

# A novel synthesis of perovskite bismuth ferrite nanoparticles

Glenda Biasotto<sup>1</sup>, Alexandre Z. Simões<sup>2,\*</sup>, César R. Foschini<sup>1</sup>, Selma G. Antônio, Maria A. Zaghete<sup>1</sup>, Jose A. Varela<sup>1</sup>

<sup>1</sup>Laboratório Interdisciplinar em Cerâmica (LIEC), Departamento de Físico-Química, Instituto de Química, Universidade Estadual Paulista, UNESP, CEP: 14800-900, Araraquara, São Paulo, Brazil <sup>2</sup>Universidade Estadual Paulista- UNESP - Faculdade de Engenharia de Guaratinguetá, Av. Dr. Ariberto Pereira da Cunha, 333, Bairro Pedregulho, CEP 12516-410– Guaratinguetá, São Paulo, Brazil

Received 17 February 2011; received in revised form 12 September 2011; accepted 19 September 2011

## Abstract

Microwave assisted hydrothermal (MAH) method was used to synthesize crystalline bismuth ferrite (BiFeO<sub>3</sub>) nanoparticles (BFO) at temperature of 180°C with times ranging from 5 min to 1 h. For comparison, BFO powders were also crystallized by the soft chemistry route in a conventional furnace at a temperature of 850°C for 4 h. X-ray diffraction (XRD) results verified the formation of perovskite BFO crystallites while infrared data showed no traces of carbonate. Field emission scanning microcopy (FE/SEM) revealed a homogeneous size distribution of nanometric BFO powders. MAH method produced nanoparticles of 96% pure perovskite, with a size of 130 nm. These results are in agreement with Raman scattering values which show that the MAH synthesis route is rapid and cost effective. This method could be used as an alternative to other chemical methods in order to obtain BFO nanoparticles.

Keywords: bismuth ferrite, nanoparticle, microwave assisted hydrothermal synthesis, Pechini method

#### I. Introduction

Perovskites and related compounds are widely investigated because of their multiferroic, photocatalytic, and magnetic properties which are useful for applications in thin-film capacitors, nonvolatile memories, nonlinear optics and photoelectrochemical cells [1-4]. Most perovskite phases are prepared by solid-state reactions between the corresponding oxides at temperatures above 1000°C. Recently, solution based methods were extensively developed for synthesis of various perovskite nanomaterials [5]. One of the very few multiferroics with a simultaneous coexistence of ferroelectric and antiferromagnetic order parameters in perovskite structure, bismuth ferrite has attracted much attention since 1960. BiFeO, (BFO) has a ferroelectric Curie temperature  $T_c$  of 850°C and an antiferromagnetic Neel temperature of 370°C [6,7]. However, potential applications for BFO in the memory devices, sensors, satellite communications, optical filters and smart devices are limited due to its low insulation resistance caused by the reduction of the Fe<sup>3+</sup> species to the Fe<sup>2+</sup> formation of species and oxygen vacancies for charge compensation [8,9]. Although great advances have been achieved for BFO thin films prepared by the pulsed-laser deposition (PLD) method [10,11], it was hard to avoid generating impurity phases by the conventional solid-state reaction in bulk materials. BFO perovskites could be only stabilized within a narrow temperature range. To date, the synthesis of single-phase BFO ceramics is still a challenging issue. In the solid-state route, nitric acid leaching was required to eliminate impurity phases such as Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and Bi<sub>25</sub>FeO<sub>40</sub>, after the calcination of mixed bismuth and iron oxides [12] which resulted in coarser powders and a poor reproducibility. Most recently, Wang et al. [8] and Pradhan et al. [13] prepared pure BFO phase ceramics by a rapid liquid-phase sintering technique. The crystallization temperature of BFO above the ferroelectric Curie temperature  $T_c$  (in these methods) was required, which implied that the volatil-

