Chapter- 4

Synthesis, characterization and transport properties of Nd-doped barium zirconium titanate
(BaNdxZr0.2Ti0.8-xO3)

4.1 Introduction

In previous chapter, detailed study of neodymium (REM) has been presented. Its role as dopant has been also discussed and proved beneficial. In this chapter our aim is to study effect of neodymium doping in barium zirconium titanate complexes. The site of doping has been also changed, which modified all the existing characteristics of barium zirconium titanate (BZrT).

In recent years, Pb-free perovskite materials have been studied extensively for their use in the field of dielectrics, pyroelectrics, ferroelectricity and piezoelectricity (Uchino et al., 2003), (Ye et al., 2008), (Pardo, 2011). Barium Zirconium Titanate (BZrT) with customarily ranging atomic proportions has been considered as best candidate in the said fields because its properties entirely depend upon the role played by carriers (electrons and holes) in transition mechanisms and these carriers exhibit extended tailing in density of state (DOS) on doping of different elemental concentrations by forming deep and shallow levels below the conduction band (Chou et al., 2007). These levels have been shown to be significantly dependent on ratio of Zr4+/Ti4+ as well as presence of rare earth elements in the compound as dopants. Ferroelectric Relaxor behaviour has been induced on substitution of rare-earth elements (Sagar et al., 2012). Kumar et al.,(Kumar, 2011) investigated interrelationship between the phase structure and dielectric behaviour of the lead substituted barium zirconium titanate Ba1-xPbxTi0.90Zr0.1O3 complex and found rise in Curie temperature with lead content. The
broadening of dielectric peaks near transition temperature and further its frequency dependent nature suggested a diffuse type phase transition in samarium (Sm) doped BZrT (Ghosh et al., 2014). With Ytterbium as dopant, ferroelectric phase transition of BZrT ceramics shifted from higher temperature to lower temperature as also Curie temperature altered with dopant content. At normal temperatures, the cubic phase has been shown to be more stable. Sagar et al., (Sagar, 2010) explained temperature dependence of resistivity. The diffuse phase transition behaviour of the ceramics at higher Nd content is shown to be significant for composition-induced diffuse transition.

Resultantly, the versatile properties of ceramics due to change in atomic compositions in BZrT compound formations and the doping techniques have given researchers a very precious tool. Different workers however differed in characterising doping adequacies for optimal properties of ceramics. A need is always felt to work out modalities that define signatures for synthesis and optimized doping for better ceramics. Present work is focussed on evolving more effective approach on synthesis of BaNdₓZr₀.₂Ti₀.₈ₓO₃ through solid state route with neodymium doping (x = 0.00, 0.05, 0.1 and 0.2) as dopants. The widely varying doping amounts are specifically chosen to visualise nature and extent of structural deformations in compound symmetry and subsequent change in their properties. The samples so prepared have been examined for phase formations using X-ray diffraction method. Elemental compositions are confirmed through energy dispersive spectroscopy. The Field Emission Scanning Electron Microscope is used for morphology of the ceramics, so formed FTIR spectroscopy has been performed on the samples for absorption information. The samples have been finally put to test for their electrical and optical properties under various stressing situations; such as temperature and frequency and to their usefulness.
4.2 Sample preparation

The chemicals of BaCO$_3$, TiO$_2$ and ZrO$_2$ with 99.5% purities and Nd$_2$O$_3$ with 99.9% purity were procured from Sigma Aldrich, Inc. USA. Barium zirconium titanate (BZrT) compound has been obtained from these chemicals through solid-state route. BZrT has been identified and analyzed for structure description and purely for information purposes only. Further, Nd$_2$O$_3$ has been introduced in the BZrT as dopant by taking all amounts in stoichiometric proportions. Nd-doped barium zirconium titanate (BaNd$_x$Zr$_{0.2}$Ti$_{0.8-x}$O$_3$) compound has been prepared for $x = 0.00, 0.05, 0.1$ and 0.2 doping amounts of Neodymium.

For homogenizing the materials, the samples were hand milled each separately for 12 hours in dry as well as acetone media using agate mortar and pestle. Samples were calcined at 950 °C on alumina boats in Macho-Nabertherm-C-42 oven. The process of heating was carried out for 2 hours in the presence of air. Samples were allowed to cool on their own and hand milled again for 2 hours for mixing and further in vinyl chloride as binder. After drying the mixture, pellets of 10 mm diameter and 2 mm thickness were formed under a 5.5 tons of pressure using standard hydraulic, graded press. Pellets were finally made to sinter at 1450°C by keeping heating rate as 10 °C per minute for four hours and allowed to cool down to normal temperature at same rate.

