# Chapter-II

## 2.1 Introduction

As pointed out in Chapter I, synthesis of phase pure $Bi(Ni_{1/2}Ti_{1/2})O_3$ has been a hard task as high pressure during high calcination temperature is required to synthesize pure perovskite phase [Zhu et al. (2013)]. A number of unwanted impurity phases like $Bi_2O_3$, $NiO$ and $Bi_4Ti_3O_{12}$ are reported to appear for high temperature calcination at ambient pressure [Okuda et al. (1994); Inaguma and Katsumata (2003)]. However, perovskite phase of BNT can be stabilized under ambient pressure synthesis by formation of its solid solution with other ferroelectric ceramics such as $PbTiO_3$ (PT) [Choi et al. (2005)], $Pb_{(1-x)}Sr_xTiO_3$ [Kang et al. (2012)], $BaTiO_3$ [Fujii et al. (2012)], $SrTiO_3$ [Kang et al. (2012)] etc. forming a solid solution of $Bi(Ni_{1/2}Ti_{1/2})O_3$ with other perovskites not only helps to reduce the unwanted impurity phases but also can enhance the resistivity, magnetic and ferroelectric properties [Choi et al. (2005); Kang et al. (2012); Hu et al. (2010)]. This Chapter presents the details of synthesis of phase pure $(1-x)Bi(Ni_{1/2}Ti_{1/2})O_3$-$xPbTiO_3$ ((1-x)BNT-xPT) solid solution in the selected composition range $0.35 \leq x \leq 0.55$ using solid state reaction method. We observed that the substitution of $PbTiO_3$ in $Bi(Ni_{1/2}Ti_{1/2})O_3$ is very effective in completely suppressing/reducing the formation of the impurity phases by solid state reaction method.

## 2.2 Characterization Tools

X-ray diffraction technique is a powerful tool used to characterize and refine the structure and different phases present in any material. Powder diffraction patterns are the characteristic of given materials and each mareial produces its own diffraction pattern which is distinct from any other material. The great advantage of powder x-ray diffraction technique is also found in the chemical analysis, stress measurement, study of phase equilibrium, determination of particle size and in-situ measurements. In the present work, the calcined and sintered powders were characterized for structure and phase analysis using powder x-ray diffraction measurements. X-ray diffraction (XRD) measurements were carried out using an 18kW rotating anode (CuKα) based Rigaku (Japan) powder diffractometer operating in the Bragg-Brentano geometry and fitted with a graphite monochromator in the diffracted beam. The microstructure (grain size) of the sintered sample was characterized using a field emission gun scanning electron microscope (SEM) Supra 40, ZEISS (Germany) attached with energy dispersive x-ray (EDS) analyzer. A thin gold film was sputter-coated under vacuum on the sintered pellets before SEM examination. Gun voltage was varied during the SEM analysis to get the better resolution in the images.

Synthesis of (1-x)BNT-xPT solid solution in the composition range $0.35 \leq x \leq 0.55$ were carried out by conventional solid state ceramic route. Following procedures in the given sequence were used for the sample preparation and characterization:

