Chapter 6

Consolidation of the present work and literature reports and figure of merits for applications

6.1 Consolidation of the present work and literature reports

In the present work, five systems are prepared and their structural and electrical properties are studied. Since, main objective of the present work is to enhance the piezoelectric coefficient \(d_{33}\), of NBT through substitution, it is pertinent to consolidate the different systems. Each substitutional systems has yielded highest \(d_{33}\) value for one particular mole fraction. Such a mole fraction from each system is taken for consolidation. Figure 6.1 shows the variation of piezoelectric coefficient with mole fraction for all the five systems. Encircled \(d_{33}\) values are highest for each system and they are considered for further analysis.

A wide variety of cations can be substituted in the perovskite structure. Goldschmidt (1927) showed that the stability of the perovskite structure depends
on the ionic radii and is relatively independent of the valency. This is described by the tolerance factor $t$:

$$t = \frac{R_A + R_O}{\sqrt{2}R_B + R_O} \quad \hdots 6.1$$

Figure 6.1: **Piezoelectric coefficient as a function of mole fraction of five systems**

where $R_A$, $R_B$, $R_O$ are the ionic radii of the ions A, B, and O. Goldschmidt showed empirically that a material preserves the perovskite structure type as long as $t$ is between 0.78 and 1.05. If $t = 1$ the size of the A- and B-site cations perfectly matches the space provided by the oxygen anions. Lower values of $t$ indicate smaller A-site cations which favors tilting of the BO$_6$ octahedra [1]. The electrical neutrality condition leads to

$$\sum_{i=1}^{m} x_{Ai}n_{Ai} + \sum_{k=1}^{n} x_{Bi}n_{Bi} = 6 \quad \hdots 6.2$$
with \( x_{Ai} \), \( x_{Bi} \) the fractions of the ions and \( n_{Ai} \), \( n_{Bi} \) the valencies of the ions.

The stoichiometry condition gives

\[
\sum_{i=1}^{m} x_{Ai} = 1 \quad \text{......................}(6.3)
\]

\[
\sum_{k=1}^{n} x_{Bi} = 1 \quad \text{......................}(6.4)
\]

Average ionic radius of A and B-site are calculated using the formula:

\[
\sum_{i=1}^{m} x_{Ai} R_{Ai} = \overline{R}_A \quad \text{......................}(6.5)
\]

\[
\sum_{k=1}^{n} x_{Bk} R_{Bk} = \overline{R}_B \quad \text{......................}(6.6)
\]

Other factors which can be taken into account for substitution besides the ionic radii are factors such as polarizability and nature of bonds. Average polarisability of A and B-site are calculated using the formula:

\[
\sum_{i=1}^{m} x_{Ai} P_{Ai} = \overline{P}_A \quad \text{......................}(6.7)
\]

\[
\sum_{k=1}^{n} x_{Bk} P_{Bk} = \overline{P}_B \quad \text{......................}(6.8)
\]

Hence, tolerance factor, average ionic radius of A and B-site and average polarisability of A and B-site are calculated and the values are tabulated in order to find a thumb rule for enhancement of \( d_{33} \) for the selection of substitutional elements in titanate-based lead-free piezoelectric ceramics [2].

For consolidation of the present work with the literature reports, nine systems from literature with highest \( d_{33} \) values are selected and all the parameters are calculated as done for the present work. Criteria for the selection of NBT based systems from literature are; (i) systems exhibiting phase purity (ii) systems exhibiting electrical neutrality and (iii) systems maintaining rhombohedral R3c structural symmetry.
Table 6.1: Intrinsic parameters of NBT-based systems in the present work

