CHAPTER

III

XRD ANALYSIS AND TOLERANCE FACTOR

3.1 The Structure of Perovskite Type Ferroelectrics

The perovskite type ferroelectrics with the general composition ABO_3 ($BaTiO_3$, $PbTiO_3$) have in the paraelectric phase, the cubic unit cell shown in Fig 3.1. The space group isO_h^1-Pm3m. Placing the origin at an A ion the atomic coordinates are as follows:

A at 0, 0, 0;

B at 1/2, 1/2, 1/2;

3 O at 1/2, 1/2, 0; 0, 1/2, 1/2; 1/2, 0, 1/2.

With decreasing temperature the crystals transform first in to a tetragonal, polarised phase with symmetry C^1_{4v}- P4mm. The ions are displaced from their original high symmetric position along the polar axis z. Again taking A at the origin the coordinates are:

A at 0, 0, 0;

B at 1/2, 1/2, 1/2 $+\delta Z_B$;

O_I at 1/2, 1/2, δZ_{OI};

$2O_{II}$ at 1/2, 0, 1/2 + δZ_{OII}; 0, 1/2, 1/2 + δZ_{OII}

Though the structure is very simple, it proved exceedingly difficult to determine the small displacements Z. Part of this difficulty is inherent in the well-known phase problem in diffraction analysis and in the existence of a center of symmetry in the undistorted structure . Considerable difficulties arise also from the thermal oscillation parameters. The determination of oxygen parameters with X-rays is particularly difficult in the presence of much heavier lattice constituents; neutron diffraction is much more suitable tool in this case. Nevertheless the X-ray picture may provide an overall information about the tetragonal phase by providing the knowledge the values of lattice parameters'a' and the ratio 'c/a'.

3.2 The Structure of $BaTiO_3$ in Tetragonal Phase:

The first detailed X-ray analysis of untwinned crystals was made by Kanzig (71) using rather unconventional method. Instead of deducting the displacement of great number of reflections (h,k,l) Kanzig measured the change that high order (0,0,l) structure factor undergo when the crystal transforms from the cubic phase in to the tetragonal phase, the displacementsδz were determined from these changes. It was assumed that O_{II} remains undisplaced and that δZTi and δZ_{OI} have opposite signs. The parametersδz at room temperature were found to be

δzTI + 0.0114,$\delta zOI = -0.032$

[$\delta zOII = 0$ assumed]

Using conventional methods, Evans (72), through X-ray analysis of the tetragonal phase at room temperature without introducing the assumptions made in the earlier analysis, deduced two structures which are in very good agreement with the observed intensities. The first solution is very close to Kanzig's result.

$\delta ZTI = 0.012, \delta ZOI = - 0.026, \delta ZOII = 0$

The second solution gave

$\delta ZTI = 0.015, \delta ZOI = -0.024, \delta ZOII = - 0.020$

A neutron analysis was accomplished by Frazer et al (73). It led to the following parameters at room temperature

$\delta ZTI = 0.014$, $\delta ZOI = -0.023$, $\delta ZOII = - 0.014$

If a purely ionic crystal is assumed these parameters correspond to an ionic displacement polarization of 17 * 10^{-6} Coul/cm^2. A neutron diffraction study of the orthorhombic phase has also been accomplished by Shirane et al (74).

3.3 Method of Determination of Parameters 'a' and 'c'

The method we have adopted is a graphical technique and was proposed by Hull and Davey. The method is described below.
The interplaner distance 'd' corresponding to any two planes with Miller indices [h,k,l] for a tetragonal unit cell is given by the relation

$$d^2 = a^2[h^2 + k^2 + l^2/(c/a)^2]^{-1} \quad ---(3.1)$$

Now the equation 3.1 has two unknowns, viz 'a' and 'c/a' to be determined, knowing the 'd' values and corroesponfing h,k,l of the reflections in the XRD graph.The XRD graph provides knowledge about 'd' values only and therefore initially h,k,l corresponding to the reflections and the parameter c/a is determined as below.
Let d_1 and d_2 be the interplaner distances for any two plane sets with corresponding indices [h_1 k_1 l_1] and [h_2 k_2 l_2] respectively. Therefore,

$$d_1{}^2 = a^2 [h_1{}^2 + k_1{}^2 + l_1{}^2/(c/a)^2]^{-1} \quad --- (3.2)$$

Further taking logarithms on both sides of equations (3,2) . We find; and (3.3) and substracting equation 3.2 from equation 3.3

$2\ \mathrm{Log}\ d_2 - 2\ \mathrm{Log}\ d_1 = \mathrm{Log}\ [\ h_1^2 + k_1^2 + l_1^2/(c/a)] -$

$\mathrm{Log}\ [\ h_2^2 + k_2^2 + l_2^2/(c/a)^2]$ ------ (3.4)

The equation 3.4 is used for the graphical technique. Initially the graph of $\mathrm{Log}(h^2+k^2+l^2/(c/a)^2]$ for various values of c/a between 0.4 to 1.8 and for different values of h,k,l is plotted. The $\log\ [h^2+k^2+l^2/(c/a)^2]$ is plotted as abscissa, while c/a is the ordinate. While selecting the scale on abscissa, the scale is selected as a negative logarithmic scale such that $-\mathrm{Log}[\ h^2 + k^2 + l^2 / (c/a)^2]$ is plotted automatically. Usually, 10 cm equals one period of logarithm.

Now the values of 2Logd are ploted on a transparant strip.

