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Ultrafast microwave hydrothermal synthesis and characterization of Bi$_{1-x}$La$_x$FeO$_3$ micronized particles

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Abstract

In this work a microwave assisted hydrothermal method is applied to successfully synthesize lanthanum doped bismuth ferrites (BLFO, Bi$_{1-x}$La$_x$FeO$_3$ where $x = 0, 0.15, 0.30, 0.45$). The growth mechanism of the Bi$_{1-x}$La$_x$FeO$_3$ crystallites is discussed in detail. The existence of the single-phase perovskite structure for all the doped samples is confirmed by the X-ray powder diffraction patterns. A peak shift, observed at lower angle with increasing La doping concentration, indicates that the BiFeO$_3$ lattice is doped. The results of TG/DTA show a shift in the transition temperature from 805$^\circ$C to 815$^\circ$C as function of the La-doping for all the doped powders. At higher levels of La doping, $i.e.$ $x = 0.30$ and $0.45$, significant weight losses occur above 860$^\circ$C suggesting a change in the physical and chemical properties. Finally, magnetic measurements are carried out at room temperature for pure BiFeO$_3$ and Bi$_{0.85}$La$_{0.15}$FeO$_3$. The results indicate that the materials are both weakly ferromagnetic, with no significant hysteresis in the curves.

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1. Introduction

Magneto-electric multiferroic materials exhibit magnetic and ferroelectric order in the same temperature range [1]. In this class of compounds, ABO$_3$ perovskites, where $A = \text{Bi}$ and $B = \text{first row transition metal}$, deserve greater attention since their multiferroic characteristics. In particular the coupling between magnetism and electric polarization of BiFeO$_3$ (BFO) has resulted in great research interest and an increasing demand for its application in several fields of science and technology such as spintronics, high-density storage media and stable nanoscale memory elements [2–5]. According to recent studies BFO, having a suitable band gap (~2.2 eV) and excellent chemical stability, is also an important UV responsive semiconductor photocatalyst used for degradation of organic pollutants [6–8]. However, potential applications of BFO are greatly limited due to the presence of impurity phases, small spontaneous polarization, high coercive field, inhomogeneous magnetic spin...
structure, ferroelectric reliability and high defect density, low
insulation resistance caused by the reduction of Fe$^{3+}$ species to
Fe$^{2+}$ and oxygen vacancies for charge compensation [9]. To tackle
the leakage current issue of BFO, several research groups have
attempted to partially substitute the Bi in the tetrahedral or octa-
hehedral sites of BFO by lanthanide elements (La, Ce, Nd, Sm, Eu, Gd,
Tb, Dy, etc.), transition metal and alkaline earth metal. This doping
by non volatile ions controls the volatile nature of Bi in BFO, reduces
the generation of oxygen vacancies and breaks the long-range
cycloidal spin arrangement responsible for cancelling the magne-
tization in the rhombohedrally distorted perovskite structure
[10–12].

The synthesis of complex oxide systems still remain a challenge
due to the multiplicity of oxidation states, morphologies and pha-
ses. Most perovskite based materials are prepared by solid–state
reactions between the corresponding oxides at temperature above
1000°C. Other preparation procedures for perovskites and in
particular for BiFeO$_3$ are sol–gel method [13], Pechini method [14],
auto combustion, chemical co-precipitation method including
solvothermal [15] and hydrothermal [16] synthesis. One of the
major underlined problems in the preparation of single phase
bismuth ferrite perovskite-type structured is the formation of im-
purities in both the micrometre-sized and nanostructure regions.
Many studies in fact describe the formation of secondary phases
such as Bi$_2$O$_3$, sillenite-type Bi$_2$Fe$_2$O$_8$ and mullenite-type Bi$_5$Fe$_3$O$_8$
[12–15]. Moreover, the Bi perovskites under high temperatures
decompose into the parent oxides [12–15]. Finally, Bi$_2$O$_3$, the
intermediate compound necessary for the BFO and doped BFO for-
amation, easily evaporates when heated at high temperature. On the
other hand, at room temperature under applied fields of about
200 kV cm$^{-1}$ BFO and doped with different metals (i.e. La, Ag, Ca,
Mn, etc) BFO can decompose, leading to hematite Fe$_2$O$_3$ [11,17,18]. J.
Prado-Gonjal et al. [19] compared three different methods for
preparing BiFeO$_3$ polycrystals: hydrothermal synthesis, microwave
heating in the solid state and the combination of both, that is
a hydrothermal method using microwave heating. The results sug-
gest that the best materials, without high purity reactants, are
obtained in few minutes by the last procedure. In our previous
work [20], the facile microwave hydrothermal synthesis route for
BFO, reported in [19] too, was repeated and optimized by carefully
controlling the reaction conditions (alkali medium concentration,
precursors ratio, temperature and time of reaction). Briefly, the
results of this investigation suggest operating at 200°C and using
KOH concentration as mineralizer source ranging from 4 M to 8 M, a
ratio 1/1 for the metallic nitrate precursors and a time reaction of
30 min are the best reaction conditions to prepare BFO pure-phase.

