CHAPTER 2

GROWTH AND CHARACTERIZATION OF LEAD FREE
NBT-BT SINGLE CRYSTALS

2.1 INTRODUCTION

Relaxor behavior has been studied extensively in lead based perovskite complexes like lead zirconate titanate (PZT), lead magnesium niobate (PMN) and lead zinc niobate-lead titanate (PZN-PT). Due to the high piezoelectric properties these materials are found to be used in sensors, actuators and transducer applications. The presence of lead in these complexes made them to expel from the society due to the environmental aspects which are concerned and there has been a development of lead free piezoelectric materials (Eric Cross 2004). Sodium bismuth titanate (NBT), potassium bismuth titanate (KBT) and potassium sodium niobate (KNN) are some of the examples of lead free relaxor ferroelectric materials. Among all lead free systems NBT is one of the best materials (Smolenskii et al 1961).

NBT is of ABO$_3$ perovskite structure with rhombohedral crystal system. NBT shows high Curie temperature of 320°C, remnant polarization ($P_r$) = 38 $\mu$C/cm$^2$ and a coercive field ($E_c$) of 73 kV/cm (Bao-Jin Chu et al 2002; Suchanicz et al 1988). However the high coercive field increases the difficulty of poling. To improve the piezoelectric properties of NBT attention is moving towards the solid solutions of NBT. Some of the solid solutions of NBT are sodium bismuth titanate-barium titanate (NBT-BT) (Takenaka et al 1991) sodium bismuth titanate – potassium bismuth titanate (NBT-KBT)

The NBT-BT is found to have high piezoelectric performance when compared to all the solid solutions of NBT. In 1991 Takenake et al (1991) pointed out the existence of Morphotropic Phase Boundary (MPB) between the rhombohedral NBT and tetragonal BT and it is shown in Figure 2.1. MPB is a place where abrupt structural change is happening with the variation of composition. The coupling between two different energy levels at MPB increases the dipoles orientation and leads to high piezoelectric properties. In NBT-BT, MPB exists at 0.06 to 0.07 mol of BT concentration.

Figure 2.12 Morphotropic phase boundary in NBT-BT solid solution (Takenaka et al 1991)
The structure of NBT-BT is distorted perovskite with the general formula ABO$_3$. In NBT-BT, TiO$_6$ octahedron is at the centre of the cube which shares the 8-corners of the cube formed by the octahedral with sodium, barium and bismuth cations in three dimensions (Woodward 1997). Various aspects of these cations (Na, Bi and Ba) like composition, size and the corresponding charge play a key role in determining the degree of coupling between the dipoles and in the formation of micropolar regions in this type of relaxor materials. Single crystals of NBT-BT was grown and studied by many researchers. The super lattice reflection in NBT-BT was studied by Soukhojak et al (2000), the inhomogeneity issues in NBT-BT grown by flux and metal strip heated zone technique was carried out to analyze the effect in dielectric properties (Bubesh Babu et al 2008). Growth of NBT-BT crystals by top seeded solution growth was carried out by Chao Chen et al (2010).

The present chapter is concentrated on the growth of NBT-BT single crystal in MPB and its dielectric properties. The 0.96Na$_{0.5}$Bi$_{0.5}$TiO$_3$-0.06BaTiO$_3$ (NBT-BT) was grown by conventional flux technique using Bi$_2$O$_3$ as a flux. The crystal perfection was studied by X-Ray rocking curve analysis. High temperature dielectric analysis was carried out to analyze the relaxor characteristics of the grown NBT-BT crystals. Dielectric anomaly was studied using Vogel - Fulcher (V-F) and power law models.

