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Structural, morphological and surface properties of the samarium modified BiFeO₃ perovskite

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Abstract. This paper reports the synthesis of the Bi_{0.93}Sm_{0.07}FeO₃ system by the conventional method of solid-state reaction using quenching at room temperature. X-ray diffraction characterization revealed a rhombohedral perovskite structure with spatial group *R3c* (161) and an impurity phase of Bi₂Fe₄O₉. The scanning electron microscopy images show the formation of homogeneous grains with an average size of 3 μm. The energy dispersive X-ray Spectroscopy (EDS) microanalysis shows the percentage of samarium incorporated in the structure of the bismuth ferrite. The analysis of X-ray photoelectron spectroscopy (XPS) allowed us to establish the percentage of the ions Bi, Sm, Fe and O ions present in the surface of the solid in addition to confirming the oxidation state 3+ of all the cations.

1. Introduction

BiFeO₃ is an attractive multiferroic material in the industry because it is a material with structure ABX₃ perovskite with rhombohedral distortion, which generates a ferroelectric polarization and a magnetic order at room temperature, making it a potential multifunctional material [1,2]. Some of the disadvantages that this material presents, if it is to be used on a large scale in technological applications, are the high dielectric loss, the low remaining polarization and the weak magneto-electric coupling in addition to the obtaining of pure BiFeO₃, since the temperature where this pure phase is stabilized competes with other secondary phases (Bi₂Fe₄O₉, Bi₂₅FeO₄₀), which leads to a high leakage of electric current due to the difference between the ionic radii of Fe³⁺ and Bi³⁺, thus generating oxygen vacancies by the conversion of iron oxidation states [3,4]. These structural defects are usually solved by replacing the atoms of Bi and Fe with trivalent ions such as those of rare earths, that give the material greater structural stability [5,6]. One of the elements that generates high stability is the Samarium. This element decreases the band gap and Fermi level, besides improving the electrical polarization in the surface of the material for possible optoelectronic applications, like in photo-catalysis for water treatments and as a material in photovoltaic cells [7–9].

For these reasons, this work describes the synthesis and structural, morphological and superficial characterization of a mixed oxide of iron and bismuth modified with samarium synthesized by the solid-state reaction method, providing relevant information of the compositional study of the surface for possible optoelectronic applications.



2. Experimental

The $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ system was synthesized by the solid-state reaction method (SSR). The reagents used (Bi_2O_3 , Sm_2O_3 and Fe_2O_3 , 99.999%) were purchased from Sigma-Aldrich. Stoichiometric amounts of each precursor oxide were weighed and dried. The oxides were mixed and macerated for 3 hours in an agate mortar. The homogenized oxides were ground at a pressure of 5.0 MPa for one minute and calcined at 700 °C for 10 hours. The calcined system was homogenized for 2 hours and sintered at 830 °C for 20 hours, followed by quenching at room temperature [10]. The structural characteristics of the synthesized sample were analyzed by means of X-ray diffraction (XRD) in a PANalytical X'Pert PRO MPD diffractometer, equipped with Ultra-Fast X'celerator detector and Bragg-Brentano configuration, using Cu K α radiation ($\lambda=1.5418$ Å). The pellet samples were analyzed in 2θ range from 10° to 70°. The morphological characteristics and the elemental analysis were performed by use of scanning electron microscopy (SEM) in a JEOL JSM-5300 microscope equipped with a detector for chemical analysis by means of energy dispersive X-ray (EDX). Surface elemental composition of the synthesized pellet was analyzed on an X-ray photoelectron spectrometer PHOIBOS WAL with monochromatic Al K α radiation (1486.6 eV) light source provided by SPECS. A constant energy beam of 10 eV was used in data acquisition. The charge effects in the XPS spectra were corrected using the value of the binding energy of carbon 1s peak at 284.5 eV [11].