## 2.3. Samples Preparation

Samples used in the present work were prepared by conventional solid state ceramic route. AR grade $Bi_2O_3$ (Himedia, $\geq$99.5%), $NiCO_3.2Ni(OH)_2$ (Qualigens, 42.78%), $TiO_2$ (Himedia, $\geq$99%), PbO (Himedia, 98%) were used as initial ingredients. Pure NiO obtained from the heating of $NiCO_3.2Ni(OH)_2$ at $550^0C$ for 1 hour was used as reactant. XRD patterns of the ingredients $Bi_2O_3$, $TiO_2$, PbO and NiO are shown in Fig.2.1. Stoichiometric proportions of all the ingredients required for a particular composition were mixed in zirconia jars containing zirconia balls for 6 hours using a planetary ball mill (Retsch, Germany). Analytical reagent grade acetone was added in optimum amount to powder mixture for wet mixing. Heat treatments for calcination were carried out at $850^0C$ in alumina crucibles using a muffle furnace. Multi-step (2-3 times) calcinations at $850^0C$ were done to prepare the single phase (1-x)BNT-xPT. Cold compaction of calcined powder was done using a steel die of 12mm diameter and a uniaxial hydraulic press at an optimized load of 65kN. 2% polyvinyl alcohol solution in water was used as binder. The green pellets were kept at $500^0C$ for 10 hours to burn out the binder and then sintered at $950^0C$ for 3 hours in closed alumina crucible. Calcined powder of the same composition was kept inside the closed crucible as sacrificial powder for preventing the loss of volatile Bi and Pb oxides during sintering. For x-ray characterizations, sintered pellets were crushed into fine powder and then annealed at $500^0C$ for 10 hours to remove the residual strains introduced during crushing.
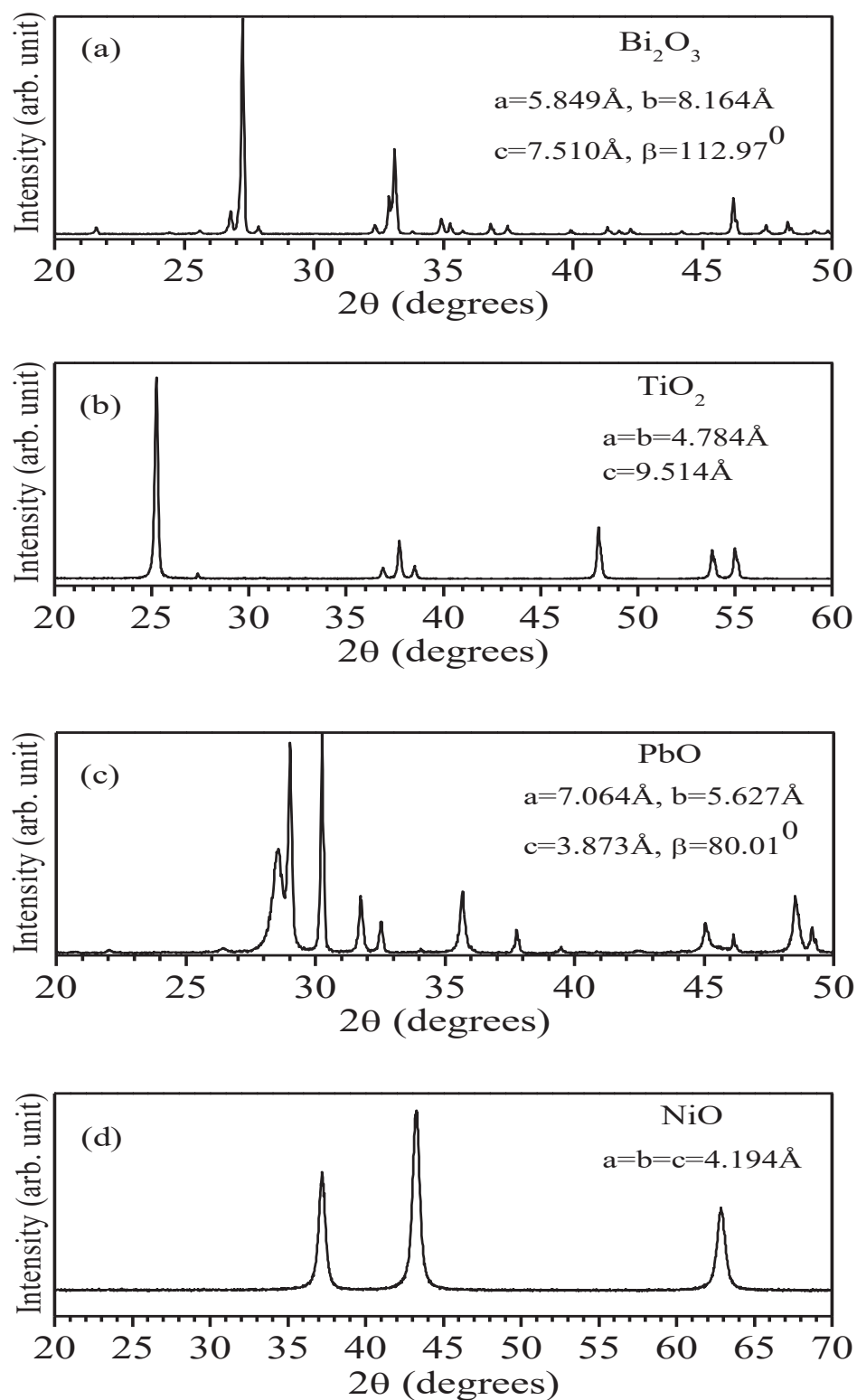
**Fig.2.1.** XRD patterns of reactant powders used for synthesis of (1-x)BNT-xPT: (a) $Bi_2O_3$ (b) $TiO_2$ (c) PbO and (d) NiO.