In all, in these two paper indicate the microwave hydrothermal
synthesis as a new, very fast, reproducible and environment-
friendly method to prepare pure BFO. Based on the authors’
knowledge dielectric heating with microwave assisted equipment
has never been applied to the synthesis of La-doped bismuth
ferrite. Here in this paper we study the microwave assisted hy-
drothermal synthesis: a fast co-precipitation reaction involving the
simultaneous occurrence of nucleation, growth, coarsening, and
eventually agglomeration processes which could represent a novel
approach to prepare nanostructures lanthanum doped bismuth
ferrite (BLFO). The main characteristic of this synthetic process is, in
fact, its widely recognized ability to enhance powder crystallinity
leading to a very homogenous particle size distribution with
respect to the conventional hydrothermal approach [21,22]. Indeed
when dielectric heating is applied via microwave (MW) irradiation,
the homogeneity of the temperature distribution reached inside
the reaction batch strongly favours the homogeneous versus het-
ergeneous nucleation mechanism. These advantages are even
more evident if compared with the “ceramic route”, where

extended periods dedicated to grinding and firing of solid prec-
cursors followed by annealing are necessary. The aim of this paper
is to report the efficiency of the microwave assisted hydrothermal
approach to obtain single-phase lanthanum modified bismuth
ferrite powders Bi$_{1-x}$La$_{x}$FeO$_3$ (BLFO) with x = 0.05, 0.30 and 0.45.
The use of a multi-mode MW applicator equipped with tempera-
ture and pressure control system permitted a careful and detailed
study of the influence of the experimental conditions (heating rate,
temperature and pressure into the reactor) on the BLFO phase
purity and properties. Moreover the total control of the above
mentioned experimental variables allowed a very good reproduc-
ibility of the optimized process performed at 200°C in terms of
phase purity and particle size. In particular, as shown in our pre-
vious paper [20], precursors composition, mineralizer concentra-
tion, hydrothermal temperature, heating rate and time play
important roles in the synthesis of these perovskites on the crys-
tallinity and morphology of Bi$_{1-x}$La$_{x}$FeO$_3$ crystallites.

2. Experimental section

2.1. Materials and microwave-assisted hydrothermal method

All the analytical grade (≥99.7%) chemicals used, bismuth nit-
rate, Bi(NO$_3$)$_3$·5H$_2$O, iron nitrate, Fe(NO$_3$)$_3$·9H$_2$O, lanthanum nit-
rate La(NO$_3$)$_3$·6H$_2$O and potassium hydroxide, KOH, were
purchased from Sigma Aldrich (Milan, Italy) and used without
further purification of analytical grade.

Bi$_{1-x}$La$_x$FeO$_3$ micronized particles with x = 0.05, 0.15, 0.30 and 0.45
were prepared from the nitrate salts as cation precursors and KOH
as mineralizer via a microwave assisted hydrothermal method
optimized by our research group for undoped compounds [20].

Bi(NO$_3$)$_3$·5H$_2$O, La(NO$_3$)$_3$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O were added to a
8 M KOH aqueous solution in a Teflon® reaction vessel under
vigorous magnetic stirring.

