



Microwave–hydrothermal synthesis of the multiferroic BiFeO₃

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ABSTRACT

In this work, three different methods for preparing BiFeO₃ polycrystals are compared: hydrothermal synthesis, microwave heating in the solid state and the combination of both, that is a hydrothermal method using microwave heating. The best materials, without high purity reactants, are obtained in few minutes by the last procedure, a new, very fast, reproducible and environment-friendly method of synthesis, which is described and discussed here.

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1. Introduction

Magnetoelectric multiferroic materials exhibit magnetic and ferroelectric order in the same temperature range. Among these compounds, ABO₃ perovskites where A = Bi and B = transition metal of the first row, i.e., Fe, deserve much attention because of their multiferroic possibilities, where spontaneous magnetic order – ascribed to the transition metal – and ferroelectric polarization – due to the lone-pair carried by bismuth – might be combined in a single phase material. These materials offer wide potential applications in information storage, such as spintronic devices and sensors where both electric and magnetic polarizations can be coupled [1,2].

BiFeO₃ is a well known multiferroic compound having simultaneous ferroelectric and weak ferromagnetic properties above room temperature. This material shows a rhombohedrally distorted perovskite structure (see Fig. 1). The space group R3c of BiFeO₃ allows, simultaneously, for a ferroelectric atomic displacement below 1083 K and for a weak-canted-ferromagnetism below a 643 K (Néel temperature) [3]. A synchrotron radiation structure refinement and a detailed explanation of its remarkable magnetoelectric properties appear in Ref. [4].

This material is quite difficult to be prepared either as single crystals or as a pure polycrystalline powder. According with the Bi₂O₃–Fe₂O₃ phase diagram, BiFeO₃ is an incongruently melting compound [5,6] and the kinetics of phase formation in the Bi₂O₃–Fe₂O₃ system can easily lead to the appearance of impurities such as

Bi₂₅FeO₄₀ and Bi₂Fe₄O₉ when preparing it by the ceramic procedure [7–11]. Moreover, according to Valant et al. [11], “the successful synthesis of single phase powder essentially depends on the purity of the starting materials”, these authors using some high purity reactants (99.9995%). The impurities formed during the heating process cannot be removed with further heat treatments. Previous works to overcome this problem involved different techniques such as sol-gel [12,13], coprecipitation [14], Pechini’s autocombustion [15,16], hydrothermal [17–19], and so on, but these methods are based on complex solution processes or involve toxic precursors.

In this work three different methods of synthesis for BiFeO₃ polycrystals are described and compared: hydrothermal, microwaves and the combination of both, that is, a hydrothermal method with microwave heating. This method, extensively used in analytical chemistry to dissolve poorly soluble materials, was proposed in the early nineties by Komarneni et al. [20,21], and demonstrated to be very efficient – on the grounds of kinetic reasons – for the synthesis and processing of ceramic powders, binary or ternary oxides. Nevertheless, to our knowledge, the application of this method for the synthesis of inorganic materials is not much extended. In our case, as later shown, the best results are obtained by this combined method of synthesis.

2. Experimental

2.1. Synthesis

In all cases the metal sources were Bi(NO₃)₃·5H₂O (Merck, 98%) and Fe(NO₃)₃·9H₂O (Merck, 98%). Three different routes have been followed.

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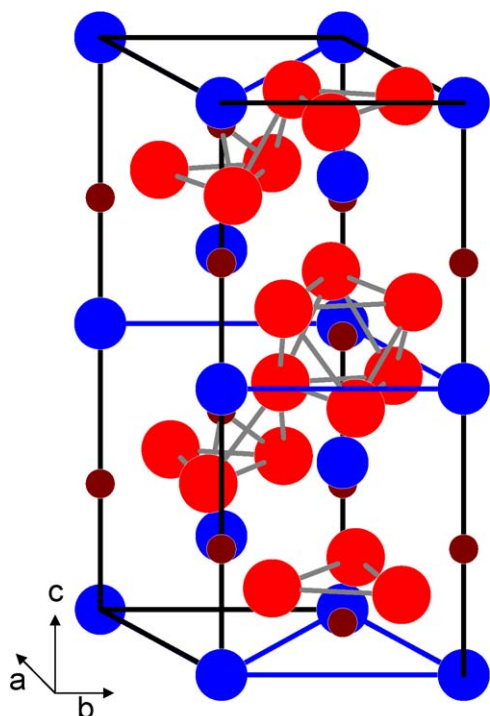


