PHASE DIAGRAM, CRYSTAL STRUCTURE AND STRUCTURE PROPERTY CORRELATIONS IN $(1-x)Ba(Cu_{1/3}Nb_{2/3})O_3$-$(x)PbTiO_3$ CERAMICS

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By

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CHAPTER 7

Summary and Future Scope

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7.1 Summary of the Thesis

In the present work, the crystal structure, microstructure, dielectric, ferroelectric, and piezoelectric properties of a previously unexplored solid solution (1-x)$Ba(Cu_{1/3}Nb_{2/3})O_3$-(x)$PbTiO_3$ ceramics have been investigated, in the complete compositional range. The solid solution exhibits a unique crystal structure evolution and has phase coexistence of two different kinds in the different composition regions, characterizing many phase boundaries. The synthesized solid solution compositions have been characterized for phase purity and compositional constituents using XRD, EDS and XPS studies. A correlation of dielectric, ferroelectric and piezoelectric properties with crystal structure, microstructure and compositional content has been established, which can help best exploit the solid solution compositions in technological applications. Additionally, it has been shown that the dielectric, ferroelectric and piezoelectric properties of the solid solution can also be greatly improved by using additives such as MnO_2. Some of the highlights and important conclusions of the present thesis are as follows:

7.1.1 Discovery of RT Crystal Structure for the Entire Composition Range of (1-x)$Ba(Cu_{1/3}Nb_{2/3})O_3$-(x)$PbTiO_3$ Ceramics

The crystal structure solution/determination has been done considering different plausible crystal structures and combinations of phase coexistence for various compositions using Rietveld structure refinement form the XRD data. With increasing PT content, the solid solution exhibits different crystal structures which are as follows:

(i) A tetragonal structure (*P*4*mm)* for x = 0, end component $Ba(Cu_{1/3}Nb_{2/3})O_3$.

(ii) A cubic structure (*Pm*-3*m*) in the range $0.05 \leq x \leq 0.55$.

(iii) A coexistence of cubic and tetragonal structures ('*Pm*-3*m* + *P*4*mm*') in the range $0.59 \leq x < 0.62$.

(iv) A coexistence of two tetragonal structures ('*P*4*mm* + *P*4*mm*') in the range $0.62 \leq x < 0.65$.

(v) A coexistence of monoclinic and tetragonal structures ('*Pm*+ *P*4*mm*') in the range $0.65 \leq x \leq 0.85$.

(vi) A coexistence of two tetragonal structures ('*P*4*mm* + *P*4*mm*') in $0.90 \leq x < 0.975$.

(vii) A tetragonal structure (*P*4*mm*) for x = 1; end component $PbTiO_3$.

Considering the phenomenological differences between the phase coexistence of monoclinic and tetragonal structures in the composition range $0.65 \leq x \leq 0.85$, the solid solution exhibits seven phase boundaries at room temperature.

7.1.2 Discovery of Crystal Structure of (1-x)$Ba(Cu_{1/3}Nb_{2/3})O_3$-(x)$PbTiO_3$ Ceramics from Cryogenic (15K) to High-Temperatures (1073K)

Even though both the end components of the solid solution exhibit the same tetragonal symmetry (*P*4*mm*) at RT, a total of seven phase boundaries have been discovered for as-prepared ceramics, as mentioned above. Using Rietveld structure refinement from the powder XRD data from the laboratory and synchrotron, it was found that some of these phase boundaries are nearly temperature independent showing a so-called morphotropic nature. As the temperature increases, the crystal structure of the solid solution undergoes phase transitions into higher symmetry phases in the sequence of Monoclinic-Tetragonal-cubic crystal structures. A single high temperature

phase transition was observed predominantly in the composition regions $0 \leq x \leq 0.70$, $0.95 \leq x \leq 1$, while two such phase transitions were observed in the phase-separated region, $0.75 \leq x \leq 0.90$, above room temperature as confirmed from the Rietveld analysis of the XRD data and investigations of dielectric properties. Below RT, the solid solution was found to be stable, and a minimal effect of temperature on the crystal structure was observed on most of the compositions, except cubic structured ceramics. Many compositions of the solid solution, in fact, showed negligible thermal contraction from ~450K to 15K temperature, showing promising fatigue-free behaviours for ferroelectric devices within the temperature range.

7.1.3 Construction of New Phase Diagram

Based on the temperature-dependent dielectric studies and the XRD data analysis by the Rietveld structure refinement for various compositions at different temperatures, a new phase diagram has been established for this newly discovered solid solution, for the first time (see Fig 7.1). This temperature vs. composition phase diagram is created for the compositional range of $0.50 \leq x \leq 1$ in a temperature range of 15K - 1073K. The rest of the composition range ($0 \leq x \leq 0.50$), with cubic structure at room temperature, has not been investigated for the phase diagram studies due to their lesser relevance for ferroelectric, piezoelectric applications. The newly constructed phase diagram of $(1-x)Ba(Cu_{1/3}Nb_{2/3})O_3$-$(x)PbTiO_3$ ceramics is reproduced below in Fig 7.1.