The scales selected for $\mathrm{Log}[\ h^2 + k^2 + l^2 /(c/a)^2]$ and 2 log d are the same. Now the transparent strip is slided over the graph of $\mathrm{Log}[\ h^2 + k^2 + l^2 / (c/a)^2]$ and c/a, such that each 2logd value matches with some $\mathrm{Log}[\ h^2 + k^2 + l^2 / (c/a)^2]$ values. This will occur only for a c/a value, as seen from equation 3.4. The corresponding parameters c/a and h,k,l value are determined for every value of the interplaner distance. Using this information the parameters 4 a , c and c/a are calculated.

In the present investigation, we have tried to index the following planes and have determined the values of parameters c, a and c/a. The planes selected are (1,0,0),(0,0,1)..........

3.4 Tolerance Factor

For the body centered perovskite structure an empirical relation is defined on the basis of the geometric consideration, which is expected to predict the possibility of the tetragonal distortion. The parameter that is defined through this relation is the tolerance factor, t(75) where t- is given by

$$t = \frac{[\ R_A + R_O]}{(2)^{1/2}[R_B + R_O]} \qquad --(3.5)$$

Where R_A, R_B and R_O are the radii of large cation, small cation and anion respectively. Referring to Fig 3.1 for the unit cell of the perovskite, the length $R_A + R_O$ should be $(2)^{1/2}*a$, where 'a' is the lattice parameter. The length $R_B + R_O$ equals length 'a'. Therefore, for the cubic system

$$t = \frac{[\ R_A + R_O]}{(2)^{1/2}[R_B + R_O]} = 1 \qquad -------(3.6)$$

The system may exhibit a tetragonal distortion if $[\ R_A + R_O] > (2)^{1/2}*[R_B + R_O]$ i.e. $t > 1$. It is to be noted that the factor determined above is based on the hard sphere model, and one would treat the tolerance factor only qualitatively to predict the occurrence of the ferroelectricity.

We have modified this relation to calculate the tolerance factor for fractionally substituted solid solutions, where t is defined as

$$t = x\ t_s + (1-x)\ t_p \qquad -----------(3.7)$$

Here x is the molar concentration and t_s and t_p are the tolerance factors for the substituted and parent species. The tolerance factors calculated for the systems

$Ba\ Ti_{(1-x)}Sb_{x/2}Mn_{x/2}O_3$ and

$Ba\ Ti_{(1-x)}Sb_{x/2}Co_{x/2}O_3$ are given in table 3.1. From the table it is observed that the t is independent of x for SbMn composition, while for the SbCo composition it increases slowly with x. At this juncture what one would predict is as below.

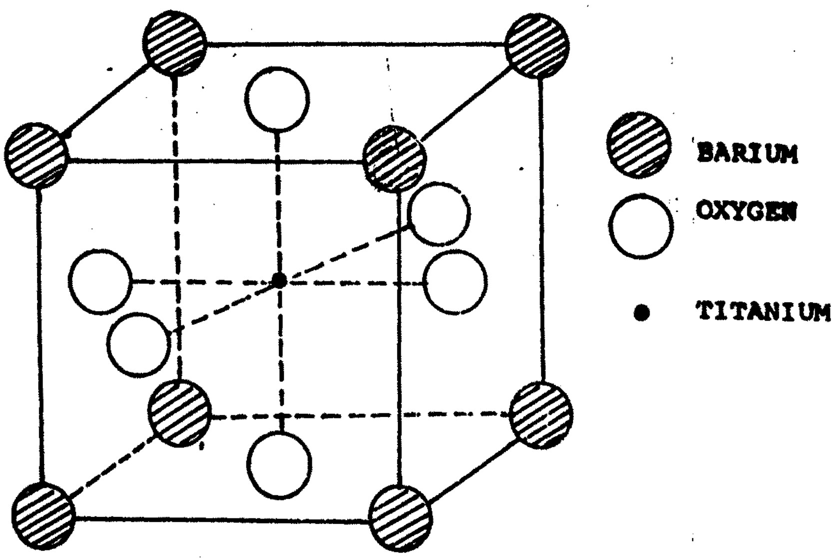

Fig. 3.1 : THE UNIT CELL OF THE CUBIC PEROVSKITE TYPE STRUCTURE $BaTiO_3$

Table No. 3.1 : Variation Tolerance Factor with Concentration

x	t	
	SbCo	SbMn
0.00	0.9530	0.9530
0.020	0.9532	0.9530
0.050	0.9534	0.9530
0.100	0.9538	0.9530
0.200	0.9544	0.9530
0.400	0.9558	0.9530

The ferroelectric behavior exhibited by the SbMn and SbCo compositions should be mainly due to the polarizability of the statistically distributed Ti, Mn, Sb and Co ions and the geometric factors do not favor any additional contribution to the ferroelectricity of the compositions studied.

3.5 The Structural Investigation:

The X-ray diffractographs of the presintered and final sintered compounds are determined and the structural parameters are calculated using the graphical method (Section 3.3) The Fig. 3.2 to 3.8 show the diffraction patterns for a few selected compositions as indicated in the figure captions. A few observations are note-worthy.

i) The reflection for 'd' nearly $4A^{o}$ is not split up to show separate reflections for plane(0,0,1) and (1,0,0) . But the peak is sufficiently wide and the reflections mask each other. The remaining part of the diffractograph confirm the structure to be

