

CHAPTER-II

***Synthesis of Phase Pure (1-x)BiFeO₃-
Pb(Fe_{0.5}Nb_{0.5})O₃ (BF-xPFN) Solid
Solutions***

2.1 Introduction

In this chapter, we present the details of synthesis of phase pure $(1-x)\text{BiFeO}_3-x\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (BF-xPFN) solid solutions in the composition range $0.1 \leq x \leq 1.0$ by solid state reaction method. The synthesis of pure BiFeO_3 has been continuing a challenge because easily formation of unwanted impurity phases $\text{Bi}_2\text{Fe}_4\text{O}_9$ [Kumar et al. (2000)], $\text{Bi}_{25}\text{FeO}_{39}$ [Lebeugle et al. (2007)] and $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$ [Pradhan (2005)] during their calcinations and sintering processes. On the other hand, the formation of unwanted pyrochlore phases e.g. $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ and $\text{Pb}_2\text{Nb}_2\text{O}_7$ [Lejeune and Boilot (1982), Jenhi et al. (1998)] during the synthesis of $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ makes it more difficult to synthesize phase pure $(1-x)\text{BiFeO}_3-x\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ samples. The $\text{Bi}_2\text{Fe}_4\text{O}_9$ (Bi-deficient) and $\text{Bi}_{25}\text{FeO}_{39}$, $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$ (Bi-excess impurities) are formed during the calcinations stage at BF end compositions of BF-xPFN solid solutions. These impurities are controlled by optimizing the calcinations temperature and time. There was no impurity phases formed during the calcinations of the PFN end compositions. The intermediate compositions of BF-xPFN are also calcined successfully without impurities. The sintering of BF-xPFN pellets were carried out in the closed alumina crucibles. The powder of same compositions are used as a spacer powder to control the evaporation of Bi during the sintering of $0.10 \leq x \leq 0.70$ compositions while calcined PbZrO_3 powder was used as a spacer powder for sintering of $0.80 \leq x \leq 1.0$ compositions to control the formation of pyrochlore phases due to evaporation of Pb.

2.2 Characterization tools

X-ray diffractometer is a powerful instrument used to characterize and identify the different phases present in any material. The simplicity and advantage of X-ray powder diffraction method can be given as follows (i) the powder diffraction pattern is characteristic of a given substance, (ii) each substance in a mixture produces its own pattern independent of others and (iii) the method is capable of quantitative and qualitative analysis of the phases present in a given mixture. In the present case, the calcined and sintered powders were characterized for the presence of different phases in the BF-xPFN compositions synthesized during this thesis work. X-ray diffraction (XRD) measurements were carried out using an 18 kW rotating anode ($\text{CuK}\alpha$) based Rigaku (RINT 2000/PC series) powder diffractometer operating in the Bragg-Brentano geometry and fitted with a graphite monochromator in the diffracted beam.

2.3 Synthesis of $(1-x)\text{BiFeO}_3-x\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (BF-xPFN)

BF-xPFN compositions with general formula $(1-x)\text{BiFeO}_3-x\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ with x in the range $0.10 \leq x \leq 1.0$ were synthesized through conventional solid state reaction route. The conditions and sequences used in the sample preparation are as follows:

2.3.1 Precursors

Analytical reagent grade reagents Bi_2O_3 (99.5%, Himedia), Fe_2O_3 (99%, Himedia), PbCO_3 (99.5%) and Nb_2O_5 (99.0%, Himedia) were taken as the initial raw materials in the present work. All the powders were having purity $\geq 99\%$.

XRD patterns of the reagents used, Bi_2O_3 , Fe_2O_3 , PbCO_3 and Nb_2O_5 , are shown in Fig. 2.1. PbCO_3 was obtained from aqueous solution of $\text{Pb}(\text{NO}_3)_2$ using $(\text{NH}_4)_2\text{CO}_3$ (99%) as the precipitant. Thermogravimetric analysis of PbCO_3 was carried out to determine the exact assay (PbO content) of the powder. The assay of PbO was found to be 99.5%. For thermogravimetric analysis, platinum crucibles were used.

2.3.2 Mixing and milling

The reacting species in the stoichiometric ratio were thoroughly mixed in an agate mortar-pestle in the presence of AR grade acetone for 2-3 hours. The mixtures were then ball milled (Retsch GmbH & Rheinische, Germany) for 6 hours using zirconia jars and zirconia balls with AR grade acetone as the mixing media.

