

CHAPTER- V

***High Temperature Ferroelectric
Phase Transition in BF-0.2PFN
Solid Solutions***

5.1 Introduction

Amongst the magnetoelectric multiferroics, BiFeO₃ is unique as it has got the highest ferroelectric polarization (50 to 100 μC/cm² measured on insulating single crystals) [Lebeugle et al. (2007), Lebeugle et al. (2007b)], highest ferroelectric Curie temperature ($T_C \sim 1103\text{K}$) [Kaczmarek et al. (1975)] and highest Neel temperature ($T_N \sim 643\text{K}$) [Roginskaya et al. (1966)] for G type antiferromagnetism with an incommensurate cycloidal magnetic ordering in the [110]_h direction [Sosnowska et al. (1982)]. It has been shown in recent years that ferroelectricity in this compound arises due to lone pair stereochemistry of Bi 6s orbitals [Hill (2000)] and not due to the covalency effects of Fe-O bonds [Cohen (1992)]. Recent work of Singh et al [Singh et al. (2008)] on a BiFeO₃ based system has provided direct atomic level evidence for magnetoelectric coupling of intrinsic multiferroic origin in terms of an isostructural phase transition accompanying the development of magnetic order leading to significant shifts of atomic positions and excess polarization. Magnetoelectric coupling of intrinsic multiferroic origin has also been demonstrated in single crystals through switching of the direction of the cycloidal magnetic order by electric field [Singh et al. (2008), Lebeugle et al. (2008)].

While there has been considerable progress in the understanding of the magnetoelectric coupling and the magnetic structure of BiFeO₃, the stability field of its room temperature phase and the sequence of the structural phase transitions it undergoes as a function of temperature continue to remain controversial and has

a long history too, as discussed in the recent literature [Arnold et al. (2009), Kornev et al. (2009), Palai et al. (2008), Haumont et al. (2008), Selbach et al. (2008), Kornev et al. (2007), Haumont et al. (2009)]. There is unanimity on the room temperature structure of α -phase of BiFeO_3 that is rhombohedrally distorted perovskite structure in the $R3c$ space group and $a\bar{a}a\bar{a}$ (in Glazer's notation [Glazer (1972) and (1975)]) tilt system. The controversial issues currently under intense debate are [Arnold et al. (2009), Kornev et al. (2009), Palai et al. (2008), Haumont et al. (2008), Selbach et al. (2008), Kornev et al. (2007)]: (i) Is there a β -phase of BiFeO_3 to which the room temperature α -phase in the $R3c$ space group transforms at the ferroelectric/ferroelastic T_C ? (ii) What is the space group of this β -phase? (iii) Is there an unambiguous evidence for the existence of the paraelectric/paraelastic cubic phase (γ -phase) prior to melting /decomposition of BiFeO_3 ? The controversy about the structure of the β -phase can be assessed from the fact that as many as five different space groups, $I4/mcm$ [Kornev et al. (2007)], $C2/m$ [Haumont et al. (2008)], $Pbnm$ [Arnold et al. (2009)], $R\bar{3}c$ [Selbach et al. (2008)] and $R3m$ [Maitre et al. (2004)] have been proposed in the literature. Barring references [Palai et al (2008)] and [Haumont et al. (2006)], who have reported the existence of the γ -phase mainly on the basis of Raman scattering studies, the other workers could not capture the existence of the γ -phase in their structural studies.

In pure BiFeO_3 it is very difficult to identify unambiguously the crystal structure of the so-called β and γ phases at high temperatures, because BiFeO_3 is unstable at the reported α to β and β to γ transition temperatures and gradually decomposes into $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{25}\text{FeO}_{39}/\text{Bi}_{25}\text{FeO}_{40}$ [Palai et al. (2008), Maitre et

al. (2004), Patel et al. (2010)] followed by the onset of melting slightly above 1200 K [Palai et al. (2008), Maitre et al. (2004)]. The partial decomposition and off-stoichiometry of BiFeO₃ due to the volatility of Bi⁺³ at high temperatures close to the melting point seems to be largely responsible for the existing controversy about the existence of the intermediate β-phase and the stability of the cubic γ-phase.

In order to capture unambiguously the sequence of structural phase transitions of BiFeO₃, it is imperative to bring down the structural phase transition temperatures below its decomposition temperature. In the present work, we have achieved this objective by forming a solid solution of BiFeO₃ (BF) with Pb(Fe_{1/2}Nb_{1/2})O₃ (PFN). The solid solution system 0.8BiFeO₃-0.2Pb(Fe_{1/2}Nb_{1/2})O₃(BF-0.2PFN) is isostructural with the α phase (R3c) of BF at room temperature and undergoes the structural phase transition at very much lowered temperatures. Because of the lowered phase transition temperature, we have found an unambiguous structural evidence for a paraelectric/paraelastic cubic phase (space group: Pm $\bar{3}$ m) to which the ferroelectric/ferroelastic rhombohedral (space group: R3c) phase transforms without any decomposition problem in this system. Our results differ from those on pure BiFeO₃ [Arnold et al. (2009), Palai et al. (2008), Haumont et al. (2008), Selbach et al. (2008), Kornev et al. (2007)] in the sense that we do not find any evidence for the so-called ‘β’ phase in stoichiometric monophasic perovskite composition of BF-0.2PFN, but it is not possible to confirm whether this difference is due to the addition of 20% PFN or it is intrinsic to pure BiFeO₃. The R3c to Pm $\bar{3}$ m transition is shown to be of first order as revealed by the coexistence of two phases over a wide temperature range

($\Delta T \sim 100$ K) and a discontinuous change in the unit cell volume. A brief discussion on the implications of the R3c to $Pm\bar{3}m$ direct transition from the point of view of Landau theory of structural phase transitions is also presented.

