Chapter 3
X-Ray Diffraction Analysis

3.1. Introduction

BNT is a ferroelectric having a rhombohedral structure (R3m) at room temperature (9,11,26) with a = 3.891 $\pm$ 0.002 A° and α = 89° 36' $\pm$ 3' and it changes to an antiferroelectric above 200 °C. X-ray diffraction, however, does not show superlattice lines indicating a multiple unit cell characteristic of an antiferroelectric (12,14). The reason given was that the distortion so small that it was impossible to differentiate the reflections. Moreover, there is no apparent optical change in the twin structure in this range and the phase above this transition is still disputable. It may be a rhombohedral phase on account of the shortage of evidence on any phase transition in an x-ray investigation (25) in the vicinity of 200 °C. There may be a concurrent between the tetragonal and rhombohedral phases exhibiting above and below this region (25,26). There is a transition to the paraelectric tetragonal phase (P4mm) at 320 °C (12)and it changes to the paraelectric cubic phase (Pm3m) at 520 °C (15) . From the x-ray diffraction pattern, Zvirgzds et al. (12) computed the lattice parameters of BNT single crystals as listed in Table 5.

Table 5. The lattice parameter from x-ray diffraction patterns (12)

Temperature (°C)	Symmetry	Parameter, (nm)
597	cubic	a_c = 0.39128
397	tetragonal	a_t = 0.39004
		c_t = 0.39057
197	pseudocubic	a_r = 0.3891 α= 90°
17	rhombohedral	a_r = 0.38848 α= 89°54'

Ivanova et al. (24) determined the structure of BNT ceramic and found that the 310 lines splitted into two peaks. This peak is used in order to detect the rhombohedral structure and the lattice parameter of BNT obtained by CrKα radiation was 3.891 $\pm$ 0.002 A$°$ and α was 89$°$ 36$'$ $\pm$ 3$'$.

With increasing the concentration of Pb for the BNT-PT solid solution, the structure at room temperature changes from rhombohedral to tetragonal. There is a different result on the boundary between these two phases for different concentrations of Pb, as 0-10% by Isupov (20) and 13% by Sakata (14) in that they prepared the samples in different ways and variable lead loss. In addition, their phase boundary did not seem to agree with their dielectric work since the sharp of the dielectric constant as a function of temperature in the tetragonal phase should be approximately like that of PbTiO$_3$

From Kuharuangrong' s work (6), the x-ray patterns at room temperature of the BNT-PT solid solution showed a single phase for all the sintered materials, as shown in Fig. 19 (6). These results indicated that BNT, 10% Pb and 15% Pb doped BNT had the same strucrture. However, the structure of 17% Pb doped BNT became tetragonal as shown by the splitting of 100 and 200 into two components with a larger intensity for the high angle peak. The phase boundary was defined as that composition in which the two phases were present in equal quantity. This result was in a good agreement with the dielectric data of this solid solution. The room temperature structure of BNT and 10% Pb doped BNT by a cubic approximation had a lattice constant of 3.889 A$°$ (6) and was 3.900 A$°$, respectively (6). The results of 111, 220, and 310 reflections for 10% Pb doped BNT were identical with those of BNT. For 17% Pb doped BNT, the structure at room temperature was tetragonal with the parameter a = 3.890 $\pm$

0.002 A° and c = 3.971 ± 0.002 A° . Above the Curie point this tetragonal material became cubic as indicated from the doublet of 200 changed to single peak of the cubic phase. As the temperature increased, the lattice parameters changed with increasing a and c. Finally, when the temperature was 460–468 °C, the structure became cubic and the lattice constant was 3.923 ± 0.001 A° (6).

In 1996, Park (13) checked the rhombohedral distortion with the sintered sample. It was found that a lattice parameter of BNT was 3.886 A° and 89.6°. The rhombohedral phase can be distinguished by a diminished splitting peak in the 111 peak obviously shown at a composition of 14% Pb doped BNT. In addition, an obvious split in 200 peak can be found in 14% Pb indicating that the symmetry should be tetragonal. Therefore, it could be suggested that the MPB of Pb doped BNT lied in the composition range near 14% Pb at room temperature. In contrast, Kuharuangrong's work (6) was shown that the splitting of both 100 and 200 of tetragonal phase appeared as 17% Pb were doped.