<sup>\*</sup> Corresponding author: tel: +55 12 3123 2765

fax: +55 12 3123 2800, e-mail: alezipo@yahoo.com

ization of bismuth was difficult to avoid. In addition, Ghosh et al. [14] produced pure phase bismuth ferrite nanopowders by the tartaric acid based sol-gel method coupled with an additional calcination process. Thus, it is crucial to synthesize and investigate single-phase BFO-based solid solution with no other ferroelectric end member. To date, two main methods are reported to prepare single phase BFO ceramics; one method involves rapid liquid phase sintering and the other method uses leaching of the impurity phase with dilute nitric acid. These methods lead to ceramics with high leakage current, which is the main obstacle for its practical applications. So, an alternative method for preparing high quality BFO ceramics is desired. Chen et al. [15] utilized a low-temperature hydrothermal synthesis route to fabricate single-phase BiFeO<sub>3</sub> (BFO) crystallites. Effects of the initial KOH concentration, reaction temperature and duration time on the phase evolution as well as the particle size and morphologies of BFO crystallites were systematically investigated. They obtained perovskite BFO crystallites at the temperature of 200°C using a KOH concentration of 4M. Scanning electron microscopy observation revealed a homogeneous size distribution of submicron BFO powders. The ferroelectric Curie temperature of our hydrothermal BFO crystallites was determined to be 825°C by differential thermal analysis. Hydrothermal reactions utilized to form crystalline BFO powders were based on the dissolution-crystallization process. Han et al. [16] reported about tunable hydrothermal synthesis of bismuth ferrites with various morphologies. Well defined Bi<sub>12</sub>Fe<sub>0.63</sub>O<sub>18.945</sub> crystals and nano- and submicrometer-sized BiFeO<sub>3</sub> and Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> particles with different regular shapes were obtained by carefully controlling hydrothermal conditions. All the synthesized samples were found to be phase pure by XRD. The diffraction patterns of BiFeO<sub>3</sub> were indexed as a rhombohedrally distorted perovskite (JCPDS No. 86-1518) with a space group of R3c and lattice parameters of a = 5.582(4) Å and c = 13.876(7) Å. Chen *et* al. [17] synthesized large-scale polyhedral bismuth ferrite (BiFeO<sub>3</sub>) particles by the hydrothermal method under a series of experimental conditions. XRD revealed that BiFeO<sub>3</sub> powders had a perovskite structure. Scanning electron microscopy images showed that different BiFeO<sub>2</sub> particles were formed, such as sphere, octahedron, truncated octahedron, cubo-octahedron and truncated cube. Experimental results showed that the concentration of KOH, reaction time as well as heating and cooling rates had important impact on the size and morphology of the BiFeO<sub>2</sub> particles. The formation mechanism and change process of the large-scale polyhedral BiFeO, particles were discussed in detail. The BiFeO, obtained showed ferroelectric behaviour and magnetic response, which verified the multiferroic property of the BiFeO<sub>2</sub> crystals. The optical behaviour of BiFeO<sub>2</sub> particles revealed a band gap energy of about 2 eV, which

is smaller than for the BiFeO<sub>3</sub> bulk material due to the nanocrystalline structure.

The advantage of the soft chemical routes is that microcrystals can be synthesized at a considerably lower temperature plus energy saving and cost effective benefits. Among the chemical methods, hydrothermal synthesis is often used due to its simplicity which facilitates control of grain size, morphology and the degree of crystallinity by simple changes in the experimental procedure. Microwave assisted hydrothermal (MAH) synthesis is a variation of this method and has the advantage of lower processing temperature and time and a uniform nucleation of the powders in suspension [18–20].

In this study, we investigated the conditions required for the crystallization of BFO under microwave-hydrothermal conditions to obtain homogeneous nanoparticles with a uniform particle size and low carbonate content. For comparison, BFO powder was also synthesized by a simple soft chemical solution. This study underlines the role of the preparation route on the structural and morphological characteristics of the material obtained.

#### **II. Experimental**

BiFeO<sub>2</sub> (BFO) samples were prepared using microwave assisted hydrothermal (MAH) and a soft chemical solution (SCS) methods. In the first method, BFO powders were synthesized from an equimolar mixture of Bi(NO<sub>2</sub>)<sub>2</sub> and Fe(NO<sub>2</sub>)<sub>2</sub>×9H<sub>2</sub>O in 40 ml of aqueous KOH solution (KOH was used a mineralizer and deionized water as a reaction medium). All source chemicals are of analytical grade. Iron (III) nitrate nonahydrate (99.5% purity-Merck) and bismuth nitrate (99.5% purity-Aldrich) were used as raw materials. The mixture was ultrasonically dispersed for 15 min, transferred into a sealed Teflon autoclave and then placed in a microwave furnace (CEM Corp. Matthews, NC - model MARS-5) with a frequency of 2.45 GHz and variable power up to 300 W. The temperature inside the vessel was controlled through an optical fiber sensor (Model EST-300-CEM Corp.). The hydrothermal treatment was performed at the same temperature for different soaking times. The reactions were carried out for 5 min, 30 min and 1 hour at temperature of 180°C. After the hydrothermal reaction, the autoclave was naturally cooled to room temperature. The resulting powders (insoluble in water) were separated by centrifugation and washed with de-ionized water in sequence to remove all soluble salts, and then dried in an oven at 80°C for 24 hours in air.

BFO powders were also prepared by the soft chemical solution method (also called polymeric precursor method or the Pechini method [21]) starting from the fact that certain  $\alpha$ -hydroxycarboxylic organic acids can form polybasic, acid chelates with a wide range of cat-

ions. After the addition of a polyhydroxylic alcohol and heating, the chelate transforms into a polymer, with homogeneous cation distribution. Bismuth and iron precursor solutions were prepared by adding the raw materials to ethylene glycol in a concentrated aqueous solution of citric acid under heating and stirring. Appropriate quantities of Fe and Bi solutions were mixed and homogenized by stirring at 90°C. The molar ratio of metal/citric acid/ethylene glycol was 1/4/16. In this study, an excess of 5 wt.% Bi was added to the solution to compensate for some unavoidable bismuth oxide loss during the thermal treatment. Without this additional bismuth, the pure phase could not be obtained. Most of the organic matter is subsequently eliminated at temperatures as low as 300°C; a dark residue containing reactive oxides with well-controlled stoichiometry is formed. The porous product was crushed and heated in an alumina crucible at 850°C for 2 hours to eliminate organic material residues. The resulting powder was milled in an attritor with zirconia balls in an acetone medium for 40 minutes using a procedure from the literature [22].