5.2 Experimental details

For the synthesis of the BF-0.2PFN powder, stoichiometric mixture of analytic reagent (AR) grade chemicals, Fe_2O_3 , Nb_2O_5 , $PbCO_3$, and Bi_2O_3 , with minimum assay of 99% or more, was calcined in open atmosphere at 1133K. The calcined powder was pelletized and then sintered at 1173K for 1 h in a sealed alumina crucible with calcined powder of the same composition used as a spacer powder to prevent the loss of Bi_2O_3 during sintering. There was no weight loss after sintering confirming the retention of the nominal composition even after sintering. The sintered pellets were crushed to powder and then annealed at 500°C for 12hr to remove the strains for XRD studies. High temperature x-ray diffraction (XRD) measurements were carried out using an 18 kW rotating anode (Cu) based Rigaku powder diffractometer operating in the Bragg–Brentano geometry and fitted with a graphite monochromator in the diffracted beam. The data were collected in the 2θ range 20°–120° at a step of 0.02°. The XRD data were analyzed by Rietveld refinement technique using FULLPROF [Carvajal (2010)] package. In the refinements, pseudo-Voigt function and a sixth order polynomial were used to define the profile shape and background, respectively. We have used the microstructural strain parameter and anisotropic thermal parameters similar to that in ref. [Palewicz et al. (2007)] for pure $BiFeO_3$.

5.3 Results

5.3.1 Room temperature Rietveld refinement of BF-0.2PFN

The rhombohedral structure of BF-0.2PFN in R3c space group was confirmed by Rietveld refinement using the powder XRD data. The positional coordinates of atoms in the asymmetric unit of the R3c space group are $(0,0,1/4+s)$, $(0,0,t)$ and $(1/6-2e-2d,1/3-4d,1/12)$ for $\text{Bi}^{3+}/\text{Pb}^{2+}$, $\text{Fe}^{3+}/\text{Nb}^{5+}$ and O^{2-} , respectively, using hexagonal unit cell, where the 's' and 't' parameters describe the polar cationic displacements, 'd' represents the octahedral distortion, and 'e' the angle of antiphase rotation $\Phi = \tan^{-1}4\sqrt{3}e$ [Selbach et al. (2009)]. The Rietveld fit between the observed and calculated profiles is shown in Fig.5.1, while the refined parameters are given in Table 5.1. The values of s, t, d and e parameters of BF-0.2PFN are found to be nearly comparable to the values reported for BiFeO_3 using powder neutron diffraction data [Palewicz et al. (2007)]. The octahedral tilt angle for BF-0.2PFN is slightly less ($\Phi = 10.7(2)^\circ$) than that for pure BiFeO_3 ($\Phi = 12.8^\circ$). BF-0.2PFN is thus isostructural with BiFeO_3 and may be considered as a model system to study the likely sequence of structural phase transitions in pure BiFeO_3 as well.

5.3.2 Evolution of the x-ray diffraction profile with temperature

Figure 5.2(a, b) shows the evolution of the 111 and 220 pseudocubic peaks (with respect to the elementary perovskite cell) from room temperature to 1023 K. Both the peaks are doublets for the R3c space group. The splitting of the 111 and 220 peaks persists up to 973 K and disappears in the profiles recorded at 998 and 1023 K (see Fig. 5.2).

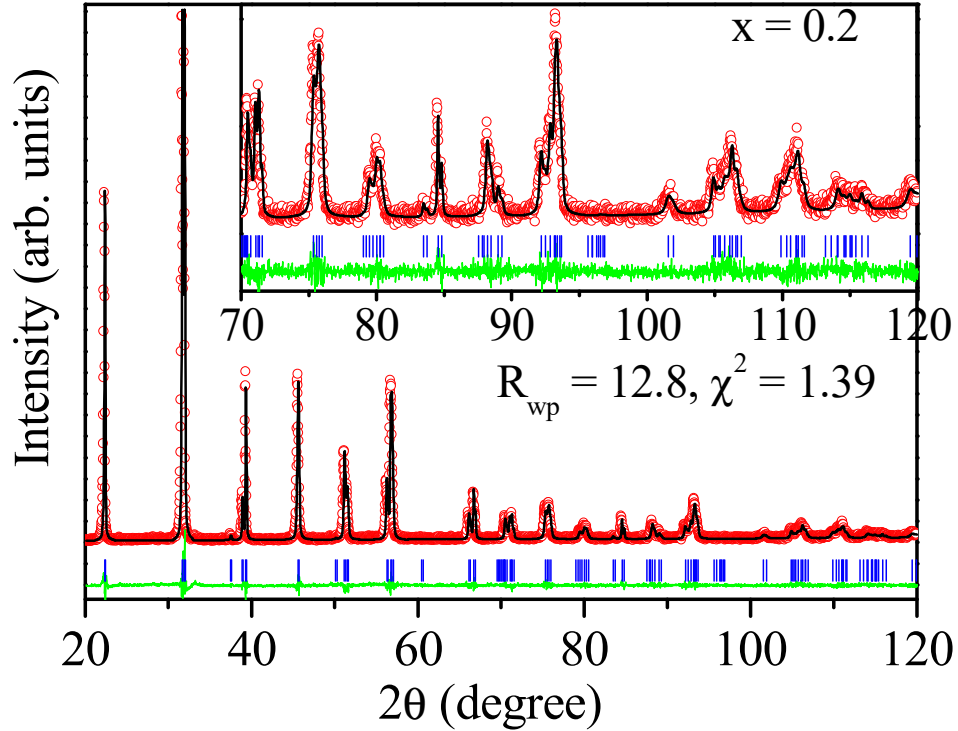


Fig. 5.1 The observed (dots), calculated (continuous line) and difference (bottom curve) plots for BF-0.2PFN obtained after full pattern Rietveld refinement. The vertical tick marks peak positions.

Table 5.1 Results of the Rietveld refinement of BF-0.2PFN at 300 K.

