AC conductivity and phase transition of the BST–BFO ceramic doped with Yb

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The homogeneity of the 0.8(Ba0.8Sr0.2)TiO3–0.2(Bi0.85Yb0.15)FeO3 ceramic, prepared by a solid-state process, was studied and quantitatively analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). At ambient temperature, X-ray diffraction shows the existence of only one perovskite phase in the tetragonal structure with the space group P4mm. The thermal variations of $\varepsilon'$ (real part of the dielectric permittivity) for this composition show extended peaks with temperature; this broadening of the peaks can be attributed to the diffuse character of the transition. As the frequency increases, $T_m$ (temperature of maximum permittivity) moves at higher temperatures, and the maximum values of $\varepsilon'$ decrease. Moreover, the impedance spectra ($\varepsilon''$ vs. $\omega$) show the presence of two arcs of circles that have been modeled with an equivalent electrical circuit. The arcs of the circles centered under the real axis ($\omega$) prove the Cole–Cole-type behavior. Each circle is associated with either the grain effect or grain boundaries. Electrical modulus analysis shows that the capacitance of the ceramic is enhanced, which is in good agreement with the results of complex impedance analysis. The AC conductivity complies with the universal power law. It disputes the modification of AC conductivity by adopting the Arrhenius-type of electrical conductivity. The temperature dependence of alternating current conductivity ($\sigma_a$) and direct current conductivity ($\sigma_{DC}$) confirms the existence of the ferroelectric–paraelectric phase transition.

1. Introduction

Ferroelectric materials are very interesting due to their simple crystalline structure. They are widely used in electronics, microelectronics and electromechanical transducers due to their piezoelectric, dielectric and thermoelectric properties.

The physical properties of the ferroelectric material Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ (BST) confer an increase in its dielectric constant of about 12 000 and a transition temperature $T_C$ of 340 K. BiFeO$_3$ (BFO) is a multiferroic material that exhibits both ferroelectric and antiferromagnetic orders. Its structure is a rhombohedral distorted perovskite (space group R3c) described by a rising Curie temperature ($T_C = 1103$ K) and an antiferromagnetic Neel temperature ($T_N = 643$ K (ref. 8)) and a spin that has been spiral modulated. In order to promote the properties of the BFO compound and reduce its defects, i.e. extreme current losses and high coercive fields, various tests have been effective, including the ion substitution test.

It has been observed in the literature that partial substitution in BFO-based ceramics by rare earths such as La, Pr, Nd, Gd, Dy and Ho at the Bi site cause a structural modification and improve the ferroelectric and ferromagnetic properties of the substituted materials. Indeed, the conductivity, ferroelectricity and magnetization are well improved, which makes the obtained compounds more useful in storage applications. In addition, Ilic et al. proved that yttrium upgrades the electric and magnetic properties.

In this paper, the main objective of our research work is to study the preliminary structural and electrical properties of BFO by ytterbium (Yb) doping in order to obtain information on the selection of materials for certain significant applications. Similarly, for this reason, we synthesized the compound 0.8(Ba$_{0.8}$Sr$_{0.2}$)TiO$_3$–0.2(Bi$_{0.85}$Yb$_{0.15}$)FeO$_3$ (BST–BiYbFO) by the solid-state method. This compound was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and complex impedance spectroscopy.

2. Experimental

Polycrystalline samples of (BST–BiYbFO) were prepared by adopting the classic solid-state reaction. The starting reagents BaCO$_3$, SrCO$_3$, Bi$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$ and Yb$_2$O$_3$ were of high purity (up to 99.9% purity, Aldrich).

These precursors were ground in a planetary mill for 2 hours in ethanol to homogenize the solution and reduce the particle size; the powders obtained were calcined at 770 °C for
3 h. The resulting solution was ground again and pelleted under 3 ton per cm² and finally sintered at 970 °C for 3 h.