2.2 EXPERIMENTAL TECHNIQUES

2.2.1 Synthesis of Polycrystalline NBT-BT

Growth of 0.96Na$_{0.5}$Bi$_{0.5}$TiO$_3$-0.06BaTiO$_3$ single crystals consists of two steps. First one is the synthesis of polycrystalline NBT-BT powder by solid state reaction method and the second one is the growth of NBT-BT single crystals by flux technique. Raw oxide and carbonate powders with higher than 99.9 % purity were used as starting materials consisting of
Na$_2$CO$_3$, Bi$_2$O$_3$, BaCO$_3$ and TiO$_2$. The well mixed powders with the composition of 0.96Na$_{0.5}$Bi$_{0.5}$TiO$_3$-0.06BaTiO$_3$ were calcined at the 900°C for 12 hours in air. Followed by grinding NBT-BT polycrystalline powder was synthesized at 1200°C with 24 hours dwelling. The perovskite structure of the synthesized powder was confirmed by powder XRD. Then the polycrystalline powder was then ground with 30 wt% of excess Bi$_2$O$_3$ and it acts as self flux for the growth.

To decide the thermal cycle for growth, Differential Thermal Analysis (DTA) was carried out for 30 wt% of flux added NBT-BT in a N$_2$ atmosphere using TA instruments, Q 600 SDT model. The DTA curve shown in Figure 2.2 corresponds to both while heating and cooling and the cooling/heating rate was fixed as 10°C/min.

![DTA curve of synthesized NBT-BT with the addition of 30 wt% of Bi$_2$O$_3$](image)

**Figure 2.13** DTA curve of synthesized NBT-BT with the addition of 30 wt% of Bi$_2$O$_3$
The congruent melting for NBT-BT without any flux was observed at 1262°C (Bubesh Babu et al 2008). The addition of 30 wt% Bi₂O₃ reduced the melting point to 1220°C. The first endothermic peak in Figure 2.2 represents the melting of Bi₂O₃ and the second endothermic peak corresponds to the complete melting of NBT-BT. The cooling curve shows that the nucleation starts at 1040°C. Depending on this results the growth profile followed to grow NBT-BT was decided as follows,

$$RT \rightarrow 10^\circ C/h \rightarrow 1300^\circ C \rightarrow 1300^\circ C \rightarrow 1100^\circ C \rightarrow 800^\circ C \rightarrow RT$$ (2.1)

where RT indicates room temperature.

2.2.2 Growth of NBT-BT Crystals by High Temperature Solution Growth Method

The growth was carried out in a resistive heating SiC furnace (Figure 2.3) using platinum crucible. The furnace was controlled and programmed by Eurotherm PID controller with the accuracy of 0.01°C. After the growth run the crystals were harvested from the crucible using hot conc. HNO₃ for several hours. The photographs of as grown and the harvested crystals were shown in Figure 2.4. Each growth has resulted about 10-15 crystals of several dimensions. The maximum crystal dimension was found to be $1.5 \times 1.3 \times 1 \text{ cm}^3$. Crystalline structure of the grown crystal was studied using powder XRD with the CuKα radiation of wavelength 1.5060 Å with step time of 1 s and step size 0.02° was maintained all over the experiment. The dielectric constant as a function of temperature in the range 30°C to 450°C for 5 different frequencies 1 kHz, 5 kHz, 10 kHz, 50 kHz and 100 kHz has been determined using LCR meter (HIOKI 3532-50, Japan).
Figure 2.14  SiC resistive heating furnace used for the growth of NBT-BT single crystals

Figure 2.15 (a) As grown and (b) harvested NBT-BT single crystals

2.3 RESULTS AND DISCUSSION

2.3.1 Structural and Surface Studies

To understand the intermediate phase formation and the reaction mechanism during the synthesis of polycrystalline powder of NBT-BT, the
calcined powders was analyzed by powder XRD. Figure 2.5 shows the XRD patterns of NBT-BT calcined at 900°C, 1200°C, and for the single crystal. One intermediate phase is observed around 49° in the NBT-BT calcined at 900°C and it corresponds to BaTiO$_3$ phase. However the calcinations at 1200°C yield a NBT-BT polycrystalline material. The BT diffuses into the NBT lattice to form a complete solid solution. For single crystals the XRD analysis is carried out on the as grown crystal. The harvested crystals are crushed into fine powders using agate mortar. The obtained XRD patterns are well matched with the existing reports (Chao Chen et al 2010; Bubesh Babu et al 2008).