The vessel was placed in an ETHOS TC (Milestone Italia, Ber-
gamo, Italy) multimode microwave applicator, operating at the
frequency of 2.45 GHz and equipped with temperature and pres-
sure monitoring devices. The reaction mixture was heated up to
200°C in 15 min then this temperature was maintained for 30 min.
The source power was 500 Watt (for two vessels). After cooling
down to room temperature, the products were centrifuged and
washed several times with 1 M HNO$_3$ deionized water solution to
eliminate impurities and un-reacted starting compounds, and
finally dried at 110°C overnight in a conventional oven.

2.2. Powder characterization techniques

The dried powders were characterized by X-ray diffraction
(XRD) analysis (PANalytical, X’Pert PRO diffractometer, Almelo, The
Netherlands) using Ni-filtered Cu Ka radiation (k = 1.5405 Å). The
XRD patterns were collected, in the range 10°–90° at room tem-
perature, to investigate the crystal structures of BFO with different
La doping proportions.

The powder morphologies were examined by Scanning Electron
Microscopy (Scanning Electron Microscopy (ESEM, Quanta-200 Fei,
Oxford Instruments)) after Au sputtering.

Thermal analysis was performed using a differential thermal
analyzer (DTA) STA 429 CD, NETZSCf, Selb, Germany) to study the
phase transition. All the samples were placed in alumina-cru
cibles and the measurements were performed with a heating/cooling
rate of 10°C/min from room temperature to ~900°C in nitrogen at-
mosphere. The thermo-balance was flushed for 15 min with ni-
trogen prior to heating.

Raman spectra were acquired using a spectrometer equipped
with an He–Ne laser illumination (Horiba Jobin Yvon LabRAM,
though there is no literature evidence of its application to the synthesis of lanthanum doped bismuth ferrite. It is generally agreed that the crucial points of the based bismuth ferrite perovskites synthesis are the dissolution of the precursors (i.e., Bi(NO\textsubscript{3})\textsubscript{3}:5H\textsubscript{2}O, La(NO\textsubscript{3})\textsubscript{3}:6H\textsubscript{2}O, Fe(NO\textsubscript{3})\textsubscript{3}:9H\textsubscript{2}O) and of $\alpha$-bismuth oxide (reactive intermediate), vital processes to reach the super-saturation. The basic mechanism to describe this processes is “dissolution-crystallization” [16], in which the dissolution of the reactants is strongly dependent on a mineralizer i.e. KOH, and crystallization only occurs in the supersaturated fluid.

As we observed in our previous work, and in agreement with literature, the alkali concentration in synergistic cooperation with high temperature and high pressure, plays a key role in the whole process as responsible of the crucial substrates dissolution [20]. In fact, with high alkali concentration (> M) the dissolution of the nitrate-precursors and of the reaction intermediate $\alpha$Bi\textsubscript{2}O\textsubscript{3} are promoted. This brings to the Bi$^{3+}$ ions formation, which reacts with Fe(OH)\textsubscript{3} leading to the BiFeO\textsubscript{3} multiferroic phase [16,19,20].

The crucial step is the achievement of the so-called super-saturated fluid condition in which the Bi$^{3+}$ concentration in the alkali solution exceeds the saturation point, as detailed in Equation (2) of mechanism detailed below. Rod-like $\alpha$-Bi\textsubscript{2}O\textsubscript{3} particles gradually dissolve into Bi$^{3+}$ ions, and this higher degree of super-saturation, useful to overpass the energetic barrier, results in a higher nucleation rate of BLFO. Finally, as indicated in Equation (3), they eventually react with amorphous iron and lanthanum (III) hydroxide leading to the $\text{Bi}_{1-x}\text{La}_x\text{Fe}_2\text{O}_5$ multiferroic phase.

\[
\text{Bi(NO}_3\text{)}_3 + \text{La(NO}_3\text{)}_3 + \text{Fe(NO}_3\text{)}_3 + 9\text{KOH} \rightarrow \text{Bi(OH)}_3 + \text{Fe(OH)}_3 + \text{La(OH)}_3 + 9\text{KNO}_3
\]  \hspace{0.5cm} (1)

\[
\text{Bi(NO}_3\text{)}_3 + \text{La(NO}_3\text{)}_3 + \text{La(OH)}_3 + 6\text{KOH} \rightarrow 2\text{Bi(OH)}_3 + 3\text{K}_2\text{O}
\]  \hspace{0.5cm} (2)

