Thermal and Structural Characterization of Lead Free Relaxor Bismuth Sodium Titanate: Processing Optimization for Phase Pure Material

K. S. Ojha, K. N. Singh and P. K. Bajpai[*]

Advance Materials Research Laboratory, Department of Pure & Applied Physics
Guru Ghasidas Vishwavidyalaya, Bilaspur-495009, (C. G.) India

*Corresponding Author:
Prof. P. K. Bajpai
Head & Dean
Department of Pure & Applied Physics
Guru Ghasidas Vishwavidyalaya, Bilaspur-495009
Chhattisgarh, India

Abstract:

Bismuth Sodium Titanate (BNT), was synthesized using solid state reaction route by optimizing the sintering temperature and controlling the heating and cooling rate during calcination and sintering. The phase evolution was studied by calcining the precursor materials at varying temperatures and analyzing the phase at each temperature though XRD. The calcined phase pure material was obtained at 800°C. The calcined powders sintered at different temperatures in the range 850-1000°C when analyzed through XRD shows sintering optimization at 950°C ($\approx$81%). The rhombohedral structure was stabilized and the estimated lattice parameters closely match with those reported earlier. The phase transitions sequence was confirmed using DSC. The coexistence of two phases in large temperature range and heat of formation due to antiphase and in-phase tilting is significantly different. The ferroelectric-antiferroelectric phase transition is not structural in character.

Keywords: Lead free relaxor, X-ray diffraction, differential scanning calorimetry, Phase transition

1. Introduction

Perovskite-based ceramic materials are being investigated due to their device applications [1, 2]. Most of these materials are lead bearing compounds which for environmental, health and social reasons are not preferred in devices and attempts are being made to eliminate the lead content from these materials. Bismuth Sodium Titanate, $(Bi_{0.5}Na_{0.5}TiO_3)$, is considered to be one of the excellent candidates among the lead- free ferroelectric materials with large remnant polarization, high Curie temperature and shows diffuse phase transition [3]. In addition to DPT, two more phases, cubic and tetragonal in the temperature ranges from 500°C to 540°C and the tetragonal and the rhombohedral phases from 255°C to 400°C are experimentally observed [4]. Crystal structures in cubic, tetragonal and rhombohedral phase of BNT have been studied [5]. The ferroelectricity in BNT ceramic is attributed to $(Bi_{1/2} Na_{1/2})^{2+}$ ions, especially Bi^{3+} ions at the 'A' site of the perovskite structure and due to rhombohedral symmetry below 200^0C. The peculiar phase transition behavior of BNT has attracted considerable attention and the different dielectric anomalies and electrical state of each phase has been examined [6, 7].

The peculiarity of BNT phase transition between 200°C and 300°C in the context of incommensurate polar ↔ commensurate polar phase transition with increasing temperature has been discussed [8] and it has been suggested that the size of the incommensurate phase to be of the order of nanometers, accounting for the structural disparity between the incommensurate phase with low symmetry and the ordered rhombohedral to tetragonal matrix. Phase transition in BNT is an exceptional case of ferroelectric phase transition in that the point group of ferroelectric phase is not a subgroup of a high temperature paraelectric (PE) phase.

In spite of these studies, the information about the nature of the phase transitions in BNT is still not coherent after several different explanations for the peculiarities of phase transition behaviour. Another problem due to these peculiarities is associated with BNT

based relaxors is the very low packing (sinter-ability). Therefore, the synthesis of BNT ceramics, using solid-state reaction, is attempted under controlled calcination and sintering conditions to determine the structural and phase characterization to understand the peculiarities of phase transition behaviour.

2. Experimental

2.1. Synthesis of the BNT Powders:

The stoichiometric amounts of Na_2Co_3, Bi_2O_3 and TiO_2 (Loba Chem., purity 99.9%) were used as starting materials. The oxides and carbonates were mixed thoroughly and calcined in silica crucible at 400ºC, 600ºC and 800ºC for 4 hours at each temperature. The calcined powder exhibiting single phase was pressed into pellets. The pellets were then sintered at temperatures 850ºC, 900ºC, 950ºC and 1000^0C for 4 hours at each temperature. The pellets sintered at different temperatures were used for XRD analysis for sintering optimization.