3. Results and discussion

Figure 1 shows the X-ray diffraction pattern (XRD) in pellet of the BiFeO_3 sample modified with 7% bismuth. The semiquantitative analysis of the experimental diffraction pattern reveals the formation of two structural phases, which correspond to $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ in 90% and $\text{Bi}_2\text{Fe}_4\text{O}_9$ in 10%. $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ has a perovskite structure with a rhombohedral crystalline system, spatial group $R3c$ (161), lattice parameters $a = b = 5.577$ Å, $c = 13.861$ Å according to the reference diffraction pattern ICSD No. 86-1518. The peaks marked with the red symbol in Figure 1 are attributed to the secondary phase $\text{Bi}_2\text{Fe}_4\text{O}_9$ (ICSD file no. 74-1098) present in the ceramic material synthesized by SSR method in accordance with Chermahini *et. al* [12]. The scheme of the $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ perovskite structure is revealed in Figure 2. The diagram shows the chains of face-sharing FeO_6 octahedra orientated along the c-axis [13].

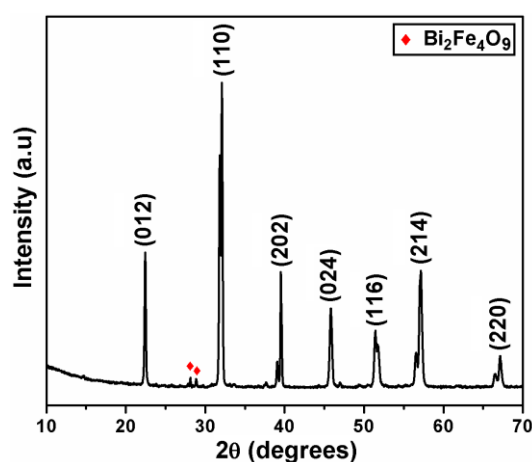


Figure 1. X-ray diffraction pattern of $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ system.

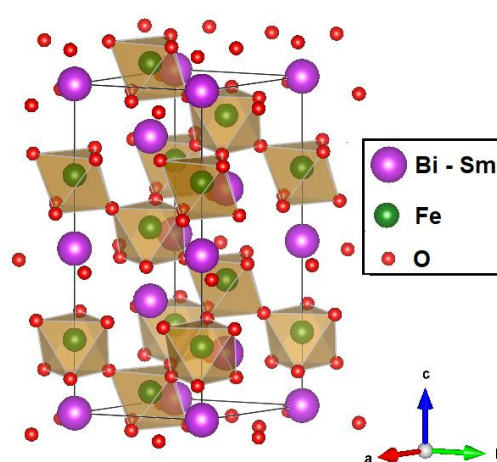


Figure 2. Schematic structure obtained with VESTA software of $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ sample.

The surface morphology of the samarium modified with bismuth ferrite was analyzed with the scanning electron microscopy images shown in Figures 3(a) and (b). The micrographs reveal the formation of homogeneously distributed grains characteristic of the sintering and cooling process to which the material was exposed, generating narrower grain boundaries at the surface level without morphological modifications, indicating that samarium is incorporated in BiFeO_3 , as stated in previous

works [14]. Figure 3(c) presents the frequency histogram of the agglomerates shown in Figure 3(a), which shows a unimodal distribution with micrometric grain sizes of 3 μm on average at the surface of the synthesized oxide.

