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# Relaxations in $Ba_2BiTaO_6$ ceramics investigated by impedance and electric modulus spectroscopies

João Elias Figuereido Soares Rodrigues [a], Carlos William de Araujo Paschoal [a,*], Eder Nascimento Silva [a], Kathryn A. Mince [b], Michael W. Lufaso [b]

[a] Departamento de Física – CCET, Universidade Federal do Maranhão, Campus do Bacanga, 65085-580, São Luis -MA, Brazil
[b] Department of Chemistry, University of North Florida, 1 UNF Drive, Jacksonville, FL 32224, USA

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ABSTRACT

Impedance spectroscopy analysis of the dielectric properties of a $Ba_2BiTaO_6$ ceramic was performed in the temperature range from room temperature to 500 K. The sample was prepared using conventional solid state synthesis under air and the X-ray diffraction shows the presence of $Ba_5Ta_4O_{15}$ as a minor secondary phase (0.09%). The impedance data clearly show contributions of the grain and grain boundary. The results indicate that the conduction in $Ba_2BiTaO_6$ is due to hopping of oxygen vacancies and that the impurities not influence the conduction mechanism.



## 1. Introduction

The ordered double perovskites $Ba_2BiM^{5+}O_6$, where $M^{5+}$ = $Bi^{5+}$, $b^{5+}$ and $Ta^{5+}$, have attracted much attention since the discovery of superconductivity in solid solutions of the $BaBiO_3$ compound [1–5]. The interest in the compounds where $Sb^{5+}$ and $Ta^{5+}$ are substituted for $Bi^{5+}$ ions [6–10] emerged after the confirmation of the $Bi^{4+}$ disproportionation [11–13] in the $BaBiO_3$ perovskite. The structural properties of $BaBiO_3$ were extensively investigated [6–9], notably in the seminal work of Kennedy et al. [6] where the authors showed, using high resolution neutron powder diffraction, that $BaBiO_3$ undergoes three structural phase transitions (SPT). At temperatures higher than 820 K the aristotype structure for the ordered double perovskite, with space group $Fm\bar{3}m$, is observed. Below 523 K its structure transforms into a rhombohedral $R\bar{3}$ structure that is stable down to 132 K. For temperatures below than 132 K the structure transforms into a monoclinic $I2/m$ structure. Finally, at 35 K there is a new SPT where the phase transforms into another monoclinic structure with space group $P2_1/n$. However, for $M^{5+}$ = $Sb^{5+}$ and $Ta^{5+}$ only two SPT are observed, with the compounds not exhibiting the lowest symmetry monoclinic phase $P2_1/n$ [6,7,9]. The $R\bar{3} \rightarrow I2/m$ structural phase transition is also induced by application of high-pressure [7,10,14].

Electrical investigations in double complex perovskites in the radio frequency range have shown important features such as defect ordering induced relaxor ferroelectric behavior [15] and a giant dielectric constant [16]. However, only recently have the electrical properties of $Ba_2BiM^{5+}O_6$, where $M^{5+} = Sb^{5+}$ and $Ta^{5+}$, been investigated. Castro et al. [17] characterized the temperature dependence of electrical properties of a $Ba_2BiSbO_6$ ceramic sample using impedance spectroscopy, showing that the conductivity in this compound is due to oxygen vacancies. The dielectric properties of $Ba_2BiSbO_6$ was also characterized by Sundaresan et al. [18]. More recently, Mandal and Sundaresan [19] have characterized the dielectric properties of $Ba_2BiTaO_6$ showing also that oxygen vacancies are the main contributor to the conductivity of this compound. Therefore, as pointed out by Mandal and Sundaresan [19] it is hard to obtain pure $Ba_2BiTaO_6$ compounds using the conventional solid state route under air atmosphere. In that study the samples were synthesized under argon atmosphere. However, the preparation of compounds to be utilized in bulk devices occurs on a large scale and therefore must have a low cost, which is not easily achieved for synthesis under an inert atmosphere. It is of interest to investigate the physical properties of $Ba_2BiTaO_6$ mixed with a minor secondary oxide phase resulting from the synthesis under air. Mandal and Sundaresan [19] measured the temperature dependence of the electrical properties. However, as suggested by Zhou and Kennedy [9], the SPT $R\bar{3} \rightarrow Fm-3m$ exhibited by $Ba_2BiTaO_6$ is possibly ferroic and such measurements under isothermal conditions is desired to avoid domains effects in the measurements. Therefore, this work is complementary to that

* Corresponding author. Tel.: +55 98 3301 8291; fax: +55 98 3301 8204.
*E-mail address:* paschoal@ufma.br (Paschoal).

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Mandal and Sundaresan [19]. Also, we have discussed the electrical properties of this compound of the viewpoint of the modulus spectroscopy, that permit us conclude interesting features about the relaxational process in $Ba_2BiTaO_6$ and, for the first time, modeling the conductivity of this compound. In this work we have performed the impedance and modulus spectroscopies analyses of the dielectric properties of $Ba_2BiTaO_6$ ceramics obtained by conventional solid state route at high temperatures under isothermal conditions. The synthesis of samples under air show the presence of a low amount (0.09 wt%) of $Ba_5Ta_4O_{15}$ as a minor secondary phase.

## 2. Experimental procedure

Samples were synthesized by solid-state reaction in air using stoichiometrically weighed high-purity $BaCO_3$ (99.95%), $Bi_2O_3$ (99.975%), and $Ta_2O_5$ (99.99%). Reagents were ground under acetone using an agate mortar and pestle. Samples were heated at 800 °C for several cycles and then 850 °C, with intermediate grinding. Phase purity was examined using X-ray powder diffraction with data collected by a Rigaku Ultima III X-ray diffractometer with Cu K$\alpha$ radiation. The polycrystalline powder was uniaxially pressed into pellets of 13 mm diameter and sintered at 850 °C. The density of the pellets was 94% of the theoretical density of $Ba_2BiTaO_6$.

