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# BiFeO<sub>3</sub> synthesis by conventional solid-state reaction

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**Abstract**—BiFeO<sub>3</sub> is a multiferroic material with the perovskite structure which is promising for use in sensors and transducers. Single phase production of BiFeO<sub>3</sub> remains a challenge, however. In this study, the optimal calcination temperature to obtain close to single phase powder was determined to be 750 °C. The sintering temperature of 775 °C was also found to obtain high density ceramics (≈ 95 % of theoretical density). It is shown that off-stoichiometry of bismuth oxide in precursors effects the content of secondary phase. Impedance spectroscopy indicates that the content of secondary phases has a large effect on the electrical conductivity BiFeO<sub>3</sub>.

**Keywords**—bismuth ferrite; multiferroic; perovskite; solid state reaction; impedance spectroscopy

## I. INTRODUCTION

Bismuth ferrite (BiFeO<sub>3</sub>), and the solid solutions based on it, are promising multiferroic materials for use in sensors and transducers. In particular BiFeO<sub>3</sub> is of interest due to the high Curie temperature, T<sub>C</sub>, of 825 °C [1]. This allows for the possibility of using it as a lead-free high temperature piezoceramic [2]. Although bismuth ferrite was discovered in the late 1950s, obtaining it in a single phase form is challenging due to the formation of the stable secondary phases of Sillenite (Bi<sub>25</sub>FeO<sub>39</sub>) and Mullite (Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>) [3]. The presence of these secondary phases leads to large electrical leakage currents, which imposes serious restrictions on its use in industry. Due to the high coercive field required to pole this material, it is important to increase its insulating properties [4]. Therefore, before studying the electrical properties, it is necessary to obtain high-density ceramics as free from secondary phases as possible. In previous works, various methods of obtaining pure bismuth ferrite were used, such as solid-state synthesis [5], rapid liquid reaction [6], mechano-chemical activation [7], wet-chemical methods [8] as well as others. But the formation of secondary phases could not be avoided in any of them. To eliminate secondary phases, leaching in nitric acid [9] was proposed, which shows good results, but probably leads to uncontrolled changes in the composition of the material which will impact the defect chemistry.

In this work, we focus on the optimization of making BiFeO<sub>3</sub> ceramics, by classic solid-state reaction, for future investigations of the defect chemistry. The effect of the calcination temperature on phase formation has been studied. Furthermore, the influence of excess Bi<sub>2</sub>O<sub>3</sub> addition is investigated. Impedance spectroscopy on the as-made ceramics

has been performed to investigate the influence of phase purity on the electrical properties.

## II. EXPERIMENTAL PROCEDURE

BiFeO<sub>3</sub> samples with and without 1 mol% excess Bi were prepared by a solid-state reaction from premilled Bi<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> powder in the appropriate ratios. Milling was performed using 2 mm Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> balls in hexane using a Retsch PM100 planetary ball mill. The powders were dried and calcined at a range of temperatures between 700 and 825 °C in air for 1 h with a heating rate of 600 °C/h. The reacted powder was ground again and pressed into pellets using a uniaxial press. After that, the samples were sintered at temperatures between 750 °C to 850 °C in air for 1 h at a heating rate of 600 °C/h.

Phase purity of the BiFeO<sub>3</sub> powders was analysed by X-ray diffraction analysis using a Rigaku Miniflex 600 table top diffractometer and Cu K $\alpha$  radiation at room temperature. The density was determined by the Archimedes' method in water. The microstructures of sintered ceramics were investigated using scanning electron microscopy (SEM), using a Jeol JSM-7500F field emission scanning electron microscope. For electrical measurements, gold electrodes were deposited on the ceramics by DC sputtering using a Quorum Q300T sputter coater. Electrical measurements were performed with a Novocontrol Alpha Dielectric Analyzer in the frequency range from 1 Hz to 10 MHz at temperature from 25 to 200 °C.

## III. RESULT AND DISCUSSION

Although solid-state synthesis of bismuth ferrite has been well studied by many groups, reproducing these results is not a trivial task due to the high sensitivity of this material to the temperature profile of calcination and sintering. Therefore, before studying the material properties, it is necessary to optimize the methods of sample preparation.