2.2. Characterization:

The X-ray powder-diffraction (XRD) patterns were obtained with Rigaku MiniFlex diffractometer using Cu-Kα radiation within range of 20° to 80° with a step of 0.2° and a counting time of 2 s. The phase transition behaviour of calcined BNT powder was measured with Differential Scanning Calorimeter (DSC-60, Shimadzu, Japan) in the temperature range from 30ºC to 510ºC at the rate of 10ºC/minute.

3. Result and Discussion:

3.1. Structural Characterization:

. The XRD patterns of the sample calcined at 400°C, 600°C and 800°C are shown in Figure 1. For the sample calcined at 400°C, XRD peaks due to Bi_2O_3, Na_2CO_3 and TiO_2 were detected, while the one that calcined at 600°C showed the peaks due to Bi2O3, Na_2CO_3, and TiO_2 along with BNT phase. The XRD pattern of sample calcined at 800°C showed the pure

BNT ceramic phase. The phase pure material stabilized in rhombohedral structure. The lattice parameters, observed peaks indexing along with d-spacing are tabulated in Table 1.

In order to optimize the sintering, the XRD patterns of the sintered material at each sintering temperature are measured and shown in Figure 2. The lattice parameters obtained after each sintering were used to calculate the density of the unit cell and compared with the experimental density measured using Archimedes method. It is observed that the density of the material increases with increasing temperature up to 950°C and then start decreasing. The maximum density observed at 950°C is 81.3% that of theoretical density as shown in Table 2.

3.2 Phase Transitions Characterization:

Figure 3 shows the DSC thermograph of Bismuth Sodium Titanate. It shows two exothermic peaks with broad temperature range having maxima at 324°C and 498°C. The first DSC peak starts at 334°C and spans up to 344.4°C. The small heat of transition associated with the peak (2.45 J/g) shows that the phase transition is dominantly second order. The second peak ranges between 459.7°C to 514.4°C and is accompanied by relatively large heat of formation (1.7kJ/g). The observed thermal peaks match closely with reported phase transitions. However, no peak is observed around 200°C where dielectric anomaly is observed.

Phase transitions sequence in BNT has been studied widely by neutron powder diffraction study [5] and reports that with decreasing temperature, BNT transforms from cubic Pm3m to tetragonal *P4bm* and then to rhombohedral *R3c* with coexistence regions between them. The sequence of phase transitions from the high temperature prototypic cubic structure (above 813°K), to a tetragonal phase that coexists with cubic phase between 813-773°K. Below this temperature, the system exists in pure tetragonal phase up to 673°K. Between 673-528°K, both tetragonal and rhombohedral phases coexist. Structure remains pure rhombohedral in the temperature range (5-528°K). Coexisting tetragonal/cubic (773-

813°K) and rhombohedral/tetragonal phases thus have a temperature range of 40 and 145°K respectively. The rhombohedral *R3c* space group with $a_H = 5.4899$ (2) A^0, $c_H = 13.0605$ (8) A^0 is polar with parallel cation displacements along the [111] pseudo cubic direction along with antiphase a$^-$a$^-$a$^-$ oxygen octahedral rotations with a tilt angle $\omega = 8.24°$ (4). The tetragonal phase, space group P4bm, with $a_T = 5.5179$ (2) A^0, $c_T = 3.9073$ (2) A^0 possesses an unusual combination of in phase, a^{0}a^{0}c$^+$ oxygen octahedral tilts $\omega = 3.06°$ (2), and anti-parallel cation displacements along the polar axis. The transition from ferroelectric to antiferroelectric phase reported at 493°K is not associated with structural changes. XRD results in the present study at room temperature gives rhombohedral phase with close values of lattice parameters as observed in the earlier reports. Thus, the endothermic peaks observed in DSC measurements at 597°K ranging between 607-617.4°K and at 771°K spanning between 733-787°K matches very closely with the coexisting region of rhombohedral/tetragonal phase and cubic/tetragonal phases, respectively. Non-observance of peak in 493°K region associated with ferroelectric-antiferroelectric phase transition further confirms the non-structural character of this phase transformation. Further, the heat of formation associated with tetragonal-rhombohedral phase transformation is relatively small. This may be due to the fact that large oxygen octahedral tilt is in antiphase in which the adjacent octahedra are tilting oppositely, thus compensating the energy requirement to a large extent. This may also be due to much larger range of temperature in which two phases coexist.