The x-ray diffraction usually uses to determine the crystal parameters of the phases, both the lattice parameters and the crystal structure. The bragg angles determine the lattice parameter and the intensities identify the type of elements. The collection of these data is a critical operation, because preferred orientation effects in the x-ray diagrams. To prevent this problem, one should sieve the powder to be analyzed directly through a 100 mesh (150 μm) sieve (23).

This study is concerned with the structure and the phase boundary at room temperature of the BNT–BaT and (0.90BNT-0.10PT)–BaT solid solution from XRD MODEL JDX-8030, JEOL, JAPAN

3.2. Results and Discussion

The x–ray patterns at room temperature show a single phase for all the materials of $(1-x)$BNT–BaT and $(1-x)(0.90$BNT–0.10PT$)-x$BaT solid solutions, as shown in Fig.20. These results also indicate that BNT, 5% Ba doped BNT, 0.90BNT–0.10PT and 5% Ba doped 0.90BNT–0.10PT have the same structure. In relevance to the result from DTA analysis as shown in Fig 1. the reaction of 5% Ba doped BNT completes before reaching the calcining temperature such that the x–ray pattern in Fig.20 shows the single phase. However, at 10% Ba doped BNT, there are the other peaks in the front of 110, 111, 200 and 211. This may be an evidence of a second phase in which it was clearly shown from three peaks at 110, as shown in Fig.21. The result from XRD, as seen in Fig.22 shows standard $BaTiO_3$ peaks fitting with this position. In addition, the elememts of the second phase are Ba and Ti as same as the result from EDS.