The grown NBT-BT crystals are in perovskite structure and it is having rhombohedral structure with R3c space group. The lattice parameters are $a = b = c = 3.951$ Å and $\alpha = \beta = \gamma = 90.5^\circ$.

The obtained NBT-BT crystals are yellow in color with near cubic morphology in most of the crystals. In some parts of the crystals step like morphology as shown in Figure 2.6 was observed when analyzing through the optical microscope.

2.3.2 X-ray Rocking Curve Analysis

High resolution X-ray diffraction (HRXRD) is a significant tool to determine the crystalline perfection of the single crystals. The Full Width at Half Maximum (FWHM) of the rocking curve is the most important parameter to decide the crystal quality. Figure 2.7 shows the X-ray rocking curve of the (001) plane reflection for the as grown crystal.
Figure 2.16 Powder XRD patterns of polycrystalline and single crystal NBT-BT

Figure 2.17 Optical microscope image of as grown NBT-BT single crystal
The X-ray rocking curve was obtained by means of PANalytical X’Pert Pro MRD equipped with a Ge (220) monochromator and triple axis proportion detector. The FWHM value of the (001) peak is 4.72 arc min. As a solid solution of rhombohedral NBT and tetragonal BT, NBT-BT crystals have some structural distortion. Therefore the line broadening of the rocking curve might be attributed to lattice distortion as well as the growth defects. However the present value is lower than the FWHM of 7 and 18 arc min for NBT-BT crystal grown from single flux and double flux systems respectively (Bubesh Babu et al 2008) which confirms the grown crystals are having improved crystal quality.

2.3.3 Dielectric Analysis

The single crystals were cut and polished for even surface and then electroded using colloidal silver paste. The samples were annealed at 200°C
for 30 min to get proper adhesion. This annealing would help to minimize the significant change in the electrode response to the temperature during the measurements. Capacitance (C) and dielectric loss (tan δ) as a function of temperature are measured for unpoled as grown NBT-BT single crystals as the frequency was increased. Relative dielectric constant ε’ (real part of the dielectric constant) was calculated from the capacitance using the following Equation (2.2),

\[ \varepsilon' = \frac{C \cdot l}{\varepsilon_0 \cdot A} \]  

(2.2)

where \( l \) is the thickness of the sample in m, \( A \) is the area of electroded surface in m², \( \varepsilon_0 \) is the permittivity of vacuum 8.854×10⁻¹² F/m. The C and tan δ measurement are carried out as the sample is heated from 300 K to 725 K. Figure 2.8 shows the temperature and frequency dependence of the real part of dielectric constant (ε’) upon heating. Two dielectric anomalies are visible in the dielectric plot. The first peak at 442 K corresponds to the ferroelectric to antiferroelectric transitions and the temperature is called as depolarization temperature \( T_d \). This phase transition is still controversy. The X-ray or the neutron diffraction studies show that this is due to the co-existence of rhombohedral and tetragonal phases and there is no antiferroelectric phase change (Suchanicz & Kwapulinski 1995; Jones & Thomas et al 2002). However recently TEM studies on NBT ceramics explained the antiferroelectric property, in addition to that, temperature dependent ferroelectric studies on NBT crystals shows the double hysteresis (Dorcet et al 2008; Sun et al 2011). According to the model suggested by the Dorcet (2008) NBT-BT single crystals can show the transformation from rhombohedral ferroelectric to tetragonal antiferroelectric. The polarization of the sample disappears after \( T_d \), hence the \( T_d \) plays an important role in determining the practical applications of NBT-BT single crystals.
The second hump in the dielectric plot attributed to the transition from antiferroelectric to paraelectric state and the temperature where the dielectric constant reaches its maximum (T_m) (Chao Chen 2010). It can be seen from the Figure 2.8, the dielectric constant shows an obvious frequency dispersion and exhibit broad dielectric peaks with the maximum at T_m= 595 K and ε_{mn} = 4783 (for 1 kHz). These results indicates that the as grown NBT-BT crystals are relaxor ferroelectric. The T_m value in the present study is higher than the previously reported values (Bubesh Babu et al 2008; Wenwei Ge et al 2008). Hong Liu et al (2008) reported that the maximum dielectric constant of NBT single crystals is about 2500 and the phase transition temperatures T_d and T_m is at 498 K and 630 K respectively.

