

CHAPTER-IX

***Phase Diagram, Summary of the
Work and Suggestions for Future
Work***

9.1 Phase diagram of the BF-xPFN solid solution system

Several workers have studied the structure of BF-xPFN solid solutions but no phase diagram of the BF-xPFN solid solutions have been reported due to lack of systematic and comprehensive study on this system. The temperature dependent dielectric permittivity, magnetization measurements and structural studies using laboratory x-ray, synchrotron x-ray and neutron diffraction data discussed in the preceding chapters have enabled us to construct a phase diagram for BF-xPFN system in the whole composition range shown in Fig. 9.1. The ferroelectric transition temperature (T_C) for pure BiFeO₃ is taken from the literature [Kaczmarek et al. (1975)]. However, for $x = 0.20$, we have estimated the T_C from the XRD and NPD studies described in the chapters V & VI. We have also used ferroelectric T_C and T_N reported for some BF-xPFN compositions by the earlier workers [Bührer (1962), Smolenskii and Yudin (1965), Bhat et al. (1974)] which is indicated by circle in Fig. 9.1. The antiferromagnetic transition temperature for $x = 0.80$ is found to be $T_N \sim 335$ K as discussed in chapter VII, which is larger than $T_N \sim 300$ K reported by Smolenskii and Yudin (1965). The ferroelectric T_C decreases linearly with increasing x up to second morphotropic phase boundary $x = 0.80$ with a change in slope at the first morphotropic phase boundary while for $x > 0.90$ the ferroelectric T_C increases with increasing x . The magnetic transition temperature T_N also decreases linearly with increasing x up to $x = 0.87$

composition. It means BF-xPFN is G-type canted antiferromagnet at room temperature in the composition range $0.0 < x \leq 0.87$. The present study resolves the controversies about the room temperature crystal structures of BF-xPFN and the structural phase boundaries using XRD, SXR and NPD as well as magnetization and dielectric characterizations. The R3c to average cubic phase transition occurs at the first morphotropic phase boundary at $x = 0.40$ instead of R3c to P4mm transition reported in the literature. The controversies related to the existence of the ferroelectric phase transition (peak in the temperature dependent dielectric plot) in cubic phase region $0.40 \leq x \leq 0.90$ is resolved by the local structure study using high resolution high energy synchrotron x-ray diffraction data collected in the cubic phase region. It has been shown that A-site and O-site ions of the cubic ABO_3 perovskite are locally displaced from their ideal cubic position. The local displacement of the A-site and O-site ions produces local electric dipoles which gives the ferroelectric T_C in the cubic phase of BF-xPFN. The room temperature structure of BF-xPFN in the composition range $0.40 \leq x \leq 0.80$ is shown to be average cubic with off-site disorder of Bi^{3+}/Pb^{2+} along $\langle xxz \rangle$ and O^{2-} along $\langle 110 \rangle$ directions while in the composition region $0.80 \leq x \leq 0.90$ the average crystal structure is still cubic but Bi^{3+}/Pb^{2+} shifted along $\langle xxx \rangle$ direction. It has been reported that the ferroelectric to paraelectric phase transition for pure BF follow $R3c \rightarrow R3c + Pbnm \rightarrow Pbnm$ path while the $Pb(Fe_{0.5}Nb_{0.5})O_3$ doped BF-0.2PFN solid solution follow $R3c \rightarrow R3c + Pm\bar{3}m \rightarrow Pm\bar{3}m$ path.