Fig. 1 shows the X-ray diffraction patterns of BiFeO<sub>3</sub> ceramics calcined at different temperatures. In all samples, the major phase is the perovskite bismuth ferrite, but it contains different concentrations of the two secondary phases: one rich in bismuth – Bi<sub>25</sub>FeO<sub>39</sub> and one iron rich – Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>. By comparing the intensity of the most intense peaks of the secondary phases with the major peak of the bismuth ferrite (110) (Fig. 2) the amount of each secondary phase present in each sample could be estimated. The peaks of Bi<sub>25</sub>FeO<sub>39</sub> decrease with increasing temperature, while the peaks of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> increase. This may be due to the loss of bismuth

during the synthesis. We have determined that the lowest concentration of both secondary phases was obtained for the sample calcined at 750 °C.

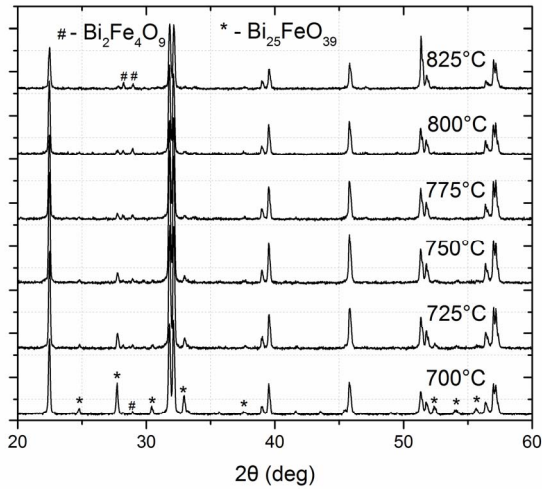


Fig. 1. X-ray diffraction patterns of bismuth ferrite synthesized at different temperatures.

Fig. 3 shows the relative density and the SEM micrographs of the fracture surfaces of the samples prepared by the conventional sintering. For each temperature 10 samples were prepared. SEM micrographs clearly show an increase in grain size with increasing temperature. At temperatures above 825 °C, the morphology of the samples is radically different, which is due to the proximity to the melting point of  $\text{Bi}_{25}\text{FeO}_{39}$  [1]. When sintering at temperatures of 825 and 850 °C, two separate microstructures can be observed in coexistence: square cuboid particles and smooth shapeless crystallites. The shapeless crystallites can be attributed to bismuth ferrite and the bismuth-rich phase. The square cubic crystallites are likely to be an iron-rich phase that has a high melting point[10]. The maximal average density of 95% has been observed for the sample sintered at 775 °C. The XRD patterns before and after sintering show no change in the composition.

However, bismuth ferrite obtained in this way still contains a high amount of secondary phases. Therefore, a 1% excess of bismuth oxide was added to the precursors to compensate for the loss of Bi which might occur during the sintering process to increase the phase purity of bismuth ferrite. The XRD pattern of the sample calcined and sintered from the stoichiometric precursors (Fig 4a) shows both secondary phases  $\text{Bi}_{25}\text{FeO}_{39}$  and  $\text{Bi}_2\text{Fe}_4\text{O}_9$ . But in the XRD pattern of the sample with excess bismuth (Fig. 4b) secondary phase peaks are not detectable at the level of background noise.

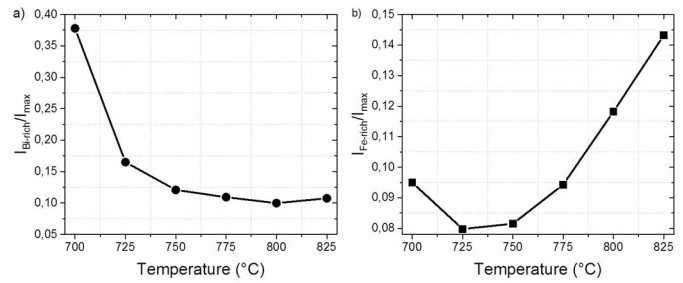


Fig. 2. Comparison of intensities of secondary phases with the major peaks of bismuth ferrite. (a –  $\text{Bi}_{25}\text{FeO}_{39}$ , b –  $\text{Bi}_2\text{Fe}_4\text{O}_9$ )

The electrical properties of the  $\text{BiFeO}_3$  ceramics and the sample with 1 mol% excess of Bi have been investigated by impedance spectroscopy. Fig. 5 shows the results of impedance measurements at different temperatures for the samples that correspond to the XRD patterns shown in Fig. 4.