Fig. 1. BiFeO₃ unit cell. The rhombohedrally distorted perovskite structure is described with the corresponding hexagonal cell parameters. Colour codes: blue (Bi), red (O) and purple (Fe). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

2.1.1. Hydrothermal method

A procedure slightly modified from that described in Ref. [18] for the synthesis of BiFeO₃ has been used. A mixture of nitrates, using a 10% weight excess of the bismuth nitrate (barely soluble in these conditions) in order to displace the equilibrium towards the product formation, with 40 ml KOH 4 M, used as mineralizer, was ultrasonically dispersed for 30 min and transferred into a Teflon-lined stainless steel autoclave. The hydrothermal treatment was performed at 200 °C and autogeneous pressure (15 bars, the water vapour pressure at this temperature) during 24 h. After the hydrothermal reaction, the autoclave was allowed to cool down to room temperature. Finally, the products were decanted and leached with HNO₃ 2 M, rinsed with water to eliminate the remaining impurities and dried at 100 °C in a conventional oven.

2.1.2. Microwave route of synthesis

The procedure used is analogous to that described in Ref. [22] for the synthesis of Ni/NiO nanomaterials and performed in this work for the first time to prepare BiFeO₃. The reagents used in this study were the mixture of nitrates with carbon black (added to enhance microwave absorption). Different weight percentages of

carbon black (5% C or 10% C), were mixed with the salts, mechanically homogenized and compacted in pellets of 12 mm diameter. The pellets were put in a porcelain crucible and placed inside another larger one stuffed with mullite. Worth to note, the microwave source is a domestic microwave oven, operating a 2450 MHz frequency and 800 W power. After 30 min of microwave irradiation an amorphous powder is obtained which is, in a second step, heated at 500 °C in air for 24 h in a conventional furnace.

2.1.3. Microwave–hydrothermal synthesis

A commercial Milestone ETHOS 1 apparatus, operating at 2450 MHz, the same frequency used in domestic microwave ovens but fully automatized and therefore, capable of programming and adjusting the most important reaction parameters (pressure, power–temperature and time), equipped with a stirrer motor and a twist board was used. The reactions were carried out in double-walled vessels consisting of an inner Teflon container and an outer shell of high strength polymer. Two vessels, at least, were simultaneously used: one as reference, equipped with the temperature and pressure sensors, and another to equilibrate the rotating system; 20 ml of 4 M KOH solution, 1.05 g of iron nitrate and 1.52 g of bismuth nitrate were placed in each autoclave. The heating program used was as follows: a heating slope to 200 °C for 15 min, then 30 min at 200 °C and finally a slow cooling range for 15 min. The pressure limit was also set at 15 bars and the power limited to 800 W, keeping all the time the system under vigorous agitation. Finally, the products were decanted and leached with HNO₃ 2 M, rinsed with water to eliminate remaining impurities and dried at 100 °C in a conventional oven.

2.2. Characterization

Samples were characterized by powder X-ray diffraction (XRD) performed on a X'Pert MPD Philips instrument, using Cu K α ₁ radiation obtained with a Cu curved monochromator, operating at 45 kV and 40 mA. For the less pure samples, cell parameters were calculated using the CheckCell software [23]. For preliminary Rietveld analysis, only performed on the samples obtained by the microwave/hydrothermal method, a Philips X'Pert PRO ALPHA1 of Panalytical B.V. instrument with Cu K α ₁ radiation with primary curved Ge111 monochromator and speed X'Celerator detector was used. For cell parameters measurements and phase identification, the angle step and the counting time were 0.02° (2 θ) and 9 s, respectively. Fullproof software was used for profile fittings and cell parameter refinements [24]. Samples were also examined by scanning electron microscopy (SEM) on a Jeol 6400 microscope equipped with an EDAX Inc. energy-dispersive X-ray detector for microanalysis.