<table>
<thead>
<tr>
<th>S.No</th>
<th>NBT</th>
<th>$x$</th>
<th>$d_{33}$</th>
<th>Average ionic radius</th>
<th>Average ionic radius</th>
<th>Tolerance Factor</th>
<th>Average polarisability of A-site</th>
<th>Average polarisability of B-site</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NBT-BMZ</td>
<td>0.01</td>
<td>112</td>
<td>1.3446</td>
<td>0.6062</td>
<td>0.9675</td>
<td>3.9816</td>
<td>2.9236</td>
</tr>
<tr>
<td>2</td>
<td>NBT- BMT</td>
<td>0.04</td>
<td>108</td>
<td>1.3432</td>
<td>0.6073</td>
<td>0.9665</td>
<td>4.0464</td>
<td>2.8978</td>
</tr>
<tr>
<td>3</td>
<td>NBT- BMZ- BMT</td>
<td>0.025</td>
<td>105</td>
<td>1.3437</td>
<td>0.6085</td>
<td>0.9661</td>
<td>4.1472</td>
<td>2.9067</td>
</tr>
<tr>
<td>4</td>
<td>NBT- BFO</td>
<td>0.01</td>
<td>98</td>
<td>1.3446</td>
<td>0.6045</td>
<td>0.9683</td>
<td>3.9816</td>
<td>2.9288</td>
</tr>
<tr>
<td>5</td>
<td>NBT:Rb</td>
<td>0.015</td>
<td>92</td>
<td>1.3495</td>
<td>0.605</td>
<td>0.9698</td>
<td>4.0124</td>
<td>2.93</td>
</tr>
<tr>
<td>6</td>
<td>NBT</td>
<td>0</td>
<td>74</td>
<td>1.345</td>
<td>0.605</td>
<td>0.9681</td>
<td>3.96</td>
<td>2.93</td>
</tr>
</tbody>
</table>
Table 6.2: Intrinsic parameters of NBT-based systems from the literature reports

<table>
<thead>
<tr>
<th>S.No</th>
<th>NBT</th>
<th>x</th>
<th>(d_{33})</th>
<th>Average ionic radius of A-site</th>
<th>Average ionic radius of B-site</th>
<th>Tolerance factor</th>
<th>Average polarisability of A-site</th>
<th>Average polarisability of B-site</th>
<th>Ref. No</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NBT-BA</td>
<td>0.08</td>
<td>130</td>
<td>1.3414</td>
<td>0.5994</td>
<td>0.9695</td>
<td>4.133</td>
<td>2.759</td>
<td>[13]</td>
</tr>
<tr>
<td>2</td>
<td>NBT:Li</td>
<td>0.16</td>
<td>108</td>
<td>1.3226</td>
<td>0.605</td>
<td>0.9602</td>
<td>3.864</td>
<td>2.93</td>
<td>[14]</td>
</tr>
<tr>
<td>3</td>
<td>NBT-BMN</td>
<td>0.007</td>
<td>94</td>
<td>1.3447</td>
<td>0.6056</td>
<td>0.9677</td>
<td>3.975</td>
<td>2.925</td>
<td>[15]</td>
</tr>
<tr>
<td>4</td>
<td>NBT:La</td>
<td>0.0172</td>
<td>91</td>
<td>1.3337</td>
<td>0.605</td>
<td>0.9641</td>
<td>3.962</td>
<td>2.93</td>
<td>[16]</td>
</tr>
<tr>
<td>5</td>
<td>NBT-NN</td>
<td>0.02</td>
<td>88</td>
<td>1.3459</td>
<td>0.6057</td>
<td>0.9681</td>
<td>3.917</td>
<td>2.951</td>
<td>[17]</td>
</tr>
<tr>
<td>6</td>
<td>NBT-BCW</td>
<td>0.005</td>
<td>80</td>
<td>1.3463</td>
<td>0.6056</td>
<td>0.9683</td>
<td>3.972</td>
<td>2.906</td>
<td>[18]</td>
</tr>
<tr>
<td>7</td>
<td>NBT-CT</td>
<td>0.02</td>
<td>75</td>
<td>1.3449</td>
<td>0.605</td>
<td>0.9680</td>
<td>3.944</td>
<td>2.93</td>
<td>[19]</td>
</tr>
<tr>
<td>8</td>
<td>NBT-BS</td>
<td>0.02</td>
<td>74.7</td>
<td>1.3411</td>
<td>0.6078</td>
<td>0.9664</td>
<td>4.003</td>
<td>2.928</td>
<td>[20]</td>
</tr>
<tr>
<td>9</td>
<td>NBT</td>
<td>0</td>
<td>74</td>
<td>1.345</td>
<td>0.605</td>
<td>0.9681</td>
<td>3.96</td>
<td>2.93</td>
<td>[4]</td>
</tr>
</tbody>
</table>
From table 6.1 and 6.2 it is found that (i) increasing the average ionic radius of A-site, increasing the average ionic radius of B-site, (ii) simultaneous decrease of average ionic radius of A-site and increase of B-site, and (iii) decrease of both A and B-sites enhances the piezoelectric coefficient. Tolerance factor is not a major factor in improving $d_{33}$. Increase in average polarisability of A-site and decrease in polarisability of B-site is the key factor in increasing piezoelectric coefficient in present and literature reports. Therefore, a thumb rule for the selection of substitutional element to obtain better piezoelectric coefficient is substitution of high polarisable ions in the A-site and low polarisable ions in the B-site.

