Effect of Ni doping on structural and dielectric properties of BaTiO$_3$

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Polycrystalline samples of Ba$_{1-x}$Ni$_x$TiO$_3$ (BNT), where $x = 0, 0.03, 0.05, 0.07$ and $0.10$ have been synthesized by solid-state reaction technique. No phase change in the crystal structure has been observed with Ni doping in barium titanate up to $x = 0.10$, however a decrease in crystallite size, lattice strain, $cla$ ratio and grain size has been found with Ni doping. The different results presented may be related to, and are explained by, the grain size and its distribution in the ceramic bulk. Ni doping in BaTiO$_3$ exhibit many interesting features, such as shift in transition temperature, increasing diffuse phase transition and decreasing dielectric constant. The evolution from a normal ferroelectric phase transition to a diffuse phase transition has been observed with increasing Ni concentrations. The dielectric study of samples poled in magnetic field (data shown for BNT, $x = 0.03$ here) suggests that $T_c$ and maximum dielectric constant increase with increasing magnetic poling strength along with decreasing nature of diffusivity thus showing multiferroic nature.

Keywords: Ceramics, X-ray diffraction, Dielectric properties, Grain size, Diffuse phase transition

BaTiO$_3$ (BT) is one of the most common ferroelectric material with a wide range of applications including micro-electro mechanical systems (MEMS), multilayer ceramic capacitors (MLCs), PTC thermistors, piezoelectric transducers, microwave devices, different type of storage information devices, infrared sensors$^{1-4}$ etc. BaTiO$_3$ has a general ABO$_3$ type structure where A and B are cations of different sizes, with the 6 fold coordinate B cation in the middle, the 12 fold coordinate A cation in the corner and the anion, commonly oxygen, in the centre of the face. The packing of the ions can be thought of as the A and O ions together forming close-packed array. The phase of BaTiO$_3$ at room temperature is tetragonal and it transforms to cubic phase above 130$^\circ$C. It also exists in orthorhombic phase at 0$^\circ$C and in rhombohedral phase below -90$^\circ$C. Above 1460$^\circ$C, BaTiO$_3$ exits in hexagonal phase$^5$. Although the primitive cube is the idealized structure, differences in radius between the A and B cations can alter the structure to a number of different so-called distortions, of which tilting is the most common one. With perovskite tilt the BO$_6$ octahedron twists along one or more axes to accommodate the difference. The ferroelectric properties of ABO$_3$ type perovskite ceramics (here barium titanate) can be efficiently controlled by doping with different doping elements$^{6-9}$.

The possible applications of Ni doped barium titanate (hereafter BNT) materials in the bulk form are still explored over a wide range of compositions and controlled ion substitutions. Few reports are available on this issue where the micro-structural changes in Ni doped barium titanate$^{10}$, dielectric characteristics of Ni-ion doped BaTiO$_3$ nanoparticles$^{10}$ (Ni is doped at Ti-site), exaggerated grain growth in Ni doped BaTiO$_3$ (Ni concentration ~0.7 mol%) to study$^{11}$ hexagonal phase in BaTiO$_3$ dielectric characteristics of BT co-doped$^{12}$ with Ni and Nb, electrical transport properties of Mn and Ni doped BT at high temperature$^{13}$, valence change and phase stability of Ni doped BT annealed in O$_2$ and H$_2$ are discussed$^{14}$. The ionic radii of Ni$^{2+}$ ($r_{6}^{2+} = 0.69$Å) is less than both the ions Ba$^{2+}$($r_{6}^{2+} = 1.35$Å) and Ti$^{4+}$($r_{6}^{4+} = 0.61$ Å) and hence it can occupy both A and B sites. As per our literature survey no systematic dielectric study of Ni-doped BaTiO$_3$ has been reported. In this paper, the synthesis, characterisation and dielectric properties of Ni-doped BT have been studied and the effect of magnetic field on the dielectric properties of BNT has been analysed.