3. Results and discussion

The conditions used and the products obtained for the three methods described are summarized in Table 1.

Table 1

Conditions used for the three methods of synthesis described: (a) hydrothermal synthesis (HS); (b) microwave-solid state (MWSS) and (c) microwave/hydrothermal synthesis (MWHs).

Method	T (°C)	P (bar)	Time	Products (as prepared)	Products after annealing in air, 24 h, 500 °C
HS	200	15	1 day	BiFeO ₃ + Bi ₂ O ₃	–
			4 days	BiFeO ₃ + Bi ₂ O ₃ + Bi ₂ Fe ₄ O ₉	–
			5 days	BiFeO ₃ + Fe ₂ O ₃	–
MW-SS	–	–	10 min	Amorphous	BiFeO ₃ + Bi ₂ O ₃ + Fe ₂ O ₃
			20 min	Amorphous	BiFeO ₃ + Bi ₂ O ₃ + Fe ₂ O ₃
			30 min	Amorphous	BiFeO ₃ + Bi ₂ O ₃ + Fe ₂ O ₃
MW-HS	200	15	30 min	BiFeO ₃	–

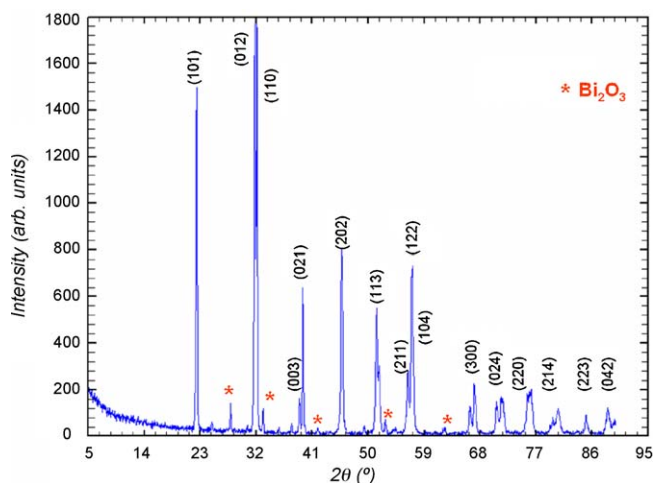


Fig. 2. Powder X-ray diffraction pattern of BiFeO₃ prepared by the hydrothermal method (1 day, 200 °C, 15 bars).

3.1.1. Hydrothermal

For the hydrothermal reactions, reactants, concentration, pH, total volume, pressure and degree of filling of the autoclave have been kept constant, the only variable being the heating time. BiFeO₃ is always obtained as a brown-reddish powder, although impurified with different phases as specified in Table 1. Fig. 2 shows the corresponding XRD patterns of the products obtained after 1 day of heating and leaching the materials obtained with diluted nitric acid, with bismuth oxide as the only impurity (~14%), while longer treatments result in partial decomposition of the desired material in non-soluble impurities such as Bi₂Fe₄O₉. Moreover, it has to be said that this method of synthesis is not very reproducible, probably due to the poor solubility of bismuth nitrate in alkaline conditions which turns a full reaction difficult, leading in some cases to other impurities such as FeOOH. As a consequence, the yield is far from 100%. Cell parameters (S.G. R3c) of the sample of BiFeO₃ obtained by this method are $a = b = 5.580(4)$ and $c = 13.832(2)$, in quite good agreement with those reported in the literature (JCPDS 86-1518). The average particle size, as obtained using the Debye–Scherrer formula, is ~33 nm.

3.1.2. Microwave-solid state

The choice of the nitrates as precursors for the microwave-assisted reaction in the solid state was based on their easy decomposition at moderate temperatures, their high electrical polarization due to non-centrosymmetrical structures and their simple compositions and availability. Fig. 3a shows the XRD pattern corresponding to the sample after 30 min of irradiation; the product is amorphous and black coloured (due to the presence of remnant carbon). After a heating treatment in air at 500 °C for 24 h, the samples become brown-red in colour and crystalline as shown in the corresponding XRD patterns (Fig. 3b). The impurities observed are Bi₂O₃ and Fe₂O₃ (produced by decomposition of the corresponding nitrates) which indicates a partially uncompleted reaction. Cell parameters for the 30 min microwaved sample BiFeO₃ are $a = b = 5.587(2)$ and $c = 13.8924(4)$ (S.G. R3c), again in reasonable agreement with those reported in the literature (JCPDS 86-1518) although bigger than the parameters reported above for the hydrothermal sample. The estimate proportions of BiFeO₃, Bi₂O₃ and Fe₂O₃ are 72%, 19% and 9%, respectively. The average particle size, as obtained using the Debye–Scherrer formula, is ~35 nm.