## 2.3.1 Precursors, Mixing, Milling and Calcination

AR grade $Bi_2O_3$, $TiO_2$, PbO and NiO powders were hand mixed in an agate mortar-pestle in the stoichiometric ratio. Before weighing of reactants, they were heated at $100^0C$ for 30 minutes to remove the moister if any. The mixtures were then ball-milled (Retsch, Germany) for 6 hours. After hand mixing and ball milling, the mixture was dried and then calcined at different temperatures and time to optimize the calcination temperature and time. To study the reaction mechanism for the formation of the perovskite phase of (1-x)BNT-xPT solid solutions, the composition 0.48BNT-0.52PT was calcined at $750^0C$ and $850^0C$ for 6 hours. The XRD pattern of the sample calcined at $750^0C$ and $850^0C$ are shown in Fig.2.2. XRD patterns in Fig.2.2 demonstrate that the reaction starts at $750^0C$ as the XRD peaks corresponding to perovskite phase (marked with P) are seen but prominent XRD peaks for $Bi_2O_3$, $TiO_2$, NiO and PbO are also seen. In addition, large number of intermediate phase peaks marked with asterisk (*) in Fig.2.2 are also detected in the XRD pattern calcined at $750^0C$. For the calcination at $850^0C$, the sample is nearly pure perovskite phase with two very weak impurity reflections. A comparison of comparison of Fig.2.1 and Fig.2.2 suggest that no diffraction peaks corresponding to $Bi_2O_3$, $TiO_2$, PbO and NiO reactants are present in the XRD pattern. All the peaks in the XRD pattern of 0.48BNT-0.52PT powder obtained after calcination at $850^0C$ can be index with the perovskite cell except very weak intensity (< 2%) impurity peaks near $2\theta \sim 28^o$-$29^o$ (marked with asterisk) shown in Fig.2.2. As discussed in Chapter I,
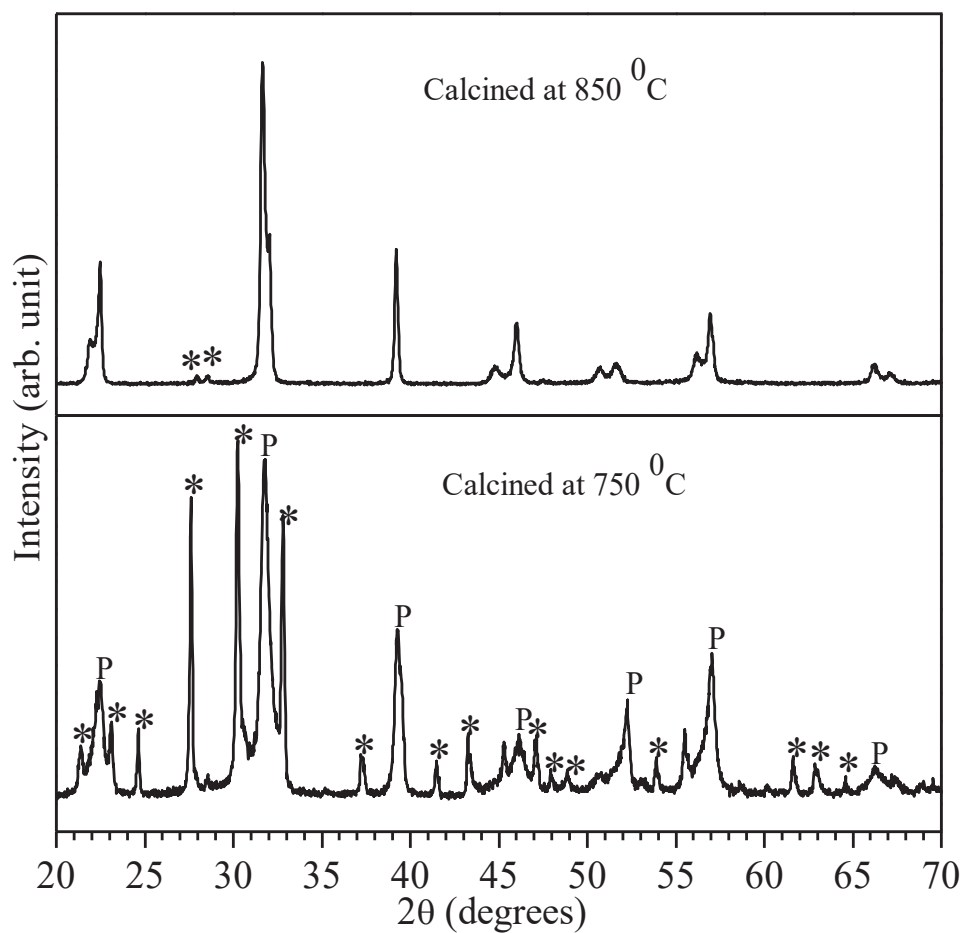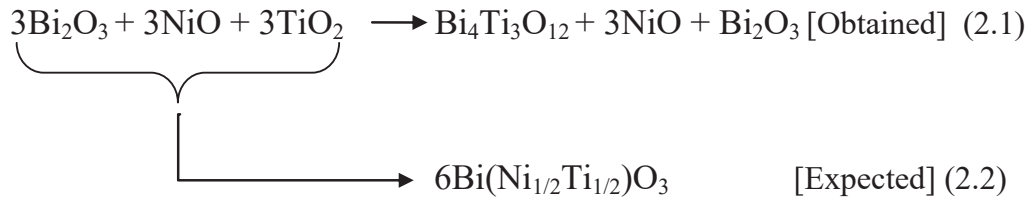
**Fig.2.2.** XRD patterns of 0.48BNT-0.52PT powder obtained after calcination at $750^0$C and $850^0$C using $Bi_2O_3$, $TiO_2$, PbO and NiO as starting ingredients. XRD peaks corresponding to perovskite phase are marked with 'P'. Peaks marked with asterisk (*) correspond to intermediate phase peaks.