The powders obtained were characterized by Xray powder diffraction (XRD) using a (Rigaku-DMax/2500PC, Japan) with Cu-K $\alpha$  radiation ( $\lambda$ =1.5406 Å) at 0.02 °/min. For Rietveld analyses, XRD data were collected under the following experimental conditions: 40 kV, 30 mA,  $20^{\circ} \le 2\theta \le 80^{\circ}$ ,  $\Delta 2\theta = 0.02^{\circ}$ ,  $\lambda Cu k_{a}$ monochromated by a graphite crystal, divergence slit of 2 mm, reception slit of 0.6 mm and step time of 10 s. The Rietveld analysis was performed with the Rietveld refinement program DBWS-941 1 [23]. The profile function used was the modified Thompson-Cox-Hastings pseudo-Voigt where  $\eta$  (the Lorentzian fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum. TG-DTA analyses were carried out with a Netzsch-409 STA apparatus at a heating rate of 20 °C/min under flowing air. Infrared spectroscopy (Model 400-IR/FT, IMPACT) was used to detect carbonates in bismuth ferrite powders. Raman spectra were collected with Bruker RFS-100/S Raman spectrometer with Fourier transform; a 1064 nm YAG laser was used as the excitation source, and its power was kept at 150 mW. Microstructural characterization was performed by FE-SEM (Supra 35-VP, Carl Zeiss, Germany).

#### **III. Results and discussion**

To determine the best annealing conditions and to evaluate the crystallization temperature necessary to obtain a single bismuth ferrite phase by the soft chemical method, thermal analyses were performed using TG-DTA analyses of the BFO powder obtained by microwave assisted hydrothermal method at 180°C for 1 hour (Fig. 1a). The existence of three stages, corresponding to the weight and energy change, can be observed in

nt	Parameters	BFO - SC	BFO – MAH
efineme Index	$R_{_{WP}}[\%]$	11.12	24.2
	$R_{exp}$	7.06	20.2
Re	S	1.57	1.2
Atomic Positions	A1	0; 0; 0.06722	0; 0; 0.06722
	A2	0; 0; 0.21091	0; 0; 0.21091
	B1	0; 0; 1/2	0; 0; 1/2
	B2	0; 0; 0.37099	0; 0; 0.37099
	O1	1/4; 1/4; 0	1/4; 1/4; 0
	O2	1/4; 1/4; 1/4	1/4; 1/4; 1/4
	O3	0; 0; 0.43786	0; 0; 0.43786
	O4	0; 0; 0.32536	0; 0; 0.32536
	05	1/4; 1/4; 0.11165	1/4; 1/4; 0.11165
S <sub>0ee</sub>	Bi (A1)	1.00000	1.00000
	О	0.93700	0.91700
Lattice Pa- rameter	<i>a</i> [Å]	5.6206	5.5806 (3)
	<i>c</i> [Å]	13.6924	13.8699 (7)
	V [Å <sup>3</sup> ]	374.57	374.38
	t	0.935	0.915
Perovskite [mol%]		$97.5 \pm 0.5$	$96.03 \pm 0.5$
Stoichiometry		BiFeO <sub>3</sub>	BiFeO <sub>3</sub>
Refinement		BiFeO <sub>2.7</sub>	BiFeO <sub>2.6</sub>

Fig. 1a. The first region (25-200°C) corresponds to the loss of physisorbed water; the second region (200-350°C) corresponds to the loss of surface hydroxyl groups. Finally, the weight loss above 500°C is due to the decomposition of the nitrate species. Figure 1b shows the TG-DTA curve of the BFO resin from room temperature up to 1000°C which was obtained by the polymeric precursor method. Two stages, corresponding to the weight and energy change, can be observed in Fig. 1b. The first characterized stage (from 25°C to 230°C) with a small weight loss is related to the elimination of excess ethylene glycol and water formed during the esterification process. The second stage (from 380°C to 500°C) is related to the decomposition of the polymeric metal-carboxylate complexes and to the formation of a metal oxide phase. The DTA curve shows strong exothermic peaks at ~420°C and ~620°C, which are correlated to a weight loss that must be considered as the crystallization of the residual amorphous phase.