Experimental Procedure

The compositions Ba$_{1-x}$Ni$_x$TiO$_3$, where $x = 0, 0.03, 0.05, 0.07$ and $0.10$ were prepared by conventional

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method based on solid state reaction of mixed oxides, using required amount of analytical grade reagents BaCO$_3$, TiO$_2$, NiO as starting materials. The weighed individual reagents were homogeneously mixed in acetone media. The well-mixed powder was then calcined at 1200°C for 2 h, in alumina crucible. Calcined powder was pressed into cylindrical pellets of 1-2 mm thick and 8 mm diameter at a pressure of \( \sim 31.2 \times 10^6 \) Pa, using uniaxial hydraulic press. These pellets were then sintered at 1250°C for 5 h. Crystal structure and phase identification of the powder of sintered pellets was carried out by X-ray diffractometer (Brucker D8 Advance) using Cu-K$\alpha$ radiation (\( \lambda = 1.5418 \) Å), the microstructure and the composition analysis were investigated using field emission scanning electron microscope (FE-SEM) with energy dispersion X-ray spectrooscope attached (FEI, Quanta 200). The compositional analysis was carried out at different spots on the samples by applying accelerating potentials of 15 kV and 20 kV. Sintered pellets were polished and flat surface were coated with high purity silver paste and then dried at 120°C for 30 min, before taking electrical measurements. Dielectric measurements were conducted on an automated HIOKI 3532-50 Hi Tester, LCR meter. Dielectric permittivity were acquired in the frequency range 100 Hz - 1 MHz as a function of temperature (\( T \)) in a temperature range 35-200°C, where the sample undergoes the ferroelectric to paraelectric phase transition.

**Results and Discussion**

A typical X-ray diffraction (XRD) pattern of powder of all the sintered samples is shown in Fig. 1. Diffraction peaks occurred at slightly smaller angles when the specimens were doped with Ni ion and, although appreciable scatter existed in the c-axis values, the data did seem to indicate a lengthening of the a-axis and shortening of the c-axis to produce a more cubic structure with little change in cell volume. At first sight the XRD patterns of higher concentration of Ni$^{2+}$ doped BT samples, could be thought that the patterns fit well with the peak position of standard BT cubic phase (JCPDS file n-79-2263) since the splitting of cubic peak at \( 2\theta = 45.235 \) into tetragonal peaks (002) at \( 2\theta = 44.853 \) and (200) at \( 2\theta = 45.339 \) (JCPDS file 05-0626) is not observed. However, from a more careful examination of the patterns, it is evidenced that the broadening of the peaks of a same diagram does not increase regularly with Bragg angle \( \theta \), i.e., does not obey to the Scherrer’s equation$^{8, 15}$. This observation suggests that the lattices of the studied structures, initially cubic, have undergone a low tetragonal deformation. But the specimens do not show any phase involving the NiO compound up to \( x = 0.10 \). Thus, it appears that the Ni$^{2+}$ ions with the given concentration are totally soluble in BT lattice with the possibility of the Ni$^{2+}$ (\( r_{6}^{2+} = 0.69 \) Å) ions substituting both Ba$^{2+}$ (\( r_{6}^{2+} = 1.35 \) Å) and Ti$^{4+}$ (\( r_{6}^{4+} = 0.61 \) Å) sites due its small ionic radius. The unit cell parameters were calculated and the data is given in Table 1. The linear particle size (\( L \)) and lattice strain (\( \eta \)) was calculated using following Scherrer’s equation$^{8, 15}$ and data is given in Table 1.

\[
\beta_{1/2} \cos \theta = \frac{K \lambda}{L} + \eta \sin \theta
\]

where \( K = 0.89 \), \( \beta_{1/2} \) is full width at half maxima. The lattice strain was calculated from slope of sin \( \theta \) versus \( \beta_{1/2} \cos \theta \) plot. From the data it is observed

![Fig. 1—X-ray diffraction patterns of Ba$_{1-x}$Ni$_x$TiO$_3$](image)
that Ni doping decreases the crystallite size, unit cell parameters and lattice strain in BT, which may be due to replacement of large ionic radii of Ba $^{2+}$ ($r_{Ba}^{2+} = 1.35\text{Å}$) ion by smaller ionic radii Ni $^{2+}$ ($r_{Ni}^{2+} = 0.69\text{Å}$) ion.