In the same way, x–ray pattern of 5% Ba doped 0.90BNT–0.10 PT shows the single phase, as shown in Fig.23 that fits with the complete reaction depicted by DTA analysis. Nevertheless, for 10% Ba doped 0.90BNT–0.10PT, the x–ray pattern looks like to 10% Ba doped BNT, as depicted in Fig.21. From SEM photomicrograph and EDS analysis, they also shows second phase that fits with this result from XRD. XRD pattern also shows $BaTiO_3$ second phase in 10% Ba doped 0.90BNT–0.10PT.
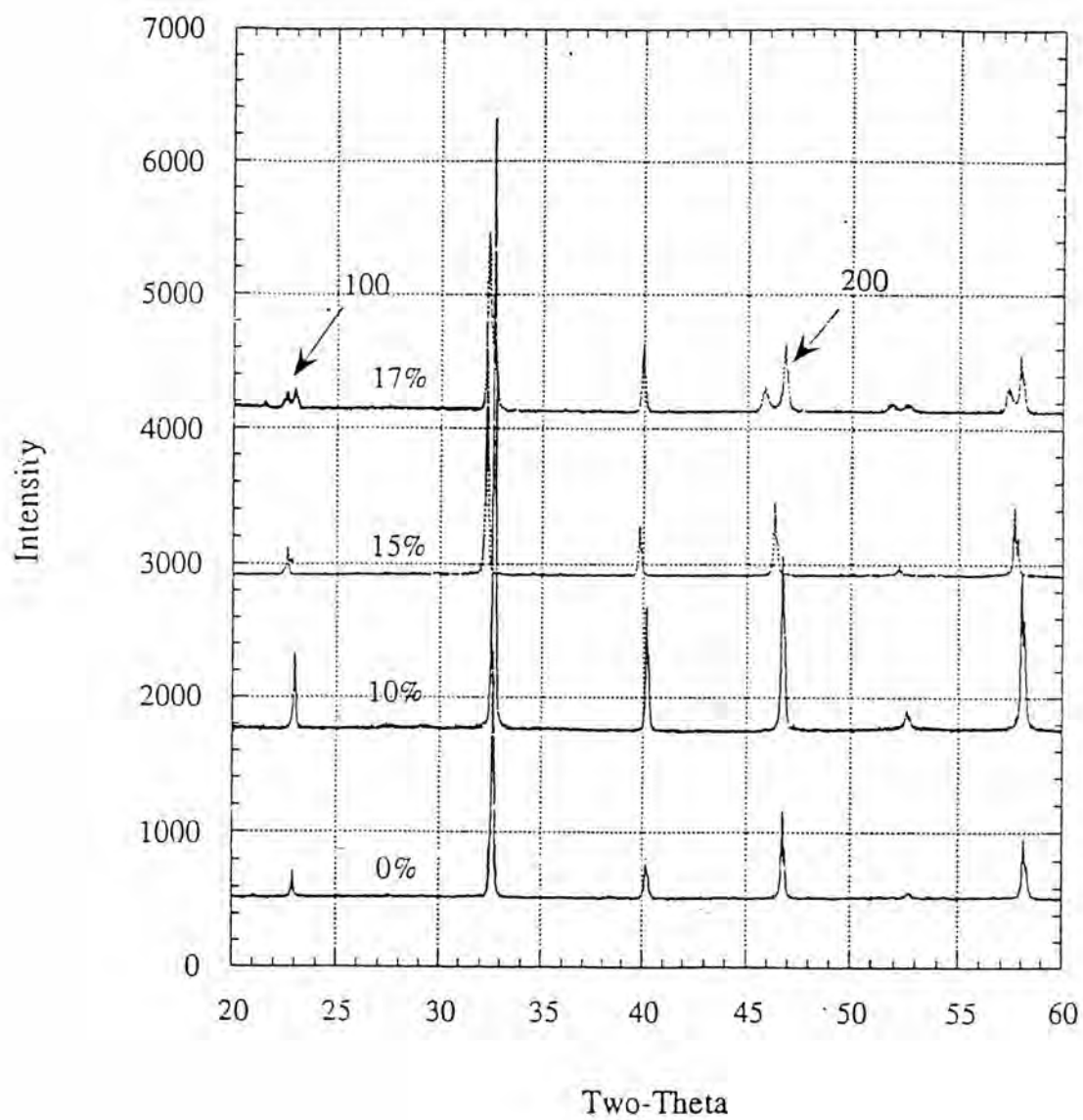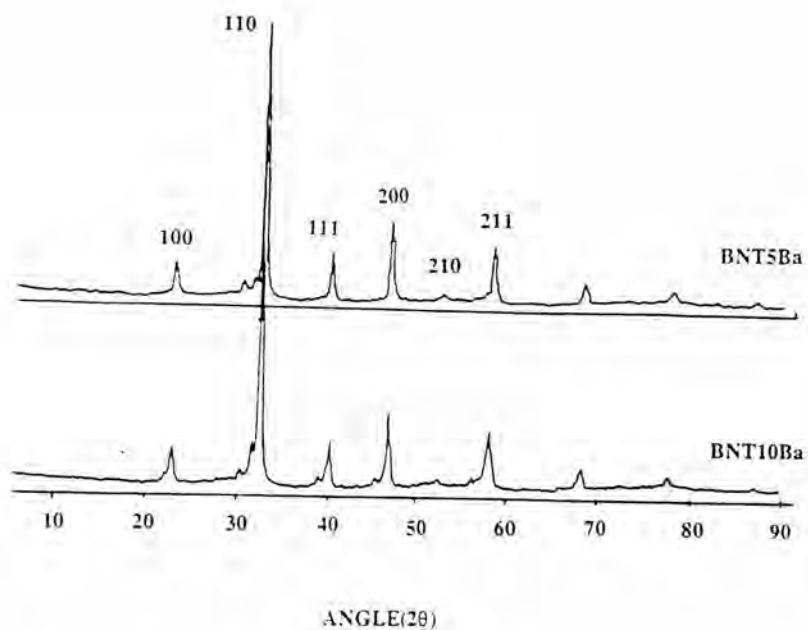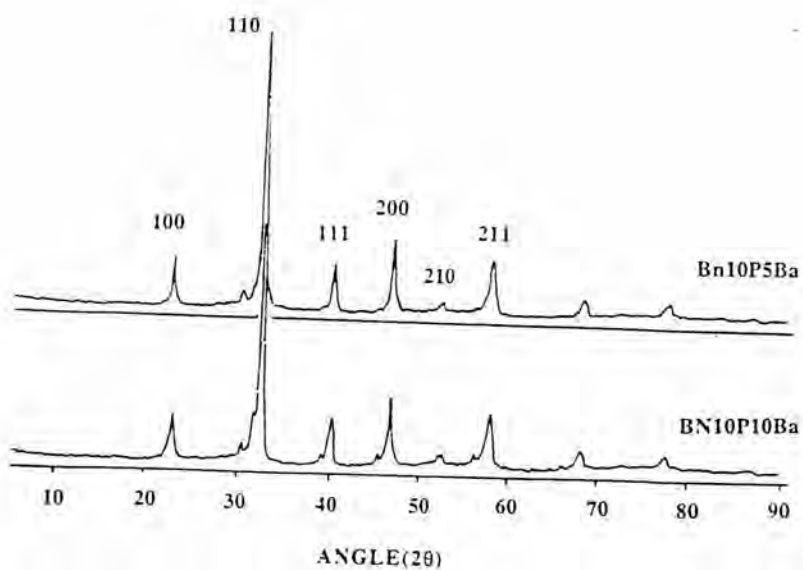
Fig.19 XRD patterns of (1–x)BNT–xPT at room temperature (6)