XRD patterns of BFO powders synthesized by MAH method at 180°C at different times using an initial KOH concentration of 4M are shown in Fig. 2a. Diffraction peaks resulting from BFO powders synthesized for 1 hour can be indexed mainly with BFO according to the powder data of JCPDS card no.86-1518. These peaks



Figure. 1. TG/DTA curves of BFO nanoparticles synthesized by: a) microwave assisted hydrothermal method at 180°C for 1 h and b) soft chemical method and calcined at 300°C for 4 h

revealed that BFO crystallites had a perovskite structure belonging to the polar R3c space group [24,25] which indicates that the hydrothermal technique was successfully used to produce almost pure crystalline nanoparticles. However, the presence of an impurity phase, such as  $Bi_{2}Fe_{4}O_{0}$  was detected in addition to the major BFO phase for specimens hydrothermally treated for 5 min and 30 min. The BFO powders obtained by the MAH process lead to a reduction in processing time. Small variations observed in the XRD pattern can be associated with distortions in the lattice which possibly can be associated with the rapid formation kinetics of BFO powders due to the influence of microwave radiation during the MAH processing [26]. For comparison, the crystallinity of BFO obtained by the polymeric precursor method and calcined at 850°C for 4 hours was studied by XRD analyses. The XRD data reveal that BFO obtained by the soft chemistry method has an orthorhombic perovskite structure. The presence of  $Bi_{24}Fe_2O_{20}$ 

as a minor phase (marked with \*) is presented as a low level impurity phase.

In this study, the Rietveld refinement technique was used to investigate the crystal structure of the BFO powder (Table 1 and Fig. 3). Data were collected from nanoparticles obtained by microwave assisted hydrothermal method at 180°C for 1 hour and the powders synthesized by the soft chemical method and calcined at 850°C for 4 hours. Table 1 illustrates the  $R_{uuv}$  $R_{exp}$  and S indexes, as well as the lattice parameters (a)and c) and the unit cell volume (V). In both treatments, the atomic positions obtained by Rietveld analyses belong to the ICSD card (86-1518) with a space group of R3c. The quantitative phase analyses of powders for the orthorhombic phase were calculated according to the reference of Young and Wiles [23]. For the impurity (Bi<sub>2</sub>Fe<sub>4</sub>O<sub>0</sub>), we have obtained from the refinement  $R_{hrave}$ 20.4% and a space group of Pbam with unit cells equal to a = 7.939(5), b = 8.520(6) and c = 6.007(4). The re-



Figure 2. XRD pattern of BFO powders synthesized by: a) microwave assisted hydrothermal method at 180°C for 5 min, 30 min and 1 h and b) soft chemical method and calcined at 850°C for 4 h



Figure 3. Rietveld refinement of BFO nanopowders synthesized by: a) microwave assisted hydrothermal method at 180°C for 1 h and b) soft chemical method and calcined at 850°C for 4 h

sults confirmed that the BFO powder crystallized in the orthorhombic phase with no changes during the refinement. Hydrothermal treatment at 180°C for a long soaking time causes a structural distortion of the BFO lattice due to covalent interaction which originates from the strong hybridization between Fe 3*d* and O 2*p* orbitals. From the low *S* values ( $S = R_{wp}/R_{exp} = 1.2\%$ ) it can be assumed that the refinement of the BFO powder obtained by microwave assisted hydrothermal method at 180°C for 1 hour was successfully performed with all the investigated parameters close to literature data [27].

FTIR spectra of crystalline BFO powders derived from the hydrothermal reaction are shown in Fig. 4a. The broad band at 3000–3600 cm<sup>-1</sup> is the result of antisymmetric and symmetric stretching of  $H_2O$  and  $OH^$ bond groups, while a band at 1630 cm<sup>-1</sup> corresponds to the bending vibrations of H<sub>2</sub>O [28,29]. The band at around 1384 cm<sup>-1</sup> was due to the presence of trapped nitrates [30]. Specifically, strong absorptive peaks at 400-600 cm<sup>-1</sup> are attributed to the Fe-O stretching and bending vibration which is characteristic of octahedral FeO<sub>6</sub> groups in the perovskite compounds. The formation of a perovskite structure can be confirmed by the presence of metal-oxygen band [31,32]. Residual water and hydroxy groups are usually detected in the as grown samples and further heat treatment is necessary for their elimination. It is well known that the hydroxylation of metal ions and the deprotonation can be accelerated by raising the solution temperature or pressure [33]. The crystallized nanoparticles were found to have OH<sup>-</sup> ions due to the alkali used under the present reaction conditions. In hydrothermal-microwave processing



Figure 4. FT-IR spectra of a BFO nanoparticles synthesized by: a) microwave assisted hydrothermal method at 180°C for 1 h and b) soft chemical method and calcined at 850°C for 4 h



Figure 5. Raman spectra of BFO nanoparticles synthesized by: a) microwave assisted hydrothermal method at 180°C for 1 h and b) soft chemical method and calcined at 850°C for 4 h

the high frequency electromagnetic radiation interacts with the permanent dipole of the liquid (H<sub>2</sub>O), which initiates rapid heating from the resultant molecular rotation and permanent or induced dipoles in the dispersed phase cause rapid heating of the particles which results in a reaction temperature in excess of the surrounding liquid-localized superheating [34]. The band at around 830 cm<sup>-1</sup> was due to the presence of traces of trapped NO<sub>2</sub><sup>-</sup> ions in the BFO nanoparticles [35]. Infrared spectra of the BTO powder synthesized by SC method and calcined at 850°C for 4 hours were recorded (Fig. 4b). Typical band characteristics of oxygen-metal bonds were observed in the 450-640 cm<sup>-1</sup> region. The sample is free of carbonates. This result is satisfactory from a technological point of view since many properties are dependent on the purity of the raw powders, especially carbonate traces which may result in porous ceramics due to CO<sub>2</sub> elimination. The O-H bond stretching near 3400 cm<sup>-1</sup> could be attributed to adsorbed water due to the contact of the sample with the environment.

