Structural, Optical and Dielectric properties of Nickel substituted Barium Titanate ceramics.

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Abstract. In present study, this paper describes the fabrication of Ba$_{1-x}$Ni$_x$TiO$_3$ (X=0, 0.05, 0.10) nanomaterial’s synthesized by chemical route sol-gel method. Their structural, optical and dielectric properties have been investigated as a function of sintering temperature. Dielectric measurements of the sintered sample were carried out for the composition over the frequency range of 10Hz - 10$^7$Hz. X-ray diffraction technique reveals that the formation of single phase crystalline structure. The presence of O-H stretching, NO$_3^-$, C-H bending modes and C=O stretching were verified by the Fourier transform infra-red spectroscopy for Ni substituted BaTiO$_3$.

1. Introduction
Since the discovery of BaTiO$_3$ in early 1940s, this material has been used for a wide range of scientific and industrial applications such as capacitors, ultrasonic transducers, pyroelectric infrared sensors, and positive temperature coefficient (PTC) resistors, etc [1-3]. For the application of doped BaTiO$_3$ ceramics as a capacitor material apart from a good density, a high dielectric constant and low loss factor have to be achieved. Barium titanate is a classical example of a ferroelectric crystalline material. Firstly, it is chemically and mechanically very stable, secondly it exhibits ferroelectric properties at and above room temperature and finally it can be easily prepared and used in the form of ceramic polycrystalline samples [4]. However, the effect of the specific impurity on the electrical conductivity depends on the substitution site as well as on the nature of the defect/electronic charge compensating defect. In the present work we have studied that the structural, dielectric and FTIR properties of BaTiO$_3$ and doped BaTiO$_3$ with one transition element Ni$^{2+}$ (0.05, 0.10 respectively) [5].

2. Experimental Details
Polycrystalline sample with composition of Ba$_{1-x}$Ni$_x$TiO$_3$ (x=0.05, 0.10) have been prepared by chemical route sol-gel method. The precursor Barium nitrate, Titanium nitrate, Nickel nitrate were taken in stoichiometric ratio. We mixed all materials in beaker and dissolved in de-ionized water. The mixture is slowly heated on magnetic stirrer and citric acid is added. The pH value is adjusted 7 by adding ammonia solution. If pH value is below 7, no gel is formed. The formed gel was dried on furnace and then gets a powder form which calcined at 900$^\circ$C for 2 hrs.
3. Result and Discussion

3.1. Structural Analysis

The room temperature X-ray diffraction pattern (Fig 1) and XRD data (Table 1) of Ba$_{1-x}$Ni$_x$TiO$_3$ (x=0.05, 0.10) confirm the single phase tetragonal Barium Titanate structure. All peaks are identified as tetragonal BaTiO$_3$ in space group P4mm. The lattice parameters BaTiO$_3$ were refined to $a=b=4.01\text{Å}, c=4.04\text{Å}$ and Ba$_{1-x}$Ni$_x$TiO$_3$ where (x=0.05, 0.10) were refined to $a=b=4.01\text{Å}, c=3.99\text{Å}$ and $a=b=4.01\text{Å}, c=4.00\text{Å}$ and reported value of $a=b=3.994\text{Å}, c=4.033\text{Å}$ corresponding to tetragonal-BaTiO$_3$ are compared and Nickel doped BTO are seen to reduce the constant cell volume (Table 1).

3.2. Fourier transform Infra-red Spectroscopy Analysis

FTIR analysis was carried out at 900$^\circ$C for detection the presence of the functional groups. By using this analysis the reaction mechanisms during the sol gel process can be detected. The FT-IR spectrum of the undoped and doped powder presented in Fig 2 shows the presence of the band located at 542 cm$^{-1}$ specific to the vibration mode of the Ti-O bond in the TiO$_6$ octahedra. The characteristic absorption band at 3486 cm$^{-1}$ is assigned to the O-H stretching vibration in water and confirms that the existence of the water in the BaTiO$_3$ and doped BaTiO$_3$ ceramics. The main bands specific to the ionic NO$_3^-$ (866 cm$^{-1}$ and 1425 cm$^{-1}$) introduced in the system by the catalyst and by the Barium and Nickel source, Ba(NO$_3$)$_2$, Ni(NO$_3$)$_2$·6H$_2$O in the case of the doped precursors, were also identified. The absorption bands at 1013, 1042, 1062 cm$^{-1}$ can be considered as C-H bending modes and the very small band at 1739, 1749 cm$^{-1}$ assigned to the C=O stretching mode of an ester bond. These two bonds can be related to the formation of the citrate complex during synthesis.