2.3.3 Calcinations

After proper mixing (hand mixing and ball milling), mixture was kept at least for 12 hours to completely evaporate the acetone which was used during ball milling. The dried powder was gently collected and used for calcinations. The calcinations were carried out in an alumina crucible at different temperature by using global furnace capable of going up to ~ 1600 K.

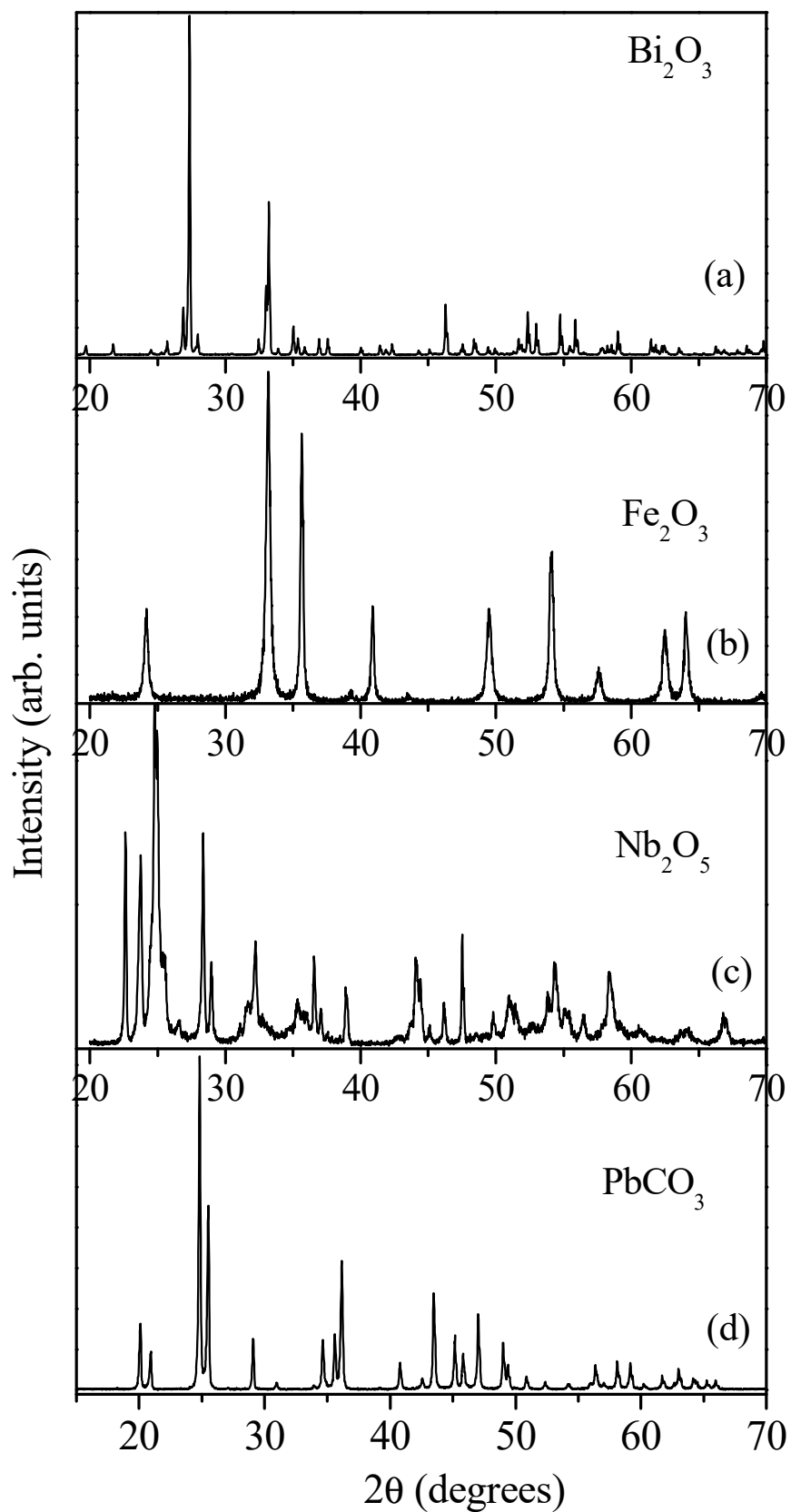


Fig. 2.1 XRD patterns of the chemicals used (a) Bi₂O₃ (b) Fe₂O₃ (c) Nb₂O₅ and (d) PbCO₃ for synthesis of the BF-xPFN samples.