Raman scattering has proven to be a valuable technique to obtain information about local structures within materials. Raman spectra of the BFO nanoparticle obtained by MAH method at 180°C for 1 hour are illustrated in Fig. 5a. The modes located at 212, 316, 377, 445, 537 and 635 cm<sup>-1</sup> are caused by the internal vibration of FeO<sub>6</sub> octahedra, whereas modes below 200 cm<sup>-1</sup> must be attributed to different sites occupied by bismuth within the perovskite units. The bands located at 97 cm<sup>-1</sup>, 120 cm<sup>-1</sup> and 145 cm<sup>-1</sup> are related to Bi atoms of the perovskite layer and correspond to a rigid layer. These modes are probably due to a distortion in the A site caused by the bismuth ion. This distortion into the A site of the perovskite enhances the Jahn-Teller distortion of FeO<sub>6</sub> octahedra. On the other hand, Raman modes located above 200 cm<sup>-1</sup> are responsible for distortions and vibrations of FeO<sub>6</sub> octahedra. Vibrational modes of the powder obtained in the hydrothermal microwave tend to disappear when compared to the powders obtained in the conventional furnace (Fig. 5a) which can be related to structural disordering at short range, as well as a phase transition for an ordering crystal structure. The fast structural organization of BFO powder processed by MAH method can be related to the heating process which occurs from the interior to the surface. The microwave energy is transformed into heat through the interaction between molecules and atoms with the electromagnetic field. This interaction results in an internal and volumetric heating of the powders which promotes the formation of temperature gradients and heat flows [36]. Raman spectrum of the BFO powder obtained by SC method and calcined at 850°C for 4 hours is illustrated in Fig. 5b. The presence of Raman-active modes can be used to evaluate the degree of structural order at shortrange. The modes located above 200 cm<sup>-1</sup> are caused by internal vibrations of FeO<sub>6</sub> octahedra, whereas the internal vibrations below 200 cm<sup>-1</sup> are related to Bi atoms of the perovskite layer and corresponds to a rigid layer. Raman results are in agreement with XRD data; therefore, small changes observed in the spectra can be associated with the preparation method, average crystallite size and the degree of structural order.

The effect caused by thermal treatment in the morphology and shape of the grains was evaluated by SEM analysis (Fig. 6). SEM images of specimens synthesized by MAH method at 180°C for 1 hour are shown in Fig. 6a. According to the image, most of the grains of BFO powders are homogeneous with an individual particle size of approximately 130 nm. However, BFO powders reveal a few large particles with an irregular shape. The variation of grain morphologies may be an evidence of the formation of impurity phases. Nanometric and isotropic BFO crystallites obtained in this study are quite different from the previous study, where BFO powders agglomerated into a cubic shape with the side size of 45 mm under hydrothermal conditions [20]. The growth of large cubic grains is usually preferred for the hydro-



Figure 6. FE-SEM images of BFO nanoparticles synthesized by: a) microwave assisted hydrothermal method at 180°C for 1 h and b) soft chemical method and calcined at 850°C for 4 h

thermal lead zirconate titanate (PZT) particles [37]. In the hydrothermal process, the presence of an alkaline medium was found to be essential. In our case, a critical annealing time could exist after which the formation of impurity phases was favoured, and the formation of pure BFO was highly dependent upon this formation. The "dissolution and crystallization" process can be utilized to describe the hydrothermal reaction [38]. During the hydrothermal treatment, Bi3+ and Fe3+ hydroxides underwent an attack by KOH to dissolve and reacted at high temperatures and pressures, and then precipitated as insoluble ceramic oxide particles from the supersaturated hydrothermal fluid. If the temperature and pressure conditions are carefully maintained during the duration of the experiment, neither etching of BFO crystals nor the formation of a second phase is observed. Therefore, the dissolution and crystallization process continued in supersaturated fluid in such a way that the system was self-stabilizing. We conjecture that the dissociation of bismuth and iron hydroxide and the formation of ionic complexes might prevent the growth of BFO crystallites and limit the size of BFO particles to the nanometric range. The agglomeration process was attributed to Van der Waals forces. To reduce the surface energy, the primary particles have a tendency to form nearly spherical agglomerates, in a minimum surface to volume ratio [39]. This type of grain structure is common in oxide, ferrite and titanate ceramics [40-47] which is a result of an abnormal/discontinuous grain growth, also called an exaggerated grain growth. In abnormal growth, some grains grow faster than other grains with increasing sintering temperature. Abnormal grain growth may be the result of: (1) the existence of second phase precipitates or impurities, (2) materials with high anisotropy in interfacial energy and (3) materials with high chemical equilibrium [48]. In the hydrothermally derived BFO, which crystallizes in an orthorhombic structure, it can be assumed that the abnormal grain growth comes from factor (1) and (3) due to the existence of two-phase structure. At intermediate temperatures, a higher degree of agglomeration was noted which could be due to the favoured nucleation process at higher OH<sup>-</sup> concentration with no separation of particles which is due to a low reaction temperature. The random aggregation process between the small particles can be related to an increase in effective collision rates between small particles by microwave radiation [49] which indicates that microwave energy favours an anisotropic growth caused by the differences in the surface energies on the different crystallographic faces [50]. Possibly, the imperfections or differences between the height and width of these particles can be associated with the influence of microwave energy during the BFO phase growth process. A large number of elongated and circular agglomerates which are typical of chemical methods are evident in Fig. 6b. BFO presents a mixture of rod-like and plate-like grains. The rod-like grains might originate from an anisotropic behaviour of bismuth ferrite. There is no evidence of liquid-phase segregation at the grain boundaries which indicates that the polymeric precursor method facilitates the attainment of the phase at low sintering temperature with particles distributed in a nanometric matrix. By rough estimation and using the Sherrer formula, it was found that the individual crystallite size was approximately 30 nm.