At room temperature (RT), X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 diffractometer using Cu K emission = 1.5460 Å in the angular range of 10° < 2θ < 80° with 10 s for each step of 0.02° around the structure to determine the composition. The FullProf⁹–¹¹ software was used to analyze the XRD profiles. The morphologies and sizes of the samples were studied directly with a Hitachi SU70 Merlin SEM at an acceleration voltage of 3 kV, equipped with an EDXS energy-dispersive X-ray spectrometer, which was used for the elemental analysis of the different phases. For electrical measurements, the BST-BiYbFO powder was pressed into disks about 8 mm in diameter and 1 mm thick. The electrical properties were measured by an impedance analyzer (TEGAM 3550) in the temperature and frequency ranges of 473–753 K and 100 Hz–2 MHz, respectively.

3. Results and discussion

3.1. X-ray, SEM and EDX characterization

Fig. 1 shows the XRD pattern of the compound BST–BiYbFO recorded at RT. The peaks were successfully indexed using the FullProf program in the tetragonal system with the space group P4mm. The parameters were a = b = 3.9737 Å, c = 3.9840 Å, α = β = γ = 90° and V = 62.9085 Å³, with a reliability factor of χ² = 2.91, which is consistent with the literature.²²

Analysis of the synthesized powders by XRD and SEM allows us to control the formation of the desired phase and the solid solution boundaries.²³ These additional studies can distinguish the elements or phases present in our compound through the detection of backscattered electrons. From the SEM micrographs in Fig. 1 (with a resolution of 2 μm (top) and 5 μm (bottom)), it can be seen that the sample consists of uniform grains with a dimension of about 3.5 μm. It is also observed that the grains are compactly distributed over the surface with some porosity present.

The corresponding EDX analysis confirms that all elements are present in the material (Table 1), as indicated in Fig. 2. In addition to the presence of Ba, Sr, Bi, Fe and O, the spectra clearly show the successful Yb doping in BST–BFO. No other impurities were found in the EDX analysis, confirming the clarity of the sample.

Table 1 : Quantitative analysis of the 0.8(Ba₀.₈Sr₀.₂)TiO₃–0.2(Bi₀.₈5Yb₀.₁₅)FeO₃ ceramic

| Elements  | Weight % | Atomic % |
|-----------|-----------|-----------|
| O         | 19.79     | 54.99     |
| Ti        | 26.17     | 24.3      |
| Fe        | 5.03      | 4         |
| Sr        | 7.57      | 3.84      |
| Ba        | 35.56     | 11.51     |
| Yb        | 4.54      | 1.17      |
| Total     | 99.56     | 100       |

Fig. 1  XRD pattern for the tetragonal ceramic 0.8(Ba₀.₈Sr₀.₂)TiO₃–0.2(Bi₀.₈5Yb₀.₁₅)FeO₃ at room temperature and SEM micrographs of the ceramic surface.
3.2. Dielectric study

Investigation of the dielectric allows for the determination of the ferroelectric phase transition temperature and the nature of the relaxing ferroelectric behavior of BST–BIFo.

Fig. 3(a) shows the variation of the real component of the dielectric permittivity \( \varepsilon'_r \) with frequency. As the frequency increases, \( \varepsilon'_r \) continues to decrease. For high temperatures, i.e. at 693 K, \( \varepsilon'_r \) is about 6200 at 125 Hz and then becomes more or less stabilized down to above 10 MHz. The maximum value of \( \varepsilon'_r \) changes with frequency, leading to a dispersion effect. Two plateaus are observed, with one occurring in the lower-frequency region (\( 10^2 \– 10^4 \) Hz) and another in the higher-
frequency region ($10^4$–$10^6$ Hz) for all the measured temperatures. For electronic ceramics, both grains and grain boundaries provide non-ignorable effects on the electrical properties.

In fact, at lower frequencies, the pattern can be attributed to various types of polarizations in which the space charges are able to follow the frequency of the applied field given that they have enough time. These space charges are generally concentrated in the grain boundaries. On the contrary, at higher frequencies, these space charges do not have sufficient time to undergo relaxation, it is the effect of the grains that intervenes in this case. High values of dielectric permittivity are observed only at high temperatures and very low frequencies, which may be due to the free charge build-up at interfaces within the bulk of the sample (interfacial Maxwell–Wagner polarization) and the interface between the sample and the electrodes (space charge polarization). These results are similar to those found by Patil et al.