The impedance and modulus spectroscopic measurements of the ceramic pellets with silver parallel electrodes obtained by the deposition of silver paste were performed using a Solartron frequency response analyzer model 1260 coupled to a dielectric interface Solartron model 1296. The measurements were carried out in the frequency range from 1 Hz up to 1 MHz and in the temperature range from room temperature up to 500 K. The temperature measurements were performed in an EDG 10P furnace under air.

## 3. Results and discussion

Peak splitting is evident in the high angle peaks of the powder X-ray diffraction pattern. Indexing of the diffraction peaks were consistent with the rhombohedral double perovskite that crystallizes in space group $R\bar{3}$. The refined crystal structure of $Ba_2BiTao_6$ agrees well with that reported by Wallwork et al. [7]. A

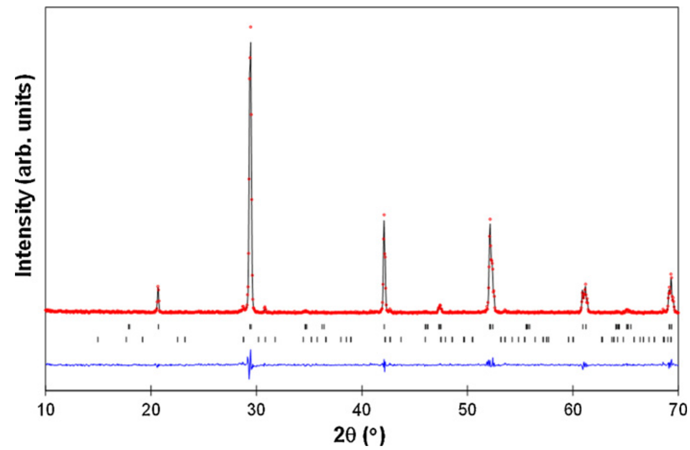


**Fig. 1.** Observed X-ray powder diffraction data (circles) along with the calculated diffraction pattern (line) obtained from Rietveld refinement. At the bottom of the figure the difference plot (Iobs–Icalc) is shown as a blue line. Vertical bars on the bottom indicate the positions of allowed Bragg reflections for rhombohedral (R-3) $Ba_2BiTaO_6$ (top set) and $Ba_5Ta_4O_{15}$ (bottom set). The weight fraction of $Ba_5Ta_4O_{15}$ determined from the refinements is 0.09(1)%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

minor secondary phase of $Ba_5Ta_4O_{15}$ is present and the weight percent determined from the refinements is 0.09(1)%, which formed as a result of the sintering process. The structure of $Ba_5Ta_4O_{15}$ was obtained from the literature and the fractional coordinates were fixed in the refinements [20]. The rietveld refinement of the sample is shown in Fig. 1.

Fig. 2 shows the impedance complex plane obtained for the $Ba_2BiTaO_6$ ceramics. A distorted impedance arc at low temperatures is observed, similar to that observed by Mandal and Sundaresan [19]. This distorted arc is expanded in two arcs at intermediate temperatures and, at high temperatures, the relaxation frequency associated to an impedance arc increases sufficiently so this arc disappears (left arc). These features are common in ceramic samples and are modeled by two arc electrical circuits, which consist of a resistor in parallel with a constant phase

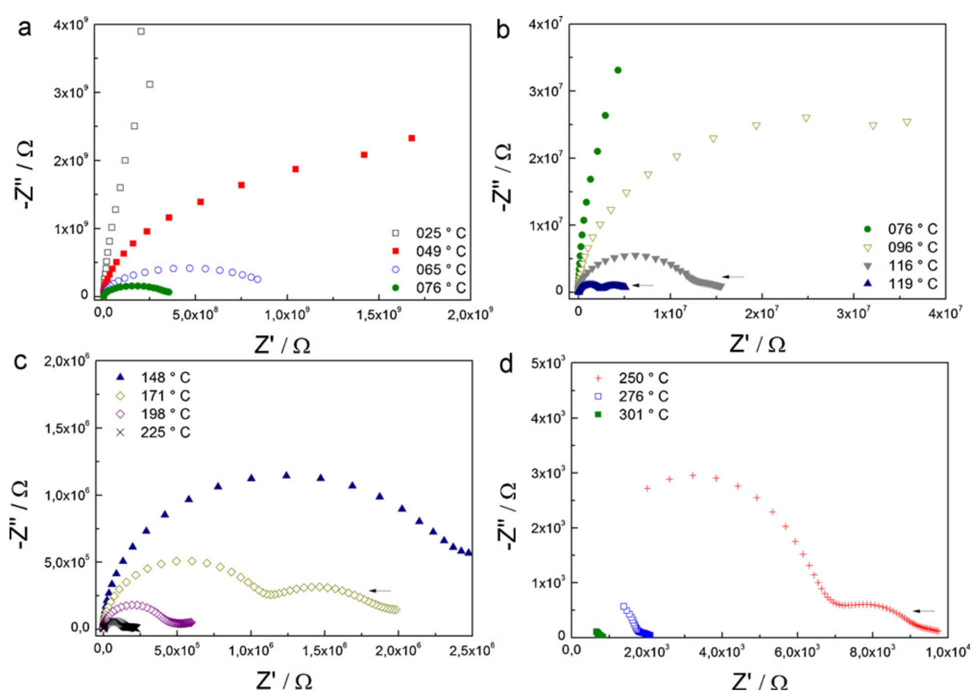


**Fig. 2.** Complex impedance plot obtained for the $Ba_2BiTaO_6$ ceramics at several temperatures.