \AA}$ , which are comparable with the values given in JCPDS 72-1019. Finally, within the limit of the XRD technique, no bismuth and/or titanium based secondary phases could be detected in the XRD patterns. EDS analysis was performed on the powder calcined at 850 °C (detailed in the supplementary information), indicating that elemental balance of the starting chemicals was kept while neither segregation nor presence of second phases could be detected.

Figure 2 shows the thermogravimetric analysis (TGA) of the gelled ink coupled with the dilatometry plot of a pellet composed of powder calcined at 500°C for 1 hour. The TGA curve exhibits a strong mass loss between room temperature and 300°C due to organic burn off. From 300 to 850 °C no mass loss can be detected indicating that the bismuth oxide, trapped in the sol gel, does not evaporate even at high temperature, for which such phenomenon was observed [9]. A pure BiT phase can thus be obtained as the necessary stoichiometric ratio to obtain this phase is preserved. The sintering behavior of the pellet was studied by using a dilatometry measurement. No shrinkage is occurring between room temperature and 600 °C; a small expansion (0.1%) can however be noticed in that temperature range, due to chemical reactions and/or crystal lattice rearrangements. The shrinkage starts from 600°C and the highest size reduction is recorded between 700 and 800°C, leading to 14% shrinkage. Measured density is 6.79 g/cm<sup>3</sup>, which is in good agreement with literature [19].

Figure 3 shows the dielectric constant measurement of a BiT pellet calcined at 850°C together with measurements performed on powders synthesized by other processing routes [2,20,21]. We measured permittivity in powder (powder calcined at 850°C). The average value of the dielectric constant at room

temperature for this sample is 227 (value fitted linearly) which is approximately 20% higher than those obtained on samples synthesized by other techniques and reported in Figure 3. This result emphasizes the importance of the powder preparation method and demonstrates that using the hybrid concept “sol-gel + colloids” leads to enhanced material properties.

## Conclusion

In this study bismuth titanate  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powder was synthesized for the first time by suspending bismuth oxide particles in a stable titanium based sol-gel solution, followed by a heat treatment. Pure *c*-axis oriented bismuth titanate was obtained after calcination at 850 °C. With this technique bismuth is trapped into a sol gel a matrix and cannot evaporate allowing the synthesis of pure BiT without secondary phases in a one step process. The dielectric constant was determined using impedance measurements and was evaluated as 20% higher than previously observed values.

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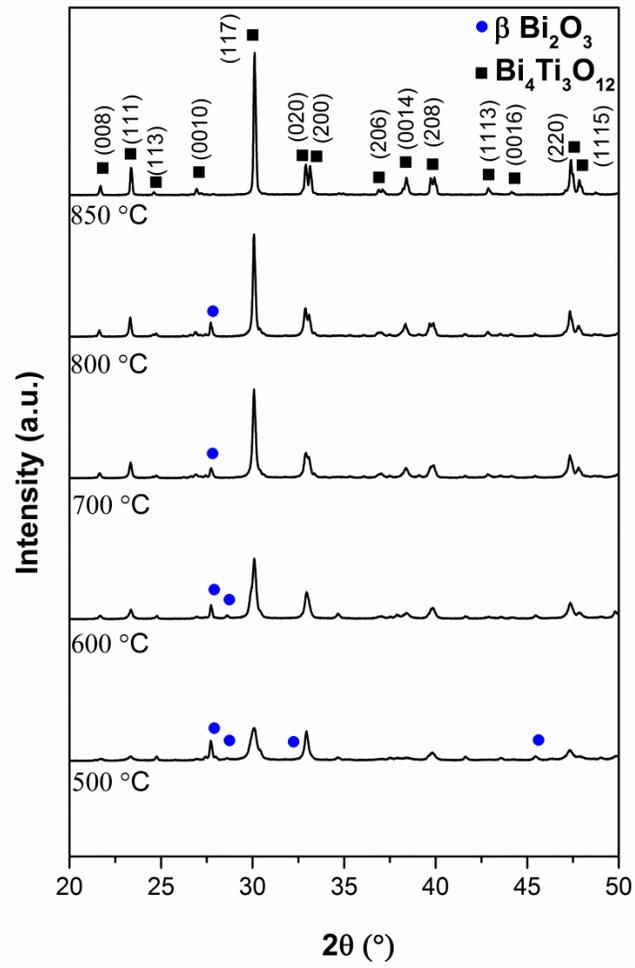


Figure 1: X-ray diffraction patterns of BiT powders after calcination at different temperatures.