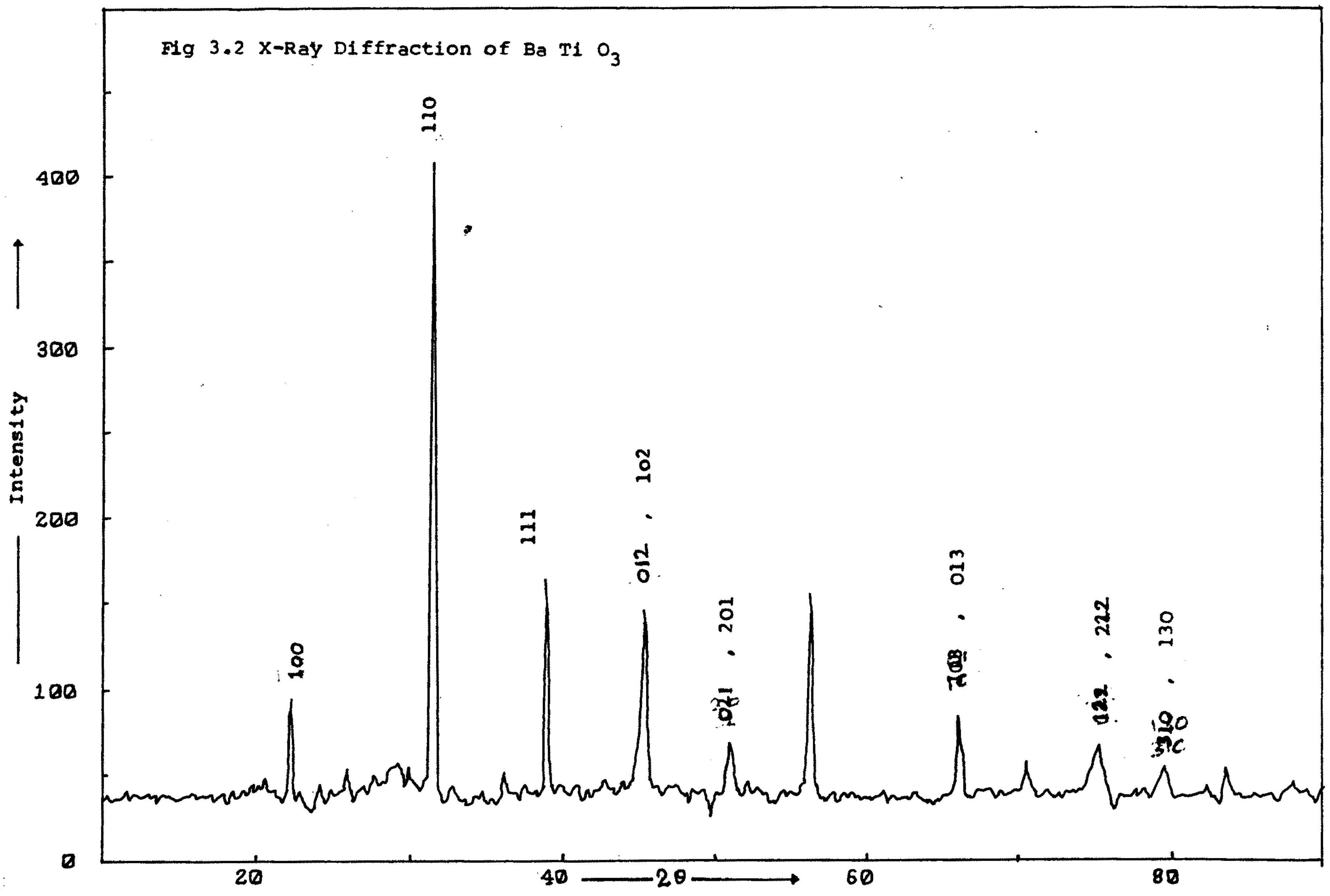

Fig 3.2 X-Ray Diffraction of Ba Ti O_3

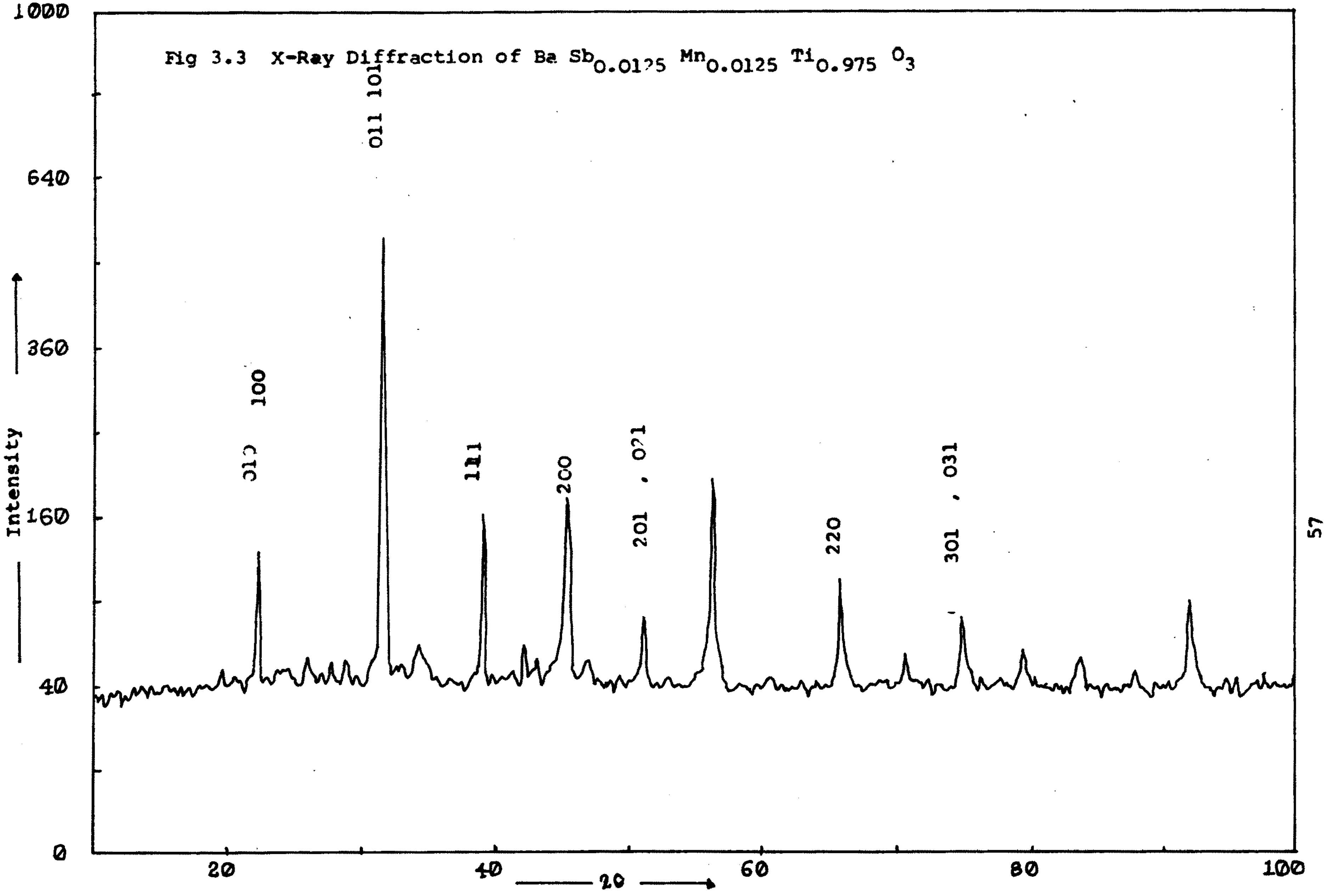

Fig 3.3 X-Ray Diffraction of Ba $Sb_{0.0125}$ $Mn_{0.0125}$ $Ti_{0.975}$ O_3

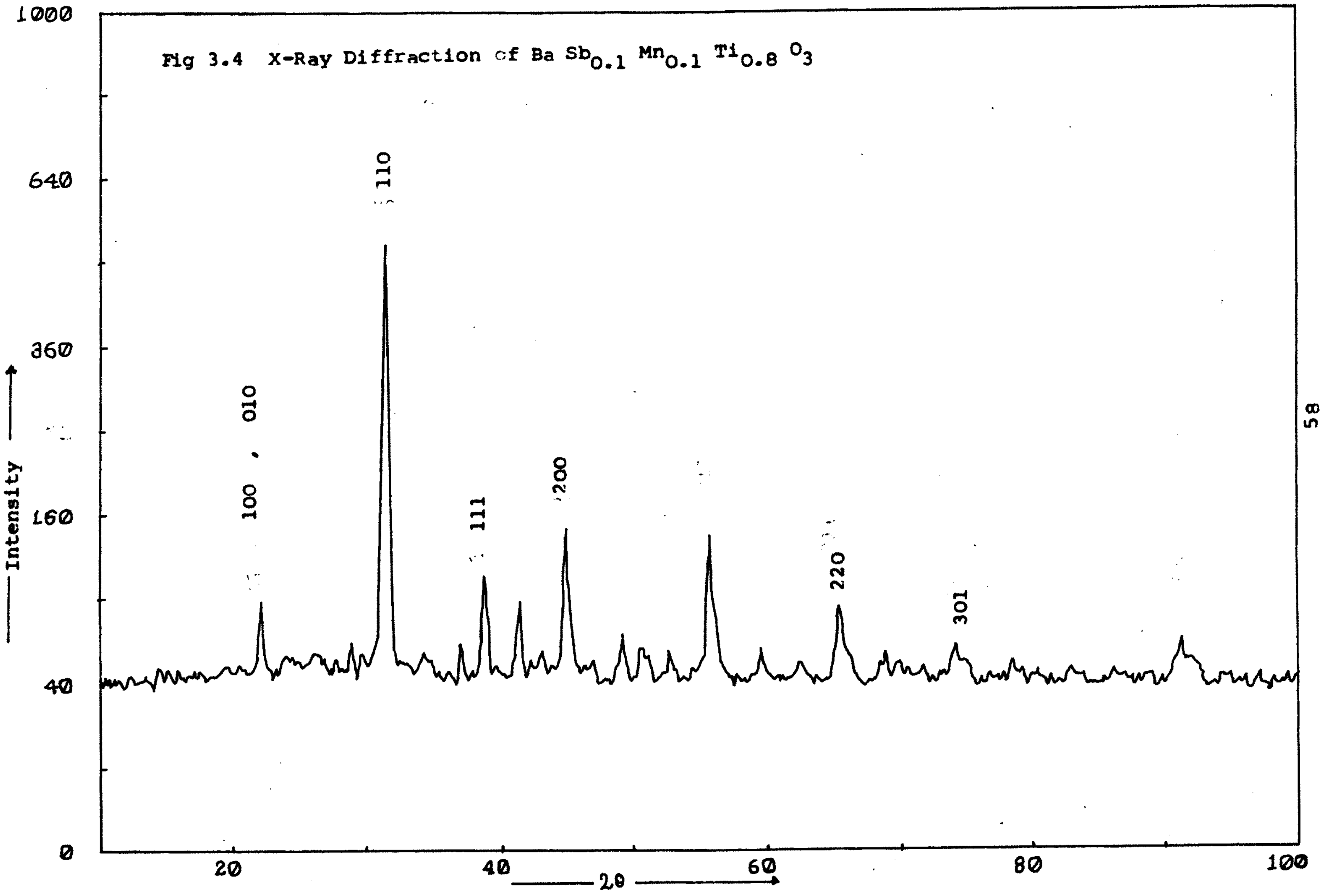

Fig 3.4 X-Ray Diffraction of Ba $Sb_{0.1}$ $Mn_{0.1}$ $Ti_{0.8}$ O_3

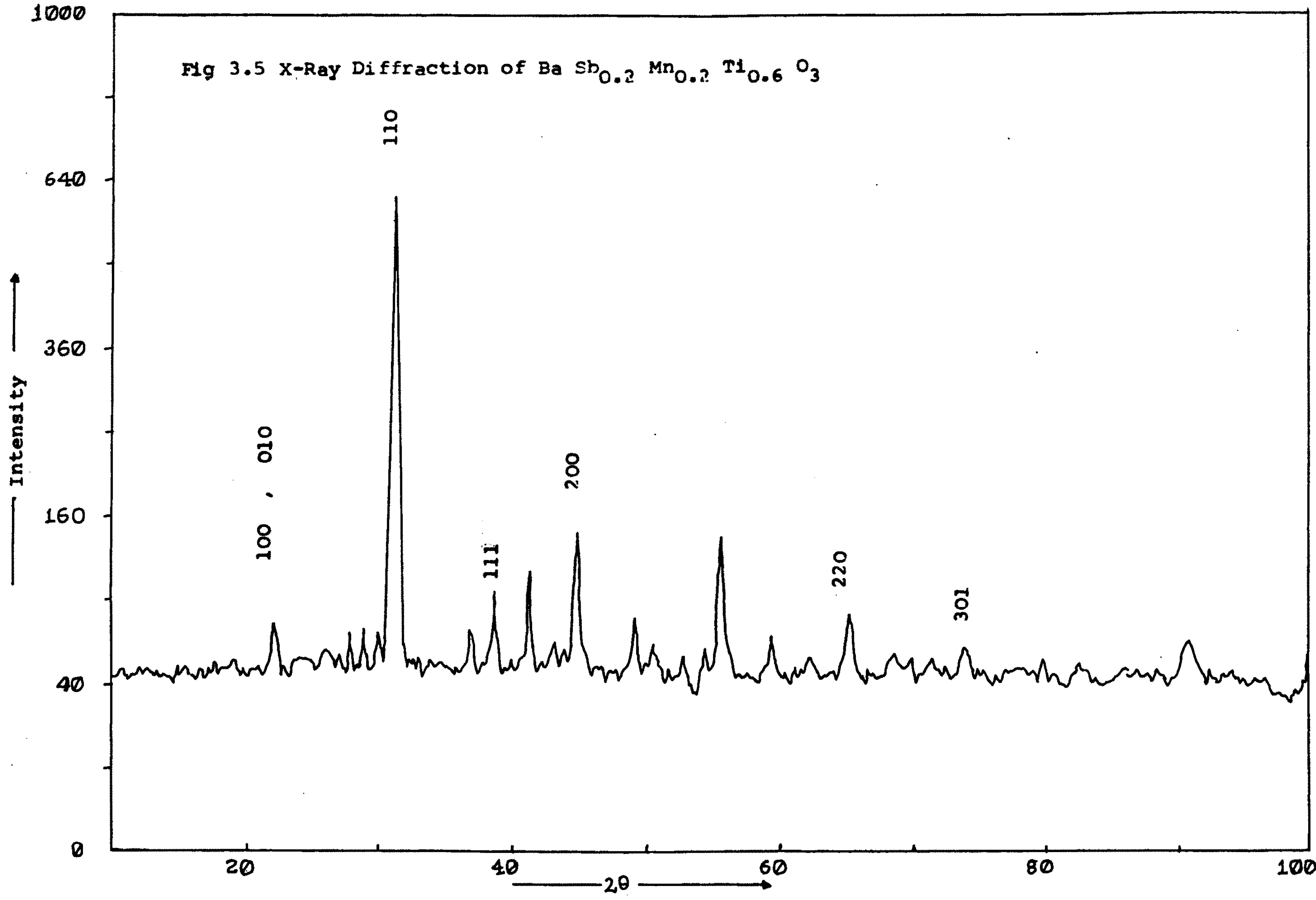

Fig 3.5 X-Ray Diffraction of Ba $Sb_{0.2}$ $Mn_{0.2}$ $Ti_{0.6}$ O_3

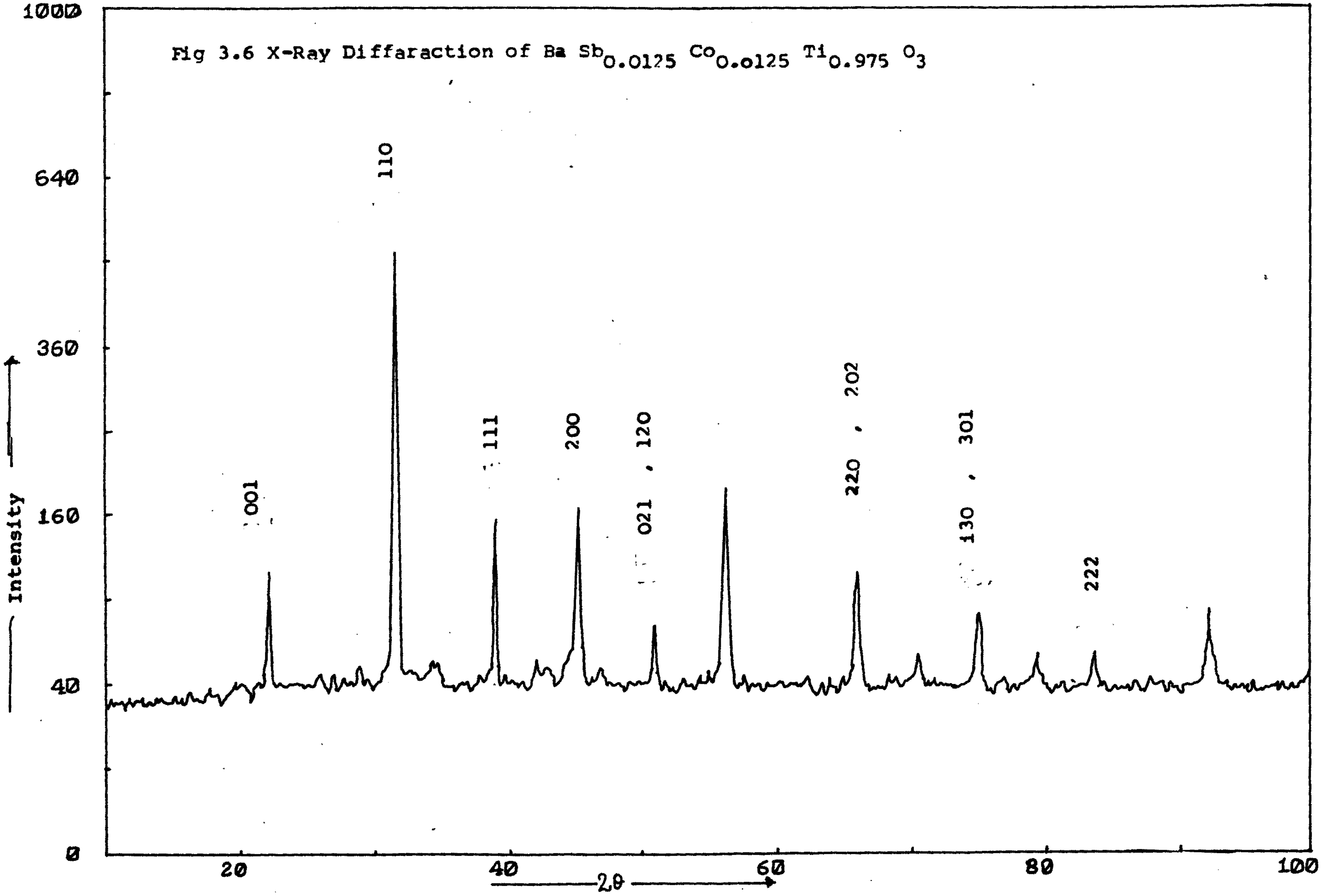

Fig 3.6 X-Ray Diffaraction of Ba $Sb_{0.0125}$ $Co_{0.0125}$ $Ti_{0.975}$ O_3

