Synthesis, structural characterization and functional properties of Sr$_{0.5}$Ba$_{0.5}$Nb$_{2-x}$Fe$_x$O$_6$ ceramic powders

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Received: September 21th, 2020. Received in revised form: May 10th, 2021. Accepted: June 8th, 2021.

Abstract
Sr$_{0.5}$Ba$_{0.5}$Nb$_{2-x}$Fe$_x$O$_6$ (SBNF) ceramic powders for $x=0.00$, $x=0.02$ and $x=0.03$ were synthesized using coprecipitation method. The structure of the SBNF single phase with $x=0.02$ was identified by X-ray diffraction and Rietveld refinement; the morphology and size of the particles were observed by TEM and SEM-EDS microscopy. Electrical characterization showed that Fe doping did not cancel the typical ferroelectric relaxor behavior and magnetic characterization showed a weak ferromagnetic response, which suggest that the samples obtained can be considered as multiferroic.

Keywords: SBNF; coprecipitation method; ferroelectric relaxor; multiferroic.

1. Introduction

The Sr$_{1-y}$Ba$_y$Nb$_2$O$_6$ system was presented in 1960 by Francombe [1] as a ferroelectric material in the range of 0.25 $< y < 0.75$, with a tetragonal tungsten-bronze (TTB) structure at room temperature. The compound has the form [$(A_1)_{2}(A_2)_{2}C_4][[(B_1)_{2}(B_2)_{8}]O_{30}$ and consists of 10 ordered oxygen octahedrons, forming 3 types of interstitial places (A1, A2 and C) occupied by Sr$^{2+}$ and Ba$^{2+}$ cations [2]. The B1 and B2 sites, occupied by Nb, are located inside the octahedron. Researchers found that even if the SBN compound is a ferroelectric material, upon doping it with iron it acquires a ferromagnetic behavior, which does not cancel its ferroelectric behavior [3]. Therefore, the doping of SBN compound with iron results in the multiferroic property. Several methods have been proposed for the synthesis and processing of SBN ferroelectric ceramics, including solid-state synthesis, gel citrate, Pechini and controlled
The controlled precipitation method is based on aqueous media reactions containing stoichiometric predetermined amounts of the precursors (salts). Additionally, Cho et al. [11,12] and Kshirsagar et al. [13] studied the effect of Fe doping on the ferroelectric and ferromagnetic properties of Sr0.5Ba0.5Nb2−xFexO6 prepared by a solid-state reaction method. These groups reported that the synthesized materials maintained the bronze tungsten structure at low Fe values (x = 0.03). In addition, a multiferric response was reported when x = 0.03. Few materials with multiferroic properties are known to date; therefore, it is relevant to carry out studies to synthesize these materials and characterize their properties. In this study, we synthesized and characterized Sr0.5Ba0.5Nb1.98Fe0.02O6 powders by the controlled coprecipitation method. Structural characterization showed monophasic powders and electrical and magnetic characterizations showed that Fe incorporation did not suppress the ferroelectric behavior of the samples and generated a ferromagnetic character, this indicates that a multiferric material was obtained.

2. Experimental conditions

We obtained powders with a stoichiometry corresponding to Sr0.5Ba0.5Nb2O6 (SBN), Sr0.5Ba0.5Nb1.97Fe0.03O6 (SBNF3). Strontium carbonate (SrCO3, Aldrich 99.9%), Barium carbonate (BaCO3, Mallinckrodt 99.9%), Iron II oxalate (FeC2O4.2H2O, Alfa Aesar 95%) and Niobium pentoxide (Nb2O5, Aldrich 99.9%) were used as precursors. All precursors were previously determined by the equivalence and saturation pH (pHeq = 7 and pHsat = 10, respectively).