Ions	x	y	z	B (\AA^2)
Bi ³⁺ /Pb ²⁺	0.0	0.0	0.2922(3)	0.98(2)
Fe ³⁺ /Nb ⁵⁺	0.0	0.0	0.0169(5)	0.012(8)
O ²⁻	0.228(2)	0.347(3)	0.08300	1.0(3)
a=b=5.6014(4) \AA , c=13.8817(3) \AA , $\alpha=\beta=90^\circ$, $\gamma=120^\circ$				
$R_p=9.63$, $R_{wp}=14.3$, $R_{exp}=11.81$, and $\chi^2=1.47$				

These observations suggest that the α -phase of BF-0.2PFN in the R3c space group has transformed to another phase above 973 K. Further, the 220 pseudocubic profile shows a triplet structure in the temperature range 873 to 973 K. The peak positions of the two outer peaks match with the R3c peak positions while the inner

peak position matches with the singlet peak position at $T \geq 998$ K suggesting the coexistence of the rhombohedral (R3c) and the new high temperature phase over the temperature range $873 \text{ K} \leq T < 998 \text{ K}$.

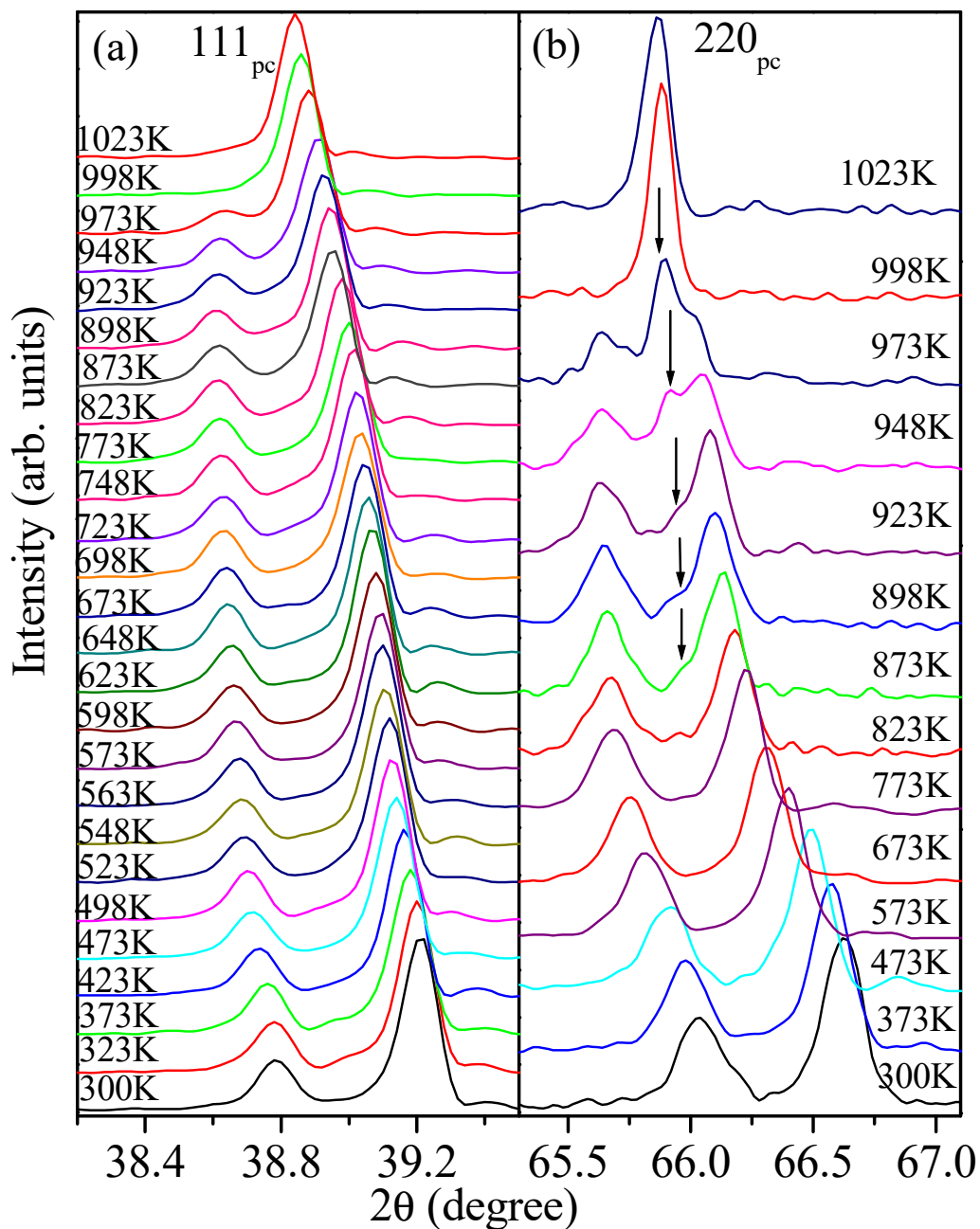


Fig. 5.2 Evolution of the x-ray diffraction profiles with temperature: (a) 111 pseudocubic reflection and (b) the 220 pseudocubic reflection. The arrows in (b) indicate the cubic peak positions coexisting with the rhombohedral peaks.

5.3.3 Rietveld refinement of the high temperature x-ray diffraction pattern: (Evidence for the first order phase transition)

For the high temperature paraelectric phase of pure and compositionally modified BiFeO₃, cubic $Pm\bar{3}m$ [Palai et al. (2008)], tetragonal $I4/mcm$ [Kornev et al. (2007)], orthorhombic $Pbnm$ [Arnold et al. (2009)] and monoclinic $C2/m$ [Haumont et al. (2008)] centrosymmetric space groups have been proposed in the literature. While the diffraction profile of BF-0.2PFN above 973 K could be indexed with cubic unit cell, the possibility of other lower symmetry space groups with pseudocubic metric relationship amongst their cell parameters cannot be ruled out. In order to determine the space group of BF-0.2PFN above 973 K, we therefore carried out Rietveld refinements considering the $Pm\bar{3}m$, $I4/mcm$, $Pbnm$ and $C2/m$ space groups proposed in the literature for pure BF. The Rietveld fits for all the four structural models are of the same quality with nearly identical χ^2 . The fact that even after using many more refinable parameters in the non-cubic structural models as compared to those in the cubic model no improvement in the Rietveld fits is observed clearly favours the choice of highest symmetry structural model i.e. the cubic model. This was further confirmed by a comparison of the refined structural parameters of the three structural models given in Table 5.2. It is evident from the values of the refined positional coordinates given in the table that the atomic shifts from the cubic positions in the tetragonal, orthorhombic and monoclinic models are within the standard deviation.