synthesis of BNT, the one component of (1-x)BNT-xPT solid solution requires high pressure (~ 5-6GPa) as well as high calcination temperature (~ $1000^0$C). It cannot be synthesized at ambient pressure calcination. Fig.2.3 shows the XRD pattern of BNT prepared by calcination at $1000^0$C under ambient pressure. The XRD pattern shows that perovskite phase perovskite phase has not formed. Reaction sequence for BNT calcined under ambient pressure is described by equations (2.1) [Inaguma et al. (2003)] and (2.2).

$$3Bi_2O_3 + 3NiO + 3TiO_2 \longrightarrow Bi_4Ti_3O_{12} + 3NiO + Bi_2O_3 \text{ [Obtained] } (2.1)$$

$$\longrightarrow 6Bi(Ni_{1/2}Ti_{1/2})O_3 \qquad \text{[Expected] (2.2)}$$

Most of the peaks shown in Fig.2.3 correspond to $Bi_2O_3$, NiO and $Bi_4Ti_3O_{12}$ phases and not due to perovskite $Bi(Ni_{1/2}Ti_{1/2})O_3$ phase. Major peaks in Fig.2.3 are indexed by $Bi_4Ti_3O_{12}$ phase (JCPDS card no. 897502). However, as shown in Fig.2.2, perovskite phase in BNT ceramics can be stabilized at ambient pressure synthesis by formation of its solid solutions with other stable perovskites. The crystal and magnetic structure of the stabilized system may be different from the initial components after the formation of solid solution. Following this route, perovskite phase of BNT ceramic has been stabilized for ambient pressure synthesis by formation of its solid solution with $PbTiO_3$, in the present thesis.
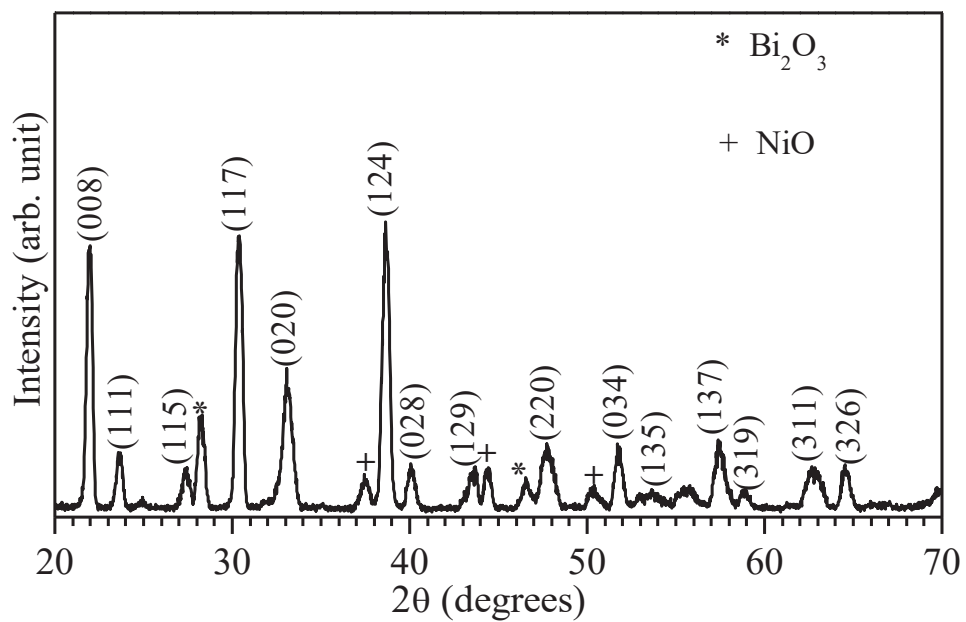
**Fig.2.3.** Powder XRD patterns of BNT prepared using AR grade $Bi_2O_3$, NiO and $TiO_2$ powders. Peaks are marked with $Bi_4Ti_3O_{12}$ phase by JCPDS card no. 897502. (*) and (+) correspond to $Bi_2O_3$ and NiO precursors.

The structure of the intermediate composition of this solid solution is entirely different from the two components namely BNT and PT. The (1-x)BNT-xPT solid solution exhibit a phase transition from pseudocubic to tetragonal structure via a monoclinic phase with increasing PT concentration.

