Dielectric Dispersion in Antimony substituted Barium Bismuth Titanate

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ABSTRACT

Barium bismuth titanate is a compound of Aurivillius family which attracts the attention of scientists due to its excellent physical properties. Antimony doped Barium bismuth titanate $BaBi_3SbTi_4O_{15}$ compound, a member of perovskite family is synthesized using solid state reaction route. This sample is calcined followed by a sintering process at 850 ºC for 6 hours. The sample is subjected to XRD analysis and got confirmation of perovskite structure in orthorhombic crystal system obtained in single phase. The change in structure is analyzed due to antimony doping at B-site. The variation of dielectric properties with temperature and frequency are analyzed. Phase transitions are found both at higher frequencies as well as low frequencies. A revised Curie -Weiss law intimates the degree of diffuseness of phase transition. The activation energy is estimated in the conductivity study as a function of temperature. The hysteresis curve for the sample confirm the ferroelectric and paraelectric phase transition.

Key words: Barium bismuth titanate, Perovskite structure, Solid state reaction, Dielectric, Activation energy.

I. INTRODUCTION

The discovery of Aurivillius materials [1] with high curie temperature play an important role for their applications in high temperature piezoelectric, pyroelectric and memory devices [2]. Different interesting physical properties of ferroelectric material of perovskite family are superconductivity, conductivity, piezoelectric and multi dielectric properties have great importance in microelectronics and telecommunication sector [3-5]. The structure of Aurivillius compound consists of n numbers of perovskites such as $(A_{n-1}B_nO_{3n+3})^{2-}$ unit cells sandwiched within $(Bi_2O_2)^{2+}$slabs along pseudo tetragonal axis (where n is an integer from 1 to 5) having general formula formula $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{2-}$. The 'A' site is occupied by large mono, di or trivalent cations (e.g., Ba^+,Na^+,K^+,Bi^{+3}) having ionic radii ~1.34 to 1.64 Å with 12 coordination number and 'B' site is filled by tetra-, penta-, or hexavalent cations (Ti^{+4},Cr^{+3},Fe^{+3}) of small dimensions with 6 coordination number [6]. Barium bismuth titanate (BBT) has attracted considerable attention for its excellent physical properties among perovskite family, which can be enhanced by doping antimony (Sb) at Bi site. The parent compound BBT has a structure of n=4 with barium & Bismuth ions at A site & titanium ions at B site of the perovskite block $[(Bi_2O_2)^{2+},(BaBi_2Ti_4O_{13})^{2-}]$ [7]. From literature survey, it reveals that, when Ba is substituted by La in BBT with different concentrations (having general formula $Ba_{1-(3/2)x}La_xBi_4Ti_4O_{15}$ (x=0-0.4)) exhibits enhancing electrical properties [8]. Farther, J. D Bobic and B. D Stojanovic have reported some significant enhancement of properties when La is doped in BBT using general formula $BaBi_{4-x}La_xTi_4O_{15}$ x=0-0.30 [9, 7]. Looking to above literature survey, Sb modified of BBT i.e $BaBi_3SbTi_4O_{15}$ is synthesized and the enhanced dielectric properties are studied.

II. Experimental

A. Sample preparation.

The polycrystalline sample $BaBi_3SbTi_4O_{15}$ has been synthesized by mixed oxide process or solid-state reaction technique. High purity ingredient powder (>99.9%) of $BaCO_3$ (M/S Sarabhai M.Chemicals pvt. ltd), TiO_2 (Merck Specialities pvt. ltd), Sb_2O_3 (Loba chemicals pvt.ltd), Bi_2O_3(Central drug house pvt.ltd) are homogenously mixed in a suitable stoichiometric mass ratio and are thoroughly grounded in