Fig. 3(b), showing the temperature ($T$) dependence of the real part of the dielectric constant ($\varepsilon_r$) at different frequencies, proves the existence of a plateau at low temperatures, which can be described as a grain or bulk response of the LBFO compound. As the frequency increases, $T_m$ (the temperature of the maximum value of permittivity) moves toward high temperatures and the maximum values of $\varepsilon_r$ decrease. In addition, a large scatter in the evolution of $\varepsilon_r$ under $T_m$ was observed. This behavior shows the relaxing character of this material. The value of $\varepsilon_r$ increases with temperature to a certain degree and shows a broad dielectric extreme at a certain temperature, $T_m = 633$ K, which is attributed to the phase transition from an antiferroelectric to a paraelectric state.

The thermal variation of $1/(\varepsilon_r')$ for this compound, presented in Fig. 3(c), shows a deviation from the Curie–Weiss law given by the equation:

$$\varepsilon_r' = \frac{C}{T - T_0} \quad T > T_C$$

Further theoretical fitting shows that in this case, the transition is diffuse and that the behavior is of the relaxor type. This is a second-order transition, where $C$ is the Curie–Weiss constant and $T_0$ is the Curie–Weiss temperature. Since ion diffusion occurs with increasing temperature, the movement of $T_C$ (i.e. the transition from the antiferroelectric to the paraelectric state) at high temperatures is most likely due to space charge polarization.

### 3.3. Impedance analysis

The behavior of the impedance spectra for different materials is often explained using Argand diagrams (Cole–Cole or Nyquist). In fact, these diagrams are particularly useful for materials that represent one or more relaxation processes, are better separated, and are comparable considering the functional forms of Debye or Cole–Cole.

Fig. 4(a) presents the Nyquist diagrams ($-Z'' = f(Z')$) for BST–BiYbFO for different temperatures (473–753 K). The experimental points of these curves are based on circular arcs that pass near the origin and have their centers below the real axis. Since the Debye plots produce semicircles centered on the real axis, this shows that the behavior of this material follows the Cole–Cole model. Any increase in temperature is accompanied by a decrease in resistance, which shows the thermal activation of the conductivity of the material. We examined the thermal evolution of the impedance plots of the BST–BiYbFO compound to verify the assignment of the grain boundaries to the high-temperature dielectric anomaly. With increasing temperature (Fig. 4(b)), the positions of the different frequencies shift from the grain semicircle (higher frequencies) to the grain boundary semicircle (lower frequencies). The anomaly observed at high temperatures could therefore be related to the oxygen vacancies present at the grain boundaries. By modeling the impedance spectra, a resistive effect of the grain boundaries greater than that of the reinforcements could be demonstrated. This confirms that this dielectric anomaly is mainly due to the oxygen vacancies associated with the grain boundaries. In order to explain the electrical behavior of the material, we prepared an equivalent circuit (inset in Fig. 4(b)) formed from a series of combinations of grains (g) and grain boundaries (gb).

The first consists of a parallel combination of resistance ($R_g$) and fractal capacitance (CPEg) with the impedance $Z_{\text{CPEg}} =$

![Image](image-url)
Impedance as a function of frequency at various temperatures. This behavior could be explained by the presence of space charges and/or ionic conduction. At high and medium frequencies, $Z'$ is independent of temperature, which reduces the influence of space charges. In fact, in the highest frequency range, all the curves merge and become independent of frequency, suggesting a possibility of space charge release.

Fig. 5(b) shows the change in the imaginary part of the impedance ($Z''$) with frequency for the BST–BFO composition at different temperatures. At higher frequencies and higher temperatures, the $Z''_{\text{max}}$ peaks change and broaden, indicating relaxation in the studied composition. This curve is useful to evaluate the relaxation frequency in materials with resistive character. The asymmetrical broadening of the peak under the influence of temperature suggests a temperature-dependent distribution of relaxation times.