The solution was sonicated for 15 min, using an ultrasound equipment (frequency 20kHz) to destroy possible aggregates, dried, macerated to get a powder, and calcined at 1200°C for 4.5-h, and at 1300°C for 4.0-h. The analysis by X-ray diffraction (XRD) was performed using a PANalytical X’Pert Pro diffractometer in continuous mode using Cu Kα (λ. 1.5406 Å) with divergence slit width of 0.2 mm. XRD patterns where measured with a steps size of 0.02, time per step of 2.0 s, 20 range of 20°-80° and analyzed according to diffraction patterns for X’Pert HighScore Reference Patterns (Barium strontium niobium oxide): 00-039-0265. The morphological general aspect of the particles was observed by transmission electron microscopy (TEM, JEOL – 1200 EX) and scanning electron microscopy (SEM - SM7001 – F JEOL). Because Nb5+ and Fe3+ cations do not have the same valence, we tested if doping affected the conduction processes inside the material by characterizing the disk-shaped samples prepared at a pressure of 343.2 MPa and synthesized at 1200 °C for 4.5-h with and without doping. The relative permittivity was measured as a function of temperature using an impedance analyzer in the temperature range of 50°C – 300°C. The measurements of magnetization vs. external magnetic field were obtained with a vibrating sample magnetometer (VSM) with a field in a range of -15 and 15 kOe, at 50 K.

3. Results and discussion

The Fig. 2 shows the XRD diffractogram for Sr0.5Ba0.5Nb2−xFexO6 samples with x=0.00, x=0.02 and x=0.03, treated at 1200 °C for 4.5-h, and pH=7. The Sr0.5Ba0.5Nb2O6 phase was obtained but the sample also contained Sr and Ba niobates, produced from previous reactions [14]. Upon iron addition, the intensity of the peaks corresponding to the secondary phases decreased. This effect was more noticeable in samples with doping x=0.02 and therefore, testing continued with this doping value.

Based on these results, we continued the process of obtaining Sr0.5Ba0.5Nb1.97Fe0.03O6 with the inclusion of a new parameter, the variation of the Sr/Ba stoichiometric ratio. This new parameter was introduced according to previous studies in which barium hexaferrites (BaFe12O19) were obtained with good results by varying the stoichiometric ratio Fe:Ba [15, 16]. The Figs. 3(a) and 3(b) show the XRD diffractograms to powders, at T=1300°C, varying the Sr/Ba stoichiometric ratio for pH=7 (Fig. 3a) and pH=10 (Fig. 3b).

As observed, the production of monophasic powders depends on pH, since only at pH=10 and Sr/Ba=0.5/0.55 (Fig. 3b), the XRD patterns showed a single phase for Sr0.5Ba0.5Nb1.97Fe0.03O6. The Fig. 4 shows the diffractogram with Rietveld refinement for the Sr/Ba=0.5/0.55. The Table 1 contains the parameters confirming the monophasic powders. The monophasic sample was obtained at lower temperature and less calcination time than reported by Köferstein [16].
Figure 2. Sr$_{0.5}$Ba$_{0.5}$Nb$_2$-$_x$Fe$_x$O$_6$ diffractograms at (a) $x=0.00$, (b) $x=0.02$, (c) $x=0.03$.
Source: The authors.

Figure 3. Diffractograms of ceramic powder Sr$_{0.5}$Ba$_{0.5}$Nb$_{1.98}$Fe$_{0.02}$O$_6$ sample obtained by coprecipitation at T=1300°C, with different Sr/Ba ratios and at (a) pH=7; (b) pH=10.
Source: The authors.

Table 1. Rietveld refinement parameters for Sr$_{0.5}$Ba$_{0.5}$Nb$_{1.98}$Fe$_{0.02}$O$_6$.

<table>
<thead>
<tr>
<th>Refined parameters</th>
<th>Sr$<em>{0.5}$Ba$</em>{0.5}$Nb$<em>{1.98}$Fe$</em>{0.02}$O$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spatial group</td>
<td>a (Å)</td>
</tr>
<tr>
<td>P4bm</td>
<td>12.490</td>
</tr>
<tr>
<td></td>
<td>b (Å)</td>
</tr>
<tr>
<td></td>
<td>12.490</td>
</tr>
<tr>
<td></td>
<td>c (Å)</td>
</tr>
<tr>
<td></td>
<td>3.953</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>616.64</td>
</tr>
<tr>
<td>Phase %</td>
<td>100</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.29</td>
</tr>
</tbody>
</table>

Source: The authors.