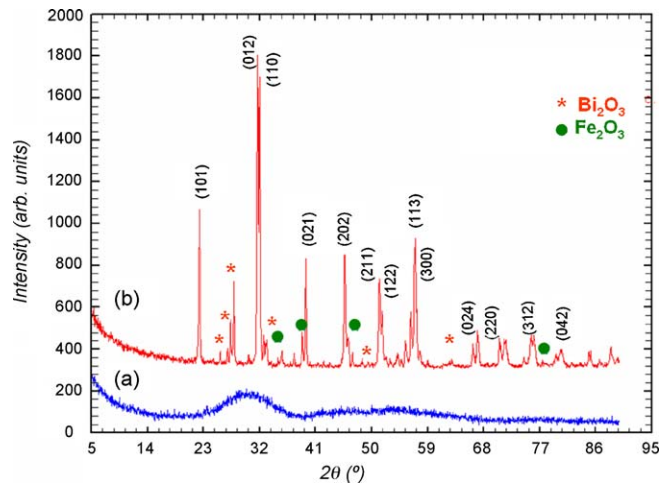


Fig. 3. (a) Powder X-ray diffraction pattern of an amorphous sample prepared by microwave irradiation (30 min) and (b) the same material yields crystalline BiFeO₃ sample after further treatment in air at 500 °C for 24 h.

3.1.3. Hydrothermal and microwaves

In this case, as described in Table 1, most of the conditions used for the conventional hydrothermal synthesis (power, T , P , pH, volume, KOH as mineralizer, etc.) have been maintained, and for the irradiation time, 30 min – optimal for the microwave-solid state procedure – has been chosen. It is interesting to point that in this case, and contrary to the conventional hydrothermal method, the yield of reaction is close to 100%; microwave radiation has, besides a different thermal profile in the autoclaves, a double absorption effect: provides heat through the reaction media (water) and decomposes the reactants (nitrates). This new, fast and fully reproducible method of synthesis yields materials of excellent crystallinity and purity as shown in Fig. 4 where the XRD pattern of a representative sample appears. All the Bragg reflections characteristic of the above-mentioned BiFeO₃ perovskite are indexed and no impurities are evident. Cell parameters, as obtained from the Rietveld profile analysis are $a = b = 5.5799(1)$ Å and $c = 13.8692(4)$ Å, in very good agreement with the values reported in the literature (JCPDS 86-1518). A full refinement will be published elsewhere. The average particle size, as deduced by using the Debye–Scherrer equation is ~35 nm. As a representative example, a SEM micrograph of this sample is shown in Fig. 5. Worth to be noted and quite differently

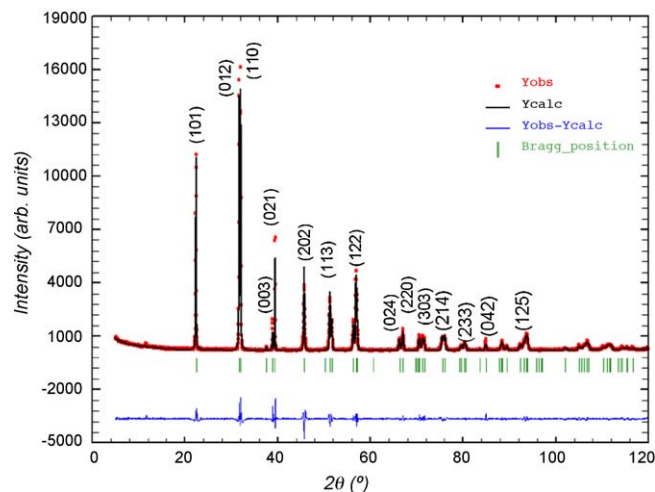


Fig. 4. Profile analysis of the powder X-ray diffraction pattern of BiFeO₃ obtained by the microwave/hydrothermal synthesis method.