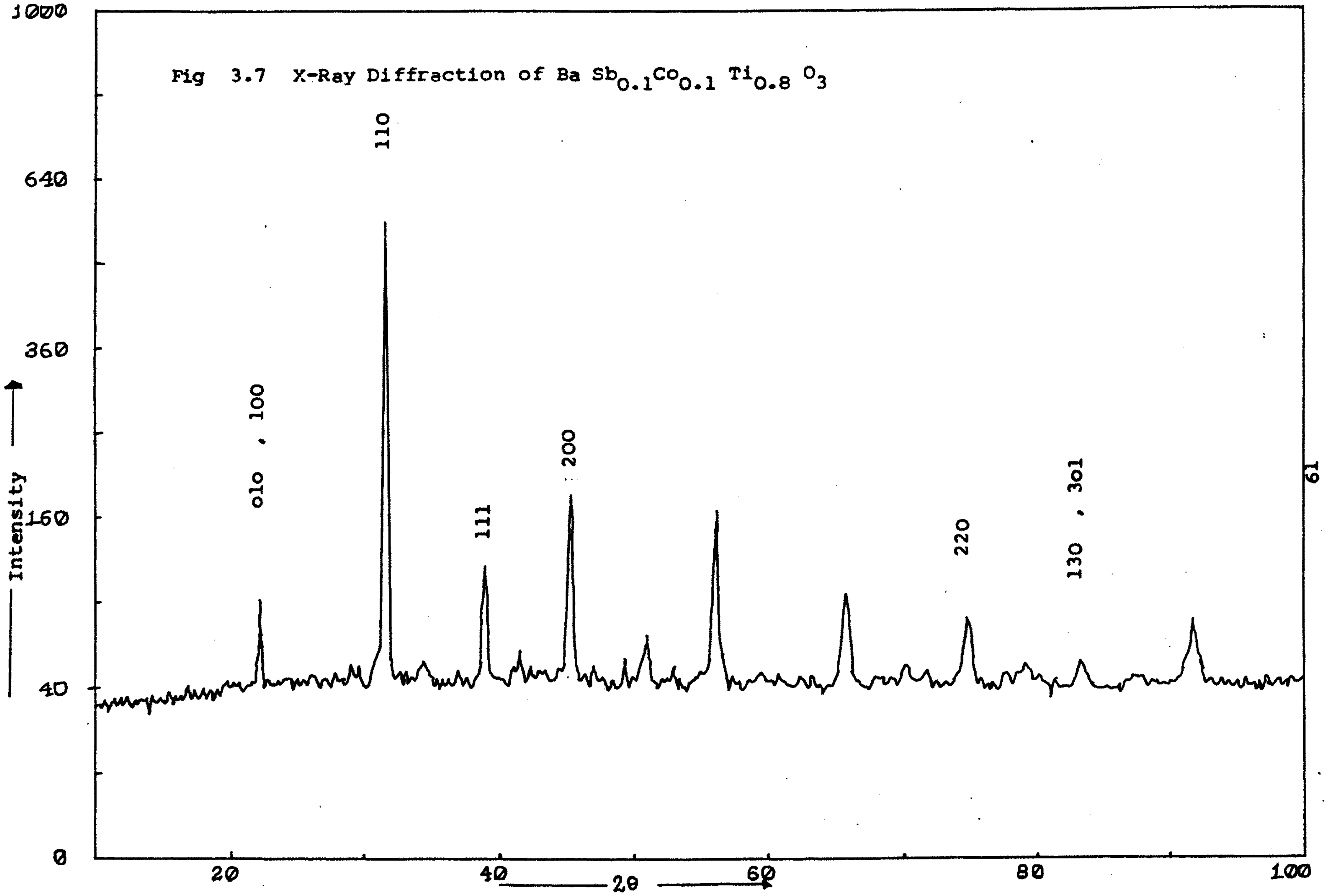

Fig 3.7 X-Ray Diffraction of Ba $Sb_{0.1}Co_{0.1}Ti_{0.8}O_3$

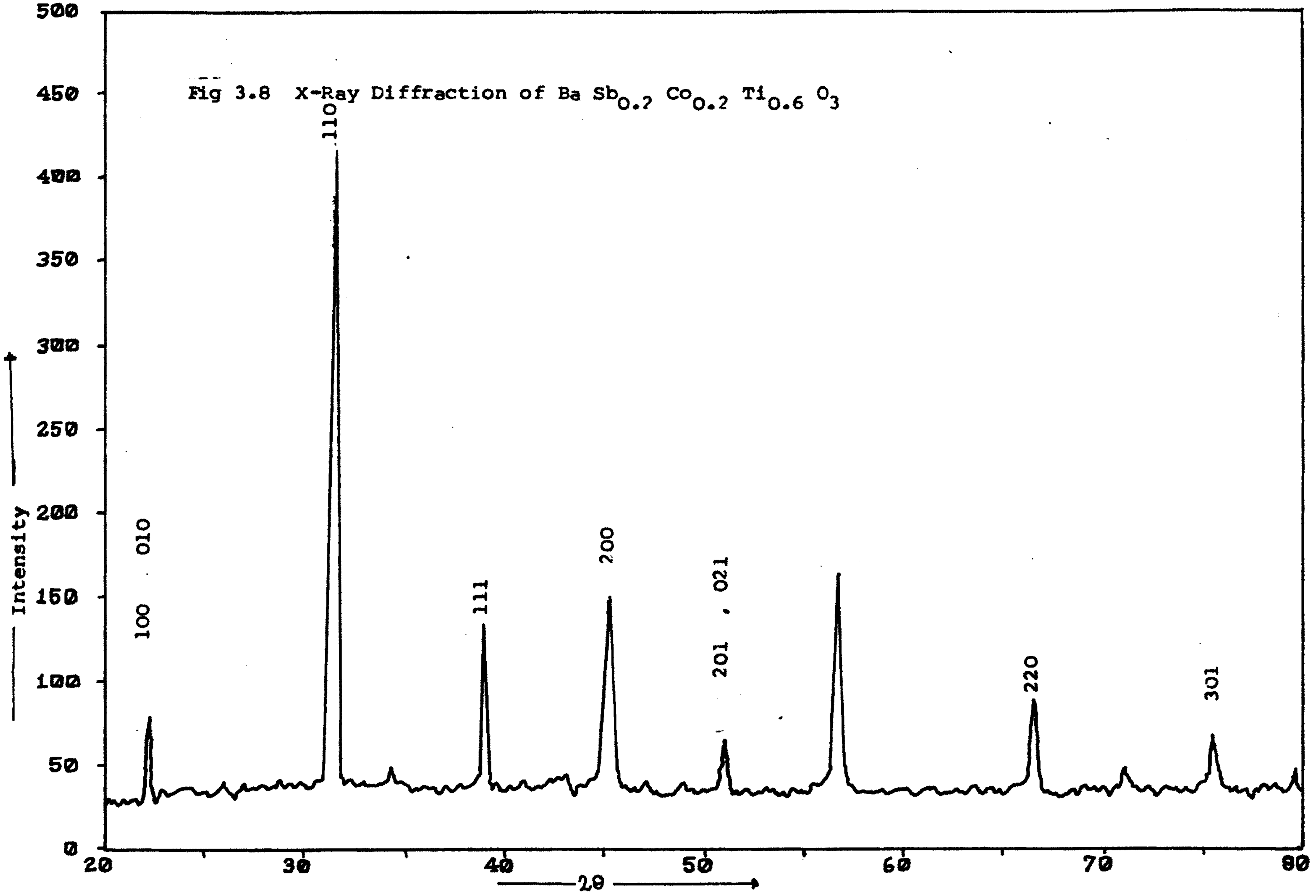

Fig 3.8 X-Ray Diffraction of Ba $Sb_{0.2}$ $Co_{0.2}$ $Ti_{0.6}$ O_3

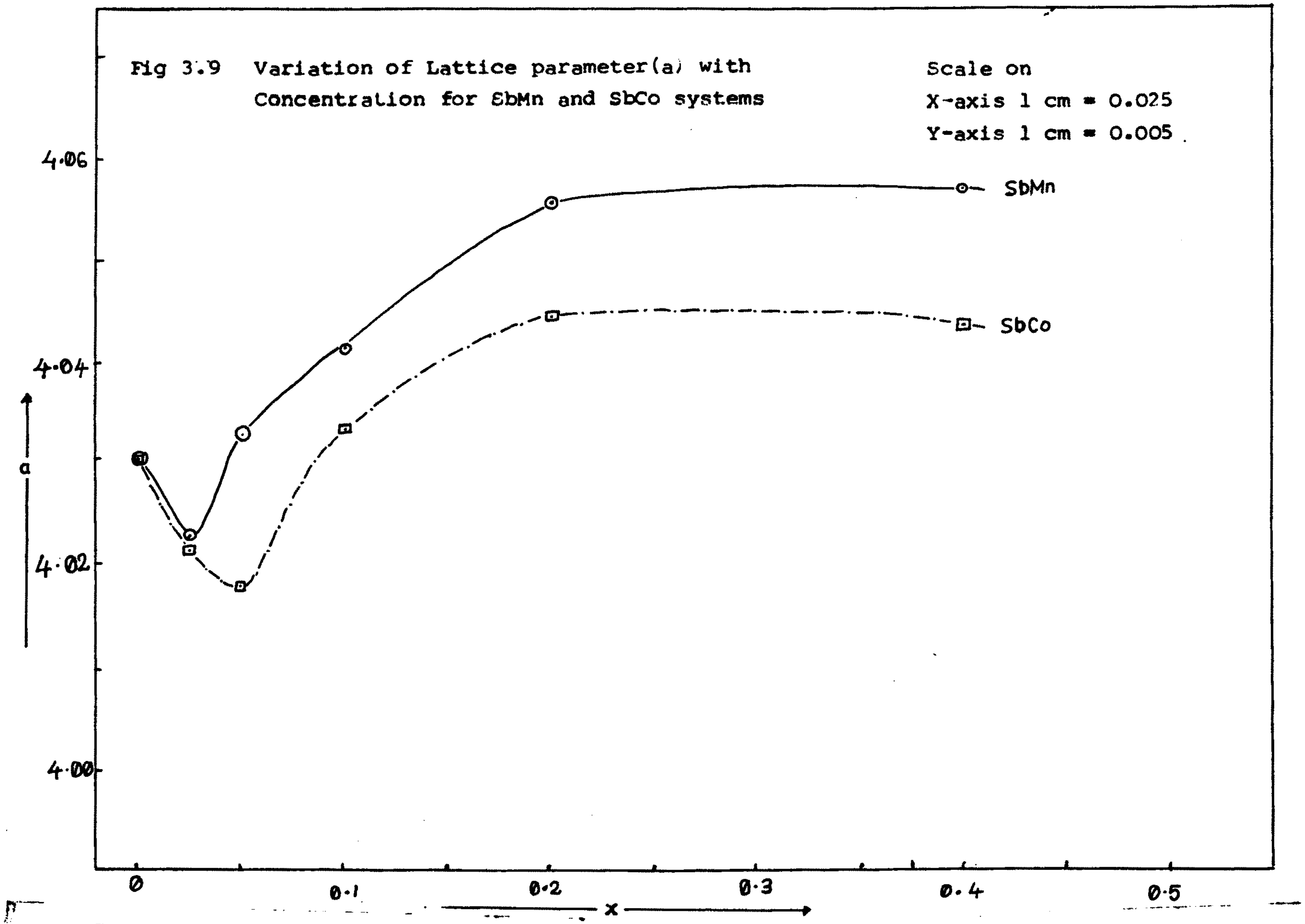

Fig 3.9 Variation of Lattice parameter(a) with Concentration for SbMn and SbCo systems

tetragonal and not a cubic one (59). It is observed the c/a ratio for all these compositions is very nearly equal to that of $BaTiO_3 \approx 1.01$.