6.2 Figures of merits for applications

Piezoelectric ceramics have been in commercial use for a long time, due to their unique ability to couple electrical and mechanical displacements, i.e., to change electrical polarization in response to an applied mechanical stress or mechanically strain in response to an applied electric field [3]. They have witnessed a tremendous growth rate over the last decade, which is in part connected to the successful transfer of the multilayer capacitor technology to manufacturing multilayer actuators. Now, displacements of tens of micrometers are available in microseconds and actuators are able to support stresses in the order of tens of megapascals. Application opportunities now abound in the areas of piezoelectric fuel injection, piezoelectric motors, piezoelectric printing machines, piezoelectrically controlled thread guides, micropositioning systems, sensors, ultrasound medical imaging and many others [4-7].

Among the piezoelectric ceramics, ferroelectric oxide ceramics are used in a very broad range of functional ceramics and form the materials base for the majority of electronic applications. These electronic applications account for more than 60% of the total high technology ceramics market worldwide. Piezoelectric
and electrostrictive responses in poled and unpoled ferroelectric and relaxor ferroelectric compositions are of importance in transducers for converting electrical to mechanical response and vice versa. Sensor applications make use of the very high piezoelectric constants $d_{ijk}$ of the converse effect, which also permit efficient conversion of electrical to mechanical response. For actuation the strong basic electrostrictive coupling can be exploited for very high precision position control and the possibility of phase and domain switching with shape memory is used in polarization controlled actuation [8].

Figure of merits for application in functional devices are tabulated by calculating the electromechanical coupling factor ($k$), mechanical quality factor ($Q_m$), piezoelectric coefficient ($d_{33}$), product of square of electromechanical coupling factor and mechanical quality factor ($k^2Q_m$) and density ($\rho$). In underwater and medical applications the acoustic impedance of the transducer should be close to that of the object under investigation. The resonant frequency ($f_r$) is related to the size of the sample ($l$), density ($\rho$) and mechanical compliance ($s$). This favours materials with lower density as better choice for high frequency transducers. Hence NBT is preferred for underwater and medical applications as its density is low ($\rho = 5.8\text{g/cm}^3$) compared to PZT ($\rho = 8.0\text{g/cm}^3$).

$$Z \propto \sqrt{\rho c} \text{ ........................6.9}$$

$$f_r = \frac{1}{l\sqrt{\rho s}} \text{ ........................6.10}$$

Critical figures of merit (FOM) for well established and impending current and future piezoelectric applications in non-resonant and resonant modes has been reported by Rodel et al. [9]. Based on that report the figures of merit for application in functional devices are identified. Major figures of merit for sensors, buzzers and motors in non-resonant modes is mechanical quality factor ($Q_m$).
Table 6.3: Figure of merits for applications