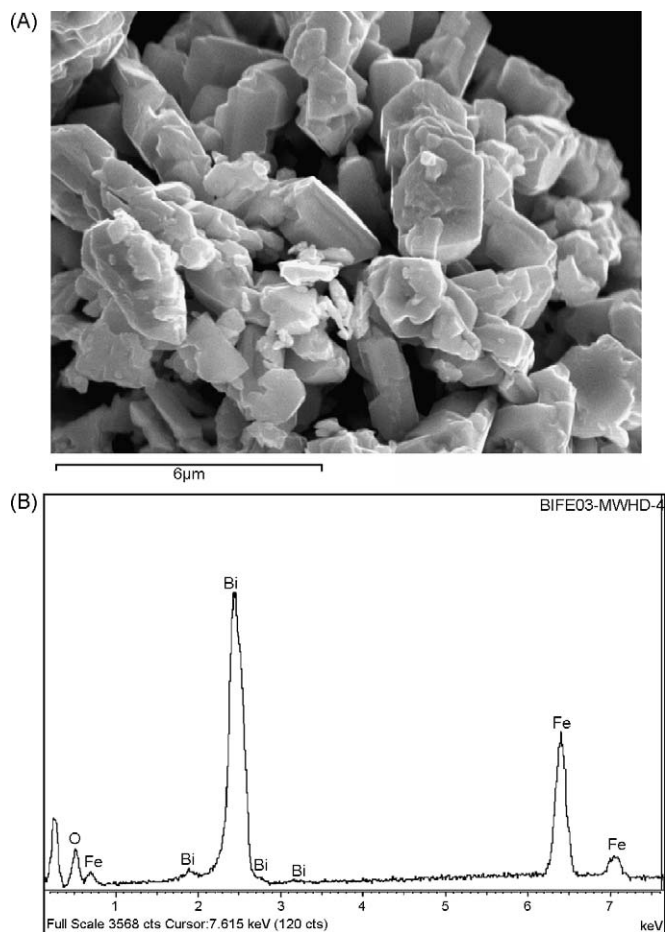


Fig. 5. (A) SEM micrograph of the BiFeO₃ phase obtained by the microwave/hydrothermal method and (B) corresponding EDS analysis.

from the above described cases, polyhedral particles are evident, some of them with hexagonal faces and sizes up to 2 μm. The corresponding microanalysis has been performed *in situ* both in an average mode and also by selecting single particles: the experimental atomic proportions of Bi, Fe and O are 22.12%, 22.35% and 55.53%, respectively which are in quite good agreement with the nominal ones (20%, 20%, 60%) if one takes into account the usual errors associated to the determination of light elements such as oxygen. Electrical and magnetic characterizations are in progress in order to check the properties of BiFeO₃ obtained by these means and compare them with those reported for this material obtained by other methods of synthesis. In this connection it has to be recalled that the literature concerning dielectric properties of BiFeO₃ is quite controversial, probably associated to the different ways of sintering used by different authors. Regarding the magnetic properties antiferromagnetism is the usual behaviour reported for BiFeO₃ but other authors claim anomalous temperature-dependent magnetization behaviour [8,10] ferromagnetism associated to nanoparticulated materials [25], etc., depending on the specific conditions of preparation or processing. A magnetic characterization

of the material obtained by the combined microwave/hydrothermal method is in progress.

4. Conclusion

BiFeO₃ can be prepared by three different ways: conventional hydrothermal synthesis, microwave-assisted solid state synthesis or the combination of both, that is, heating with microwaves an appropriate solution placed in an autoclave. This last method is optimum: it produces, without using high purity reactants at a moderate temperature (200 °C) and in a very fast way (30 min) the pure, well crystallized powder material.