## 2.3.2 Preparation of Green Pellets

As discussed in above Section, the calcined mixtures were crushed in to fine powder in an agate mortar for preparation of green pellets. The crushed powders were free from agglomerates form during calcination. The crushed powders were mixed with binder containing 2% polyvinyl alcohol (PVA) solution in the agate mortar. A cylindrical steal die of 12mm diameter was used to make the green pellets of (1-x)BNT-xPT. The calcined powders mixed with binder were kept in the cylindrical die in appropriate amount and pressed by using a hydraulic press to form the pellets. The load optimization was carried out to overcome the problem of low densification of pellets. After pellet formation, the green density was measured from geometrical dimensions. The variation of pellet density with applied load is shown in Fig.2.4. The density of pellets increases with increasing load and then levels above the applied load of 60kN. We used 65kN as the optimum load for pellet formation. Since, in thick pellets the applied load will not be uniformly distributed and may result into density variation, thin pellets of ~ (1-2)mm thickness were prepared for sintering and further characterization.
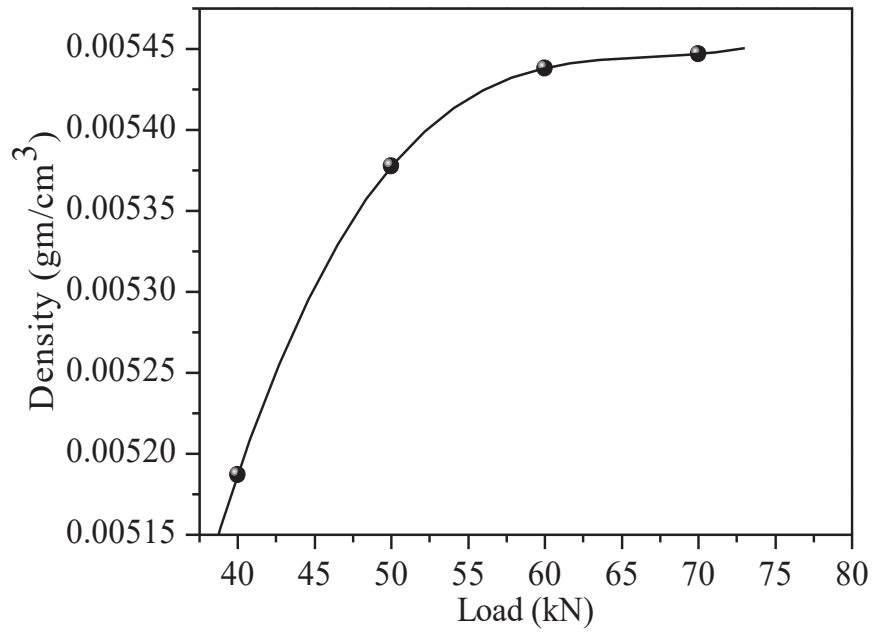
**Fig.2.4.** Optimization of load for the green pellets of 0.53BNT-0.47PT calcined at 850$^0$C.