4. Conclusions:

The preliminary structural and differential scanning calorimetric measurements performed on BNT ceramic confirms the phase pure material having phase transition sequence as recently reported by neutron diffraction study. Further, it suggests that the heat of formation associated with antiphase tilt of oxygen octahedra is much smaller than that

associated with in phase tilt and ionic displacement. It also confirms the non-structural character of ferroelectric-antiferroelectric phase transition.

References:

[1]   Cross L. E., Tang J. S., Newnham R. E., Ferroelectrics, 1980, 23, 187-191.

[2]   Nomura S., Uchino K., Ferroelec., 1983, 50, 197-202.

[3]   Rupprecht G., Bell R. O., Phys. Rev. A, 1964, 135, 748-752.

[4]   Suchanicz J., Poleder K., Kania A., Handerek J., Ferroelec., 1988, 77, 107-110.

[5]   Jones G. O., Thomas P. A., Acta Cryst. B, 2002, 58, 168-178.

[6]   Zvirgzds J. A., Kapostins P. P., Zvirgzde J. V., Krunzina T. V., Ferroelec., 1982, 40, 75-77.

[7]   Hong K. S., Park S. E., J. Appl. Phys., 1996, 79, 388-392.

[8]   East J., Sinclair D. C., J. Mater. Sci. Lett., 1997, 16, 422-425.

CAPTIONS

Figure 1.

XRD pattern of Sodium Bismuth Titanate calcined at 400°, 600° and 800°C.

Figure 2.

XRD pattern of Sodium Bismuth Titanate sintered at 850°, 900°, 950° and 1000°C.

Figure 3.

Thermal analysis of Sodium Bismuth Titanate.

Table 1.

Lattice Parameter, indexing of the observed peaks along with d-spacing of BNT sample (calcined at 800^0C).

Table 2.