### 3.4. AC conductivity studies

Fig. 6 shows the frequency dependence of electrical conductivity (AC) at different temperatures. The conductivity model is represented by two distinct regions. First, the conductivity in the low-frequency range is frequency independent, which characterizes the direct conductivity due to the displacement of the mobile charge carriers. Second, at high frequencies, the conductivity is influenced by the presence of space charges and/or ionic conduction. At high and medium frequencies, $Z'$ is independent of temperature, which reduces the influence of space charges. In fact, in the highest frequency range, all the curves merge and become independent of frequency, suggesting a possibility of space charge release.

Table 2: Extracted parameters for the circuit elements of the BST–BFO compound

| $T$ (K) | $R_g$ (Ω) | CPE$_g$ ($10^{-8}$ F) | $\alpha_g$ | $R_{gb}$ (Ω) | CPE$_{gb}$ ($10^{-9}$ F) | $\alpha_{gb}$ |
|--------|----------|---------------------|---------|----------|---------------------|---------|
| 473    | 1 726 700| 1.672               | 0.684   | 202 770  | 1.67                | 0.9245  |
| 493    | 1 343 100| 3.553               | 0.644   | 247 100  | 1.807               | 0.904   |
| 513    | 1 051 200| 5.193               | 0.6188  | 145 570  | 1.719               | 0.897   |
| 533    | 685 380  | 7.484               | 0.5762  | 64 444   | 0.981               | 0.86    |
| 553    | 407 060  | 8.982               | 0.5675  | 35 420   | 0.879               | 0.872   |
| 573    | 52 061   | 0.550               | 0.756   | 111 340  | 12.038              | 0.901   |
| 593    | 30 439   | 0.563               | 0.755   | 70 369   | 13.228              | 0.883   |
| 613    | 18 796   | 0.726               | 0.732   | 42 344   | 1.333               | 0.879   |
| 633    | 16 098   | 0.236               | 0.652   | 21 802   | 87.510              | 0.869   |
| 653    | 5670     | 0.356               | 0.807   | 15 401   | 1.353               | 0.868   |
| 673    | 5125     | 1.810               | 0.716   | 8935     | 11.790              | 0.853   |
| 693    | 3395     | 1.967               | 0.675   | 6254     | 13.146              | 0.843   |

Fig. 5: Variation of the real part $Z'$ and the imaginary part $-Z''$ of the impedance as a function of frequency at various temperatures.

Fig. 6: Variation of the AC conductivity ($\sigma_{\text{AC}}$) with frequency at selected temperatures of 0.8(Ba$_{0.8}$Sr$_{0.2}$)TiO$_3$–0.2(Bi$_{0.85}$Yb$_{0.15}$)FeO$_3$. 

\[ Z' = \left( \frac{R_g}{1 + R_g Q_u} + \frac{R_g Q_u}{1 + R_g Q_u} \sin(\alpha_g \pi/2) \right)^2 + \frac{R_u Q_u}{1 + R_u Q_u} \sin(\alpha_u \pi/2) \]

\[ Z'' = \left( \frac{R_g Q_u}{1 + R_g Q_u} \sin(\alpha_g \pi/2) \right)^2 + \frac{R_u Q_u}{1 + R_u Q_u} \sin(\alpha_u \pi/2) \]

\[ Q(\omega)^{-\alpha} \text{(ref. 41)} \text{ where } Q \text{ is a positive constant and a positive number less than or equal to 1), while the second consists of a parallel combination of resistance } (R_{gb}) \text{ and a constant phase element } (CPE_{gb}). \]
charge carriers. Second, the AC conductivity–compatible dispersion regime occurs at a higher frequency.