Table 5.2 Results of the Rietveld refinement of BF-0.2PFN at 1023 K by using $\overline{Pm\bar{3}m}$, I4/mcm, Pbnm and C2/m space groups.

	I4/mcm	Pbnm	C2/m	Pm3m
a	5.6598(2)	5.6598(3)	5.658(5)	4.0022(1)
b		5.6603(4)	5.660(4)	
c	8.0048(5)	8.0041(5)	8.003(2)	
β	90.0	90.0	90.00(1)	
Bi ⁺³ /Pb ⁺² x	0.0	0.002(3)	0.0	0.0
Bi ⁺³ /Pb ⁺² y	0.50	0.003(3)	0.0	0.0
Bi ⁺³ /Pb ⁺² z	0.25	0.2500	0.0	0.0
Bi ⁺³ /Pb ⁺² x			0.0	
Bi ⁺³ /Pb ⁺² y			0.0	
Bi ⁺³ /Pb ⁺² z			0.5	
Fe ⁺³ /Nb ⁺⁵ x	0.0	0.50	0.50(1)	0.50
Fe ⁺³ /Nb ⁺⁵ y	0.0	0.0	0.0	0.50
Fe ⁺³ /Nb ⁺⁵ z	0.0	0.0	0.74(2)	0.50
O ⁻² 1x	0.0	0.03(3)	0.0	0.0
O ⁻² 1y	0.0	0.53(3)	0.50	0.50
O ⁻² 1z	0.25	0.2500	0.0	0.50
O ⁻² 2x	0.25(1)	0.76(3)	0.0	
O ⁻² 2y	0.75(1)	0.27(3)	0.50	
O ⁻² 2z	0.0	-0.02(2)	0.50	
O ⁻² 3x			0.22(3)	
O ⁻² 3y			0.27(2)	
O ⁻² 3z			0.28(3)	
Bi ⁺³ /Pb ⁺² β	$\beta_{11}=\beta_{22}=0.050(2)$ $\beta_{33}=0.020(9)$	$\beta_{11}=0.054(5)$ $\beta_{22}=0.032(6)$ $\beta_{33}=0.024(4)$ $\beta_{12}=0.001(9)$	$\beta_{11}=0.06(1)$ $\beta_{22}=0.035(8)$ $\beta_{33}=0.019(4)$ $\beta_{13}=0.002(4)$	$\beta_{11}=\beta_{22}=\beta_{33}=0.09(1)$
Bi ⁺³ /Pb ⁺² β			$\beta_{11}=0.07(1)$ $\beta_{22}=0.035(9)$ $\beta_{33}=0.026(5)$ $\beta_{13}=-0.01(2)$	
Fe ⁺³ /Nb ⁺⁵ B	1.1(1)	1.11(9)	0.74(3)	1.2(1)
O ⁻² 1 β	$\beta_{11}=\beta_{22}=0.04(3)$ $\beta_{33}=-0.01(1)$	$\beta_{11}=0.04(9)$ $\beta_{22}=0.06(5)$ $\beta_{33}=0.02(9)$ $\beta_{12}=-0.06(4)$	$\beta_{11}=0.12(9)$ $\beta_{33}=0.04(1)$ $\beta_{33}=0.03(1)$ $\beta_{13}=0.09(1)$	$\beta_{11}=0.12(4)$ $\beta_{22}=\beta_{33}=0.13(3)$
O ⁻² 2 β	$\beta_{11}=\beta_{22}=0.04(1)$ $\beta_{33}=0.06(2)$ $\beta_{12}=-0.05(2)$	$\beta_{11}=0.01(6)$ $\beta_{22}=0.02(2)$ $\beta_{33}=0.05(3)$ $\beta_{12}=0.02(5)$ $\beta_{13}=-0.02(3)$ $\beta_{13}=0.02(3)$	$\beta_{11}=-0.04(1)$ $\beta_{22}=0.06(1)$ $\beta_{33}=0.04(1)$ $\beta_{13}=0.05(2)$	
O ⁻² 3 β			$\beta_{11}=0.02(7)$ $\beta_{22}=-0.03(1)$ $\beta_{33}=0.04(1)$ $\beta_{12}=-0.01(1)$ $\beta_{13}=0.05(4)$ $\beta_{23}=-0.09(1)$	
χ^2	1.82	1.79	1.80	1.78

This implies that irrespective of the structural model we use for refining the structure of BF-0.2PFN above 973 K, we arrive at the cubic structure in the $Pm\bar{3}m$ space group. Thus Rietveld analysis confirms the cubic structure of the high temperature paraelectric phase.

