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Reduced leakage current of multiferroic $BiFeO_3$ ceramics with microwave synthesis

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Abstract

Preparation of multiferroic $BiFeO_3$(BFO) is reported using microwave heating. The prepared sample is characterized using x-ray diffraction, scanning electron microscopy, differential scanning calorimetry and leakage current measurements. It is observed that the BFO can be prepared with microwave heating at a fast heating rate, consisting of more homogeneous microstructure and better electrical properties. Phase purity of the sample is confirmed from x-ray diffraction measurements. Uniform grain size distribution is observed for the sample prepared with microwave heating. More than an order of magnitude reduction in the leakage current is observed for the sample prepared with microwave heating as compared to conventional radiant heating.

Keywords: $BiFeO_3$; Multiferroics; Microwave heating

1. Introduction

$BiFeO_3$ (BFO), which is ferroelectric (FE, $T_C \approx 830\ ^\circ C$) and antiferromagnetic (AFM, $T_N \cong 370\ ^\circ C$), has been the focus of current research in the context of multiferroic materials [1,2]. Most of the published literature of BFO deal with the suppression of spin-cycloid to observe the spontaneous magnetization and understanding the mechanism responsible for the same [2,3]. Relatively few reports are seen in the literature dealing only with the preparation of BFO ceramics, which equally deserves the attention because of the following reasons. The challenging aspect in the preparation of BFO is in terms of improving the resistivity of the sample (decreasing the leakage current), making the phase pure sample, etc. During synthesis of BFO, the kinetics of formation always leads to a mixture of $BiFeO_3$ as a major phase along with other impurity phases. This is mainly because of the narrow temperature range in which $BiFeO_3$ stabilizes and there are a number of other phases of Bi and Fe which appear if temperature is not controlled accurately [2]. Since, Bi is highly volatile so at high temperatures it may create a Bi vacancy that leads to the formation of oxygen vacancies and other parasitic phases, which would increase the leakage current in the system. Hence, even though BFO was discovered in the 1960s and its structure and properties have been extensively studied, the low resistivity of the sample at room temperature limited the applications of this compound.

Silva et al. have recently reviewed the different approaches used in the literature to address these issues in the preparation of BFO ceramics [4]. Various methods for preparation of BFO ceramics are reported in the literature like solid-state reaction method, chemical method, rapid phase sintering method, co-precipitation method etc [4–8]. Wang et al. have reported the preparation of single phase BFO with high resistivity using a rapid liquid phase sintering technique [7]. Su et al. have reported the high-pressure synthesis of single-phase BFO, which resulted in higher resistivity, higher density and better crystallization as compared to the conventional BFO samples [8]. Recently, Deepti et al. have reported reduced leakage current in epitaxial BFO thin films with oxygen plasma treatment [9].

It is to be noted that the microwave sintering process has many unique advantages over conventional sintering processes.

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The fundamental difference is in the heating mechanism with which the samples are heated. Usually, the conventional heating (resistive heating) requires long duration for sintering the materials, which is because of the fact that heat generated by heating elements is transferred to sample via radiation, conduction and convection. Such long duration sintering may cause some of the constituent elements to evaporate. In BFO, Bi being volatile, often this leads to non-stoichiometry, oxygen deficiency, Fe^{2+} formation, etc., which would essentially increase the leakage current. Unlike conventional heating, in microwave heating the materials themselves absorb microwave energy and then transform it into heat within the sample volume and sintering can be completed in shorter times. The advantages of microwave heating over conventional heating are demonstrated in the literature for many materials [10–15].

However, only couple of reports are seen dealing with the preparation of BFO with microwave heating. Using only microwave sintering Gonjal et al. have observed an amorphous BFO phase formation with un-reacted constituents which needed further radiant heating to form a crystalline BFO ceramics and whereas with microwave-hydrothermal synthesis they could prepare phase pure BFO ceramics [17]. Joshi et al. have reported the preparation of BFO nanocubes using microwave synthesis [16]. Therefore, preparation of BFO ceramics with microwave sintering is not fully explored in the literature and in the present work we show that phase pure BFO ceramics could be produced at a faster rate using microwaves as compared to conventional heating methods. And we also show that the sample prepared by microwave heating exhibits better morphological and electrical properties as compared to that of conventional radiant heating.