(a)

(b)

Fig.20 XRD patterns of Ba doped both BNT and 0.90BNT-0.10PT at room temperature   (a) Ba doped BNT   (b)   Ba doped 0.90BNT-0.10PT
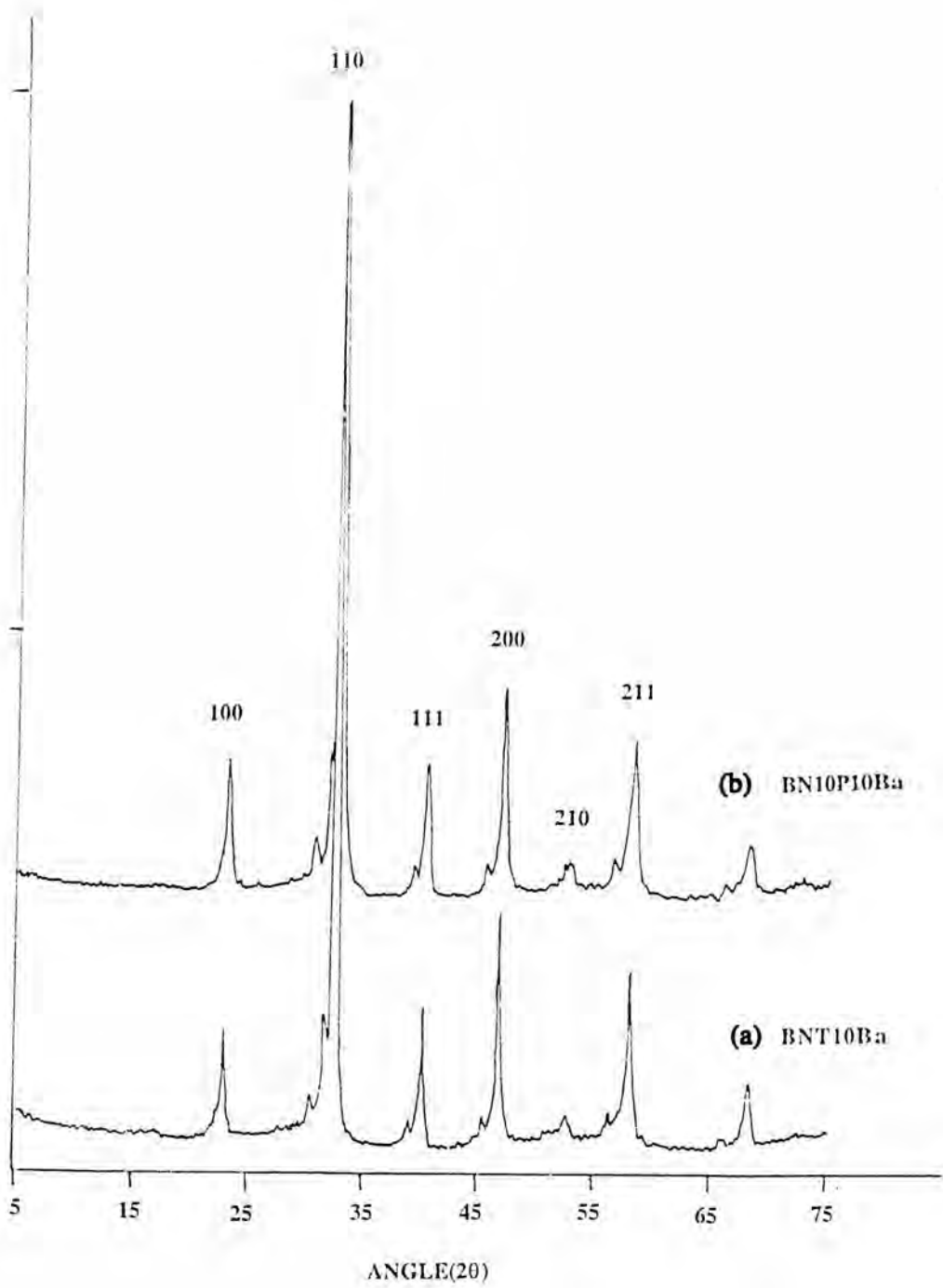