From these spectra, two processes which contribute to the electrical conductivity are noticeable. While the nature of these processes is still under discussion, there is a noticeable decrease in the conductivity of the phase pure sample when compared to the sample that contains secondary phases. This may be associated with a decrease in the concentration of bismuth and oxygen vacancies with the addition of extra bismuth.

The DC conductance was calculated by fitting the low-frequency conduction region using Jonscher's power law[11]:

$$\sigma = \sigma_{\text{DC}} + A\omega^n \quad (1)$$

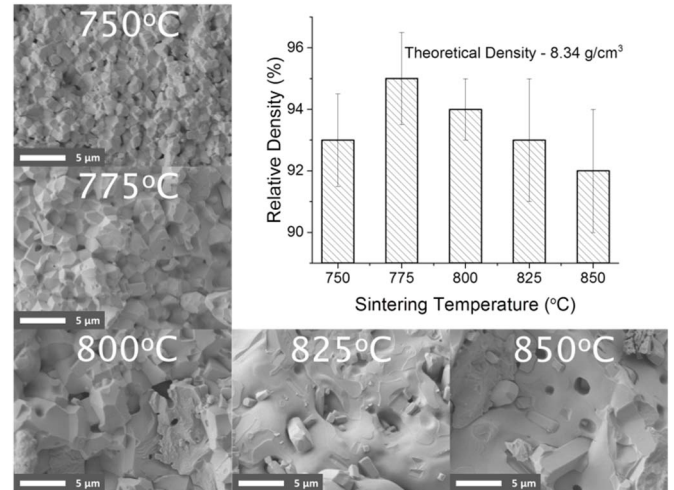


Fig. 3. SEM micrographs of structure and density measurement ceramics sintered at different temperatures.

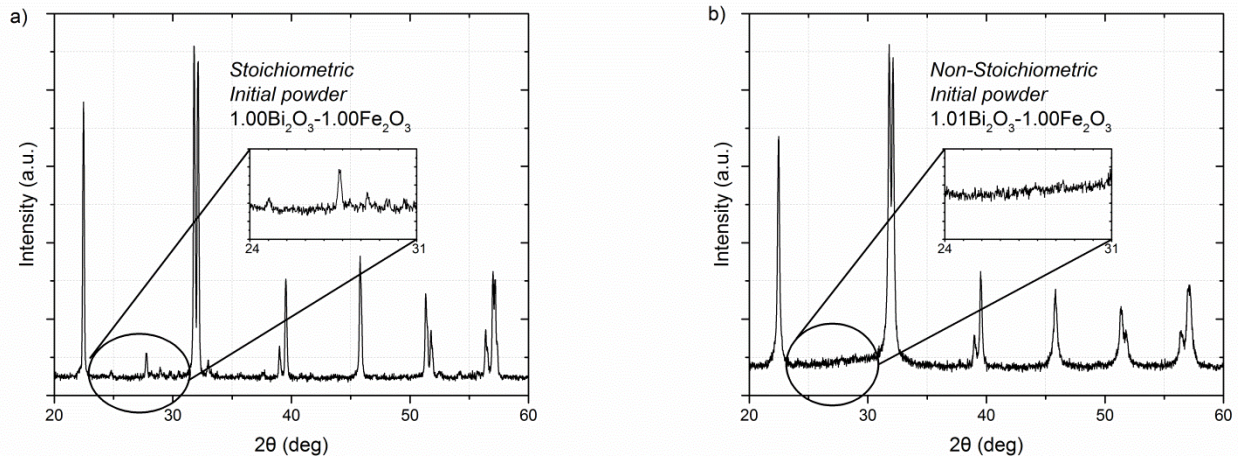


Fig. 4. X-ray diffraction analysis of samples prepared with and without the addition of extra bismuth. (a - Equal amounts of iron and bismuth in the precursor; b - 1 mol% more bismuth oxide added to precursor)

In Fig. 6 the Arrhenius plot is given for the DC conductivity of the stoichiometric and Bi-rich samples. The DC conductivity in the phase pure sample is a significantly lower than the conductivity of the sample with secondary phases. It is clearly visible from Fig. 6 that conductivity is a thermally activated process with a similar activation energy for both samples of about 0.25 eV. This strongly suggests that the conductivity mechanism for both samples is of the same nature.