<table>
<thead>
<tr>
<th>NBT Substitutional Systems</th>
<th>$x$</th>
<th>$d_{33}$</th>
<th>Density</th>
<th>$k$</th>
<th>$Q_m$</th>
<th>$k^2 Q_m$</th>
<th>Application</th>
<th>Comparative systems for selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBT-BMZ</td>
<td>0.01</td>
<td>112</td>
<td>5.89</td>
<td>0.15</td>
<td>195</td>
<td>5</td>
<td>Microphone</td>
<td>(K,Na,Li)NbO$_3$-based ($Q_m$=84)</td>
</tr>
<tr>
<td>NBT- BMT</td>
<td>0.04</td>
<td>108</td>
<td>5.96</td>
<td>0.13</td>
<td>86</td>
<td>2</td>
<td>Buzzer</td>
<td>soft PZT ($Q_m$=50)</td>
</tr>
<tr>
<td>NBT- BMZ- BMT</td>
<td>0.025</td>
<td>105</td>
<td>5.9</td>
<td>0.14</td>
<td>88</td>
<td>2</td>
<td>Actuator</td>
<td>(K,Na,Li)NbO$_3$-based ($Q_m$=84)</td>
</tr>
<tr>
<td>NBT- BFO</td>
<td>0.01</td>
<td>98</td>
<td>5.87</td>
<td>0.14</td>
<td>180</td>
<td>3</td>
<td>Sensor</td>
<td>Ba(Zr,Ti)O$<em>3$ ($d</em>{33}$=94)</td>
</tr>
<tr>
<td>NBT:Rb</td>
<td>0.015</td>
<td>92</td>
<td>5.75</td>
<td>0.13</td>
<td>83</td>
<td>2</td>
<td>Automotive sensor</td>
<td>soft PZT ($Q_m$=80)</td>
</tr>
<tr>
<td>NBT</td>
<td>0</td>
<td>74</td>
<td>5.82</td>
<td>0.14</td>
<td>149.5</td>
<td>3</td>
<td>Aerospace sensor</td>
<td>PbTiO$<em>3$ ($d</em>{33}$=60)</td>
</tr>
</tbody>
</table>
The electromechanical coupling factor ($k_p$) and mechanical quality factor ($Q_m$) [10-12] in the radial mode is found using IEEE standards:

\[ \frac{1}{k_p^2} = 0.395 \frac{f_r}{f_r-f_a} + 0.574 \] .................................. 6.11

\[ \frac{1}{Q_m} = 2\pi f_r C Z \frac{f_a^2-f_r^2}{f_r} \] .................................. 6.12

where $f_r$, $f_a$, $C$, $Z$ are the resonance and antiresonance frequencies, parallel capacitance at 1 kHz and minimum impedance at $f_r$, respectively. Resonance, antiresonance frequencies, parallel capacitance and impedance data are taken from room temperature dielectric measurements.

Table 6.3 gives the figure of merits for piezoelectric applications. Present substituted systems exhibits better mechanical quality factor in comparison with other systems such as soft PZT and (K,Na, Li) NbO$_3$. Hence present systems can be used in functional devices such as sensors, actuators, transducers, buzzers and microphones. Comparative systems for selection in table 6.3 is refered from Rodel et al. [9].

### 6.3 Conclusions

Significant factors for increasing the piezoelectric constant in non-MPB systems maintaining rhombohedral symmetry of NBT ceramics are decreasing the average polarisability of B-site and increasing the polarisability of A-site. Also decreasing the average ionic radius of A-site and increasing the average ionic radius of B-site simultaneously enhances $d_{33}$. From the present study, it is found that the thumb rule for improving $d_{33}$ in non-MPB systems is substitution of high polarisable ions in A-site and low polarisable ions in B-site. Figures of merit of the present substituted systems points out the appropriate use in functional devices such as actuators, sensors, buzzers, microphones and underwater transducers.
References