To study the reaction mechanism for the formation of the BF-xPFN solid solutions, we have initially selected BF-0.35PFN composition for calcinations. The ball milled powder were calcined at different temperatures 1053 K, 1073 K, 1113 K, 1123 K, 1133 K, 1143 K and 1158 K for 7 hours. The calcined powder was grind in to fine powders by using an agate mortar and pestle and used for the collection of x-ray diffraction patterns. The x-ray diffraction patterns of BF-xPFN powders calcined at different temperatures were recorded as shown in Fig. 2.2. The x-ray diffraction pattern collected at 1053 K was indexed by using JCPDS files. Since, there were no reflections of ingredient powders Bi_2O_3 , Fe_2O_3 , PbCO_3 and Nb_2O_5 present in XRD patterns, it means reactions were completely taken place. The major components of XRD pattern has been indexed as a main perovskite peaks of BF-0.35PFN along with two minor's phases of $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$ and $\text{Pb}_3\text{Nb}_4\text{O}_{13}$. The reflections of the impurity phases $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$ and $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ are indicated by specific symbols as shown in Fig. 2.2. The small peak located at the $2\theta \sim 37.5^\circ$ is due to the cell doubling of the main perovskite phase. In order to check the stabilities of the impurity phases, it was calcined at different higher temperatures whose XRD patterns with temperatures are given in the Fig. 2.2. It was evident from Fig. 2.2 that as the calcinations temperature was increased intensities of the x-ray peaks corresponding to the impurity phases gradually decreased and completely disappeared at 1158 K.