2. Experimental

Samples with the composition $BiFeO_3$ are prepared through chemical route starting with nitrate precursors. Stoichiometric amount of $Bi(NO_3)\cdot 5H_2O$ (99.0%), $Fe(NO_3)_3\cdot 9H_2O$ (99.5%) and tartaric acid (99.5%) were dissolved in a suitable quantity of distilled water, heated up to 80 °C in order to prepare a transparent multi-component solution. The solution was dried and burnt to obtain fluffy green coloured precipitate. Thus obtained powders were calcined at about 450 °C for two hours to remove carbon. Calcined powders were made into pellets and the final sintering was carried out at 600 °C. Two samples were made with radiant and microwave heating using a Carbolite make hybrid furnace (MRF16/22). The temperature of the sample surface was measured using a calibrated IR sensor when the microwave heating is employed and this is used to control the microwave power to maintain the sample temperature after reaching the set temperature. For calibrating the IR sensor the following method is used. Initially the sample was heated with radiant heating to the desired temperature (600 °C) and then the sample surface temperature was measured by placing a calibrated thermocouple on to the surface. After noting the exact surface temperature of the sample, the surface temperature was measured with an IR sensor and the emissivity of the sensor/controller was adjusted ($\epsilon = 0.855$) so that the IR sensor reading matches exactly with the calibrated thermocouple value. It may be noted that this procedure ensures the accuracy of temperature measured with the IR sensor, as the emissivity is expected to be different for different materials. For microwave heating, the sample was placed on a SiC plate which acted as susceptor. X-ray diffraction (XRD) measurements are carried out using D8-Discover system of M/s Brucker equipped with Cu Kα radiation $\lambda = 0.154$ nm). Leakage current measurements are carried out using a M/s Radiant Premier-II system. Scanning electron microscopy measurements (model LEO s- 440i) are carried out to study the microstructure of the prepared samples. Modulated differential scanning calorimetry (DSC) is used to determine the antiferromagnetic to paramagnetic transition temperature (T_N).

3. Results and discussions

Fig. 1 shows the temperature–time profile that is recorded during the radiant and microwave heating. In the case of microwave heating, as mentioned above the sample temperature was measured using the IR sensor. Also, one can see from Fig. 1(b) that with the microwave heating the sample temperature reached the set temperature (600 °C) within about 25 min. It is to be noted that as the IR sensor works only above 250 °C and therefore the sample temperature below 250 °C during cooling is not shown.

Fig. 2 shows the x-ray diffraction (XRD) patterns of the prepared BFO ceramics with radiant and microwave heating. The XRD data is fitted with Rietveld refinement using a FullProf program for the estimation of structural parameters. Refinement is carried out using rhombohedral lattice type with *R3c* space group and the obtained unit cell parameters are $a = 0.563 \pm 0.001$ nm and $c = 1.387 \pm 0.001$ nm. For both the samples, the observed parameters are same within experimental errors. The obtained structural parameters match well with the reported values of BFO [23].

Figs. 3 and 4 show the scanning electron microscopy (SEM) micrograph of both the samples. The inset of the figures shows the particle size distribution obtained from the SEM data using the ImageJ software [18]. The obtained distribution is fitted with the Gaussian distribution and the obtained average particle size

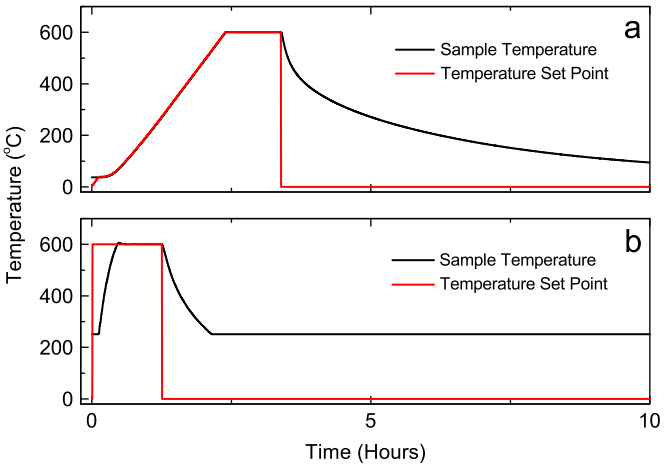

Fig. 1. Temperature–time profile recorded during (a) radiant heating and (b) microwave sintering.

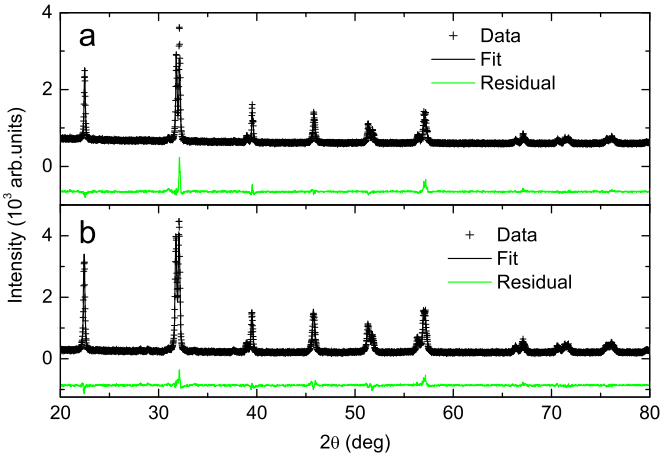

Fig. 2. X-ray diffraction patterns of prepared $BiFeO_3$ ceramics using (a) radiant heating (b) microwave heating. Symbols represent the experimental points and the solid line is the best fit to the data with Rietveld refinement.