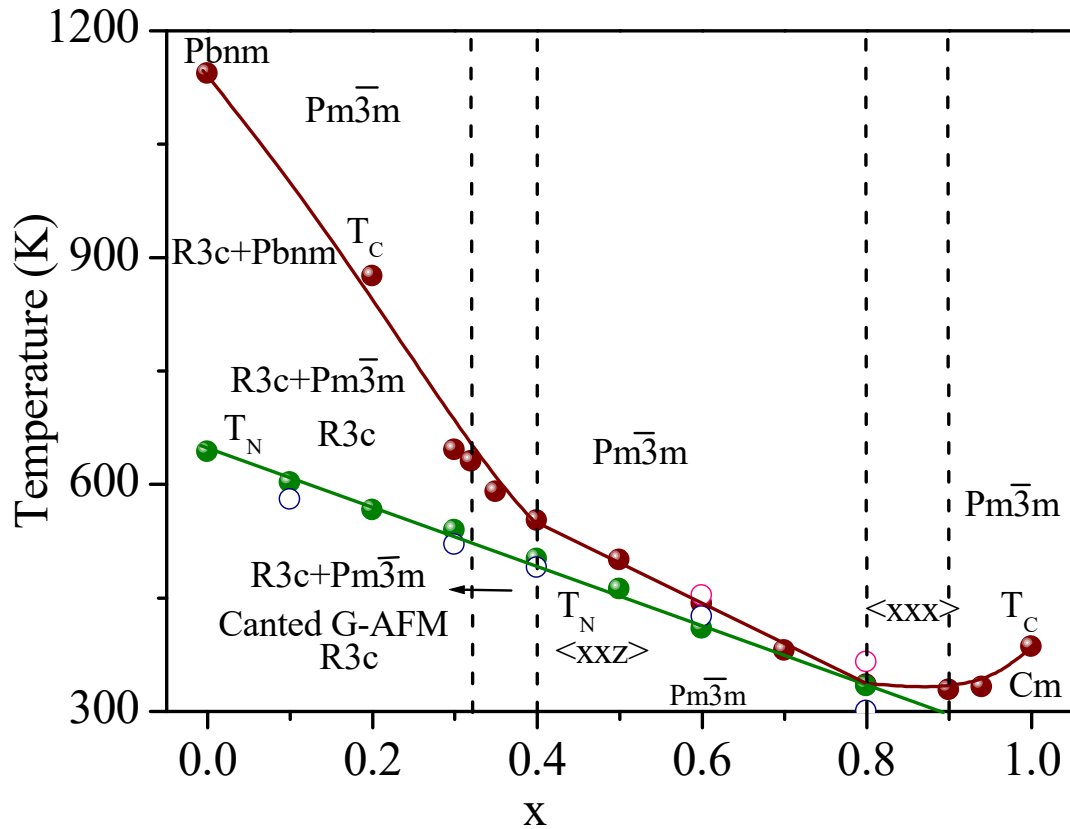


Fig. 9.1 Temperature phase diagram of BF-xPFN solid solutions. The upper solid spheres indicate the ferroelectric phase transition temperature while the lower solid spheres are due to the magnetic transition temperature. The hollow circles indicate the ferroelectric and magnetic transition temperatures which have been reported in the literature.

9.2 Summary of work

The main findings of this work are listed below:

- (i) Various compositions of BF-xPFN solid solution in the range $0.10 \leq x \leq 1.0$ were successfully synthesized by solid state reaction method.
- (ii) The room temperature crystal structure of BF-xPFN in the composition range $0.1 \leq x \leq 0.32$ is identical with BiFeO₃. It has got rhombohedral structure with R3c

space group. A morphotropic phase transition occurs in the composition range $0.32 < x < 0.40$ where rhombohedral and cubic phases coexist. This contradicts the previously reported coexistence region of $0.25 < x < 0.35$ by Zhdanova et al. (1965) with R3c+P4mm phase. The R3c + Pm $\bar{3}$ m structural model for phase coexistence with less number of parameters gives better fit in comparison to R3c + P4mm structural model. The rhombohedral (R3c) to cubic (Pm $\bar{3}$ m) phase transition is completed at $x_C \sim 0.40$. There is no evidence for a rhombohedral to tetragonal phase transition reported by Ismailzade et al. (1965). The cubic structural model with Pm $\bar{3}$ m space group was used for the Rietveld refinement of all the compositions in the range $0.40 \leq x \leq 0.90$. This model indexed all the reflections of the x-ray diffraction patterns. However, it gives very high values for the isotropic thermal parameters for the A-site and O-site ions. The anomalously high thermal parameters (B_{iso}) indicate the possibility for the positional disorder at A and O-sites. The cubic like phase in the composition range $0.40 \leq x \leq 0.90$, transforms to Cm phase for $x > 0.90$. The x-ray diffraction patterns recorded for the composition range $0.90 < x \leq 0.96$ are refined by monoclinic phase with Cm space group.