It has been suggested long back that in the ABO_3 perovskite structure the relaxor behavior originates due to the cation disordering. Furthermore, if more cations occupying the same lattice position in the unit cell, it leads to more chemical inhomogeneity with distinctive compositions and structural variations (Hong Liu et al 2008). Based on these views NBT-BT crystal is a typical relaxor ferroelectric with A-site complex ions and the relaxor characteristics are resulted from the random distribution of Na^+, Bi^{3+} and Ba^{2+} in the A-site.

A characteristic loss peak is found for all the frequencies around T_d as shown in Figure 2.8. When the phase transition from ferroelectric to anti ferroelectric is happening at T_d, the domain wall movement enhances and results in the dielectric loss peak. The rapid increase of tan δ after T_m is due to the high conductivity and it can be explained by the generation and movement of oxygen vacancies (Chao Chen et al 2010).
Figure 2.19  Variation of dielectric constant and dielectric loss as a function of temperature for various frequencies of NBT-BT single crystals

2.3.4 Modified Curie-Weiss Law Fitting

The temperature dependence of $\varepsilon'$ of a ferroelectric material obeys a Curie-Weiss law above $T_c$ (Curie temperature) which is given by,

$$\varepsilon' = \frac{C}{T - T_0}$$  \hspace{1cm} (2.3)

It shows the linear response between the $1/ \varepsilon'$ and $T$. Contrast to this $\varepsilon'$ of relaxor ferroelectric exhibits strong deviation from this law for temperature many degrees above $T_m$. The relaxor ferroelectric obeys the modified Curie Weiss law which is,
\[ \frac{1}{\varepsilon'} - \frac{1}{\varepsilon_m^*} = \frac{1}{k_B (T - T_m)^\gamma} \]  

(2.4)

where \( k_B \) is Boltzmann constant, the coefficient \( \gamma \) is diffusivity parameter and, \( \varepsilon_m^* \) is the maximum dielectric constant. Diffusivity parameter gives the degree of diffusiveness of the material at \( T_m \). For ferroelectric materials the value of \( \gamma \) is less than 1 and for relaxor ferroelectric material it is varying from 1 to 2 (Samara 2003). In the present work the dielectric data of 1 kHz are fitted to the equation (2.4) and \( \gamma \) is found to be 1.79. Figure 2.9 shows the graph between \( \ln \left( \frac{1}{\varepsilon'} - \frac{1}{\varepsilon_m^*} \right) \) and \( \ln (T - T_m) \) at 1 kHz. It shows the better diffusive nature of the grown NBT-BT single crystals.

![Graph showing modified Curie-Weiss law fit at 1 kHz of NBT-BT crystals](image)

**Figure 2.20 Modified Curie-Weiss law fit at 1 kHz of NBT-BT crystals**

### 2.3.5 Activation Energy Anomaly

The Debye medium is a classic dielectric medium. In the Debye medium the dipoles are thermally activated and there won’t be any interaction
between the dipoles. Hence the relaxation time (τ) can be said to obey the Arrhenius law,

$$\omega = \omega_0 \exp\left(-E/k_BT_m\right)$$  \hspace{1cm} (2.5)$$

where τ = 1/ω, $k_B$ is the Boltzmann constant, $\omega_0$ is the attempt frequency of a molecule (Debye frequency) and E is the activation energy. But the experimental results proved that not all the dipoles are free and there may be an interaction between the dipoles. These interactions make the dipoles to freeze at a particular temperature called $T_f$.