\[
(1-x)\text{Bi(OH)}_3 + x\text{La(OH)}_3 + \text{Fe(OH)}_3 \rightarrow \text{Bi}_{1-x}\text{La}_x\text{Fe}_2\text{O}_5 + 3\text{H}_2\text{O}
\]  \hspace{0.5cm} (3)

\[
\text{Bi(OH)}_3 + 4\text{Fe(OH)}_3 \rightarrow \text{Bi}_3\text{Fe}_2\text{O}_5 + 9\text{H}_2\text{O}
\]  \hspace{0.5cm} (4)

\[
36\text{Bi(OH)}_3 + 2\text{Fe(OH)}_3 \rightarrow \text{Bi}_{36}\text{Fe}_2\text{O}_{57} + 57\text{H}_2\text{O}
\]  \hspace{0.5cm} (5)

However, it is worthwhile to remark that high concentrations of KOH (>10 M) could cause the formation of secondary phases, Equations (4) and (5), probably due to a different thermodynamic state or to kinetic reasons connected to “dissolution and crystallization process” originating from higher pH value and solubility of $\alpha$-Bi\textsubscript{2}O\textsubscript{3} [16,22].

Other parameters that can promote the $\alpha$-Bi\textsubscript{2}O\textsubscript{3} dissolution and enhance the BLFO formation are: reaction temperature, heating rate, reaction time and presence of an inorganic agent as Na\textsubscript{2}CO\textsubscript{3} [19]. As said, only when the system exceeds a threshold temperature, the super-saturation is reached and the energy barrier transition leading to the BLFO formation. Even though the increase of the reaction time is another considered strategy to improve the dissolution of $\alpha$-Bi\textsubscript{2}O\textsubscript{3}, the drawback is the degradation of BLFO and the formation of secondary phases (Bi$_2$FeO$_{4.0}$, Bi$_2$Fe$_2$O$_{5.7}$, Fe$_2$O$_3$) [16,22].

3.2. Morphology characterization

In order to investigate the morphology of the micronized particles synthesized SEM observations were performed.

Fig. 2 a–c show SEM images of $\text{Bi}_{1-x}\text{La}_x\text{Fe}_2\text{O}_5$ ($0 \leq x \leq 0.45$) particles for selected samples. All the powders are found to be micron-sized particles that are agglomerates of micronized grains. The size and morphologies of these samples are affected by the lanthanum doping level: the images of un-doped BiFeO\textsubscript{3} particles

![Fig. 1. XRD patterns of Bi$_{1-x}$La$_x$Fe$_2$O$_5$ where x = 0, 0.15, 0.30 and 0.45 synthesized using 8 M KOH at 200 °C for 30 min.](image-url)
show an homogenous size distribution with a semi-cubic morphology in spherical aggregates characterized by a mean diameter of 20 \( \mu \text{m} \) (Fig. 2a). After the lanthanum doping with \( x = 0.15 \) (Fig. 2b), the diameter of particles is reduced to an average diameter of 5 \( \mu \text{m} \) in a homogeneous size distribution. When the La doping level increases up to \( x = 0.45 \) (Fig. 2c) the particles show irregular shape agglomerates of 10 \( \mu \text{m} \) and/or hundred micrometers. Hence, the particle morphologies and size indicate that the doped lanthanum ion has an effect on the crystallization habit of BiFeO\(_3\) particles in a microwave assisted hydrothermal method.

### 3.3. Thermal characterization

To characterize the thermal behaviour of the perovskite-structured particles Fig. 3a shows the TGA curves for all the prepared samples. The weight losses appear as a sequence of losses that occurred at nearly identical temperatures in all samples, namely at about 120 °C, 250–400 °C, 460–500 °C, 600 °C, 670 °C, 750 °C and a larger weight loss starting at 850 °C, which is likely attributed to decomposition and evaporation of Bi\(_2\)O\(_3\). As seen from the first derivative of the weight loss (DTG) in the figure, weight losses at 260–320 °C and particularly at 850 °C were relatively larger for the two higher doping levels than for the two less doped materials. In particular, the highest doping level exhibited higher weight losses in most of the steps.