### 2.3.3 Sintering

Densification of electronic ceramics is a very essential parameter to get the best response. As discussed in the above Section, the green pellets were kept at $500^0$C for 10 hours to burn out the binder and then sintered at $950^0$C for 3 hours in closed alumina crucible. The calcined powder of the same composition was kept inside the closed crucible as sacrificial powder for preventing the loss of volatile Bi and Pb oxides during sintering. The optimized sintering duration and temperature were found to be 3 hours and $950^0$C, respectively. After sintering, density of the pellets was calculated by Archimedes principle. The suspended weights of the pellets were measured in distilled water with the help of a special design hanger to hang the pellet inside the distilled water. The density of the sintered pellets was found to be greater than 97% of the theoretical density. Theoretical densities were calculated from the unit cell parameters obtained by XRD study. The bulk ceramics contains some pores and cracks, therefore the experimental density is observed to be less than the theoretical density. If the sintering temperature was increased above $950^0$C and sintering time more than 3 hours, melting of pellets started followed by the formation of impurity phases like $Bi_4Ti_3O_{12}$ due to loss of $Bi_2O_3$. The XRD patterns of sintered (1-x)BNT-xPT solid solution with compositions x=0.35-0.55 are shown in Fig.2.5. All the peaks in the XRD patterns of the sintered powders shown in Fig.2.5 could be indexed with the pure perovskite structure except for some small impurity peaks (< 2%) around $2\theta \sim 28^o$-$29^o$ which almost disappear for the higher $PbTiO_3$ concentration. Since BNT is not a stable perovskite, it is expected that impurity phases will
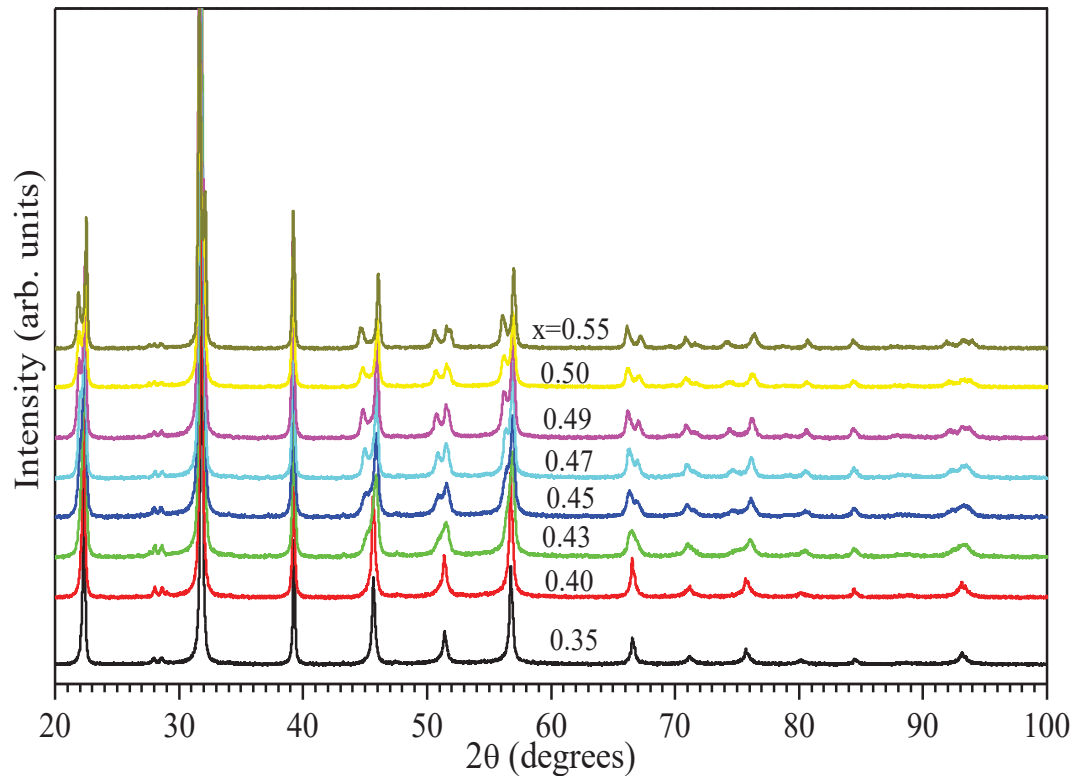