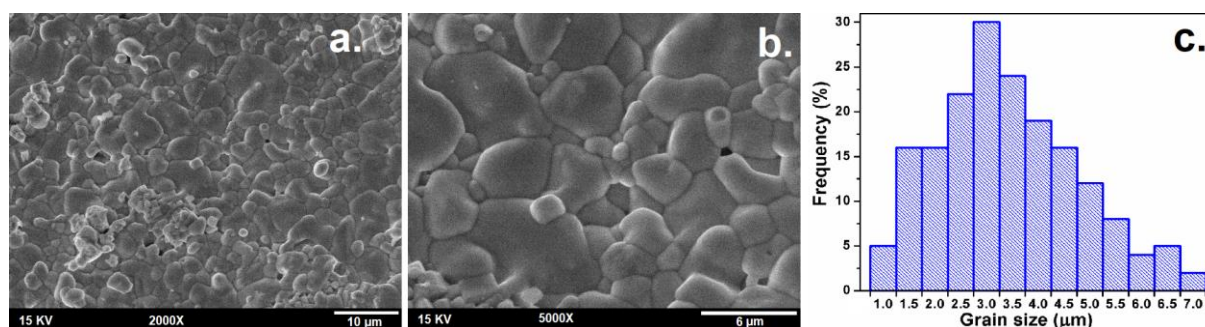


Figure 3. Scanning electron microscopy images for $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ sample at 10 μm (a), 6 μm (b) and grain size distribution data determined from SEM (c).

The appearance of samarium in the X-ray dispersive energy spectrum shown in Figure 4 allowed us to infer that Sm ions were proportionally incorporated in position A of the perovskite structure, thus validating the XRD analyzes. The mass percentage values of the different atoms are related to the proposed stoichiometry in terms of the modification of the Bi cations by Sm [15].

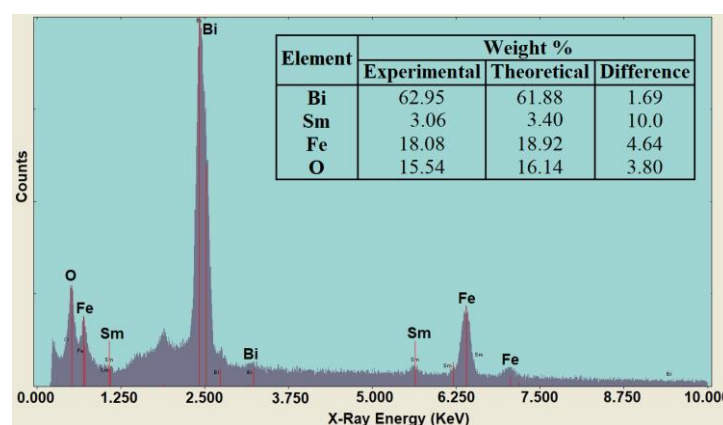


Figure 4. EDS spectrum of the $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ perovskite synthesized by the solid reaction reaction method.

The survey XPS spectrum of $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ confirmed the presence of Bi, Fe, and O ions in the sample, as shown in Figure 5(a). The photoemission peaks at 158.9 eV and 164.2 eV in Figure 5(b) corresponds to Bi $4f_{5/2}$ and Bi $4f_{7/2}$ respectively and are associated with the Bi^{3+} bond and oxygen [16]. In the case of the peaks Fe $2p_{3/2}$ and Fe $2p_{1/2}$ presents a contribution of Fe^{3+} at 711.2 eV and 735.8 eV respectively and its satellite peaks shifted 8.0 eV [17]. Besides, the O 1s contribution exhibited two peaks at binding energies of 529.1 eV for the impure phase $\text{Bi}_2\text{Fe}_4\text{O}_9$ and 532 eV for the $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ phase [18]. The high-resolution spectrum of Sm is not shown, due to the low intensity of the signals. The chemical quantification for the atomic concentration of Bi, Sm, Fe and O in the Sm-BiFeO₃ system was found to be 18.4%, 2.9%, 13.4% and 65.1% respectively.

The elemental analysis by XPS, reveals that the samarium is found in greater proportion in the surface of the synthesized ceramic material in comparison with the samarium that is present in the bulk of the compound as shown in the EDS analysis. This difference is due to the impurity present after the synthesis process. According to previous investigations [12,19], the bismuth and iron precursor oxides when

treated thermally, react to form the BiFeO_3 mixed oxide, in this process an intermediate of $\text{Bi}_2\text{Fe}_4\text{O}_9$ is formed which in turn reacts with an excess of Bi_2O_3 to form the bismuth ferrite. Therefore, the time for calcination and sintering was not enough for the processes of diffusion of the oxides of Bi, Sm and Fe to be propitiated completely and for this reason the obtaining of the solid $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ was favored in the surface and the compound $\text{Bi}_2\text{Fe}_4\text{O}_9$ was in a high ratio to the interior of the grain, confirming the XRD and EDS analyzes.