The cubic paraelectric phase coexists with the rhombohedral phase (R3c) in the temperature range 873 to 973 K. The multiplicity of the Bragg peaks (such as for 220 peak shown in Fig.5.2) due to the coexistence of the two phases can be easily misconstrued as the signature of the appearance of a lower symmetry intermediate 'β' phase. For example, Palai et al [Palai et al. (2008)] have reported the orthorhombic 'β' phase on the basis of the observation of triplet of peaks without any quantitative Rietveld fit. In order to provide quantitative confirmation to our foregoing observations about coexistence, we carried out Rietveld analysis of the full powder diffraction profile in the phase coexistence region considering all the proposed space group models in the literature i.e., I4/mcm [Kornev et al. (2007)], Pbnm [Arnold et al. (2009)] and C2/m [Haumont et al. (2008)] for the intermediate 'β' phase. Fig.5.3 shows the observed, calculated and difference profiles of pseudocubic 111, 200, 210 and 220 reflections, obtained after full pattern refinement. The I4/mcm [Kornev et al. (2007)], Pbnm [Arnold et al. (2009)] and C2/m [Haumont et al. (2008)] space groups proposed in the literature for the intermediate β - phase of BiFeO₃ may be rejected outrightly at least for BF-0.2PFN, as they are not able to account for all the observed Bragg peaks. For the sake of rigour in our analysis, we also considered coexistence of I4/mcm, Pbnm and C2/m with R3c in the temperature range 873 to 973 K. But the refined coordinates of the I4/mcm, Pbnm and C2/m converged to the cubic special

positions at the end of the refinement, similar to those for temperatures above 973 K. Thus we do not find any evidence for the so-called intermediate non-cubic ‘ β ’ phase either in coexistence with the rhombohedral R3c phase or alone in the temperature 873 to 973 K.

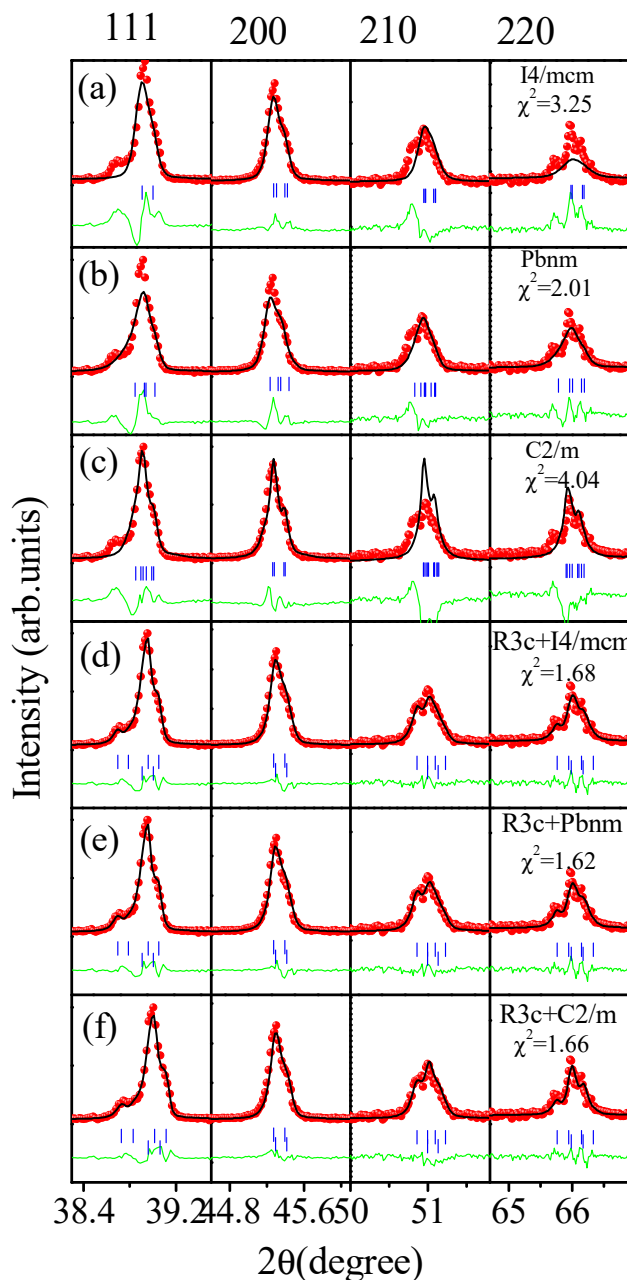


Fig. 5.3 Observed (dots), calculated (continuous line), and difference (bottom curve) profiles for a few selected pseudocubic reflections (111, 200, 210 and 220) obtained after full pattern refinements using different space groups and structural models proposed in the literature. Vertical tick marks are the peak positions.

Among the various monoclinic, tetragonal and orthorhombic space groups, proposed for the ‘ β ’ phase, evidence for the Pbnm space group has been presented by several workers in BiFeO₃ [Arnold et al. (2009)] and its solid solutions [Jiang et al. (2009), Young (1996)]. Unlike the R3c space group, belonging to the $a^-a^-a^-$ tilt system with antiphase component tilts of equal magnitude about the three pseudocubic $\langle 100 \rangle$ directions, the tilt system corresponding to the Pbnm space group is $a^-a^+c^+$. In this tilt system, the component tilts about the [100] and [010] pseudocubic directions correspond to “antiphase” rotation of the neighbouring oxygen octahedra, where the octahedra are rotated “in phase” about the [001] direction. The antiphase tilts lead to the appearance of the superlattice reflections, due to the doubling of all the three pseudocubic cell parameters, whose Miller indices with respect to the doubled cubic cell correspond to three odd (o) integers like ‘ooo’ [Glazer (1972) and (1975)]. The in-phase tilts, on the other hand, lead to cell doubling along two of the $\langle 100 \rangle$ directions perpendicular to the tilt axis. The superlattice reflections in this case have Miller indices represented by two odd (o) and one even (e) integer (i.e. ooe type) [Glazer (1972) and (1975)]. Superlattice reflections in the $a^-a^+c^+$ tilt system also arise due to antiparallel displacement of ‘A’ cation in the neighbouring ABO₃ perovskite unit cells. Such superlattice reflections have Miller indices which are represented by two even and one odd integers i.e., they are of ‘eeo’ type [Glazer (1972) and (1975)].