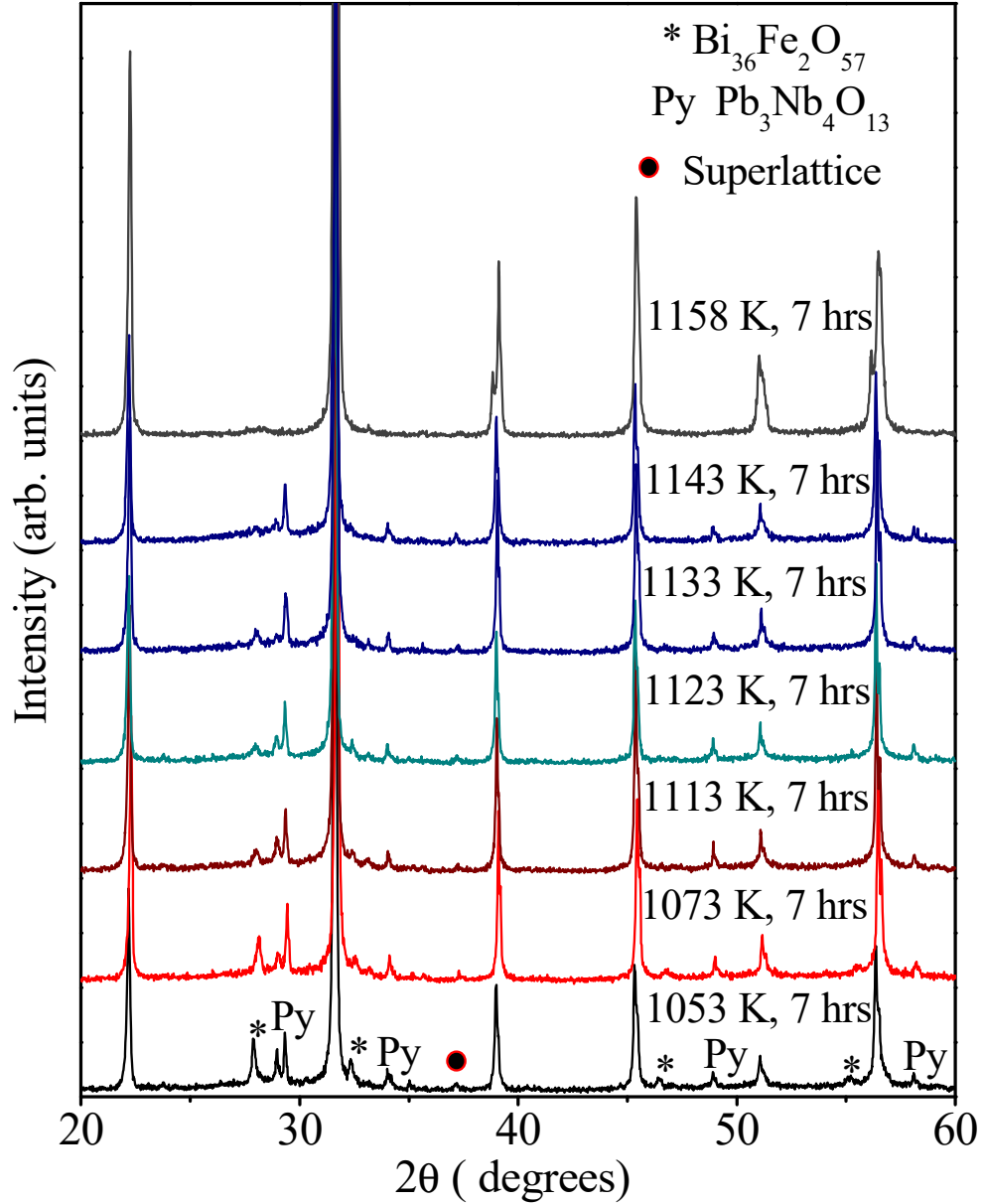


Fig. 2.2 The XRD patterns of calcined BF-0.35PFN powders at different temperatures using Bi_2O_3 , Fe_2O_3 , Nb_2O_5 and PbCO_3 as an ingredients in appropriate molecular ratio.

The small hump at $\sim 28^\circ$ is due to the Bi deficient $\text{Bi}_2\text{Fe}_4\text{O}_9$ impurity phase which probably starts to appear at sufficiently high calcination temperature. The x-ray

diffraction pattern collected at 1158 K was only due to the main perovskite phase of BF-0.35PFN along with superlattice reflections. The superlattice reflections was found in pure BiFeO₃ and its doped compound because of antiphase rotation of oxygen octahedral along the [111] direction of the perovskite phase. The 1158 K temperature was taken as an optimized calcinations temperature for the BF-0.35PFN composition. The expected calcinations temperature for other compositions was determined by an increment of 10 K in calcination temperatures with 10% increment of PFN doping and then it was optimized in similar way as for the 35% PFN doped BiFeO₃.

The optimized calcination temperatures of BF-xPFN solid solutions for x = 0.1, 0.2, 0.3, 0.35, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.94 and 0.96 are 1128, 1133, 1143, 1148, 1153, 1163, 1173, 1183, 1193, 1203, 1207 and 1210 K respectively. The XRD patterns for the calcined BF-xPFN powders are given in Figs. 2.3 and 2.4. The XRD diffraction patterns show that there are no impurity phases in the calcined BF-xPFN powder except for x = 0.10 composition.

2.3.4 Preparation of Green Pellets

After calcinations, the sample was properly crushed and mixed with an organic binder of 2% polyvinyl alcohol (PVA) solution in an agate mortar. PVA mixed powder was used for the preparation of green pellets. A cylindrical steel die of 12 mm diameter was used to make green pellets of BF-xPFN. Initially, the die was kept in a highly viscous mobile oil to prevent it from rusting. After taking out from the oil, the die was cleaned with acetone. Just before putting the powder in

the die for pressing, some stearic acid solution was used in the inner surface of the die to avoid sticking of the powder on the inner surface of the die.