The fact that the electrical conductivity for the sample with Bi excess is lower than that of the stoichiometric sample by a factor of about 1000 strongly suggests that the concentration of charge carriers is related to Bi vacancies inside  $\text{BiFeO}_3$ . Further investigation of the defect chemistry of bismuth ferrite is needed to clarify the mechanism of conductivity and to explain the low values of the activation energy for the electrical conductivity.

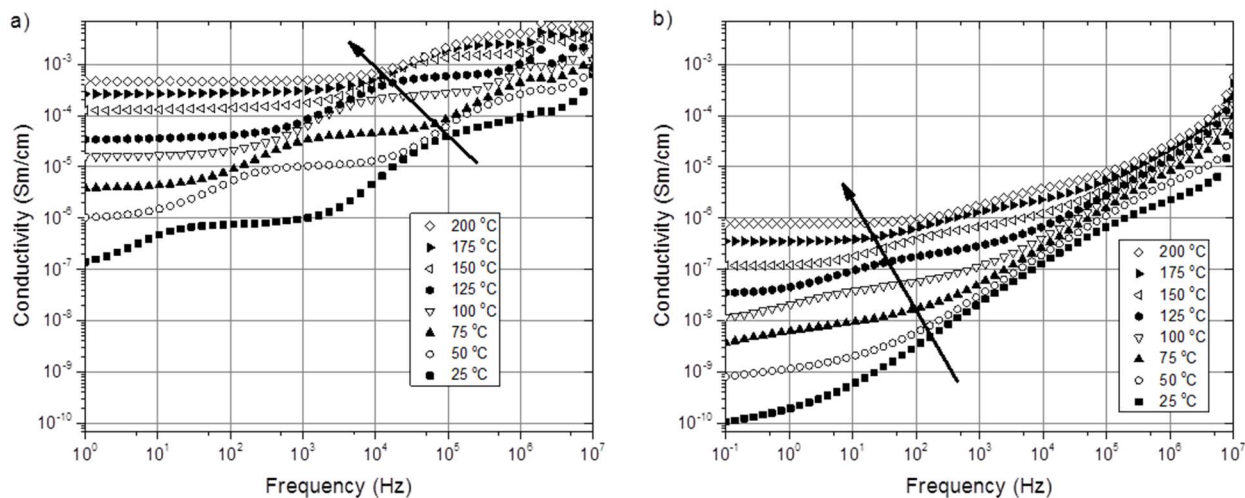


Fig. 5. AC Conductivity measurements (a - unpure  $\text{BiFeO}_3$ , b - pure  $\text{BiFeO}_3$ )



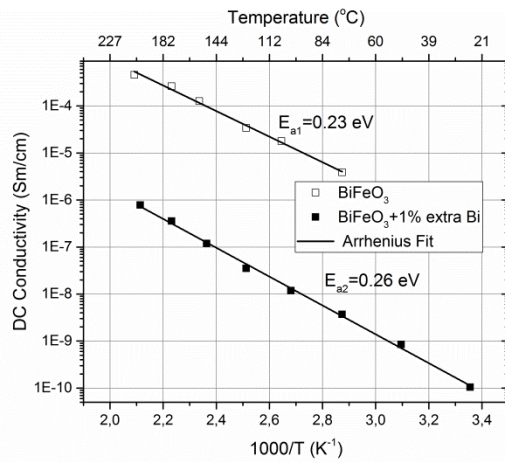


Fig. 6. Arrhenius plot of DC conductivity.

#### IV. CONCLUSION

Dense bismuth ferrite ( $\text{BiFeO}_3$ ) with a 95% relative density with a negligible amount of secondary phases can be prepared using the usual solid-state method starting from the constituent oxides. Analysis of the microstructure showed that with increasing temperature the grain size in the ceramics also increases and temperatures 800 °C cause an inhomogeneous microstructure. Samples prepared with an excess of Bi show the formation of single phase  $\text{BiFeO}_3$ . Finally, impedance spectroscopy shows that the addition of excess Bi has a large impact on the conductivity of the sample. Most likely, this is due to a reduction of bismuth vacancies arising from the preparation of ceramics.

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