If the R3c space group with $a^-a^-a^-$ tilt system transforms to the Pbnm space group with $a^-a^+c^+$ tilt system, one expects the appearance of new superlattice reflections with ‘ooe’ and ‘oeo’ indices due to the appearance of the in-phase (c^+) tilting of the octahedra about [001] direction and antiparallel cationic

displacements. We depict in Fig. 5.4 the powder XRD profiles of BF-0.2PFN in the 2θ range 20 to 35 and 35.2 to 48 degrees at seven different temperatures 300, 873, 898, 923, 948, 973 K and 998 K.

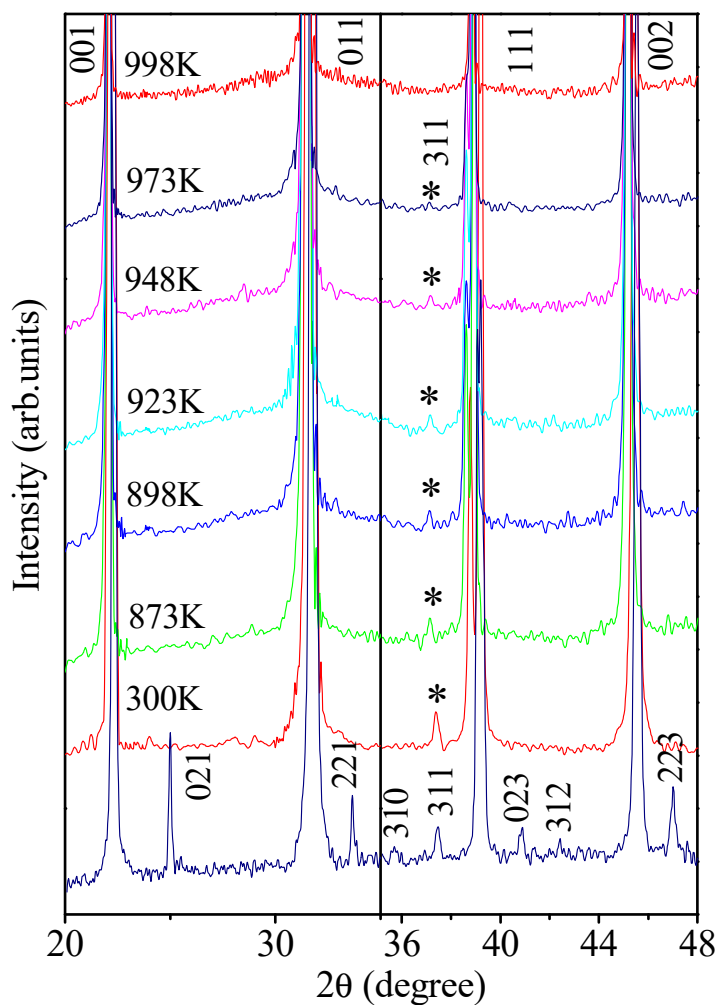


Fig. 5.4 Evolution of the x-ray diffraction profile in the 2θ range 20 to 32 and 35.2 to 48 degrees at various temperatures 300, 873, 898, 923, 948, 973 and 998 K. Asterisk indicates the 311 superlattice peak of the R3c space group. The bottom most profile corresponds to simulated pattern of BiFeO_3 using Pbnm space group and the structural parameters given in Ref. [Arnold et al. (2009)].

A simulated XRD pattern of BiFeO₃ in the Pbnm space group, obtained using the refined parameters given in the literature [Kornev (2007)], is also shown at the bottom of the figure for easy comparison. The small peak at $2\theta \approx 37.32^\circ$ bears '311' Miller indices with respect to the doubled cubic cell and results from the antiphase tilting of the oxygen octahedra. No new superlattice reflection, like '310' expected at $2\theta \approx 35.64$ or '312' at $2\theta \approx 42.41$ characteristic of the in-phase tilt of Pbnm space group and prominent 023, 223, 221 and 021 reflections, characteristic of antiparallel cationic shift in $\langle 1\bar{1}0 \rangle$ pseudocubic directions, has appeared in the 873 to 973 K temperature range. Thus we can comprehensively rule out the possibility of Pbnm space group appearing between R3c and $\text{Pm}\bar{3}m$ phases as an intermediate β -phase in BF-0.2PFN.

Having ruled out the possibility of I4/mcm, Pbnm and C2/m as β -phases of BF-0.2PFN, we also considered the $\text{R}\bar{3}c$ and R3m space groups proposed in Ref [Selbach (2008)] and [Maitre (2004)] respectively, to represent the ' β ' phase. For all the three plausible rhombohedral space groups R3c, $\text{R}\bar{3}c$ and R3m, the 220 pseudocubic peak is a doublet as shown in Fig. 5.2 for R3c at $T = 300\text{K}$. Thus the triplets of peaks observed in the temperature range 873 to 973 K in Fig.5.2 cannot be explained by pure R3c, $\text{R}\bar{3}c$ or R3m phases discussed earlier. Since the position of the middle peak marked with arrow in Fig. 5.2 matches with the position of the 220 reflection of the cubic phase stable at 998 and 1023 K, we considered $\text{R3c} + \text{Pm}\bar{3}m$, $\text{R}\bar{3}c + \text{Pm}\bar{3}m$ and $\text{R3m} + \text{Pm}\bar{3}m$ structural models in the Rietveld refinements. Fig.5.5 depicts the Rietveld fits for these three structural models for 973 K. It was found that the $\text{R3c} + \text{Pm}\bar{3}m$ structural model gives the

best fit with lowest χ^2 . The difference in the χ^2 value for this model with respect to the other two models is statistically significant as per Durbin Watson (DW) statistics [Bhattacharjee (2009)].