## **IV. Conclusions**

BFO perovskite crystallites were prepared by using the microwave assisted hydrothermal (MAH) method and the soft chemical route. Compared with the conventional solid-state reaction process, nanometric BFO particles with better homogeneity could be produced by both methods. A longer hydrothermal treatment was beneficial to inhibit the formation of any impurity phases and promote the growth of BFO crystallites into almost single-phase perovskites. The hydrothermal reaction to grow BFO crystallites with 96% pure perovskite and a size of 130 nm is described by the dissolutioncrystallization process. Rietveld refinement reveals an orthorhombic structure with a space group of R3c. SEM analyses have shown a homogeneous size distribution of nanometric BFO particles. MAH method is important not only for the use of a short treatment time and low temperature but also for the possibility to control the morphological and structural properties. Therefore, the MAH method is undeniably a genuine technique for low temperatures and short times in comparison with the previous methodologies.

Acknowledgements: The financial support of this research project by the Brazilian research funding agencies CNPq and FAPESP is gratefully acknowledged.

#### References

- T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, Y. Tokura, "Magnetic control of ferroelectric polarization", *Nature*, 426 (2003) 55–58.
- M. Zaleski, "Thermally stimulated processes related to photochromism of scandium doped sillenites", J. Appl. Phys., 87 (2000) 4279–4284.
- E. Nippolainen, A.A. Kamshilin, V.V. Prokofiev, T. Jaskelainen, "Combined formation of a self-pumped phase-conjugate mirror and spatial subharmonics in photorefractive sillenites", *Appl. Phys. Lett.*, 78 (2001) 859–861.
- P.H. Borse, U.A. Joshi, S.M. Ji, J.S. Jang, E.D. Jeong, H.G. Kim, J.S. Lee, "Band gap tuning of lead-substituted BaSnO<sub>3</sub> for visible light photocatalysis", *Appl. Phys. Lett.*, **90** (2007) 034103–034105.
- Y. Mao, T.J. Park, S.S. Wong, "Synthesis of classes of ternary metal oxide nanostructures", *Chem. Commun.*, 46 (2005) 5721–5735.