(iii) The room temperature crystal structure for different compositions of BF-xPFN has been settled by using high energy synchrotron x-ray diffraction data. The anomalously high values of isotropic thermal parameters for the A-site and O-site ions in the cubic phase are resolved by their local structure refinements. The local structure refinement in the cubic phase of BF-xPFN shows that Bi³⁺/Pb²⁺ and O²⁻ ions are not at their ideal cubic position but they are displaced

along $\langle uuv \rangle$ ($v > u$ for $x < 0.8$ and $v \approx u$ for $x \geq 0.8$ composition) and $\langle yy0 \rangle$ directions respectively. The true crystal structure at local level is found to be monoclinic. Present study, demonstrates the evidence for two MPBs for the BF-xPFN solid solution. The R3c to locally Cc phase transition occurs at the first MPB at $x \approx 0.40$ while the locally Cc to R3m phase transition occurs at the second MPB at $x = 0.80$. The R-M_A-R type of polarization rotation path occurs with x for the BF-xPFN solid solutions. The presence of structural phase boundaries is further confirmed by the room temperature dielectric plot. The composition dependent dielectric plot exhibits two peaks at $x = 0.40$ and $x = 0.80$ compositions which correspond to the two MPBs of the BF-xPFN system. A hump in dielectric constant plot at $x \sim 0.94$ indicates the average cubic with local R3m to the monoclinic phase (Cm phase) transition.

(iv) We have presented unambiguous evidence for the paraelectric cubic phase of 0.8BF-0.2PFN, which is isostructural with BiFeO₃ and does not suffer from any decomposition and melting problem faced for pure BiFeO₃. This cubic phase transforms directly into a rhombohedral phase in the R3c space group on cooling without any intermediate ‘ β ’ phase. The intermediate tetragonal [Kornev et al. (2007)], orthorhombic [Arnold et al. (2009) and Palai et al. (2008)] or monoclinic [Haumont et al. (2008)] β -phases proposed in the literature in the context of pure BiFeO₃ cannot account for the observed Bragg peaks of the XRD profiles of BF-0.2PFN. The cubic to rhombohedral phase transition is shown to be of first order character as evidenced by the coexistence of the two phases over a 100 K temperature range and a discontinuous change in the unit cell volume. Our results

suggest that both the $R(q = 1/21/21/2)$ point and $\Gamma(q = 000)$ point phonons of the cubic paraelectric/paraelastic phase have to freeze simultaneously to give the non centrosymmetric space group $R3c$ with antiphase rotated oxygen octahedra in the $a^- a^- a^-$ tilt system and off-centre displaced ions.

(v) The $R3c$ phase of BF-0.2PFN transform directly into ‘ γ ’ phase without any intermediate β -phase. The presence of 311_{pc} type of superlattice reflections across two phase region excludes the possibility of $R3m$ phase as one of the intermediate β -phase. The existence of phase coexistence in the temperature range $850 < T < 950$ along with significant jump in the unit cell volume at ferroelectric to paraelectric phase transition temperature confirms first order character of ferroelectric to paraelectric phase transitions in BF-0.2PFN solid solutions. The simultaneous appearance of the polarization and tilt order parameters below the paraelectric to ferroelectric phase transition is indicate of an unusual “trigger type” of phase transitions where two order parameters emerge simultaneously, none of which is secondary to the other. The results obtained by high temperature neutron powder diffraction study on the BF-0.2PFN samples supports our previous investigation based on laboratory source x-ray powder diffraction study.