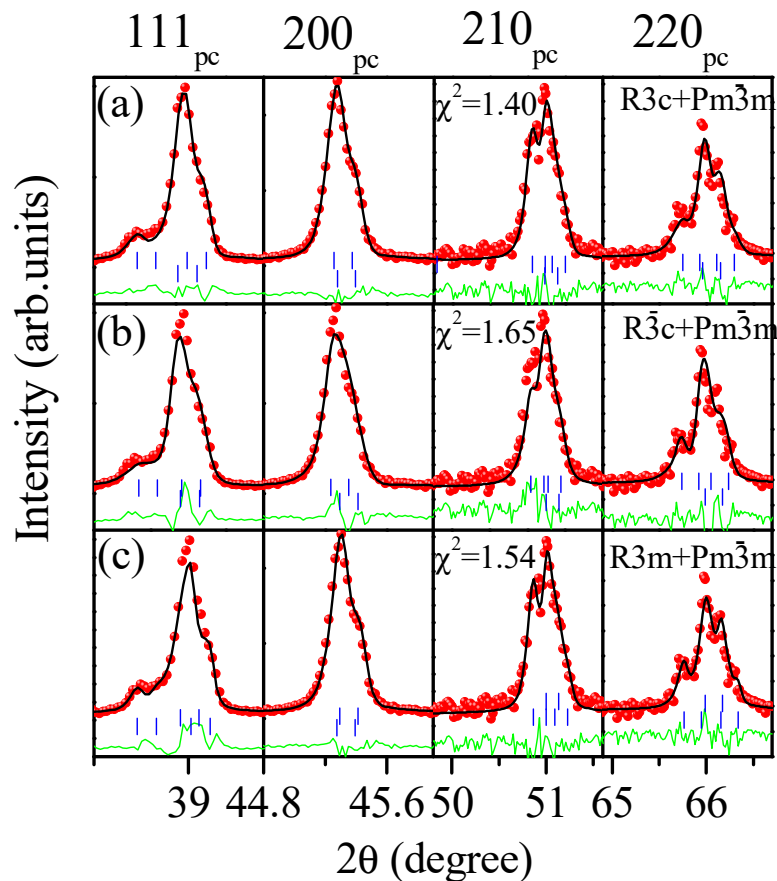


Fig. 5.5 Observed (dots), calculated (continuous line), and difference (bottom line) profiles for selected pseudocubic reflections (111, 200, 210 and 220) obtained after full pattern refinements by using $R3c+Pm\bar{3}m$, $R\bar{3}c+Pm\bar{3}m$ and $R3m+Pm\bar{3}m$ structural models. Vertical tick marks are the peak positions.

Using DW statistics we could reject the $R\bar{3}c+Pm\bar{3}m$ and $R3m+Pm\bar{3}m$ models. Our Rietveld refinements thus confirm that the room temperature $R3c$ phase transforms directly into the cubic $Pm\bar{3}m$ phase through a 100 K wide temperature range over which the two phases coexist. Rietveld analysis of the x-ray

diffractions data in the phase coexistence region, 873 to 973 K, shows that the percentage of cubic phase grows as ~ 7%, 9%, 10%, 40% and 75% with increasing temperature before complete transformation to the cubic phase in the $Pm\bar{3}m$ space group around 998 K.

The coexistence of the R3c and $Pm\bar{3}m$ phases in the 873 to 973 K range suggests that the R3c to $Pm\bar{3}m$ phase transition is of first order. If it is so, this should be reflected in the temperature variation of the unit cell parameters also. Fig. 5.6 depicts the variation of the hexagonal unit cell parameters and the elementary perovskite cell volume with temperature, as obtained by Rietveld refinements using R3c, R3c+ $Pm\bar{3}m$ and $Pm\bar{3}m$ structural models in the temperature range 300 to 823, 873 to 973 and 998 to 1023 K. It is interesting to note that the unit cell volume shows a small anomaly at the magnetic phase transition temperature T_N (see the inset), similar to that reported in $BiFeO_3$ [Haumont (2008)], $(Bi_{0.90}Ba_{0.10})(Fe_{0.90}Ti_{0.10})O_3$ [Singh et al. (2008)], and $(Bi_{0.73}Pb_{0.27})(Fe_{0.73}Ti_{0.27})O_3$ [Selbach (2009)] due to magnetoelastic coupling. More interestingly, there is a significant discontinuous change in the unit cell volume of the rhombohedral and cubic phases in the rhombohedral to cubic phase transition range confirming the first order character of this phase transition.

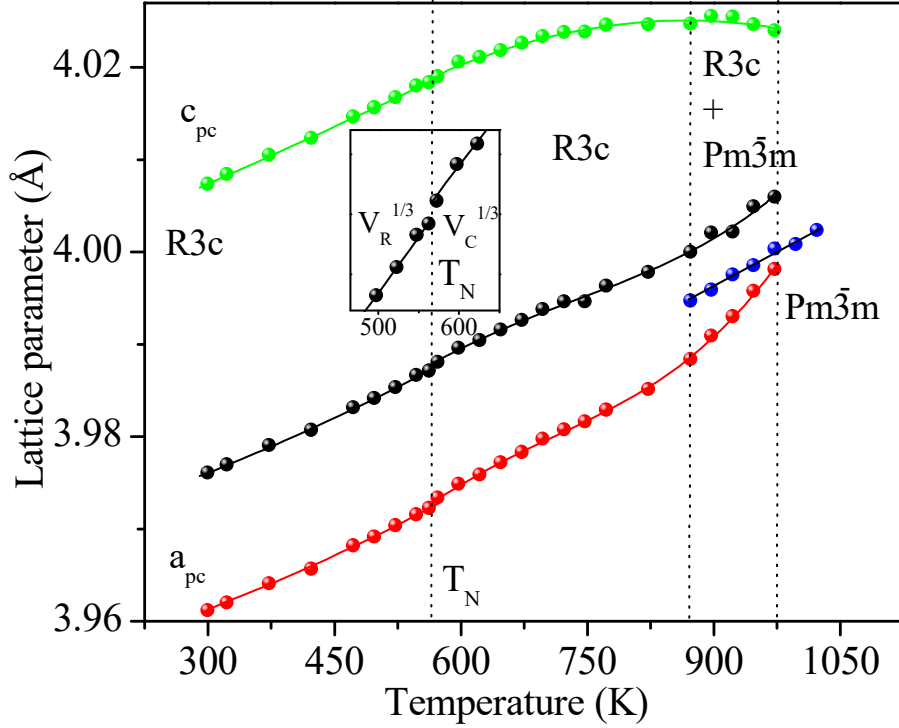


Fig. 5.6 Evolution of the unit cell parameters as a function of temperature. Inset shows small change in unit cell volume at the magnetic phase transition temperature (T_N).

