Synthesis, structural and electrical properties of BaTiO$_3$ doped with Gd$^{3+}$

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Abstract. Polycrystalline BaTiO$_3$ doped with Gd$^{3+}$ (Ba$_{1-x}$Gd$_x$Ti$_{1-x/4}$O$_3$) was synthesized using the solid state reaction method; grinding BaTiO$_3$, BaCO$_3$, TiO$_2$, and Gd$_2$O$_3$ in agate mortar, with acetone as a control medium and $x = 0.001, 0.003, 0.005, 0.01, 0.05, 0.1, 0.15, 0.20, 0.25, 0.30, 0.35$ Gd$^{3+}$ (wt. %). The powders were decarbonated at 900°C and sintered at 1400 °C for 8 hours. Tetragonality of synthesized BaTiO$_3$ doped with Gd$^{3+}$ particles were analysed by X-ray diffractometry (XRD) and Raman spectroscopy (RS). XRD results of the physical mixture of the precursor powders indicated the presence of BaTiO$_3$ phase, which increased when the temperature was increased. XRD patterns and Raman spectra revealed that the crystal phase of the obtained particles was predominately tetragonal BaTiO$_3$, intensity of Raman band at 205 cm$^{-1}$ 265 cm$^{-1}$ and 305 cm$^{-1}$ increased when Gd$^{3+}$ was increased. Capacitance of the sintering pellets was measured at 1kHz; these values were using for to calculate the relative permittivity.

Keywords: BaTiO$_3$, doped, Raman spectroscopy

Introduction
BaTiO$_3$ (BT) is a ferroelectric material with a characteristic tetragonal distortion of the cubic perovskite structure. The ferroelectric distortion is facilitated by the large size of the Ba cation. The origin of the ferroelectric property is due to a displacement of the Ti atoms and the effect is very sensitive to interatomic distances (lattice parameter). Among the most important properties that can be presented to highlight its both chemical and mechanical stability, its ferroelectric properties at room temperature considering its use as a polycrystalline ceramic [1]. (BT) is widely used in the manufacture of piezoelectric devices, electro - optical elements, ceramic capacitors and resistors PTC because have a high dielectric constant and exhibit interesting semiconducting properties when they are modified using appropriate additives [2]. High dielectric constant allows smaller capacitive components, thus offering an opportunity to shrink the size of the electronic devices [3]. The understanding of how these particular crystalline structures evolve from the tetragonal perovskite structure might enlighten a way to engineer more compounds with exagonal structure.

It is known that an appropriate amount of doping into the BT can improve structural, optical and electrical properties of the system [4, 5, 6, 7]. The doping has been studied by several authors [8, 9] and it was shown, for example, that the positive temperature coefficient of resistivity (PTCR) effect in BaTiO$_3$, doped with donors (when the substitution occurs at Ba-sites) can be significantly increased by adding small amounts of dopants. This additional doping leads to an increase of $\rho$ max/$\rho$min ratio ($\rho$ is electric resistivity) which is the most important feature to be applied. Even more, the dopants have influence in the temperature of the ferroelectric phase transition (Tc). The investigations of the dopants effect play a decisive role in
understanding the nature and in optimizing BaTiO$_3$ ceramics properties.

The main goal of this work was the investigation of BaTiO$_3$ ceramics doped with Gd$^{3+}$ using the solid state reaction method. The tetragonality of synthesized materials were analysed by X-ray diffractometry (XRD) and Raman spectroscopy (RS). Electron microscopy analysis were also used, as well as electric properties determination.

**Methodology**

Samples of BT doped with Gd$^{3+}$ were prepared according to the equation; Ba$_{1-x}$Gd$_x$Ti$_{1-\frac{x}{4}}$O$_3$, using the solid state reaction method; grinding, BaCO$_3$ (Sigma-Aldrich, cas No.513-77-9, 99.9%), TiO$_2$ (Sigma-Aldrich, cas No.13463-67-7, 99.9%), and Gd$_2$O$_3$ (Sigma-Aldrich, cas No. 278513-25G, 99.9%) in a agate mortar, with acetone as a control medium and x = 0.001, 0.003, 0.005, 0.01, 0.05, 0.1, 0.15, 0.20, 0.25, 0.30, 0.35 Gd$^{3+}$ (wt. %)

The precursors powders (BaCO$_3$, TiO$_2$ and Gd$_2$O$_3$) were dried at 200°C, before weighig. The mix of powders was placed in a alumina boat and was decarbonated at 900°C overnight and later was regrinding for 10 min in agate mortar. After that were sintered in a platinum crucible at 1400°C for 8 hours respectively using a muffle funace (Thermolyne model 46200). The purity of the products was monitored by X-ray diffraction (diffractometer Equinox 2000 Cu Kα).