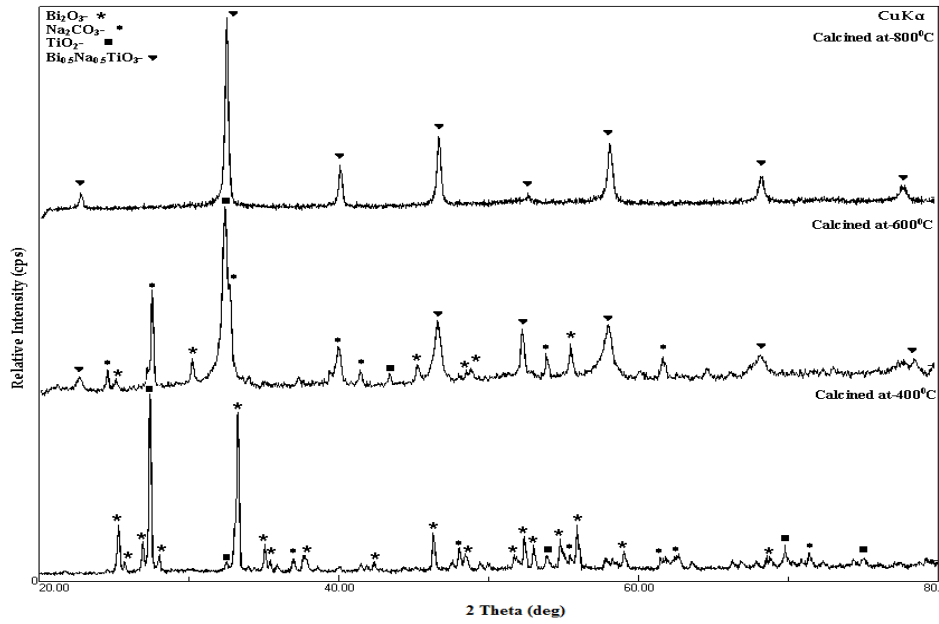Variation of experimental and theoretical densities with sintering temperatures of BNT ceramic.
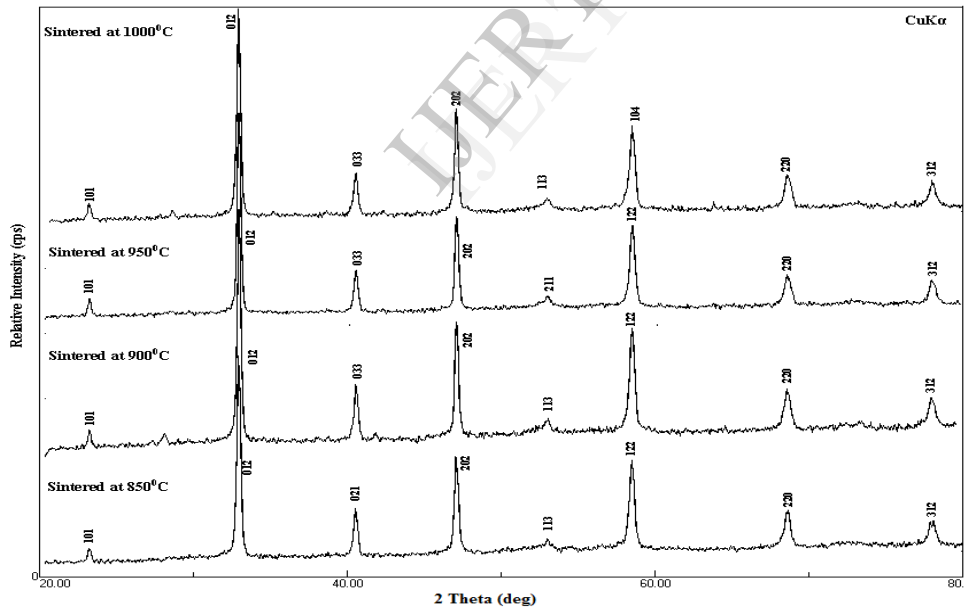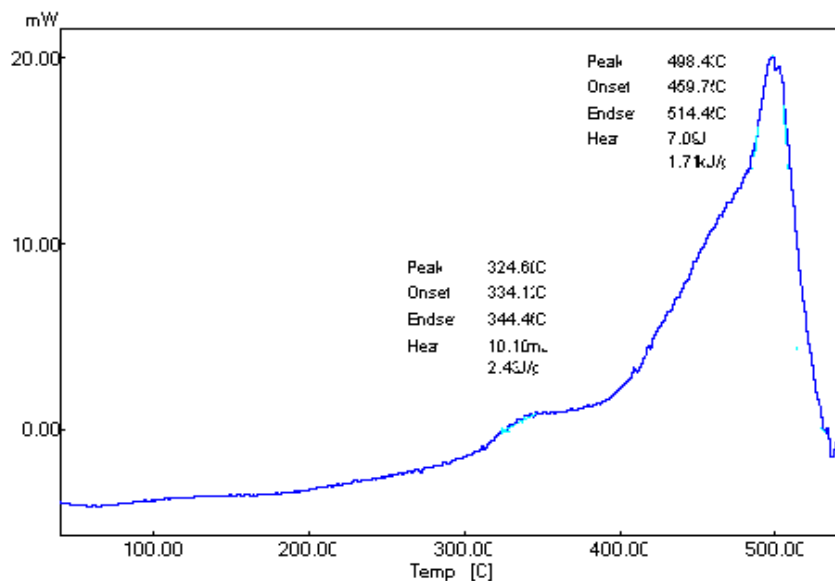
Figure 1

Figure 2

Figure 3

Table 1

Lattice Parameters			a_H= 5.4899A° c_H= 13.0605A°			
Cell Volume			V= 393.6301(A°)^3			
Standard Deviation			0.00044 A°			
Crystal structure			Rhombohedral			
Line	d-spacing (A°)		Intensity (arb)	Indices (h, k, l)	2θ degree	
	Obs.	Cal.			Obs.	Cal.
1	3.8801	3.8801	15	1 0 1	22.90	22.90
2	2.7427	2.7424	100	0 1 2	32.62	32.62
3	2.2402	2.2409	29	0 2 1	40.22	40.21
4	1.9395	1.9401	42	2 0 2	46.80	46.78
5	1.7348	1.7346	15	1 1 3	52.72	52.73
6	1.5838	1.5843	39	1 2 2	58.20	58.18
7	1.3725	1.3725	23	2 2 0	68.28	68.28
8	1.2276	1.2273	19	3 1 2	77.72	77.74

Table 2

Sintering Temperature→	850^{0}C	900^{0}C	950^{0}C	1000^{0}C
Experimental Density (gm/cm^3)	3.85	4.52	4.95	4.08
Theoretical Density (gm/cm^3)	6.13	6.17	6.09	6.03