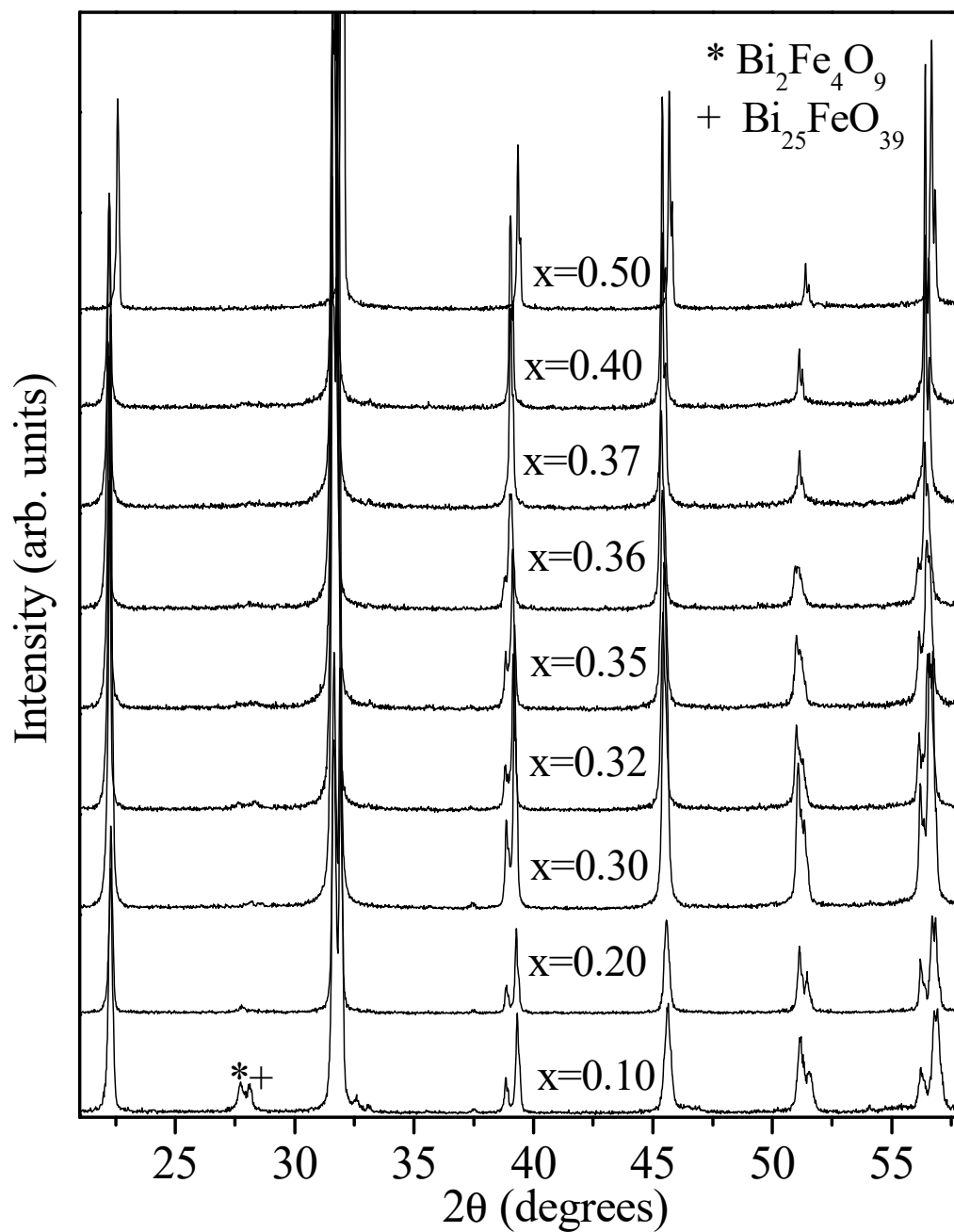


Fig. 2.3 The XRD patterns of the calcined BF-xPFN powders for x = 0.10, 0.20, 0.30, 0.32, 0.35, 0.36, 0.37, 0.40 and 0.50.

