Effect of Fe doping on the electrical properties of BaTiO₃, crystalline materials at room temperature

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Abstract. In this study, we report the room temperature electrical properties of BaFe₁₋ₓTiₓO₃ (x = 0.4, 0.5, and 0.6) crystalline materials. The materials were synthesized via a solid-state reaction. The structural properties were investigated via X-ray diffraction, showing a hexagonal perovskite structure with the P63/m space group. The room temperature electrical properties were characterized using impedance spectroscopy. The impedance data indicate a decreasing of ferroelectric behavior and the appearance of ferromagnetic behavior. The frequency spectra of the impedance show the presence of electrical relaxation in the materials, the extent of which depends on the Fe content. Doping BaTiO₃ with Fe reduces the relaxation time in the system.

1. Introduction
Among the perovskite materials, barium titanate (BaTiO₃) has received the most research attention for many decades because of its attractive properties [1]. In particular, regarding its electrical properties (e.g., ferroelectricity, piezoelectricity, and high dielectric constant), BaTiO₃ has applications in multilayer ceramic capacitors [2] and LPG sensors [3]. BaTiO₃ is a typical ferroelectric material at room temperature, with a band gap of ~3.8 eV and a transition (ferroelectric–paraelectric) temperature above 400 K [2]. The electrical behaviour of BaTiO₃ may be altered by doping [2,4]. Xu et al. [4] reported that Fe-doped BaTiO₃ ceramics exhibit ferroelectric and ferromagnetic behavior at room temperature, implying potential applications as multiferroic materials. Also, Ray et al. [1] reported that BaTiO₃ doped with Fe in the dilute limit (less than 7% Fe) exhibits intrinsic ferromagnetism above room temperature. In this study, we chose Fe-doped BaFe₂Ti₁−xO₃ (with x = 0.4, 0.5, and 0.6) and studied its structural and electrical properties via impedance spectroscopy. The materials were prepared via the solid-state reaction. As such, we can discuss the manner in which Fe doping affects the structural and electrical behavior.

2. Experimental details
Herein, we mainly analyze the effects of Ti doping (x = 0.4, 0.5, and 0.6) on the electrical properties of BaFe₂Ti₁−xO₃ materials. The samples were synthesized via the solid-state reaction using BaCO₃ (Sigma Aldrich; 98.5%), Fe₂O₃ (Sigma Aldrich; 98.5%), and TiO₂ (Sigma Aldrich; 98.5%) as precursors. The precursors were mixed and ground for 2 h to form a homogeneous powder. The homogeneous powder obtained was pressed into pellets (diameter: 12 mm) under a force of 10 kN for 5 min and calcined at 1000 °C for 12 h. Finally, the pellets were sintered under heating condition of 1200 °C for 12 h. For each sample, the crystal structure and lattice constant were identified using an X-ray diffractometer (XRD) (Philips PW 3710) with a Co Kα radiation in the 2θ range of 20°–90°. The refinement of the XRD results was investigated using the HighScore Plus software. The electrical properties were examined using an RLC-Meter (FLUKE-PM6306) in the frequency range of 100 Hz to 1 MHz at room temperature and analyzed using impedance spectroscopy.
Table 1. Results of structural analysis of BaFe\(_x\)Ti\(_{1-x}\)O\(_3\) compounds.

| Sample \(x\) | \(a=b\) (Å) | \(c\) (Å) | \(V\) (Å\(^3\)) | \(\chi^2\) |
|-------------|-------------|----------|----------------|----------|
| 0.4         | 5.707       | 14.07    | 396.8          | 1.225    |
| 0.5         | 5.699       | 14.05    | 395.1          | 1.289    |
| 0.6         | 5.701       | 14.09    | 396.5          | 1.276    |

3. Results and discussion

3.1. Structure analysis
Figure 1 displays the XRD patterns of BaFe\(_x\)Ti\(_{1-x}\)O\(_3\) with \(x = 0.0, 0.4, 0.5, \) and 0.6 at room temperature. The structural analysis was conducted using the HighScore Plus software. The analysis confirms a cubic structure for \(x = 0.0\) and a hexagonal perovskite structure with the \(P63/m\) space group for \(x = 0.4, 0.5, \) and 0.6. To be sure of the crystal structure, we calculate the Goldschmidt tolerance factor (\(t\)) for each sample [5], finding it to be 1.69, 1.75, and 1.69 for \(x = 0.4, 0.5, \) and 0.6, respectively. In other words, we have \(t > 1\) in each case, thus confirming a hexagonal structure. This indicates that substituting Fe at the Ti sites of BaFe\(_x\)Ti\(_{1-x}\)O changes the crystal structure. The obtained fitting parameters are listed in table 1, where we see a decrease in the lattice constant and lattice volume for \(x = 0.5\). This can be attributed to the differing radius of Fe\(^{3+}\) ions (60.5 pm) and Ti\(^{4+}\) ions (64.5 pm) and their positions in the lattice.

3.2. Electrical properties
Figure 2 describes the Nyquist plots of BaFe\(_x\)Ti\(_{1-x}\)O for \(x = 0.0, 0.4, 0.5, \) and 0.6 at room temperature. These show that the semicircular arc decreases with increasing Fe doping of the samples. This means that the impedance decreases as the extent of Fe doping is increased. The highest impedance is that of BaTiO\(_3\), indicating ferroelectric behavior. The doping of Fe ions at Ti sites lowers the impedance, thus lessening the ferroelectric behavior and facilitating ferromagnetic behavior. This comes from the Fe\(^{3+}\) – O\(^2-\) – Fe\(^{4+}\) exchange interaction, which causes ferromagnetic coupling between Fe ions. Thus, the increasing number of Fe ions promotes ferromagnetic behavior and inhibits ferroelectric behavior at room temperature [2].
Figure 2. Nyquist plots of BaFe\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} at room temperature.

Figure 3. Frequency dependence on (a) real and (b) imaginary impedance at room temperature for BaFe\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} compounds.

Figure 3a shows the real impedance, namely \(Z'\), for the BaFe\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} compounds at room temperature. The \(Z'\) values merge to a higher frequency region, indicating the presence of polarized of space-charge [6]. Dhak \textit{et al.} [6] reported the similar phenomena for LaMnO\textsubscript{3}-modified BaTiO\textsubscript{3} ceramics. The \(Z'\) values also decrease with the increasing of Fe content. Figure 3b shows the imaginary impedance, namely \(Z''\), for the BaFe\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} compounds at room temperature. The \(Z''\) values increase initially with frequency and exhibit a maximum before decreasing. This indicates the presence of relaxation mechanism occurring in the materials. The \(Z''\) maximum shifts to a higher frequency as increasing Fe content suggesting the Fe content reduces the relaxation time of this compound.
4. Conclusions

BaFe$_{x}$Ti$_{1-x}$O$_{3}$ ($x = 0.4$, 0.5, and 0.6) crystalline materials have been synthesized successfully by solid-state reaction. The structural properties show a hexagonal perovskite structure with the $P6_3/m$ space group. The electrical properties at room temperature show a decreasing ferroelectric behavior and the appearance of ferromagnetic behavior. They also indicate the electrical relaxation mechanism occurring in the materials, which depends on the Fe content.

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