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References

- [1] N.A. Spaldin, M. Fiebig, *Science* 309 (5733) (2005) 391–392.
- [2] W. Eerenstein, N.D. Mathur, J.F. Scott, *Nature* 442 (2006) 759–765.
- [3] T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M.P. Cruz, Y.H. Chu, C. Ederer, N.A. Spaldin, R.R. Das, D.M. Kim, S.H. Baek, C.B. Eom, R. Ramesh, *Nat. Mater.* 5 (2006) 823–829.
- [4] A. Reyes, C. de la Vega, Ma.E. Fuentes, L. Fuentes, *J. Eur. Ceram. Soc.* 27 (2007) 3709–3711.
- [5] A.K. Pradhan, K. Zhang, D. Hunter, J.B. Dadson, G.B. Loutts, P. Bhattacharya, R. Katiyar, J. Zhang, D.J. Sellmyer, U.N. Roy, Y. Cui, A. Burger, *J. Appl. Phys.* 97 (2005) 093903.
- [6] J. Yu, N. Koshikawa, Y. Arai, S. Yoda, H.J. Saitou, *J. Cryst. Growth* (2001) 231568.
- [7] X.Y. Zhang, C.W. Lai, X. Zhao, D.Y. Wang, J.Y. Dai, *Appl. Phys. Lett.* 87 (2005) 143102.
- [8] J. Chen, X. Xing, A. Watson, W. Wang, R. Yu, J. Deng, L. Yan, C. Sun, X. Chen, *Chem. Mater.* 19 (2007) 3598–3600.
- [9] S.V. Kalinin, M.R. Suchomel, P.K. Davies, D.A. Bonnell, *Am. J. Ceram. Soc.* 85 (12) (2002) 3011–3017.
- [10] Y.P. Wang, L. Zhou, M.F. Zhang, X.Y. Chen, J.M. Liu, Z.G. Liu, *Appl. Phys. Lett.* 84 (10) (2004) 1731–1733.
- [11] M. Valant, A.-K. Axelsson, N. Alford, *Chem. Mater.* 19 (2007) 5431–5436.
- [12] F. Chen, Q.F. Zhang, J.H. Li, Y.J. Qi, C.J. Lu, *Appl. Phys. Lett.* 89 (2006) 092910.
- [13] J.K. Kim, S.S. Kim, W.J. Kim, *Mater. Lett.* (2005) 4006–4009.
- [14] S. Ghosh, S. Dasgupta, A. Sen, H.S. Maiti, *Mater. Res. Bull.* 40 (2005) 2073–2079.
- [15] S. Ghosh, S. Dasgupta, A. Sen, H.S. Maiti, *J. Am. Ceram. Soc.* 88 (5) (2005) 1349–1352.
- [16] J.H. Luo, P.A. Maggard, *Adv. Mater.* 18 (4) (2006) 514.
- [17] J.-B. Li, G.H. Rao, J.K. Liang, Y.H. Liu, J. Luo, J.R. Chen, *Appl. Phys. Lett.* 90 (2007) 162513.
- [18] C. Chen, J. Cheng, S. Yu, L. Che, Z. Meng, *J. Cryst. Growth* 291 (1) (2006) 135–139.
- [19] S. Basu, M. Pal, D. Chakravorty, *J. Magn. Magn. Mater.* 320 (2008) 3361–3365.
- [20] S. Komarneni, R. Roy, Q.H. Li, *Mater. Res. Bull.* 27 (1992) 1393–1405.
- [21] S. Baldassari, S. Komarneni, E. Mariani, C. Villa, *Mater. Res. Bull.* 40 (2005) 2014–2020.
- [22] C. Parada, E. Morán, *Chem. Mater.* 18 (11) (2006) 2719–2725.
- [23] J. Laugier, B. Bochu, Checkcell—A Software Performing Automatic Cell/Space Group Determination, Collaborative Computational Project Number 14 (CCP14), Laboratoire des Matériaux et du Génie Physique de l'École Supérieure de Physique de Grenoble (INPG), France, 2000.
- [24] J. Rodríguez-Carvajal, Abstracts of the Satellite Meeting of the 15th Congress of the IUCr, Toulouse, France, 1990, 127. (<http://www.ill.eu/sites/fullprof/>).
- [25] V. Fruth, L. Mitoseriu, D. Berger, A. Ianculescu, C. Matei, S. Preda, M. Zaharescu, *Prog. Solid State Chem.* 35 (2007) 193–202.