The TEM micrograph for the Sr$_{0.5}$Ba$_{0.5}$Nb$_{1.98}$Fe$_{0.02}$O$_6$ sample with Sr/Ba = 0.5/0.55 and pH=10 (Fig. 5) shows uniform morphology and particle size, with a round shape and size around 150 nm.

The EDS analysis was done in a particular area of the material and it required several measurements for acceptable statistics. Fig. 6 shows one of the SEM micrographs and its corresponding EDS analysis. The atomic percentage has the expected proportion of the constituent ions and presents a Ba excess which agrees with the excess used for the synthesis, Sr/Ba= 0.5/0.55.
To analyze the doping effect on the electrical response of the produced material, we measured the dependency of the dielectric constant with the temperature at 50 kHz. The variation of the dielectric permittivity with temperature at two different compositions is shown in Fig. 7a. A broad dielectric peak is observed, characteristic of the relaxor ferroelectric behavior of SBN [16,17]; the temperature of maximum dielectric constant ($\varepsilon^\prime_{\text{max}}$) shifts to the right when Fe decreases: for $x=0.02$: $T_m=141.7$ °C and for $x=0$: $T_m=174.0$ °C. This agrees with previous studies reported in the literature [11-13].

The $\varepsilon^\prime_{\text{max}}$ (dielectric constant at $T_m$) increases when iron doping increases. This is expected because iron introduction should generate new conducting processes, which can be confirmed by the response in the imaginary part of the relative permittivity ($\varepsilon^\prime\prime$) vs temperature (Fig. 7b). The imaginary part of the relative permittivity measures the samples conductive behavior, i.e., the smaller the imaginary permittivity values, the more dielectric the sample will be. $\varepsilon^\prime\prime$ increases when doping increases; the introduction of iron decreases the materials dielectric response, which can be observed in Fig. 7c, which represents the behavior of the loss tangent tanδ for the Fe-doped systems. The Fig. 8 shows the behavior of the magnetization vs the external magnetic field taken at 50K for the sample Sr$_{0.5}$Ba$_{0.5}$Nb$_{1.98}$Fe$_{0.02}$O$_6$. Perhaps because of the low magnitude of maximum magnetization and high sensitivity of the VSM a noise may occur. The noise may also occur due to the fineness of the powder used for the test; nevertheless, even with the noise, a small coercivity field, close to 500 Oe is observed, characteristic of a ferromagnetic behavior [13]. The results indicate that iron doping did not inhibit the sample ferroelectric behavior and instead it gave it a ferromagnetic character. Therefore, we can say that the synthesized powders can be catalogued as multiferroic materials.
4. Conclusions

Ceramic powders of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_{1.98}\text{Fe}_{0.02}\text{O}_6$ were synthesized with the co-precipitation method, with stoichiometries corresponding to $x=0.00$, $x=0.03$, and $x=0.02$. According to the structural characterization by XRD, samples without doping showed significant presence of secondary phases, which were reduced by the addition of iron. To obtain powders of the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_{1.98}\text{Fe}_{0.02}\text{O}_6$ stoichiometry with single phase, it was necessary to vary the stoichiometry ratio $\text{Sr}/\text{Ba} = 0.5/0.55$ ratio and was confirmed by Rietveld refinement. The powders showed particles with sizes around 150 nm and uniform morphology. The electrical characterizations showed a relaxor ferroelectric behavior, even for iron-containing samples, which suggests that iron does not change the ferroelectric nature of the system. The permittivity vs temperature graphs showed a shift in the temperature ($174^\circ\text{C}$ to $141.7^\circ\text{C}$) corresponding to the maximum permittivity, which suggests incorporation of iron into the structure. The magnetic measurements showed that iron inclusion gives a small magnetic character, resulting in a hysteresis cycle with a small coercivity field; this means the iron inclusion gives a multiferric character to the sample.

Acknowledgements

The authors acknowledge the financial support from Universidad del Cauca.

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