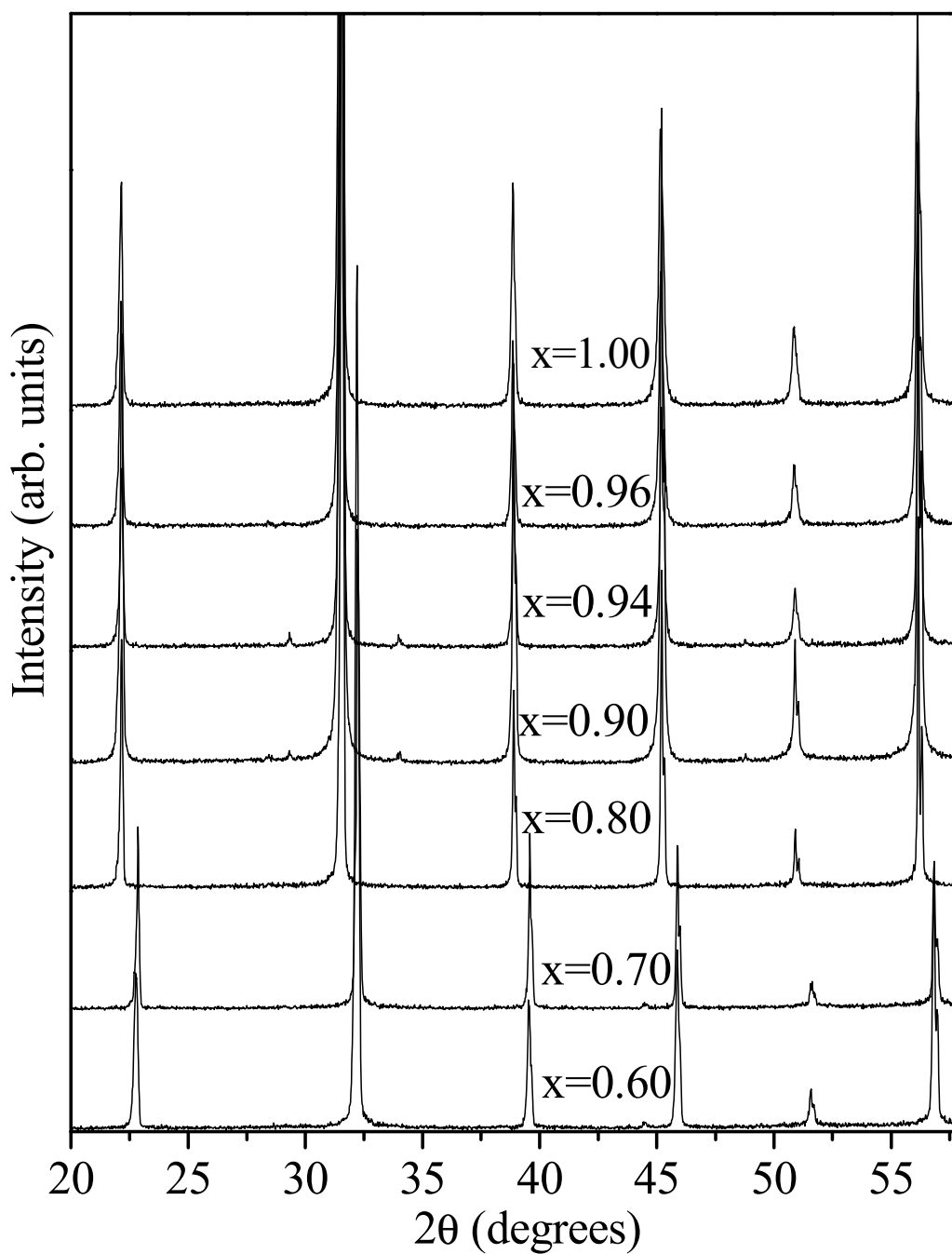


Fig. 2.4 The XRD patterns of the calcined BF-xPFN powders for $x= 0.6, 0.7, 0.8, 0.9, 0.94, 0.96$ and 1.0 compositions.

The BF-xPFN powder was put in the die and set in a hydraulic press. Then die containing powder was uniaxially pressed at an optimized pressure (for getting

maximum green density) of 65 kN in a hydraulic press. After pellet was formed, it was heated at 773 K for 12 hrs to completely evaporate the binder (PVA).

2.3.5 Sintering

The pellets called as ‘green pellets’ was kept at 773 K for 12 hours for completely burn-off polyvinyl alcohol before sintering. Sintering was performed in closed alumina crucible with calcined powder of the same composition kept inside the closed crucible as a spacer powder for preventing the loss of Bi^{3+} during the sintering for the composition range $0.1 \leq x \leq 0.70$, while equimolar mixture of PbO and ZrO_2 calcined at 973 K, powder was used for preventing the loss of Pb^{2+} for the compositions $x \geq 0.80$. PFN is sintered at very high temperature ~ 1423 K for 6 hours while the BF is sintered below its melting temperature ~ 1173 K for 1-2 hours. Therefore, the sintering temperature and time of sintering of BF-xPFN solid solutions were increased with increasing the doping of PFN for example BF-0.1PFN was sintered at 1193 K for 1 hour while BF-0.96PFN was sintered at 1423 K for 6 hours. The optimized sintering temperatures for $x = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9 are 1215, 1235, 1255, 1275, 1295, 1315, 1335 and 1355 K respectively. The sintered pellets were then crushed into fine powder. This crushed powder was annealed at 775 K for 12 hours to remove strains which may be developed during the process of crushing. This annealed powder was used for collecting the x-ray powder diffraction data. The XRD patterns of sintered BF-xPFN powder for $x = 0.1, 0.2, 0.3, 0.32, 0.35, 0.36,$ and 0.4 are given in Fig. 2.5, while for $x = 0.5, 0.6, 0.7, 0.8, 0.9, 0.94$ and 0.96 are given in Fig. 2.6.