![Figure 1. XRD pattern of pure and Ni doped BTO (0.05, 0.10) at 900$^\circ$C.](image-url)
Figure 2. FTIR spectrum of pure and Ni doped BTO (0.05, 0.10) at 900°C.

Table 1. Lattice parameter, unit cell volume, density and crystal size of Pure and Iron doped BaTiO₃.

|          | Lattice Parameter (a, b, c) | c/a | Volume (Å³) | Density (g/cm³) | Crystal Size (nm) |
|----------|-----------------------------|-----|-------------|----------------|------------------|
| BaTiO₃   | a=b=4.01, c=4.04            | 1.007 | 64.96       | 5.969           | 26.48            |
| BTNi5    | a=b=4.01, c=3.99            | 0.995 | 64.15       | 5.965           | 27.66            |
| BTNi10   | a=b=4.01, c=4.00            | 0.997 | 64.32       | 5.783           | 24.97            |

3.3. Dielectric Studies

Dielectric studies have been performed in a wide temperature range. The electric permittivity ε and dielectric loss tanδ have been measured at different frequencies for Ni (x=0.05, 0.10) doped BaTiO₃. The variation of Dielectric Constant with temperature for sample with different compositions fig shows that the Nickel doped BaTiO₃ have a prominent influence on dielectric properties. The temperature dependence (40°C to 180°C) of the dielectric parameters has been measured for Ni doped BTO (sintered at 900°C) as a function of frequency. No evidence of any structural transition in this temperature range were found which is in contrast with doped BaTiO₃. The result indicates that the dielectric constant decreased as a frequency increased from 1Hz to 10⁵Hz. Generally, the dielectric constant at low frequency is higher than those obtained at the higher frequency. The decrease in dielectric constant is due to the dipoles which cannot follow the alternation of the applied ac electric field. Loss tangent (tanδ) variation with temperature at different frequencies shows similar characteristics.
Figure 4(a). Temperature dependent Dielectric Constant of Ba_{0.95}Ni_{0.05}TiO_3 at 900°C.

Figure 4(b). Temperature dependent Dielectric tanδ of Ba_{0.95}Ni_{0.05}TiO_3 at 900°C.

Figure 5. Temperature dependent Dielectric Constant of BaTiO_3 at 900°C.
4. Conclusion

Barium Titanate and Ni (x=0.05, 0.1) doped BTO powders were prepared by Sol gel method. The synthesized powders were characterized by X-ray diffraction using a Bruker D8 Advance X-ray diffractometer. XRD patterns were obtained Cu-Kα radiation and the wavelength of X-ray was 1.54Å. The XRD patterns showed that this material crystallizes in a perovskite-type single phase tetragonal structure with space group p4mm. The XRD data has concluded that all major peaks of BTO and Ni-BTO are matching with reported XRD data, and sample is in single phase. The FTIR spectrum was measured at room temperature. The FTIR spectra of Pure BaTiO$_3$ and doped with Nickel, by the FT-IR data we get the intensity of nitrate (NO$_3^-$) and hydroxyl (O-H) peak reduced with doping of Nickel in pure BTO.

In dielectric studies no evidence of any structural transition in this temperature range were found which is in contrast with doped BaTiO$_3$. The result indicates that the dielectric constant decreased as a frequency increased from 1Hz to 10$^5$Hz. The decrease in dielectric constant is due to the dipoles which cannot follow the alternation of the applied ac electric field.

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