Fig.21 XRD patterns of 10% Ba doped both systems at room temperature
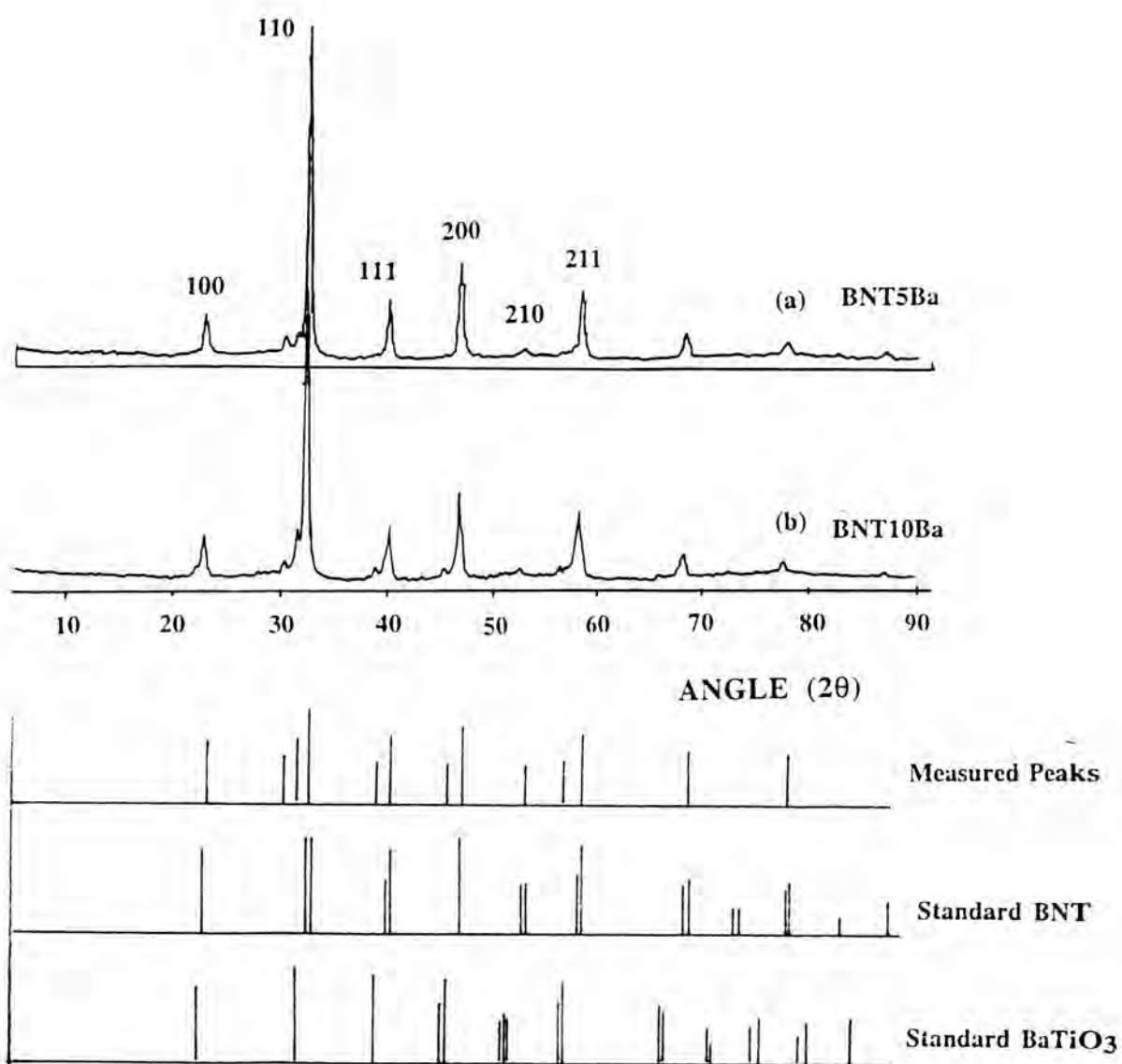(a) 0.90BNT-0.10BaT   (b) 0.90(0.90BNT-0.10PT)-0.10BaT