(vi) Weak ferromagnetism is observed in BF-xPFN solid solutions for $0.1 \leq x < 0.96$ compositions. The maximum value of the remanent magnetization $M_r \sim 0.0038$ emu/g is observed for $x = 0.10$ in the composition range $0 < x < 0.60$. The observation of the weak ferromagnetism in BF-xPFN solid solution is attributed to suppression of spatially modulated spiral spin structure of BiFeO_3 to a homogenous spin structure. We have investigated the room temperature magnetic

structure of BF-xPFN solid solutions by analyzing the neutron powder diffraction data using group theoretical representation theory. The G-type antiferromagnetic spin structure is observed both in the rhombohedral (with R3c space group) and the average cubic ($Pm\bar{3}m$ space group) phases for their magnetic structures. The composition variation of ordered magnetic moment of Fe^{3+} demonstrates that BF-xPFN is paramagnetic for $x \geq 0.87$. The magnetic transition temperature (T_N) decreases linearly with increased doping of $Pb(Fe_{0.5}Nb_{0.5})O_3$. The weak remanent magnetization observed in the BF-xPFN solid solution is attributed to canting of the spins. The canting of spins in the non-collinear $Fe^{3+}-O^{2-}-Fe^{3+}$ chain occurs due to D-M interaction. The non-collinear $Fe^{3+}-O^{2-}-Fe^{3+}$ chain arises due to the octahedral tilt in the rhombohedral phase while because of local oxygen disorder in the average cubic phase. The origin of anomalous M-T behavior with a ferromagnetic like transition well above T_N for $x \geq 0.87$ seems to be due to doping of PFN with BF whereas the weak ferromagnetism for $x < 0.87$ is due to doping of BF with PFN.

(vii) BF-0.2PFN shows weak ferromagnetism with $M_r \sim 0.0032$ emu/g at 300 K and an antiferromagnetic transition $T_N = 566$ K. Strong anomalies in the dielectric permittivity (ϵ'_r) are observed at T_N leading to change in ϵ'_r by as much as 450 at 1 MHz frequency, at which only the intrinsic contributions to ϵ'_r are observed. There is significant shift in the positions of the ions obtained from the Rietveld refinement of the nuclear and magnetic structures using neutron powder diffraction data below the magnetic transition temperature without affecting the symmetry of the high temperature paramagnetic phase of the BF-0.2PFN due to an

isostructural phase transition (IPT). The ionic polarization and the octahedral tilt angle as obtained from the nuclear structure show significant discontinuous change ($\Delta P_s \simeq 1.6(3) \mu\text{C}/\text{cm}^2$ and $(\Delta\omega \sim 0.3 \text{ degree})$ confirming first order character of the isostructural phase transition. It also reveals the presence of strong magnetoelectric and magnetoelastic coupling. The ionic part of the ferroelectric polarization as obtained from Rietveld refined coordinates scales linearly with sublattice magnetization, obtained from the refinement of the magnetic structure below T_N providing atomic level evidence for linear magnetoelectric coupling in BF-xPFN inspite of the low value of M_r .

(viii) A phase diagram of BF-xPFN solid solutions is established, using magnetic and ferroelectric transition temperatures obtained by different experimental techniques.

9.3 Suggestions for future work

(i) The origin of ferromagnetic transition well above room temperature for $x > 0.87$ needs to be investigated in a future work.

(ii) The broad peaks in $\epsilon_r'(T)$ plots indicate relaxor like diffuse transitions. This aspect needs to be explored using frequency dependent dielectric measurements.

(iii) Single crystal neutron diffraction studies are desirable to confirm spin canting and absence of spin cycloid in BF-xPFN solid solutions.