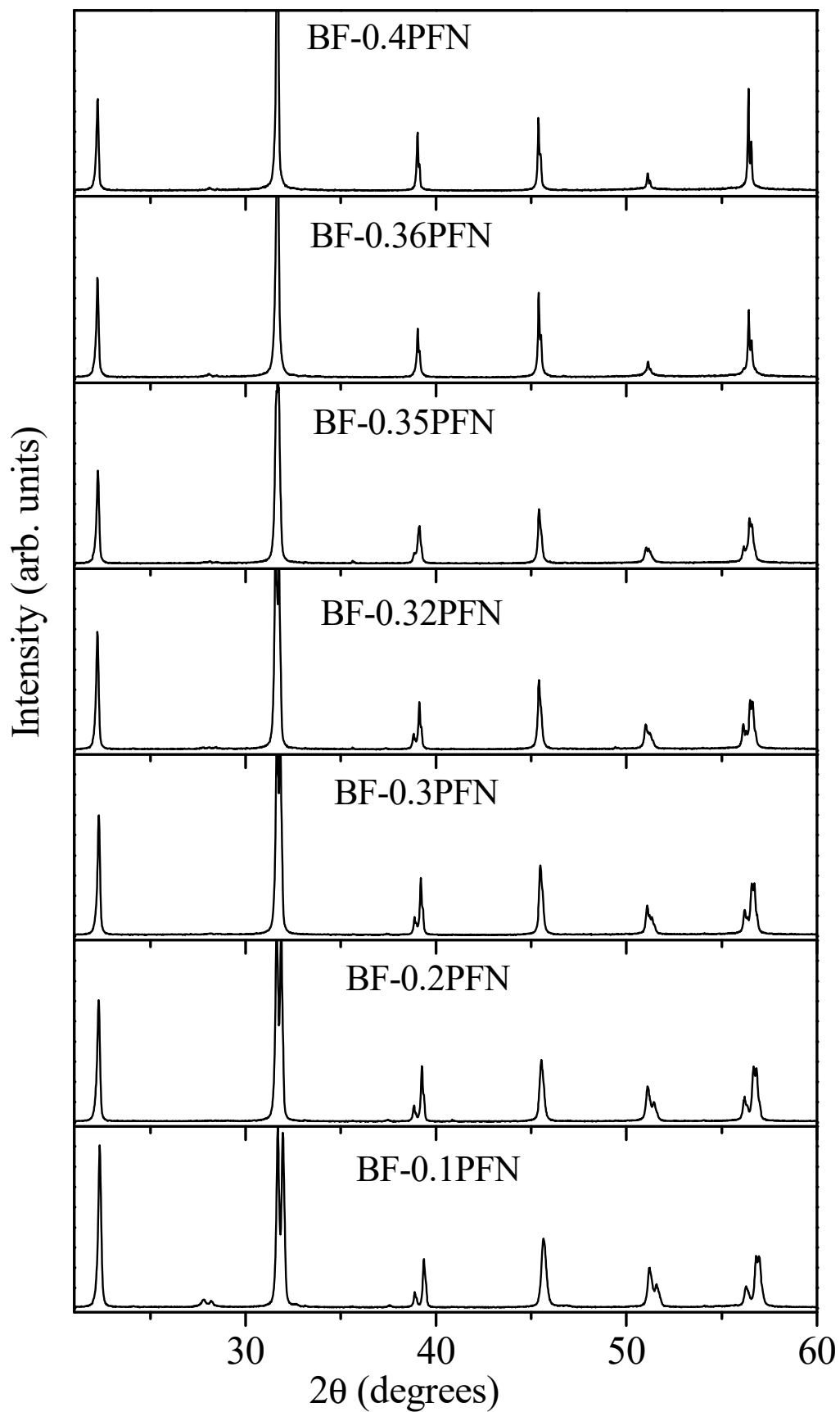


Fig. 2.5 The XRD patterns of sintered BF-xPFN for the compositions $x = 0.1$, 0.2, 0.3, 0.32, 0.35, 0.36 and 0.40.