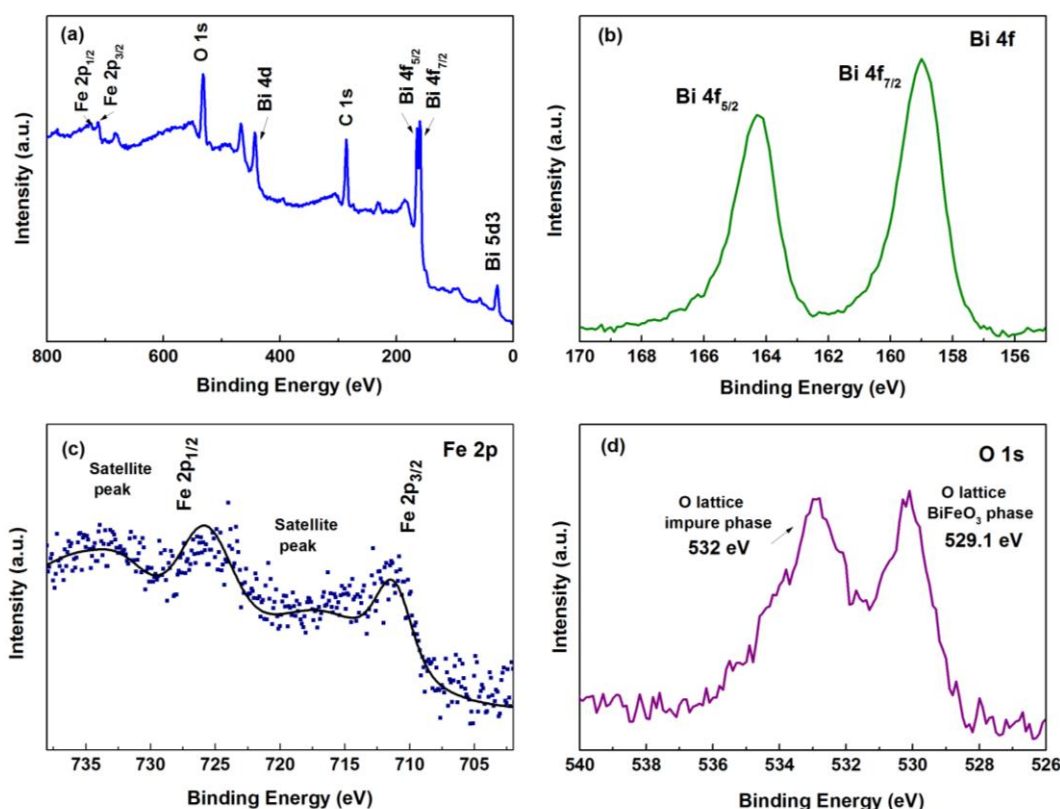


Figure 5. XPS spectra of $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ (a) survey (b) Bi 4f, (c) Fe 2p, and (d) O 1s core level

4. Conclusions

The $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ System was synthesized by the conventional solid state reaction method. The X-ray diffraction characterization demonstrates the formation of two structural phases. The main perovskite phase is 90% and the secondary phase $\text{Bi}_2\text{Fe}_4\text{O}_9$ is 10%. The analysis of SEM micrographs shows grains distributed homogeneously according to the pressing procedure and with the thermal treatments performed. The compositional analysis by EDS shows that the atomic percentage of each element is in accordance with the proposed stoichiometry for the system $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$. Finally, the analysis of the spectral components by XPS allowed us to establish that the ions Bi, Sm and Fe present oxidation states 3+ conforming a highly stable material type perovskite. In the same way, the chemical quantification of each one of the high-resolution spectra allowed us to establish that the samarium ions are found in a greater quantity on the surface, consequently, it can be inferred that the synthesis process favors the obtainment of the required phase on the surface of the solid, and that the calcination and sintering time ranges must be increased.

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