Fig.22 XRD patterns of (1–x)BNT–xBaT at room temperature

(a) x = 0.05   (b) x = 0.10

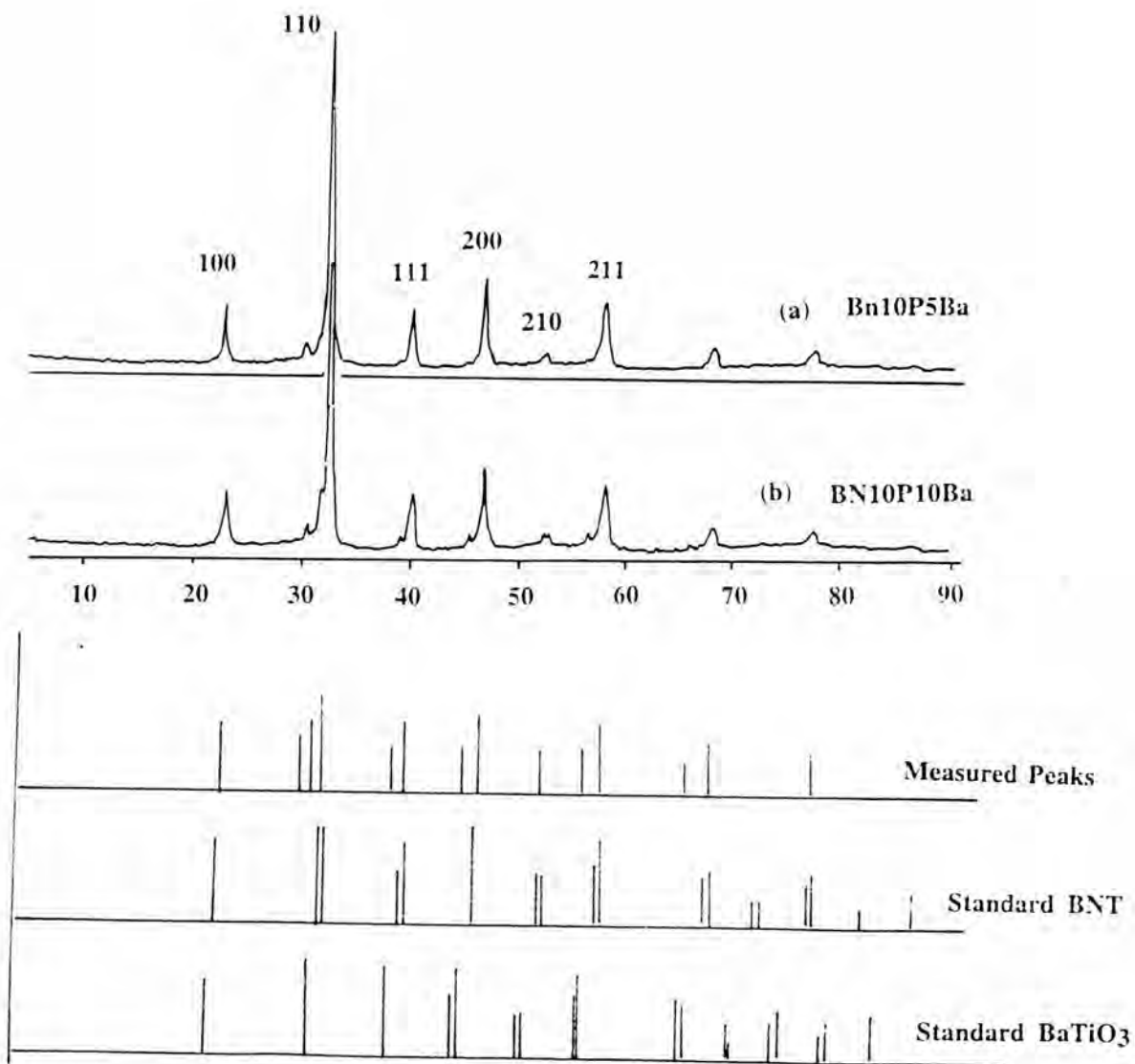Fig.23 XRD patterns of (1−x)[0.90BNT−0.10PT]−xBaT at room temperature

(a) x = 0.05   (b) x = 0.10