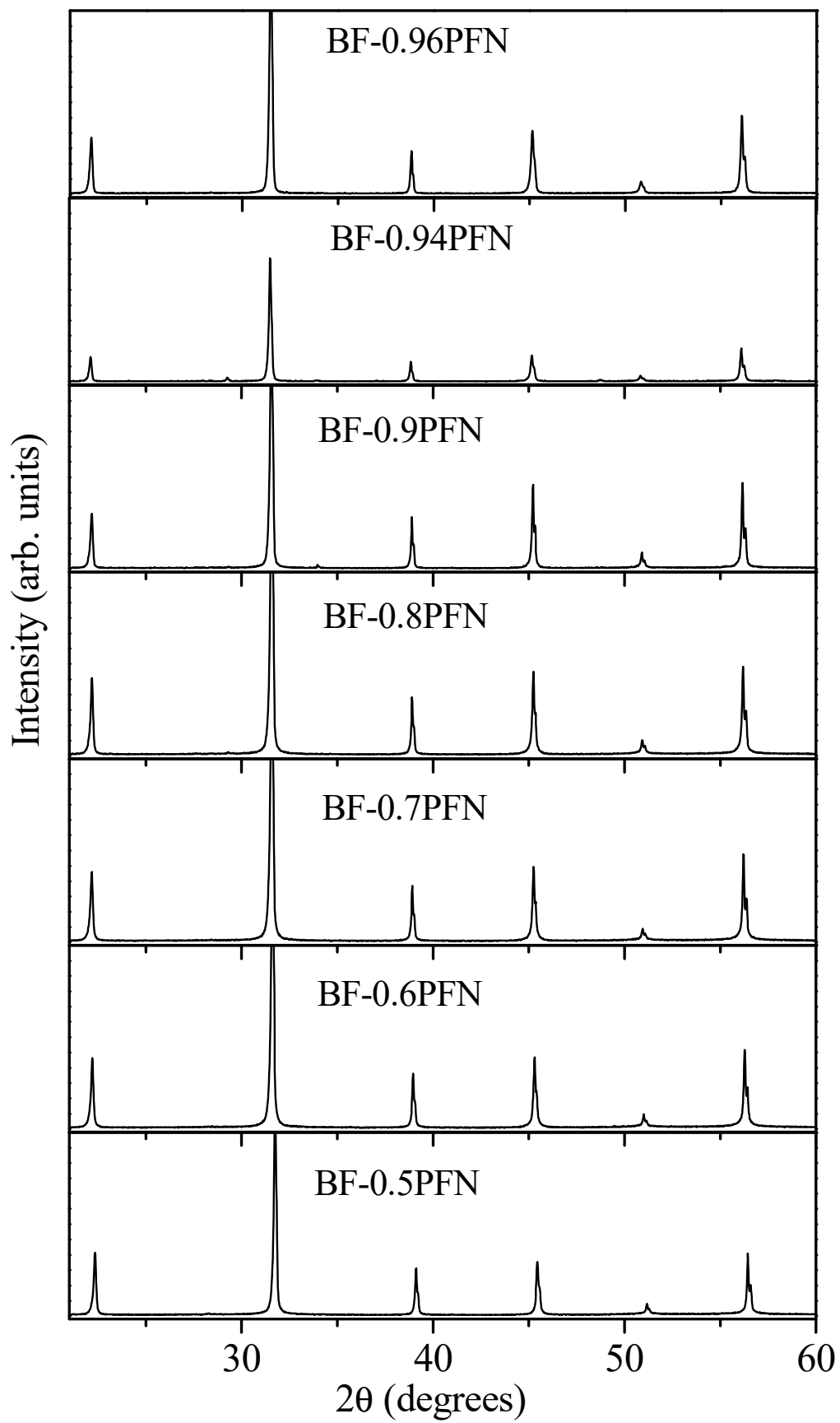


Fig. 2.6 The XRD patterns of sintered BF-xPFN for the compositions $x = 0.5$, 0.6, 0.7, 0.8, 0.9, 0.94 and 0.96.

2.4 Conclusion

All the compositions of BF-xPFN solid solution were successfully synthesized by solid state reaction method. The synthesized samples were nearly free from all the impurity phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{25}\text{FeO}_{39}$, $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$, $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ and $\text{Pb}_2\text{Nb}_2\text{O}_7$ which are commonly formed during the different stages of synthesis. Generally, PFN has been synthesized by columbite/wolframite [Swartz and ShROUT (1982), Liou et al. (2002)] precursor method to avoid the formation of pyrochlore phases. However, in present study, we have synthesized pyrochlore free Pb-rich compositions without using columbite/wolframite [Swartz and ShROUT (1982), Liou et al. (2002)] precursor route.