**Fig.2.5.** Powder XRD patterns of various compositions of (1-x)BNT-xPT solid solution sintered at $950^0$C.

appear for the lower PT concentrations of solid solution. Earlier authors have also reported the appearance of impurity phases for lower compositions [Okuda et al. (1994); Takenaka et al. (1994); Fujii et al. (2012)]. Microstructural study was carried out on the as sintered pellets to determine the grain size and uniformity of the microstructure. Fig.2.6(a) depicts the scanning electron micrograph of 0.51BNT-0.49PT ceramics calcined at $850^0$C for 6 hours. The grain size for the calcined powder is found in the range of 200nm to 300nm. Fig.2.6(b) shows the microstructure of pellet sintered at $950^0$C. As can be seen from this figure, the macrostructure is uniform, dense with grain size in the range of 0.6μm to 1.3μm. EDS spectra of calcined and sintered sample of 0.51BNT-0.49PT is shown in Figs.2.7(a) and (b). It depicts that each sample consist of bismuth (Bi), lead (Pb), nickel (Ni), titanium (Ti) and oxygen (O) ions. Since, XRD is not sensitive to detect the light atoms due to low atomic scattering factor, the average atomic percentage of oxygen atom (Z=8) cannot be determined accurately from the EDS spectrum. This inaccuracy in atomic percentage of oxygen also disturbs the atomic percentages of other atoms (Bi, Pb, Ni and Ti). The observed average atomic percentage for Bi, Pb, Ni and Ti atoms so obtained are given in Table2.1 for the calcined and sintered compositions. The calculated atomic percentages of the atoms for these compositions are also given in the Table2.1. The difference in the experimental and calculated atomic percentage values are within the accepted limit of the EDS measurements. SEM images for sintered compositions with x=0.38 and 0.45 sintered at $950^0$C for 3 hours are shown in Figs.2.8(a) and (b). The microstructure is quite dense and uniform for
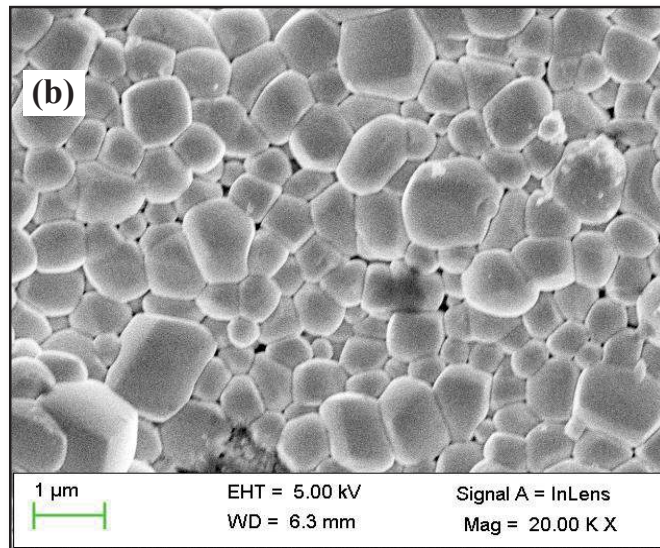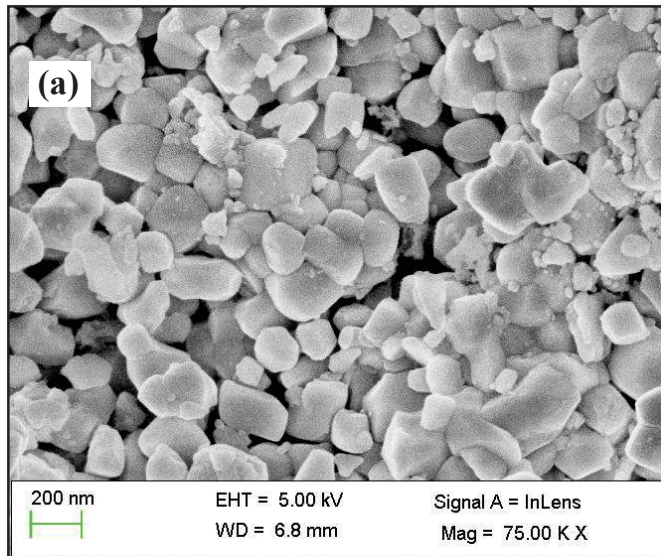
(a)