4.3 Instrumentation

Bruker Advanced D8 X-ray Diffractometer has been employed for x-ray diffraction patterns of the samples to ascertain phase formations. Diffractometer involves Cu K$_\alpha$ source ($\lambda = 1.5406$ Å) and operated at 40 kV and 40 mA in Bragg-Brentano geometry. To carry out surface morphology analysis, a field emission scanning electron microscope (FE-SEM): MIRA II LMH from TESCAN was used. Gold coating of 10 nm thickness was applied to
samples to counter charging effects by using $Q_{150}$T-S High Vacuum Turbo Pumped Sputter Coater System from Quorum Technologies. Energy dispersive spectroscopy (EDS) was performed with INCA Penta FET$_3$ from OXFORD. Dielectric measurements have been performed on Agilent precision LCR meter. For FTIR analysis, 0.20 mg of each sample mixed with 200 mg of KBr was used which was ground well for thin and transparent pellets. Agilent Technologies Cary 600 series, Model Cary 660 FTIR has been employed for optical spectroscopy of the sample.

4.4 Results and discussion

4.4.1 X-ray diffraction studies

XRD patterns obtained for sintered samples are shown in fig. 4.1. Peaks are indexed to single phase perovskite structure. The peak-patterns are matched with JCPDS card no. 36-0019. As a result, single-phase perovskite cubic structure has been identified with space group Pm3m, which is also in agreement with literature (Moura et al., 2009), (Sagar et al., 2010).
The cell parameters are observed as, $a = b = c = 4.0274(3) \text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 65.324\text{ Å}^3$; $a = b = c = 4.0275(3) \text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 65.329\text{ Å}^3$; $a = b = c = 4.0372(6) \text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 65.802\text{ Å}^3$ and $a = b = c = 4.0553(6) \text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 66.691\text{ Å}^3$ for $x = 0.00, 0.05, 0.1$ & $0.2$, respectively. An expansion in lattice parameters with increased dopant concentration is evident from above data.
This observation is further confirmed by a real negative peak shift as shown in fig. 4.2. This shift to lesser angle has indicated enormous strain in the lattice as a result of doping concentration. The increase in cell volume has thus led to expansion in the lattice size as well. A significant increase in intensity counts with doping concentration is also noticed.

4.4.2 Analysis of SEM

The SEM images, as shown in Figure for x = 0.00, 0.05, 0.1 &0.2 have revealed growth of grain size in all the samples. The surfaces of the samples appear asymmetrical while fine agglomerates have been seen in the patterns. Particle size, as calculated using Scherrer’s Formula (Patterson, 1939) comes out to be 10.12nm, 10.15 nm, 10.20 nm and 10.25 nm each for samples x = 0.05, 0.1 and 0.2. The porosity for x = 0.05 and 0.1 sample is found to have significant increase with dopant concentration which is in line with the findings of Zhang et al., (Zhang, 2013).
Further, $x = 0.2$ sample shows still higher porosity and quite a wider volume in this sample seems to have grown some fine clustered agglomerates with uneven particle distributions.

The observed significant growth in grain size with increase in proportion of neodymium dopant is also in line with XRD results, which also suggest expansion in the unit cell. However, it looks that even with marginal increase of Nd$^{3+}$ ions the constituents realign to acquire closely packed position which in turn perturbs the conditions necessary for resonant bonding. The excess dopant presence sets in impurity or imperfections in the lattice which
causes outward stress that appears at face centred sites with Nd\textsuperscript{3+} presence. The presence of impurities expands grain boundaries by virtue of enhanced grain size further leading to consistent decline in sample density. This observation also agrees well with the findings of Hsu et al., (Hsu, 2004).

4.4.3 EDS analysis

![Energy dispersive x-ray spectroscopy](image)

**Fig. 4.4**  Elemental composition information from EDS

Energy dispersive x-ray spectroscopy has been performed on the samples for elemental analysis and chemical characterization purposes where all constituents of the complex compound are represented by their corresponding peaks. The EDS analysis has shown elemental compositions in stoichiometric proportions. Presence of gold peak from gold contacts for taking SEM images is however also noticed, as shown as sample in Fig.4.4 for \( x = 0.05 \) sample.
4.4.4 Frequency dependent dielectric constant

Dielectric behaviour of the samples has been studied along frequency range of 20 Hz to 2.0 MHz at normal temperature as shown in Fig. 4.5. Within experimental errors, the values of dielectric constants with dopant concentration for 1 KHz frequency have been measured to be 985, 1065, 1153 and 1525. The dielectric properties of Nd-doped compounds have shown considerable improvement with increase in dopant concentration indicating better frequency stability.

![Frequency dependence of dielectric constant](image)

Fig. 4.5 Frequency dependence of dielectric constant

The internal stress due to increase in dopant concentration becomes more pronounced and significant enough to shift the Curie temperatures to values of around 50°C. The dopant concentration is in conformation to better quality ceramic for higher frequency operations requiring reasonable potentials at disposal.