- J.G. Ismilzade, "X-ray diffractometric detremination of the Curie temperature and temperature dependance of spontaneous polarization of hexagonal (rhomboedral) ferroelectrics", *Phys. Status Solidi (b)*, **46** (1971) K39–K41.
- G.A. Smolenskii, V.M. Yudin, "Antiferromagnetic properties of some perovskite", *Sov. Phys. JETP*, 16 (1963) 622–624.
- Y.P. Wang, L. Zhou, M.F. Zhang, X.Y. Chen, J.M. Liu, Z.G. Liu, "Room-temperature saturated ferroelectric polarization in BiFeO<sub>3</sub> ceramics synthesized by rapid liquid phase sintering", *Appl. Phys. Lett.*, 84 (2004) 1731–1734.
- 9. V.R. Palkar, R. Pinto, "Colossal magnetoresistance and other materials", *Pramana., J. Phys.*, **58** (2002) 1003–1008.
- J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig, R. Ramesh, "Epitaxial BiFeO<sub>3</sub> multiferroic thin film heterostructures", *Science*, **299** (2003) 1719–1722.
- K.Y. Yun, M. Noda, M. Okuyama, H. Saeki, H. Tabata, K. Saito, "Structural and multiferroic properties of BiFeO<sub>3</sub> thin films at room temperature", *J. Appl. Phys.*, **96** (2004) 3399–3403.
- M.M. Kumar, V.R. Palkar, K. Srinivas, S.V. Suryanarayana, "Ferroelectricity in a pure BiFeO[sub 3] ceramic", *Appl. Phys. Lett.*, **76** (2000) 2764–2766.
- A.K. Pradhan, K. Zhang, D. Hunter, J.B. Dadson, G.B. Loutts, P. Bhattacharya, R. Katiyar, J. Zhang, U. N. Roy, Y. Cui, A. Burger, "Magnetic and electrical properties of single-phase multiferroic BiFeO<sub>3</sub>", *J. Appl. Phys.*, 97 (2005) 093903–093906.
- S. Ghosh, S. Dasgupta, A. Sen, H. Sekhar, "Low-temperature synthesis of nanosized bismuth ferrite by soft chemical route", *J. Am. Ceram. Soc.*, 88 (2005) 1349–1352.
- C. Chen, J. Cheng, S. Yu, L. Che, Z. Meng, "Hydrothermal synthesis of perovskite bismuth ferrite crystallites", *J. Crystal Growth.*, **291** (2006) 135–139.
- J.-T. Han, Y.-H. Huang, X.-J. Wu, C.-L. Wu, W. Wei, B. Peng, W. Huang, J.B. Goodenough, "Tunable synthesis of bismuth ferrites with various morphologies", *Adv. Mater.*, 18 (2006) 2145–2148.
- X.-Z. Chen, Z.-C. Qiu, J.-P. Zhou, G. Zhu, X.-B. Bian, P. Liu, "Large-scale growth and shape evolution of bismuth ferrite particles with a hydrothermal method", *Mater. Chem. Phys.*, **126** (2011) 560–567.
- A. Outzourhit, M.A. El Idrissi Raghni, M.L. Hafid, F. Bensamka, A. Outzourhit, "Characterization of hydrothermally prepared BaTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub>", *J. Alloys Compd.*, **340** (2002) 214–219.
- S. Komarneni, Q. Roy, H. Li, "Microwave-hydrothermal synthesis of ceramic powders", *Mater. Res. Bull.*, 27 (1992) 1393–1405.
- 20. S. Komarneni, Q.H. Li, R. Roy, "Microwave-hydrothermal processing of BiFeO<sub>3</sub> and CsAl<sub>2</sub>PO<sub>6</sub>", *J. Eur. Ceram. Soc.*, **79** (1996) 1409–1412.

- 21. M. Pechini, U.S. Patent no. 3.330.697 (1967).
- A.Z. Simões, F. Gonzalez Garcia, C. dos Santos Riccardi, "Rietveld analysys and electrical properties of lanthanum doped BiFeO<sub>3</sub> ceramics", *Mater. Chem. Phys.*, **116** (2009) 305–309.
- R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paiva-Santos, "DBWS-9411 an upgrade of the DBWS\*.\* programs for Rietveld refinement with PC and mainframe computers", J. Appl. Cryst., 28 (1995) 366-367.
- X. Qi, M. Wei, Y. Lin, Q. Jia, D. Zhi, J. Dho, M.G. Blamire, J.L. MacManus-Driscoll, "High-resolution x-ray diffraction and transmission electron microscopy of multiferroic BiFeO<sub>3</sub> films", *Appl. Phys. Lett.*, 87 (2005) 071913–071915.
- A.G. Tutov, "Landolt-Bornstein Group III condensed matter - Numerical data and functional relationships in science and technology", *Fiz. Tverd Tela* (*Leningrad*), **11** (1969) 2682–2684.
- K.J. Rao, B. Vaidhyanathan, M. Ganguli, P.A. Ramakrishnan, "Synthesis of inorganic solids using microwaves", *Chem. Mater.*, **11** (1999) 882–895.
- S. Luo, Y. Noguchia, M. Miyayamab, T. Kudo, "Rietveld analysis and dielectric properties of Bi<sub>2</sub>WO<sub>6</sub>-Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> ferroelectric system", *Mater. Res. Bull.*, **36** (2001) 531–534.
- A.Z. Simões, B.D. Stojanovic, M.A. Ramirez, A.A. Cavalheiro, E. Longo, J.A. Varela, "Lanthanum-doped Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> prepared by the soft chemical method: Rietveld analysis and piezoelectric properties", *Ceram. Int.*, **34** (2008) 257–261.
- 29. Z.V. Gabbasova, M.D. Kuz'min, A.K. Zvezdin, I.S. Dubenko, V.A. Murashov, D.N. Rakov, I.B. Krynetsky, "Bi<sub>1-x</sub> $R_x$ FeO<sub>3</sub> (R = Rare earth): A family of novel magnetoelectrics", *Phys. Lett. A.*, **158** (1991) 491–498.
- A.V. Zalesskii, A.A. Frolov, T.A. Khimich, A.A. Bush, "Composition-induced transition of spin-modulated structure into a uniform antiferromagnetic state in a Bi<sub>1-x</sub>La<sub>x</sub>FeO<sub>3</sub> system studied using 57Fe NMR", *Phys. Solid State*, **45** (2003) 134–138.
- D. Lee, M.G. Kim, S. Ryu, H.M. Jang, S.G. Lee, "Epitaxially grown La-modified BiFeO<sub>3</sub> magnetoferroelectric thin films", *Appl. Phys. Lett.*, 86 (2005) 222903– 222905.
- J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruette, A.P. Pyatakov, "Influence of Mn and Nb dopants on electric properties of chemical-solution-deposited BiFeO<sub>3</sub> films", *Appl. Phys. Lett.*, 84 (2004) 5261–5263.
- H. Wang, J.J. Zhu, J.M. Zhu, X.H. Liao, S. Xu, T. Ding, "Fabrication of porous metal oxides for catalytic applications using templating techniques", *Phys. Chem.*, 4 (2002) 3794–3799.
- G.J. Wilson, A.S. Matijasevich, D.R.G. Mitchell, J.C. Schulz, G.D. Will, "Modification of TiO<sub>2</sub> for enhanced surface properties: Finite Ostwald ripening by a microwave hydrothermal process", *Langmuir*, 22 (2006) 2016–2027.
- 35. D.K. Agrawal, "Microwave processing of ceramics", *Curr. Opin. Solid State Mater. Sci.*, **3** (1998) 480–486.