The FE-SEM images of Ba$_{1-x}$Ni$_x$TiO$_3$ for $x = 0$, 0.03, 0.05, 0.07 and 0.10 respectively are shown in Fig. 2. From the SEM micrographs it is clear that grain distribution was uniform with least possibility of porosity throughout the sample’s surface. Also the edges of the grains are not so sharp, which confirms the melting like nature of sample (Fig. 2 a-d), moreover this melting look was found to increase with Ni doping in BT. The average grain size was determined by classical linear interception method and the data is presented in Table 1. From the data it is found that grain size decrease with Ni doping.

Table 1—Structural and dielectric properties of Ba$_{1-x}$Ni$_x$TiO$_3$

<table>
<thead>
<tr>
<th>$x$</th>
<th>0</th>
<th>0.03</th>
<th>0.05</th>
<th>0.07</th>
<th>0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>4.0115</td>
<td>4.0073</td>
<td>3.9871</td>
<td>3.9912</td>
<td>3.9951</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.0352</td>
<td>4.0242</td>
<td>4.0012</td>
<td>4.0022</td>
<td>3.9972</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.0059</td>
<td>1.0042</td>
<td>1.0035</td>
<td>1.0027</td>
<td>1.0005</td>
</tr>
<tr>
<td>Crystallite size (nm)</td>
<td>32</td>
<td>31</td>
<td>29</td>
<td>28</td>
<td>25</td>
</tr>
<tr>
<td>lattice strain</td>
<td>0.0176</td>
<td>0.0177</td>
<td>0.0102</td>
<td>0.0077</td>
<td>0.0025</td>
</tr>
<tr>
<td>Grain size (µm)</td>
<td>3.6</td>
<td>2.2</td>
<td>1.15</td>
<td>0.86</td>
<td>1.12</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.20</td>
<td>1.22</td>
<td>1.29</td>
<td>1.61</td>
<td>1.70</td>
</tr>
<tr>
<td>$\delta$</td>
<td>30.15</td>
<td>37.25</td>
<td>41.79</td>
<td>47.10</td>
<td>49.43</td>
</tr>
</tbody>
</table>

Energy dispersion X-ray spectroscopic analysis (EDX) of the $x = 0.03$ composition is shown in Fig. 3. EDX Analysis (Table 2) confirms the composition of the sample and the samples were found to be of the same composition that we have synthesized.

Figure 4 shows the variation of dielectric constant as a function of temperature for different Ni doped BT compositions at 1 kHz frequency. For normal ferroelectric, the dielectric constant increases gradually with increasing temperature up to the transition temperature ($T_c$) and then it decreases. Here the region around dielectric peak is broadened which is one of the most important characteristics of disordered perovskite structure with diffuse phase transition. This broadening is considered to be due to compositional fluctuations. The position of transition temperature ($T_c$) found to shift towards lower temperature side with increase in the Ni concentration. It was also observed that dielectric peak maxima decreases with Ni doping, in general the
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$c/a$ ratio indicates tetragonality distortion$^{16,17}$, i.e., higher the $c/a$ ratio higher will be tetragonality distortion and hence high will be dielectric constant$^{18}$.

In the present case also the peak dielectric maxima was found to follow the $c/a$ ratio trend. Further features of ferroelectric to paraelectric phase transition of different BNT samples were closely analyzed. Normal ferroelectric materials are well known to follow the permittivity versus temperature dependence described by modified Curie-Weiss law$^{18-20}$.