5.4 Discussion

The three structural models involving coexistence of rhombohedral and cubic phases correspond to the following sequence of phase transitions: (i) the ferroelectric $R3c$ phase transforms into the paraelectric phase with $R\bar{3}c$ space group, which is a centrosymmetric space group and a subgroup of the $R3c$ space group. $R\bar{3}c$ phase on heating to still higher temperatures may undergo phase transition to the paraelastic cubic phase in the $Pm\bar{3}m$ space group. This model has been proposed for BiFeO_3 in Ref. [Selbach et al. (2008)]. (ii) The $R3c$ space group of the ferroelectric phase transforms into the non-centrosymmetric $R3m$ space group as a result of untilting of the oxygen octahedra from a $a^-a^-a^-$ tilt system

to $a^0 a^0 a^0$ tilt system. The second ferroelectric phase in the $R3m$ space group finally transforms into the paraelectric cubic phase with $Pm\bar{3}m$ space group. This model has been proposed for $BiFeO_3$ in Ref. [Patel et al. (2010)]. (iii) The ferroelectric phase in the $R3c$ space group transforms directly into the paraelectric/paraelastic cubic phase in the $Pm\bar{3}m$ space group without any intermediate phase. This model is the outcome of the present investigations. Microscopically, the antiferrodistortive (from $a^0 a^0 a^0$ to $a^- a^- a^-$ tilt system) and ferroelectric phase transitions are believed to be driven by softening and freezing of the zone boundary $R(q = 1/21/21/2)$ and zone centre $\Gamma(q = 000)$ optical phonons of the cubic perovskite phase. The first scenario implies that coming from higher temperature cubic phase region, the freezing of the $R(q = 1/21/21/2)$ point phonon transforms $Pm\bar{3}m$ into the $R\bar{3}c$ space group in the $a^- a^- a^-$ tilt system as a result of an antiferrodistortive phase transition [Glazer (1972) and (1975)]. This is then followed by the phase transition from the paraelectric centrosymmetric $R\bar{3}c$ space group to the non-centrosymmetric, ferroelectric $R3c$ space group by the freezing of the $\Gamma(q = 000)$ point phonon. The likely microscopic pathway for the second scenario would be the freezing of the $\Gamma(q = 000)$ point optical phonon leading to $Pm\bar{3}m$ to $R3m$ ferroelectric transition followed by the freezing of the $R(q = 1/21/21/2)$ point optical phonon leading to $R3m$ to $R3c$ antiferrodistortive phase transition. The third scenario would involve simultaneous freezing of both $R(q = 1/21/21/2)$ and $\Gamma(q = 000)$ point optical phonons leading to a direct $Pm\bar{3}m$ to $R3c$ transition without any intermediate β phase. Our experimental observations follow the third scenario.

The observation of R3c to $\text{Pm}\bar{3}\text{m}$ direct phase transition in BF-0.2PFN is quite intriguing from the point of view of Landau theory of structural phase transitions. In this theory, a structural phase transition is driven by one primary order parameter, even though it may be coupled to a secondary order parameter [Blinic and Zeks (1974)]. The macroscopic order parameters associated with the ferroelectric and antiferrodistortive phase transitions are polarization [Blinic and Zeks (1974)] and octahedral tilt angle [Glazer (1972) and (1975)], respectively. The cubic $\text{Pm}\bar{3}\text{m}$ to rhombohedral R3c direct phase transition of BF-0.2PFN requires both the order parameters to emerge below the cubic to rhombohedral phase transition temperature simultaneously, rather than successively for scenarios (i) and (ii) discussed earlier. This implies that none of the two order parameters can be termed secondary, as both are equally important for the R3c phase to emerge from the $\text{Pm}\bar{3}\text{m}$ phase. Thus the $\text{Pm}\bar{3}\text{m}$ to R3c phase transition is an unusual type of phase transition for which no one single primary order parameter can be defined. This transition results from the cooperation of two primary order parameters. In literature, this kind of transition has been termed as ‘trigger type transition’ [Kornev and Bellaiche (2009)].

The coexistence of the R3c and $\text{Pm}\bar{3}\text{m}$ phases over a 100 K range and discontinuous change in the unit cell volume across the structural phase transition temperature confirms the first order character of this transition. The ferroelectric and antiferrodistortive phase transitions are generally regarded as second order phase transitions in the soft mode picture but may show first order character if the primary order parameters (polarization and tilt angle) are coupled to the secondary order parameter like strain [Anderson (1997)]. This coupling is usually linear in

primary order parameter and quadratic in the secondary order parameter [Levanyuk and Sannikov (1974)]. This coupling to strain renormalizes the coefficient of the fourth order term in Landau expansion, and depending on the strength of the coupling, the sign of this coefficient may change from positive to negative, which in turn may make a potentially second order transition as first order transition. It is not apriori obvious if this consideration would hold good even for the so-called ‘trigger type’ [Holakovsky (1973)] phase transitions, with no one well defined primary order parameter, assuming the coupling of the polarization and tilt angle to strain. We hope that these observations would encourage workers to develop suitable phenomenological framework for understanding such a first order, trigger type structural phase transition in BiFeO₃ based systems.

5.5 Summary and conclusions

The outcome of high temperature x-ray powder diffraction study on the BF-0.2PFN solid solution can be summarized as follows:

- (i) 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.
- (ii) 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.

(iii) 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.

(iv) 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.