This inadequacy of Debye model is taken into account in Vogel-Fulcher (V-F) model and it is given by,

$$\omega = \omega_0 \exp\left(-E/k_B(T_m - T_f)\right)$$  \hspace{1cm} (2.6)$$

where $T_f$ is the freezing temperature and also the temperature of static dielectric constant maximum (Viehland et al 1990).

In Equation (2.6) if $T_f$ equals to zero, it becomes Equation (2.5) and $T_m$ become the Curie temperature in the case of ferroelectrics regardless of the value of $T_f$. As discussed by Cheng et al V-F model fails to differentiate ferroelectrics and relaxor ferroelectrics. To overcome this lack of V-F model, Cheng et al proposed a power law,

$$\omega = \omega_0 \exp\left(-E/k_BT_m\right)^p$$  \hspace{1cm} (2.7)$$

where ‘p’ is a constant (Cheng et al 1996). When ‘p’ equals to 1 the Equation (2.7) becomes Equation (2.5) and when ‘p’ tends to infinity and $T_m$ tends to $T_c$ it explains the ferroelectric behavior of the materials. The relaxation process
is very weak for ferroelectrics. For the relaxor ferroelectric materials the ‘p’ value should be greater than 1 and the value further increases as the dielectric relaxation decreases hence the lower value of ‘p’ corresponds to the stronger relaxation. Thus the relaxation process is characterized by the value of ‘p’. The experimental values are fitted to the Equations (2.6) and (2.7) using Levenberg-Marquardt non linear fit and it is shown in Figure 2.10 and goodness of fit parameter in terms of $\chi^2$ is given in Table 2.1. The value of $\omega_o$, $E$ and ‘p’ for the grown NBT-BT single crystals is given in Table 2.1.

Table 2.4  Fitting parameters of V-F, Power law and reduced $\chi^2$ for NBT-BT single crystals

<table>
<thead>
<tr>
<th>Method</th>
<th>Attempt Frequency $\omega_o$ (Hz)</th>
<th>Activation Energy $E$ (eV)</th>
<th>Freezing Temperature $T_f$ (K)</th>
<th>$p$</th>
<th>Reduced $\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vogel–Fulcher</td>
<td>$2.28 \times 10^{10}$</td>
<td>0.029</td>
<td>569.97</td>
<td>--</td>
<td>0.216</td>
</tr>
<tr>
<td>Power law</td>
<td>$6.64 \times 10^7$</td>
<td>0.054</td>
<td>--</td>
<td>40.91</td>
<td>0.215</td>
</tr>
</tbody>
</table>

Based on the reduced $\chi^2$ value it seems that the power model gives the best fit to the present data. The attempt frequency $\omega_o$ gives the knowledge about the size and interaction between the polar clusters. For large volume of polar clusters and stronger interaction the value of $\omega_o$ will be small. That makes the $T_m$ to shift towards higher temperature side and a more broadening of the dielectric peaks. The value of ‘p’ determines the degree of relaxation and hence the rate of growth of polar clusters. More the relaxation, slower is the rate of growth of polar clusters (Vedantam et al 2003; Cheng & Katiyar 1998).
2.4 CONCLUSION

Single crystals of NBT-BT in its MPB composition have been grown by high temperature solution growth method using Bi$_2$O$_3$ as a flux. The maximum dimension for the harvested crystal was about $1.5 \times 1.3 \times 1$ cm$^3$. The perovskite structure has been confirmed by XRD analysis and the step growth was observed in optical microscope studies. The reduced FWHM of the (001) peak proved the improved crystalline perfection. Diffuse phase transition was observed from dielectric analysis and the calculated diffusivity parameter ($\gamma = 1.79$) are in acceptable range of relaxor ferroelectrics. The fitting of experimental data to the V-F and Power law models showed that the later one suits well to explain the relaxation for the present system.