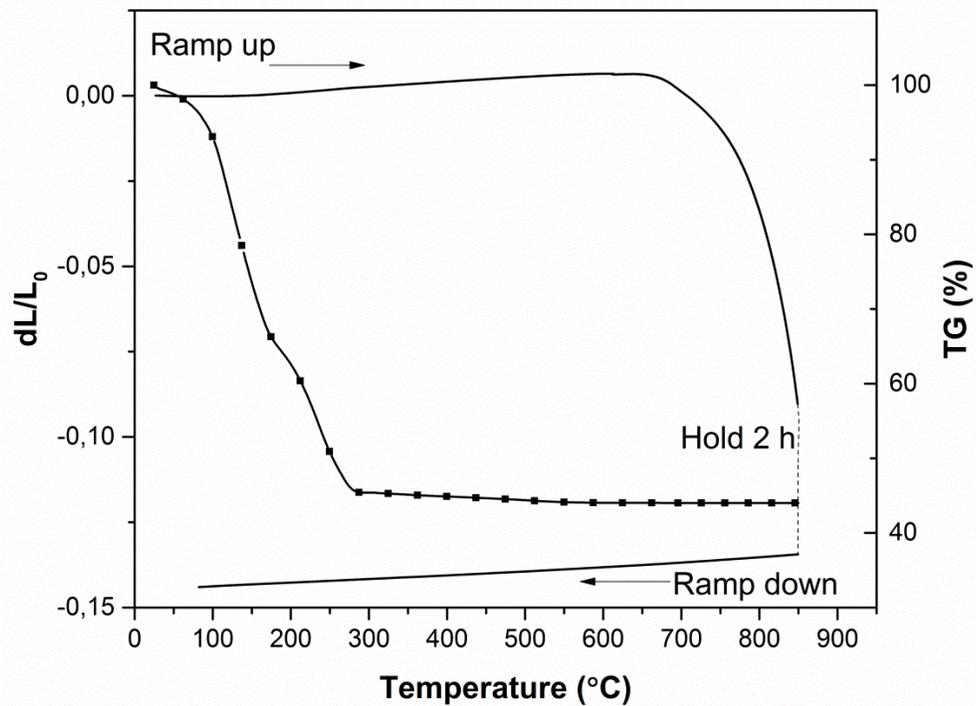


Figure 2: Thermogravimetric (symbols with line) and dilatometry (line) measurements of respectively a gelled ink and a BiT calcined at 500 °C from room temperature to 850 °C.

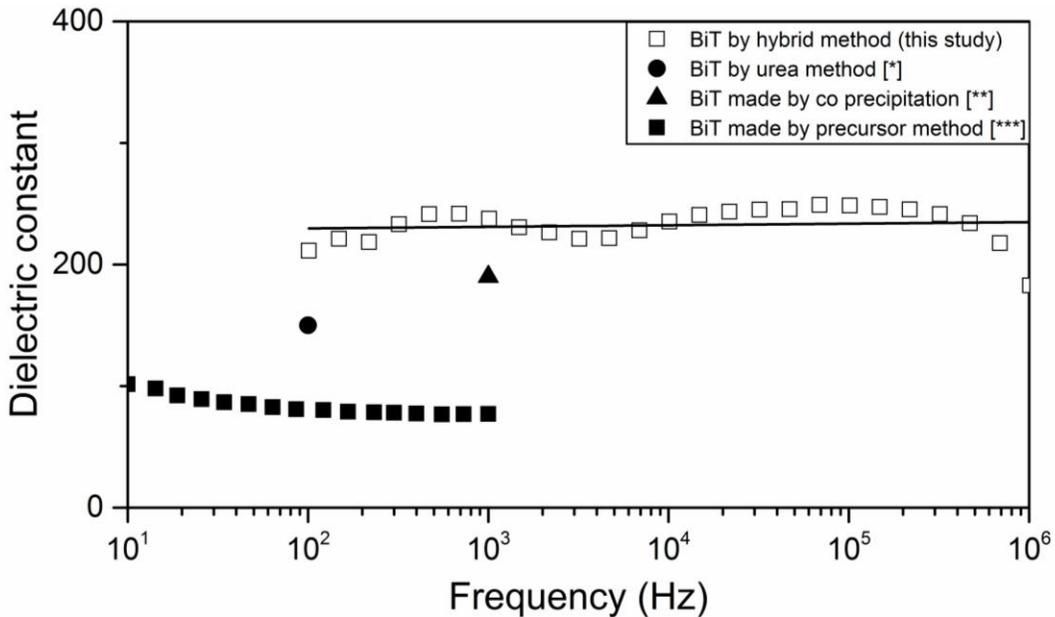


Figure 3: Dielectric measurement by impedance spectroscopy of BiT pellet calcined at 850 °C along with values reported for powder synthesized by urea method (\*=[20]), co precipitation (\*\*=[2]) and using polymeric precursors (\*\*\*=[21])