Temperature dependence of dielectric constant has been studied at fixed frequency value of 1 KHz. The results are shown in Fig.4.6.
There appears to be a change from ferro- to para-electric behaviour in the first doped sample (x = 0.05) at Curie temperature value of 390°C.

The Curie temperature of the third sample (x = 0.1) has fallen to 395°C as also the electrical permittivity at its maximum is low whereas the value of Curie temperature stands at 400°C for the fourth sample (x = 0.2). It also appears the enhanced ionocity and hopping of electrons between Nd\(^{3+}\) dopants ions and host BZrT, which favour resonant bonding as also the fluidity of charge localization at ion cores. It is the dopant concentration that supports charge transport as well as Curie value gain. Significant changes in phase transformation appear and there is noticeable temperature dependence of dielectric constant observed.
4.4.5 Frequency dependent resistivity

Frequency dependence of resistivity(Fig. 4.7) shows good response of the material at much higher frequencies, remarkably improving with dopant concentration.

![Resistivity verses Frequency](image1)

**Fig. 4.7** Resistivity verses Frequency

![Tangent loss verses Frequency](image2)

**Figure 4.8** Tangent loss verses Frequency
Tangent loss (Fig. 4.8) is quite less prevalent in the first sample which improves for higher doping concentration and makes the material better and more durable for electrical permittivity even at higher frequencies.

4.4.6 Optical behavior

![Graph showing Transmittance vs Wavenumber](image)

Fig. 4.9 Transmittance vs Wavenumber

Optical absorption spectra show absorption troughs for the three doped samples respectively at 559.255 cm\(^{-1}\), 586.253 cm\(^{-1}\) and 592.153 cm\(^{-1}\) wave numbers (Fig. 4.9). S.K. Ghosh et al., (Ghosh, 2014) however reported absorption at 543.9 cm\(^{-1}\) wave number as a fingerprint of pure BZrT powder. The shift however reveals polarization due to larger Nd\(^{3+}\) ions. It also infers that neodymium, having larger ionic radius (164 pm) substitutes titanium (132 pm) in BZrT ceramic due to which the vacancies are created at the B-site causing dramatic stress on Metal-Oxygen bond in perovskite octahedral geometry. It develops stretching of metal oxygen (M–O) vibration band at the B-site that is the reason of shift from its fingerprint value.
4.5 Conclusions

Neodymium doped compounds of barium zirconium titanate have been probed for dopant concentration effects on morphology and electrical properties of the materials. The Nd\(^{3+}\) ion dopant concentration governs stability of BZrT ceramic. The electrical permittivity is in its most acceptable form as also its stability over wide ranging frequency and temperature dependence. The Curie temperature improves showing upward trend with doping. The tangent loss is also in its lowest form. The dominance of dopant of higher ionic radius replaces titanium, as is also evident from its intensity counts under XRD-patterns, immobilizes charge movements by causing undue outward stress at face centered Zr\(^{3+}/\) Ti\(^{3+}\) locations thereby lowering the specific electrical permittivity. SEM microgram for first doped sample shows fine grain formation paving the modest route through Ti-Nd pairing. The Ti-Nd pairing with doping monitors trend of grain growth that vindicates agglomerates and uneven cluster formations. The dielectric constant over a wide frequency range thus makes the material suitable for devices operating under wider frequency bands. Tangent loss is small over a desired frequency range. Conditions of resonant bonding have shown to proactively influence electrical permittivity of the material. Dopant caused porosity triggers drastic change in dielectric behavior of the material as well as its temperature and frequency dependence. The Curie temperature shows significant change with grain size and optical absorption marginally shifted to lower wave number, probably due to formation of new Nd\(^{3+}\)-dopant arrangement. The absorption spectrum indicates M-O absorption of 559.255 cm\(^{-1}\) in IR region and appreciable change in dipole moment is observed due to new arrangements with intense IR absorption band.
The shuffling between vacancies and distortions may however account for numerous other properties of the ceramic. The dielectric and ferroelectric materials and their microstructure characteristics find strong correlation by virtue of grain size. These correlations reveal possibility of further improvements in dielectric properties of this family of ceramics. Dielectric response measurements yielded favourable electric behaviour at 1KHz frequency. By fixing the frequency at this desired value the properties of the material were exploited by varying temperature between room temperature to 550 °C. The Curie temperature obtained to be 450°C is better and above threshold value as obtained with pure compound.

**Part of This work has been published:**

*Anil Kumar, Vipin Kumar, M Gupta and SS Ghumman; Synthesis of 0.1% and 0.2% Neodymium doped barium zirconium titanate and study of their dielectric behaviour: AIP conference proceedings 1675 (2015) 030074-1-4; doi: 10.1063/1.4929290.*

----------X----------