ii) For higher values of '2O' the peaks are broadened. This feature may indicate a statistical distribution associated with the lattice parameters. The statistical distribution could be because of micro chemical inhomogeneties within a grain. Such inhomogeneties are predicted to be predominant at the grain boundary (64).

Table No. 3.2: Lattice Parameters for

$Ba\ Ti_{(1-x)}Sb_{x/2}Mn_{x/2}O_3$

Concentration	Lattice Parameters		c/a
x	a A^{o}	cA^{o}	
0.00	3.9807	---	1.01
0.025	3.9655	4.0200	1.0125
0.050	3.9863	4.0262	1.01
0.100	4.0025	4.0425	1.01
0.200	4.0316	4.0719	1.01
0.400	4.0342	4.0745	1.01

Table No. 3.3: Lattice Parameters for

$Ba\ Ti_{(1-x)}Sb_{x/2}Co_{x/2}O_3$

Concentration	Lattice Parameters		c/a
x	a A^{o}	cA^{o}	
0.025	3.9628	4.0024	1.01
0.050	3.9555	3.9950	1.01
0.100	3.9874	4.0273	1.01
0.200	4.0085	4.0486	1.01
0.400	4.0070	4.0478	1.01

The values of a,c,& c/a for these compositions are given in table 3.2 , 3.3. The $BaTiO_3$ was also prepared within the same sintering schedule and the parameters'a','c','c/a' are determined for this product also to compare systematics of variations of these parameters for the SbMn and SbCo compositions. It is observed that the c/a is insensitive to the variation in x . c/a remains constant at 1.01 at that of $BaTiO_3$.

The Fig 3.9 shows variation of 'a' with 'x' for the SbMn and SbCo systems. It is observed that the 'a' decreases initially and then increases monotonically till x =0.2. For x between 0.2 and 0.4 the variation in 'a' is very mild. Therefore we except the changes in the properties of these materials at very low values of x. With increase in the value of x, we may find a saturation in the physical parameters of these compositions. This happens to be a preliminary analysis. It is discussed in section (3.4) that the tolerance factor doesn't change much with the increasing concentration of SbCo and SbMn (The change in t is only 0.27 % for increase in x up to 0.4 for SbCo system.) The observed variation of 'a' with 'x' should therefore be correlated to modifications in the nongeometric interactions of the substituted system.