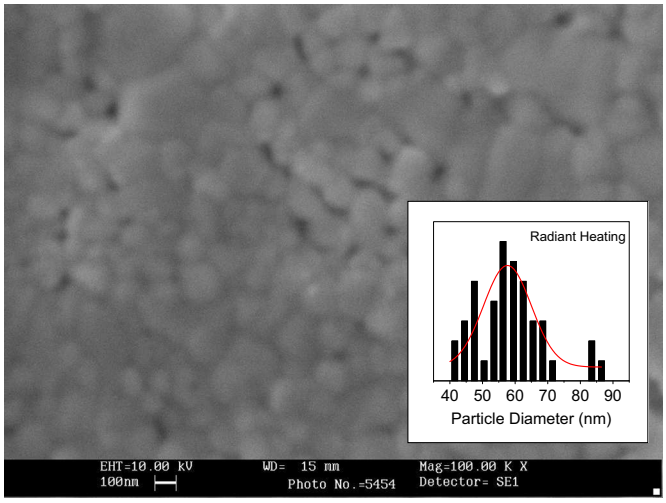

Fig. 3. SEM micrograph of $BiFeO_3$ ceramic prepared using radiant heating.

is 60.6 ± 0.3 nm with a distribution width of 7.6 ± 0.7 nm for the microwave sintered sample; 57.7 ± 1.3 nm with a distribution of 14.6 ± 3.8 nm for the radiant sintered sample. From the presented micrograph, one can clearly see that with the microwave sintering, the particle size is more uniform as compared to that of radiant heating. This can be understood in terms of the difference of heating mechanism involved with both the methods. In conventional radiant heating, energy is transferred due to thermal gradients to the material through convection, conduction and radiation of heat from the surfaces of the material and as a result there would be a thermal gradient across the sample thickness resulting in non-uniform heating and hence non-uniform particle size. In contrast, microwave energy is delivered directly to the material through a molecular interaction with the incident electromagnetic (EM) field and is the transfer of EM energy to thermal energy and is energy conversion rather than heat transfer. Since, the transfer of the energy does not rely on diffusion of heat from the surfaces, and it is possible to achieve rapid and uniform heating of thick materials with microwave heating resulting in a uniform microstructure. Such microwave effects are reported in the

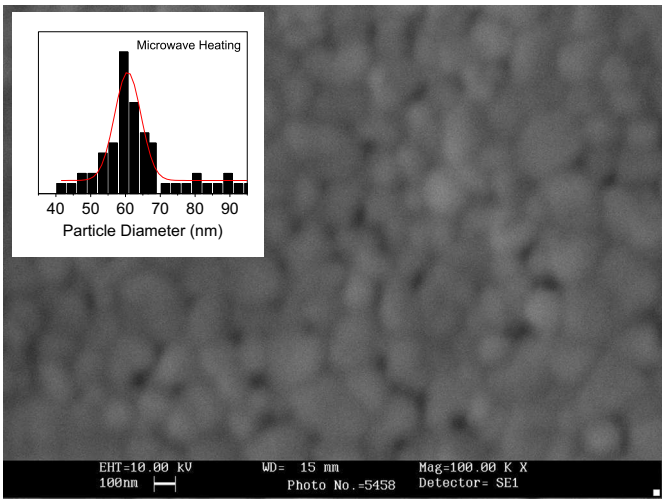

Fig. 4. SEM micrograph of $BiFeO_3$ ceramic prepared using microwave heating.

literature for various other materials. For example Yang et al. reported higher densification and uniform grain size distribution in uranium dioxide pellets sintered by microwave heating and uniform microstructure in microwave sintering of alumina–zirconia nanocomposites is reported by Menezes et al. [19,20]. The direct consequence of such a uniform microstructure is reflected in the electrical measurements of $BiFeO_3$ ceramic as discussed below.

The leakage current of both the samples viz. prepared by conventional radiative and microwave sintering is measured by subjecting the sample to a voltage of 50 V and with a soak time of 1000 ms. The data is shown in Fig. 5. As one can see from the data, the sample prepared by microwave heating exhibits less leakage current as compared to that of conventional radiative heating. More than an order of magnitude improvement is observed in the electrical properties of BFO prepared by microwave heating.