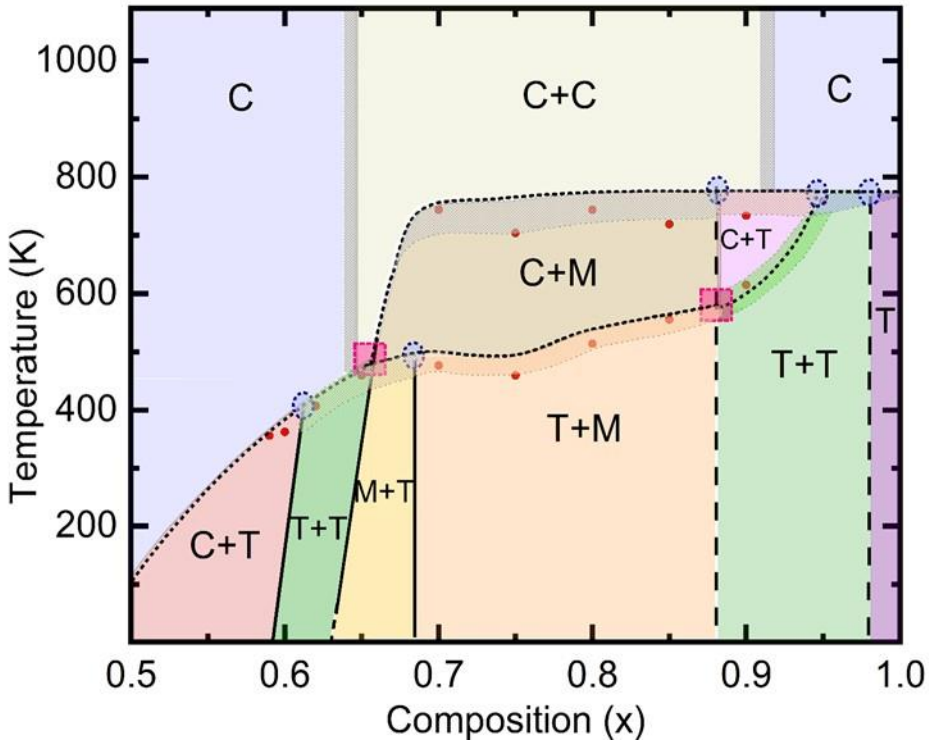

Fig 7.1 Composition versus temperature phase diagram of (1-x)BCN-(x)PT ceramics

7.1.4 Physical Properties of the (1-x)BCN-(x)PT Solid Solution

Along with the crystal structure determination of the solid solution, the present work also divulges microstructure, dielectric, ferroelectric and piezoelectric properties in as-prepared ceramics (while keeping the synthesis conditions as similar as possible) to better understand the co-relations between the structure and these properties. The microstructure reciprocated a densely populated grain structure for most of the compositions with grain size in the approximate range of 0.3-1.5μm. The solid solution exhibited good ferroelectric and piezoelectric properties in the composition range $0.70 \leq x < 1$. The enhanced responses of these properties were found near the phase boundaries. The highest of which is observed for $x = 0.70$ composition. The compositions $0.75 \leq x \leq 0.90$ show pseudocubic transitions at two different temperatures, therefore these compositions may exhibit piezoelectricity even if one

phase has gone to centrosymmetric and other remains non-centrosymmetric. By addressing the structure-property correlation, the current research may serve as the foundation for improved physical property responses in future.

7.1.5 Enhanced Responses of Ferroelectric, Dielectric and Piezoelectric Properties by the Addition of MnO_2

The tailoring effects of MnO_2 additive on a particular composition x = 0.62 of the solid solution have been studied for increasing its piezoelectric property responses. The MnO_2 modified compositions of the 0.62 compositions have been characterized for the compositional control of different structures and the chemistry of the resulting phases. The MnO_2 addition has been found to be very effective in improving the piezoelectric, dielectric and ferroelectric properties and modifying the crystal structure and microstructure of the parent compound. The study showed that the MnO_2-modified ceramic materials form defect-engineered compositions with improved piezoelectric, dielectric and ferroelectric responses. An excellent increment in d_{33} from 2.5pC/N to 72pC/N and reduced dielectric losses showed the potential of MnO_2 as an additive. The developed MnO_2-modified compositions show better properties like a high dielectric constant, low dielectric loss, variable coercivity and high piezoelectric coefficient values for different MnO_2 contents.

7.2 Future Scope

The investigations and discoveries of this thesis have revealed an interesting crystal structure evolution with composition, revealing many open questions that need to be answered in future investigations. Some important suggestions for specific work in future are as follows:

1. In chapter 5, the physical properties have been explored in as-prepared condition, keeping the sintering conditions as similar as possible; however, the best performances of the properties can be further enhanced by increasing densification and appropriate doping/additive, to compensate for the leakage current losses due to Pb, oxygen vacancies and the fluctuating valences nature of copper. As shown in chapter 6 of the thesis, that the 1wt% MnO_2 doping in the 0.62 composition of the solid solution can enhance its d_{33} response from 2.5pC to 72pC/N. This solid solution can show more promising ferroelectric characters if grain sizes are increased, leakage current is minimized and movements of domains are eased out by reducing the coercive field by critically balancing the sintering and annealing conditions.
2. The tuning of the physical properties with respect to composition can also be done in more close compositional intervals with precise exploration in order to find the maximum possible response out of the solid solution.
3. The low-temperature crystal structural and dielectric studies in the composition region $0 \leq x \leq 0.50$ are yet to be explored for their probable phase transition into low symmetry phases.
4. Theoretical studies can be done to find out the formation energy, free energy profiles and predict stable phases near the compositions having phase separation.
5. The crystal structural studies above 1073K can be performed for any possible crystal structural alteration in the compositions having phase separation.
6. The solid solution may possess different types of NPRs and ion clusters. The local probe-based studies using Raman spectroscopy, evolve TEM, nano EDAX, etc., can be done to understand different phenomena taking place in the system.