200 nm    EHT = 5.00 kV    Signal A = InLens
WD = 6.8 mm    Mag = 75.00 K X

(b)

1 µm    EHT = 5.00 kV    Signal A = InLens
WD = 6.3 mm    Mag = 20.00 K X

**Fig.2.6.** SEM image of 0.51BNT-0.49PT (a) calcined at $850^0$C for 6 hours and (b) sintered at $950^0$C for 3 hours.

**Table2.1.** Results of EDS analysis of 0.51BNT-0.49PT ceramic calcined at $850^0$C for 6 hours and sintered at $950^0$C for 3 hours. Exp. and Cal. stand for experimental and calculated average atomic percentage of atoms.

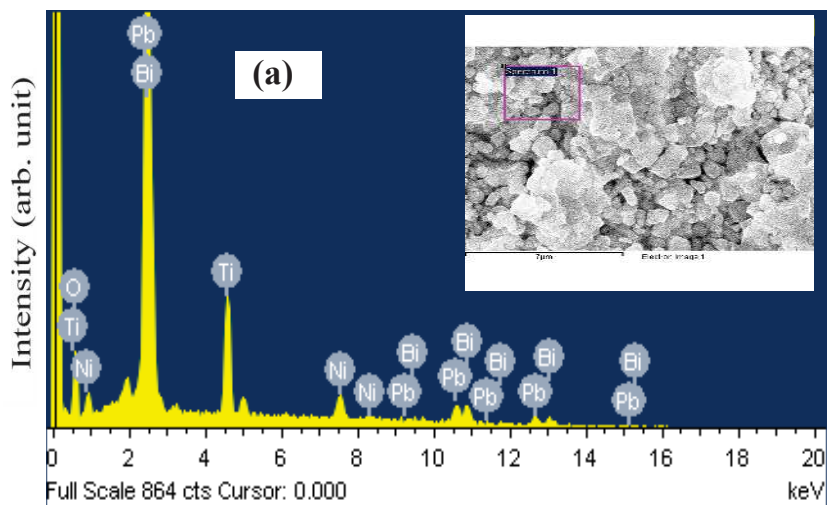| Elements | Atomic (%) Cal. | Atomic (%) Exp. (Calcined) | Atomic (%) Exp. (Sintered) |
|----------|-----------------|----------------------------|----------------------------|
| Bi | 10.2 | 10.38 | 9.75 |
| Pb | 9.8 | 9.16 | 8.86 |
| Ni | 5.1 | 5.09 | 4.7 |
| Ti | 14.9 | 15.79 | 13.85 |
| O | 60 | 59.59 | 63.24 |
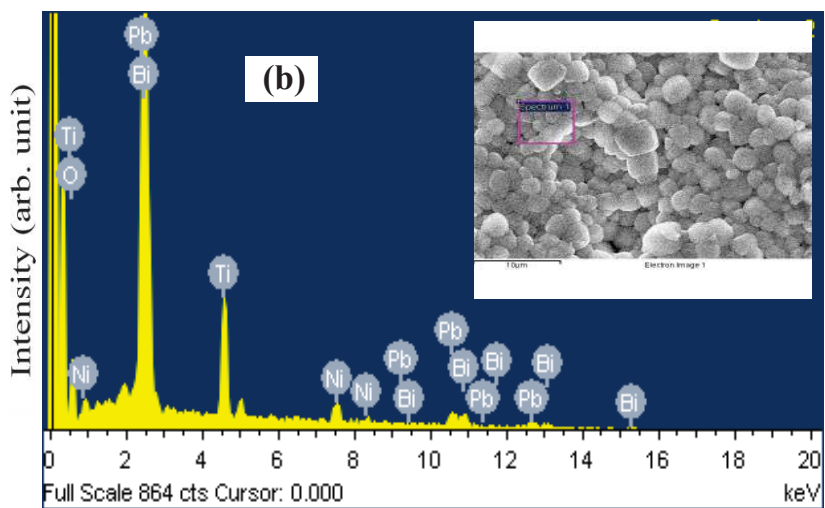
**Fig.2.7.** SEM and EDS spectra of 0.51BNT-0.49PT samples (a) calcined (at $850^0$C) and (b) sintered (at $950^0$C).
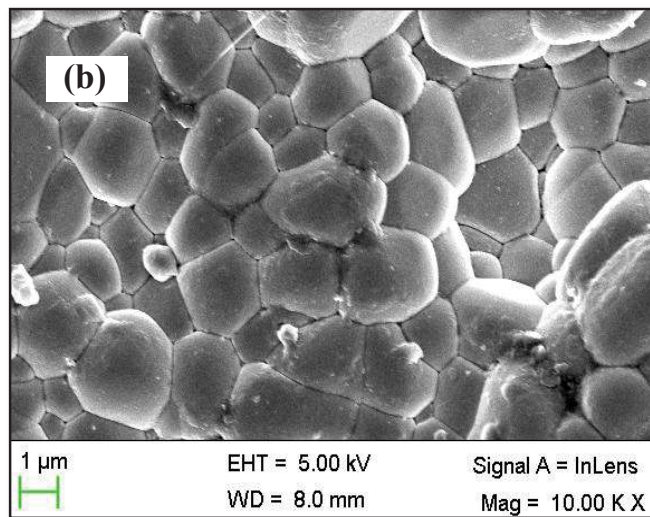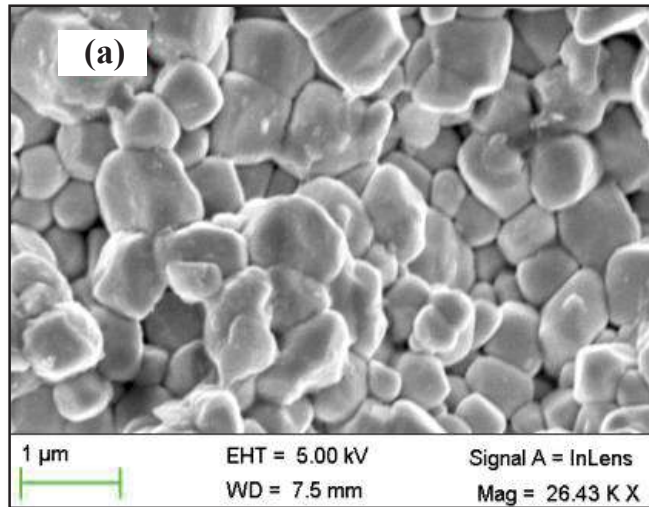
**Fig.2.8.** Scanning electron micrographs of (1-x)BNT-xPT ceramics (a) x=0.38 and (b) x=0.45 sintered at $950^0$C.

all the compositions with x=0.38 and 0.45. Linear-intercept method was used to determine the average grain size. The average grain size was found to be (0.5-1.5)μm.

## 2.4 Summary

Phase pure sample of $(1-x)Bi(Ni_{1/2}Ti_{1/2})O_3-xPbTiO_3$ were synthesized under optimized conditions by using conventional solid state reaction route. Substitution of $PbTiO_3$ has been found to be very effective in the reduction of intermediate impurity phases like $Bi_4Ti_3O_{12}$ commonly formed during the synthesis of pure $Bi(Ni_{1/2}Ti_{1/2})O_3$ under ambient pressure. The average grain size of the calcined powders was 200nm to 300nm. The average grain size of the sintered samples prepared by this method are in the range of 0.5μm to 1.5μm. Details of sample preparation of multiferroic particulate composite will be given in Chapter VI.