Usually, there can be many mechanisms, which are broadly divided into two categories viz. bulk limited and interface-limited conduction, for the leakage current in ferroelectric perovskite oxides. In BFO thin films, mechanisms, such as interface-limited Schottky emission (which arises from a difference in Fermi levels between a metal electrode and film), bulk-limited space–charge-limited conduction (arises from a current impeding space charge), and Poole–Frenkel emission (involving the consecutive hopping of charges between defect trap centers), are reported to be dominant [21,22]. However, the improved resistivity of BFO ceramics prepared with microwave sintering as compared to radiant heating, as observed in the present study, can be understood in terms of relation between grain size distribution and electrical properties of ceramics. Grains of different sizes and their boundaries are often considered to play a significant role in contributing to leakage current because of the fact that they will provide conduction pathways. The consequence of grain size distribution on the electrical properties of ceramics are reported in the literature. Lubomirsky et al. studied the modelling of space–charge effects in nanocrystalline ceramics and reported that contact between grains of very different sizes leads to charge exchange between the grains, known as heterosize charging. This will essentially influence the

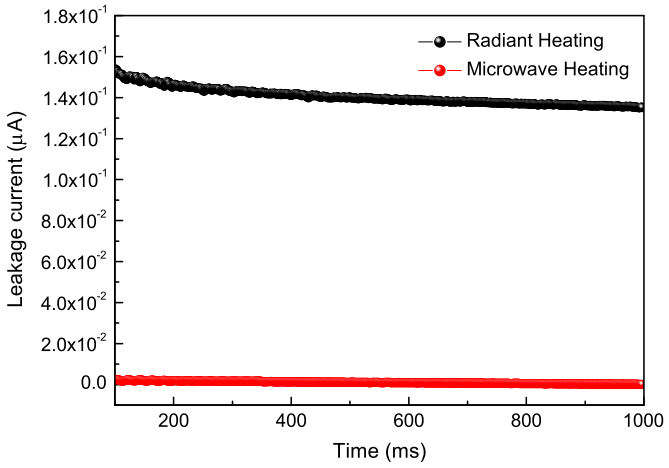

Fig. 5. Leakage current data as a function of time measured for the $BiFeO_3$ ceramic samples prepared by radiant and microwave heating. The applied voltage is 50 V and soak time was 1000 ms.

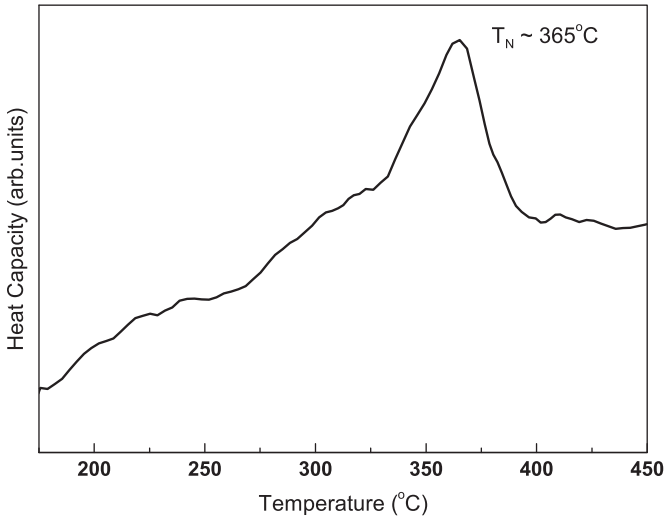

Fig. 6. DSC data of $BiFeO_3$ ceramic prepared by microwave heating showing the antiferromagnetic to paramagnetic transition (T_N).

conductivity of smaller grains and smaller grains usually conduct at lower voltages [24]. Therefore, the better uniformity of particle size distribution observed with the microwave sintering is the reason for the observed improvement of resistivity of BFO ceramic.

Finally, to look at the magnetic properties of $BiFeO_3$ ceramic prepared with microwave heating, high temperature differential scanning calorimetry (DSC) measurements are carried out across the antiferromagnetic (AFM) to paramagnetic (PM) transition. Fig. 6 shows the background subtracted DSC measurement of the BFO prepared with microwave heating. Clear peak due to AFM to PM transition is seen in the data. The Neel temperature (T_N) obtained matches well with the reported T_N value of polycrystalline BFO prepared by conventional heating [23].

In conclusion, the preparation of polycrystalline multiferroic $BiFeO_3$ (BFO) using microwave heating is presented. More than an order of magnitude reduction in the leakage current is observed for the BFO sample prepared with microwave heating as compared to conventional radiant heating. The results are explained in terms of microstructure. The obtained Neel temperature (T_N) of 365 °C matches well with the reported T_N value of polycrystalline BFO prepared by conventional heating. The fact that the microwave sintering is fast as compared to conventional heating is an added advantage in the preparation of BFO ceramics with better resistivity, which might essentially help in the application of repeated high electric fields as often required in the applications of ferroelectric materials.

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