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_{\text{max}}} + \frac{(T - T_c)^\gamma}{2\delta^2}$$

where $C$ is Curie-Weiss constant, $T_c$ is Curie temperature, $\gamma$ and $\delta$ are the diffusivity coefficients. The coefficient $\gamma$ gives information on the character of the phase transition; for $\gamma = 1$, normal Curie–Weiss law is obtained, $\gamma = 2$ describe a full relaxor state with completely diffuse phase transition and $1 < \gamma < 2$ a combined ferroelectric/relaxor state with a certain degree of diffuseness in the phase transition. The parameter $\delta$ indicates the temperature extension for the diffuse phase transition, which is correlated with the dielectric permittivity broadening. $\gamma$ and $\delta$ can be determined by the slope and interception of the graph plotted between $\ln(1/\varepsilon - 1/\varepsilon_{\text{max}})$ versus $\ln(T - T_c)$ respectively and the data is reported in Table 1. Accomplishment of the above equation means that, treatment of dielectric data above transition temperature, in logarithmic plot of the type $\ln(1/\varepsilon - 1/\varepsilon_{\text{max}})$ versus $\ln(T - T_c)$ should give linear behaviour whose slope value $(\gamma)$ are expected to be 2. But the value of $\gamma$ comes out to be in the range $1.7 > \gamma > 1.2$ for different doping concentration of Ni in barium titanate. So in this case, it may be said that the phase transition is not purely diffuse, as described by Isupov$^{18}$. From Table 1, it is found that the diffusion parameters ($\gamma$ and $\delta$) increase with Nickel doping, i.e., an increasing relaxor character and a shift of $T_c$ towards lower values with Ni doping. In the literature the appearance of this diffuseness is generally argued in terms of variation in local composition giving rise to distinct micro regions, each of which has slightly different $T_c$ for its ferroelectric-paraelectric phase transitions$^{20,21}$. The decrease in grain size and crystallite size with Ni doping further supports the argument that Ni doping might have increased the micro regions (which have different $T_c$) and thus increased the diffused phase nature of the samples.

Figure 5 shows the variation of dielectric constant as a function of temperature for various Ba$_{1-x}$Ni$_x$TiO$_3$ compositions at 1 kHz.

**Table 2—EDAX analysis of Ba$_{1-x}$Ni$_x$TiO$_3$**

| Elements | $X = 0.03$ | | $X = 0.05$ | | $X = 0.07$ | | $X = 0.10$ |
|----------|------------|---|------------|---|------------|---|------------|---|
|          | wt% | At% | wt% | At% | wt% | At% | wt% | At% |
| O K      | 16.71 | 50.38 | 19.49 | 55.14 | 27.21 | 65.32 | 19.24 | 53.53 |
| Ba L     | 51.58 | 18.11 | 50.07 | 16.50 | 44.51 | 12.45 | 45.99 | 14.91 |
| Ti K     | 29.48 | 29.68 | 28.05 | 26.51 | 25.18 | 20.19 | 30.38 | 28.23 |
| Ni K     | 02.22 | 01.82 | 02.39 | 01.84 | 03.11 | 02.04 | 04.39 | 03.33 |

**Fig. 4—Variation of dielectric constant as function of temperature for various Ba$_{1-x}$Ni$_x$TiO$_3$ compositions at 1 kHz**
0.75 and 1T poled samples respectively, i.e., the diffusivity parameters were found to decrease with increase in poling strength. As argued in the above paragraph this observation suggests that magnetic field might grow the ferroelectric domain and results to less diffusivity in the sample.

Conclusions

The system $\text{Ba}_{1-x}\text{Ni}_x\text{TiO}_3$, $x = 0, 0.03, 0.05, 0.07$ and 0.10 was prepared by solid state reaction method. No phase change in the crystal structure was observed with Ni doping in BT, however a decrease in crystallite size, lattice strain, $c/a$ ratio and grain size was found with Ni doping. All the different results presented may be related to, and are explained by, the grain size and its distribution in the ceramic bulk. Ni doping in $\text{BaTiO}_3$ exhibit many interesting features, such as shift in transition temperature, increasing diffuse phase transition and decreasing dielectric constant. The evolution from a normal ferroelectric phase transition to a diffuse phase transition was observed with increasing Ni concentrations. The dielectric study of samples poled in magnetic field (data shown for BNT, $x = 0.03$ here) suggests that $T_c$ and maximum dielectric constant increase with increasing magnetic poling strength along with decreasing nature of diffusivity.

References