The differential temperature (DTA) has been shown in Fig. 3b–c. In all the curves endothermic peaks can be found at about 120 °C, 300–320 °C, 420 °C, 800–815 °C and 850 °C, whereas the DTA-peak associated with the weight losses between 400 and 500 °C seems to be exothermic. Up to 200 °C only the Bi\(_{0.55}\)La\(_{0.45}\)FeO\(_3\) sample
presents an endothermic peak at around 187.7 °C, but it is not related to any significant loss of weight. In the pure sample BiFeO₃, an endothermic peak can be seen at about 330 °C attributed to the Neel temperature of BFO [9]. Based on the literature, the small endothermic peak at around 815 °C could be assigned to a ferroelectric-to-paraelectric phase transition [23], which has been enlarged in Fig. 3c where a significant shift in the transition temperature from 814 °C to about 793 °C as function of the La-doping is observed. Table 1 reports the numbers of extrapolated onset temperatures $T_C$ (Curie temperature), and peak area for all the

![Graphs showing TG/DTG, DTA patterns, and DTA enlargements for Bi₁₋ₓLaₓFeO₃ samples.](image-url)

**Fig. 3.** a) TG/DTG trace observed for Bi₁₋ₓLaₓFeO₃ 0 ≤ x ≤ 0.45 heated at a constant rate 10 °C/min up to 900 °C in nitrogen atmosphere; b) simultaneous DTA pattern and c) DTA enlargement in the range between 700 °C and 900 °C for all the prepared samples.
investigated powders. The $T_C$ is 813.9 °C for undoped BFO and it decreases with La doping increase. The two formulations with $x = 0$ and 0.15 retained both the peak-shape and the peak area during the cooling segment, while at higher doping levels a secondary peak started to develop at lower temperatures. This phenomenon can better be seen on the trace of the La0.45Bi0.55FeO3 and it has been highlighted in Table 1 by two values for the extrapolated onset during heating. In addition to the phase transition, samples showed minor weight losses (Table 1). Again, pure BFO and BLFO with $x = 0.15$ behave more or less identical, whereas the two higher doping levels lead to markedly higher degradation summarizing the DTA–TGA results suggest that the La 15% doping of BFO was successful, while higher doping levels lead to gradually lower thermal stability and phase purity.

### 3.4. Crystal structure characterization

Starting from the characterizations yet reported it is evident that all the samples have shown a single crystalline phase without impurity phases (XRD analysis, Fig. 1a), but at doping levels greater than $x = 0.15$ the samples, keeping the same crystalline pattern, seems to undergo structural distortions highlighted by morphological characterizations (Fig. 2) and by thermal analysis (Fig. 3). For these reasons the work has been concluded with the Raman and magnetic characterization of La0.15Bi0.85FeO3.

### 3.5. Magnetic characterization

Fig. 5 presents the magnetization as a function of field at room temperature for BFO and La0.15Bi0.85FeO3 measured as full loops (1.5T -> −1.5T -> 1.5T). The results show the expected antiferromagnetic behaviour with a weak ferromagnetic component due to crystalline or structural imperfections of the investigated samples: the magnetization of the doped sample is slightly lower than the...
undoped one. Furthermore, it is clear that there is no significant hysteresis in either sample. In fact, the hysteresis in the studied materials is a mere 0.01 T, which is close to the instrumental resolution of the VSM used.

4. Discussion & conclusions

Lanthanum-doped bismuth ferrite (Bi$_{1-x}$La$_x$FeO$_3$, $x = 0, 0.15, 0.30$, and 0.45) crystallites were successfully synthesized by an ultrafast microwave assisted hydrothermal method. The optimized microwave hydrothermal conditions allowed to promote the formation of crystalline BLFO powders at a very low processing temperature of 200 °C, which greatly reduced the synthesized temperature by about 500 °C and reaction time for the BLFO phase beyond which a perovskite degradation has taken place in terms of the thermal properties (TG/DTA) and morphology (ESEM images). Indeed the ferroelectric transition temperature decreased from the thermal properties (TG/DTA) and morphology (ESEM images).

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As conclusive remark we can state that this paper shows that the microwave assisted hydrothermal route, without the presence of catalysts and expensive equipment, has been able to ensure high purity in the products and greatly reduce the production cost. Therefore this approach offers a novel, fast and simple synthetic route for high-quality mixed oxide ceramic powders.

Acknowledgements

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