After the phase was obtained pellets were manufactured for each composition. The powder mixtures were compacted using a uniaxial pressing at 250 MPa in an 8-mm stainless steel die to produce green pellets of 3 mm thick. The pellets were sintered at 1400°C for 5 hours in air atmosphere with heating and cooling rates of 5°C/min. They were polished and cleaned in an ultrasonic bath. The morphology studies were performed in a JEOL 6300 SEM. Electrical measurements were performed on LC Meter Analyzer ELC -3133A LCM Escort, 1 KHz. Additionally, Raman studies were carried out for each sample using a spectrophotometer (Perkin Elmer Spectrum Gx); in a range of 0–1200 wavelength.

**Results and discussion**

**X-ray diffraction**

Due to the difference of ionic radii between gadolinium (r(Gd$^{3+}$) = 1.02 Å, and titanium r (Ti$^{4+}$) = 0.68 Å) the lattice will expand to some extent. This may be one of the reasons why the XRD reflections shift to lower angles (Figure 1 and Figure 2) at $2\theta = 65.7$ and $x \geq 0.15$ sintering at 1400 ºC. It can be seen from Figure 1 that the diffractograms shows a double peak at $2\theta \approx 45$ indicating the presence of tetragonal ferroelectric phase (JCPDS 050626) for the diffractograms when the Gd$^{3+}$ content was $0.001 \leq x \leq 0.3$. This phase disappears for the sample with Gd$^{3+}$ content $x = 0.35$, however, secondary phase was found when the Gd$^{3+}$ content was higher than 0.15 observed in the peak $2\theta \approx 32$. Determination of the cubic – hexagonal transition temperature was complicated by the presence of a wide metastable persistent region. The phase(s) present after heat treatment was found to be dependent not only on the quenching temperature, but also on the initial phase composition of the sample and thermal history.

![Figure 1. XRD Diffractograms for (Ba$_{1-x}$Gd$_x$Ti$_{1-\frac{x}{4}}$O$_3$) powders sintering at 1400°C during 8 h for different values of x.](image)
Raman spectroscopy
Raman spectroscopy (RS) was used to study the phase transition of Gd$^{3+}$ doped BaTiO$_3$ ceramics. RS is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system [8]. Figure 3 shows the Raman spectra for BaTiO$_3$ doped with several Gd$^{3+}$ concentrations prepared by the solid state reaction. The graphs show the characteristic Raman peaks of the tetragonal ferroelectric phase of BaTiO$_3$ [9, 10, 11] located at 205 cm$^{-1}$ (E(TO + LO), A1(LO)), 265 cm$^{-1}$ (A1(TO)), 304 cm$^{-1}$ (B1, E(BO + LO)), 513 cm$^{-1}$ (A1(TO), E(TO)) and 717 cm$^{-1}$ (A1(LO), E(LO)). When the Gd$^{3+}$ concentration in BaTiO$_3$ is enough to cross through the tetragonal-cubic phase transition point, all the active Raman modes in the tetragonal phase (P4 mm) are inactive in the perfect cubic phase (Pcm 3) according to forbidding of Raman selected rules. However, the broad A1 (TO) band at 513 cm$^{-1}$ persist into the cubic phase above TC, which is attributed to intrinsic disorder in the cubic phase, and they become broad and weak with increasing Gd$^{3+}$ content [3, 12].

Dielectric and ferroelectric measurements
Figure 4 shows the results of relative permittivity obtained at 1 kHz of frequency for the compositions prepared in the range of 0 ≤ x ≤ 0.35. The maximum permittivity values were recorded for the samples with x = 0.001, 0.003 and 0.005. It is observed that the three compositions indicated the same Tc value (90°C), however the maximum value of k was recorded for the sample with x = 0.005 (10560). Furthermore, the compositions of x = 0.010 and x = 0.050 showed Curie temperature values of 50 to 45°C with permittivity values of 4042.1 and 6073.7 respectively. In some cases, was observed an inflection at 120°C, indicating the presence of barium titanate. For the composition x ≥ 0.1 the peak of maximum permittivity was not observed because the Tc is shifted to values below room temperature.
Figure 4. Relative Permittivity against temperature of capacitors, prepared by \((\text{Ba}_{1-x}\text{Gd}_x\text{Ti}_{1-x/4}\text{O}_3)\) to 1 kHz \(0 \leq x \leq 0.35\)

Morphology and microstructure

Figure 5 shows SEM-EDS images of Gd\(^{3+}\) doped BaTiO\(_3\) sintering at 1400°C for the samples with \(x = 0\), \(x = 0.15\) and \(x = 0.35\). It can be observed the presence of Gd in the EDS spectrum. The SEM images of the samples indicate that Gd\(^{3+}\) does not influence drastically the microstructure. All the samples reveal comparable grain sizes, around 10 \(\mu\)m, (Figure 5 b) and c). Only for the case of \(x = 0\), (Figure 5 a) one can observe grain size greater than 100 \(\mu\)m. Also can be seen a relatively homogeneous microstructure with higher amounts of intergranular porosity, this may be due to the behavior of Gd\(^{3+}\) in the BaTiO\(_3\) ceramics. In the image detail (Figure 6) can be observed this characteristic. [13]

The summary of semiquantitative compositions for all samples is shown in the Table 1. The EDS investigations show that the ceramics BaTiO\(_3\) + x wt. % Gd\(^{3+}\) (0.001 \(\leq x \leq 0.35\)) contain Ba, Ti, O and Gd elements near their surfaces. No other impurity element has been detected in the spectrum.