- H. Zhang, X. Fu, S. Niu, Q. Xin, "Synthesis and luminescent properties of nanosized YVO<sub>4</sub>: *Ln (Ln=Sm, Dy)*", *J. Alloys Compd.*, 457 (2008) 61–65.
- M. Traianidis, C. Courtois, A. Leriche, "Mechanism of PZT crystallisation under hydrothermal conditions. Development of a new synthesis route", *J. Eur. Ceram. Soc.*, **20** (2000) 2713–2720.
- E. Shi, C.T. Xia, W.Z. Zhong, B.G. Wang, C.D. Feng, "Crystallographic properties of hydrothermal barium titanate crystallites", *J. Am. Ceram. Soc.*, 80 (1997) 1567–1572.
- Y.B. Khollam, A.S. Deshpande, A.J. Patil, H.S. Potdar, S.B. Deshpande, S. Date, "Microwave-hydrothermal synthesis of equi-axed and submicron-sized BaTiO<sub>3</sub> powders", *Mater. Chem. Phys.*, 71 (2001) 304–308.
- 40. J. Yoo, "The effects of microstructure on  $Ba_{1-x}Sr_xTiO_3$  pyroelectric materials for pyroelectric and bolometer infrared sensors", *Ph.D. Thesis*, University of Auckland, 1999.
- A.Z. Simões, E.C. Aguiar, A.H.M. Gonzalez, J. Andrés, E. Longo, J. A. Varela, "Strain behavior of lanthanum modified BiFeO<sub>3</sub> thin films prepared via soft chemical method", *J. Appl. Phys.*, **104** (2008) 104115-1–104115-6.
- A.Z. Simões, L.S. Cavalcante, C.S. Riccardi, J.A. Varela, E. Longo, "Improvement of fatigue resistance on La modified BiFeO<sub>3</sub> thin films", *Curr. Appl. Phys.*, 9 (2009) 520–523
- A.Z. Simões, M.A. Ramírez, C.S. Riccardi, E. Longo, J.A. Varela, "Ferroelectric characteristics of Sr-Bi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> thin films grown on Pt/Ti/SiO<sub>2</sub>/Si substrates

by the soft chemical method", *Mater. Lett.*, **60** (2006) 2020–2023.

- A. Z. Simões, M.A. Ramírez, C.S. Riccardi, A.H.M. Gonzalez, E. Longo, J.A. Varela, "Synthesis and electrical characterization of CaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> thin films deposited on Pt/Ti/SiO<sub>2</sub>/Si substrates by polymeric precursor method", *Mater. Chem. Phys.*, 98 (2006) 203–206.
- 45. A.Z. Simões, A.H.M. Gonzalez, E.C. Aguiar, C.S. Riccardi, E. Longo, J.A. Varela, "Piezoelectric behavior of SrRuO<sub>3</sub> buffered lanthanum modified bismuth ferrite thin films grown by chemical method", *Appl. Phys. Lett.*, **93** (2008) 142902–142904.
- A.Z. Simões, C.S. Riccardi, L.S. Cavalcante, J.A. Varela, E. Longo, "Size effects of polycrystalline lanthanum modified Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> thin films", *Mater. Res. Bull.*, 43 (2008) 158–167.
- A.Z. Simões, M.A. Ramírez, A.H.M. Gonzalez, C.S Riccardi, A. Ries, E. Longo, J. A. Varela, "Control of retention and fatigue-free characteristics in CaBi<sub>4</sub>. Ti<sub>4</sub>O<sub>15</sub> thin films prepared by chemical method", *J. Sol. State Chem.*, 179 (2006) 2206–2211.
- 48. S.-J.L. Kang, Sintering Densification, Grain Growth & Microstructure, Elsevier, Oxford, 2005, p. 265.
- M. Godinho, C. Ribeiro, E. Longo, E.R. Leite, "Influence of microwave heating on the growth of gadolinium-doped cerium oxide nanorods", *Cryst. Growth Des.*, 8 (2008) 384–386
- 50. J. Geng, Y. Lv, D. Lu, J.-J. Zhu, "Sonochemical synthesis of  $PbWO_4$  crystals with dendritic, flowery and star-like structures", *Nanotechnol.*, **17** (2006) 2614–2620.