Jonscher's law is commonly used to explain the phenomenon of conductivity dispersion:

\[ \sigma_{AC}(\omega) = \sigma_{DC} + A\omega^S \] (3)

where \( \sigma_{DC} \) denotes DC conductivity, \( A \) is a temperature-dependent constant, and \( S \) denotes the degree of mobile ion interaction.

\[ \sigma_{AC}(\omega) = \frac{\sigma_S}{1 + (\omega\tau)^2} + \sigma_S(\tau\omega)^2 + A\omega^S \] (4)

where \( S \) is the conductivity at low frequencies, \( \sigma_S \) is a high-frequency estimate, and \( \tau \) denotes the characteristic relaxation time.

3.5. DC electrical conductivity

Electrical conductivity depends on the slightly bound charged particles that move through a material under the effect of a continuous electric field. The following relationship can be used to calculate electrical conductivity (DC) from resistance (\( R \)):

\[ \sigma_{DC} = \frac{e}{S \times R} \] (5)

where \( e \) and \( S \) respectively are the thickness and the surface of the pellet and \( R \) is the resistance determined by the fit of the curve \(-Z' = f(Z')\). The variation of \( \ln(\sigma_{DC} \times T) \) versus \( 1000/T \) is plotted in Fig. 7. The Arrhenius law\(^{33} \) describes the study of DC conductivity as follows:

\[ \sigma_{DC} \times T = A \exp \left( \frac{-E_a}{K_BT} \right) \] (6)

where \( A \) is the pre-exponential factor, \( K_B \) is the Boltzmann constant and \( E_a \) is the activation energy. The activation energy has been deduced from a linear adjustment at the data points. The phase transition is determined by the change of the curve's slope at 633 K. In the ferroelectric zone, the activation energy is \( E_{I} = 0.44 \) eV, while in the paraelectric region, it is \( E_{II} = 0.68 \) eV.

This behavior is also common to semiconductor oxides and perovskites,\(^{64,65} \) where there is usually a change in the low-temperature conduction mechanism.

3.6. Modulus

Macedo et al. first developed the modulus formalism in 1972. This formalism has been applied to the study of material electrical characteristics. It is used to determine the relaxation times of the conductivity. The complex modulus is expressed as:

\[ M^* = j\omega\varepsilon_0\varphi = M' + jM'' \] (7)

Fig. 8 shows the variation of the imaginary part \( M'' \) of the complex modulus as a function of the real part \( M' \) at different temperatures. The influence of grains and grain boundaries is related to the two observed semicircles, consistent with previous findings.

Fig. 8(a) shows the change in the real part \( M' \) of the electrical modulus as a function of frequency at different temperatures. It is observed that, at low frequencies, the values of \( M' \) are very low.
(from $10^6$ Hz). The spectra of $M'$ present rapid decreases according to the equation: $M' = \varepsilon'/(\varepsilon'_2 + \varepsilon''_2)$. Moreover, the increase in $M'$ is due to the accumulation of charges at the electrode–electrolyte interface, i.e. it is space charge 

polarization.\textsuperscript{87,88}

The fluctuation of the imaginary part $M''$ of the electrical modulus as a function of frequency at various temperatures is shown in Fig. 8(b). These fluctuations are found in two temperature ranges: $T < 633$ K and $T > 633$ K. This confirms the existence of the two conduction domains. In the first domain, the maxima of the curves are not of the same levels, and in the second domain, the maxima of the curves decrease when the temperature increases. Moreover, these spectra present asymmetrical relaxation peaks whose maxima shift towards high frequencies when the temperature increases.\textsuperscript{69,70}

**4. Conclusion**

In this study, the interaction of the structure and electrical properties of the BST–BiYbFO ceramic prepared by solid-state technology has been studied.

According to X-ray diffraction, the sample shows a tetragonal structure with a space group of $P4mm$. Dielectric measurement showed a relaxing ferroelectric behavior at the phase transition temperature of 633 K. The analysis of the impedance spectra showed a relaxing ferroelectric behavior at the phase transition temperature increases. Moreover, these spectra present asymmetrical relaxation peaks whose maxima shift towards high frequencies when the temperature increases.

**Conflicts of interest**

Authors declare that they have no conflict of interest or personal relationships that could have appeared to influence the work reported in this paper.

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