It is noted that the content of Gd increases as “x” increases. On the contrary, with “x” content increasing, the Ba and Ti contents decrease. This can be explained by an amphoteric behavior in BaTiO\(_3\) [14], e.g. they have as an acceptor when Ti-site is substituted or as donor when the substitution occurs at Ba-sites.

Yongping et al. [14] reported that the thermodynamic conditions, such as the partial pressure of oxygen in the sintering atmosphere and temperature, play an important part in the distribution of rare earth elements with amphoteric behavior in A-site or B-site of BaTiO\(_3\) [15, 16].

Figure 5. SEM-EDS micrographs of BaTiO\(_3\), doped with different Gd\(^{3+}\). a) BaTiO\(_3\), b) \(x = 0.15\), c) \(x = 0.35\).

Table 1. Semiquantitative chemical composition (SEM-EDS) of sintering powders at 1400°C, 0 \(\leq x \leq 0.35\). (Wt. %)

<table>
<thead>
<tr>
<th>Muestra</th>
<th>Ba</th>
<th>Ti</th>
<th>O</th>
<th>Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO(_3)</td>
<td>68.46</td>
<td>25.31</td>
<td>6.22</td>
<td>0</td>
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<tr>
<td>x=0.001</td>
<td>65.64</td>
<td>23.98</td>
<td>10.31</td>
<td>0.07</td>
</tr>
<tr>
<td>x=0.003</td>
<td>61.41</td>
<td>21.93</td>
<td>16.41</td>
<td>0.25</td>
</tr>
<tr>
<td>x=0.005</td>
<td>61.87</td>
<td>20.13</td>
<td>17.66</td>
<td>0.34</td>
</tr>
<tr>
<td>x=0.010</td>
<td>58.03</td>
<td>20.51</td>
<td>20.74</td>
<td>0.72</td>
</tr>
<tr>
<td>x=0.050</td>
<td>54.38</td>
<td>21.15</td>
<td>21.75</td>
<td>2.72</td>
</tr>
<tr>
<td>x=0.100</td>
<td>50.81</td>
<td>22.74</td>
<td>13.03</td>
<td>13.42</td>
</tr>
<tr>
<td>x=0.150</td>
<td>48.68</td>
<td>19.33</td>
<td>15.85</td>
<td>16.14</td>
</tr>
<tr>
<td>x=0.200</td>
<td>46.64</td>
<td>19.22</td>
<td>9.83</td>
<td>24.31</td>
</tr>
<tr>
<td>x=0.250</td>
<td>41.01</td>
<td>19.14</td>
<td>12.83</td>
<td>27.02</td>
</tr>
<tr>
<td>x=0.300</td>
<td>38.88</td>
<td>19.01</td>
<td>12.37</td>
<td>29.74</td>
</tr>
<tr>
<td>x=0.350</td>
<td>36.02</td>
<td>19.11</td>
<td>10.92</td>
<td>33.95</td>
</tr>
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</table>
Conclusions
The BaTiO$_3$ doped with Gd$^{3+}$ ($\text{Ba}_{1-x}\text{Gd}_x\text{Ti}_{1-x/4}\text{O}_3$) $x = 0.001, 0.003, 0.005, 0.01, 0.05, 0.1, 0.15, 0.20, 0.25, 0.30, 0.35$ Gd$^{3+}$ (wt.%) were investigated by XRD, Raman spectroscopy (RS) and electric measurements.

It was confirmed by XRD a double peak at $2\theta \approx 45$ indicating the presence of tetragonal ferroelectric phase for the diffractograms when the Gd$^{3+}$ content was $0.001 \leq x \leq 0.3$. This phase disappears for the sample with Gd$^{3+}$ content $x = 0.35$. The Raman results shown the characteristic Raman peaks of the tetragonal ferroelectric phase of BaTiO$_3$ located at $205$ cm$^{-1}$ ($E(TO + LO)$, $A1(LO)$), $265$ cm$^{-1}$ ($A1(TO)$), $304$ cm$^{-1}$ ($B1$, $E(TO + LO)$), $513$ cm$^{-1}$ ($A1(TO)$, $E(TO)$) and $717$ cm$^{-1}$ ($A1(LO)$, $E(LO)$). The maximum permittivity values were recorded for the samples with $x = 0.001, 0.003$ and $0.005$.

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References