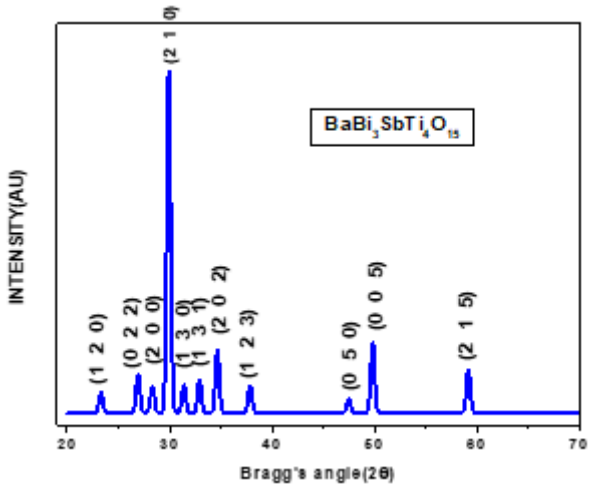
an agate mortar in air medium for 3 hrs followed by wet methanol medium for 2 hrs. The grounded mixture is calcined at 850 ºC in an alumina crucible for 12 hrs. The calcined powders are reground into fine powder with polyvinyl alcohol (binding agent) and pelletized into cylinders of diameter ~1cm & thickness of 1-2mm in a hydraulic press at a pressure 4 $\times 10^6$ Nm^{-2}. Then sintering of the pellets are carried on at 875 ºC for 12 hrs in a high temperature furnace.

B. Characterization

The creation of new compound is verified by XRD analysis. The X-ray diffraction pattern of the sample is recorded using a diffractometer (Rigaku,Miniflex) at room temperature with CuK_α radiations (λ=1.54A^O) in broad range of Bragg's angle 2θ ($20^o \leq 2\theta \leq 80^o$) with scattering rate 3º/minute. For dielectric characterization, both sides of the sintered samples are polished with emry paper and electroded with silver paint. The sintered pallets are then fired at 130ºC for 30 minutes before taking measurement in order to remove moisture in the pallets. The electrical properties are measured at different frequencies of 1kHz ,5KHz, 10kHz and 50KHz up to 1000KHz using a HIOKI-3532-50LCR Hitester in a large temperature range (30ºC to500ºC) with a rate of heating 2 ºC/minute. The PE loops of the sample are measured in automatic PE loop tracer (Marine India).

III. RESULTS AND DISCUSSIONS

A. Structural and microstructural studies.



d_{obs}	d_{cal}	h	k	l
3.813	3.812	1	2	0
3.312	3.30	0	2	2
3.141	3.142	2	0	0
2.984	2.986	2	1	0
2.848	2.847	1	3	0
2.719	2.719	1	3	1
2.586	2.590	2	0	2
2.375	2.381	1	2	3
1.914	1.916	0	5	0
1.829	1.830	0	0	5
1.561	1.56	2	1	5

Figure 1 Room Temperature XRD and 'd' spacing values with h k l of $BaBi_3SbTi_4O_{15}$

The XRD pattern of $BaBi_3SbTi_4O_{15}$ at normal temperature are as in the Fig 1. The XRD analysis confirms the formation of single-phase new compound with a variation in XRD pattern of the ingredient oxides [8]. The reflection peaks of the XRD graphs are noted by using 'peak fit' computer software. By listing 2θ values of the peaks, the value of lattice parameters, volume and interplanar spacing (both observed and calculated) are estimated by using POWD MULT software [10]. As seen from literature survey the parent compound has a tetragonal structure at room temperature [9]. But Nalini et al. [11] have noticed an orthorhombic structure of BBT sample. The orthorhombic structure is also confirmed by Irie and coauthors [12] of the same BBT compound. By taking into account to the best agreement of interplanar spacing (d) ($\Delta d = d_{obs} - d_{cal}$=minimum) an orthorhombic structure is confirmed in Sb modified BBT compound. The lattice parameter of the unit cell (orthorhombic) are found to be a=6.2869 Å, b=9.58 Å ,c=9.1499 Å with volume 551.08 Å^3.The volume of the Sb modified compound is decreased as the ionic radius of Sb is less than that of Bismuth. The size of particle (P) of calcined sample is calculated from the widening of peaks of XRD graphs applying Scherer's equations $P = k\lambda/\beta_{1/2} \cos\theta_{hkl}$, k=constant =0.89, λ=1.54 Å, $\beta_{1/2}$ =diffraction peak width at half intensity. Crystal size is found by taking average of all the data of P and is calculated as 19.38 nm.

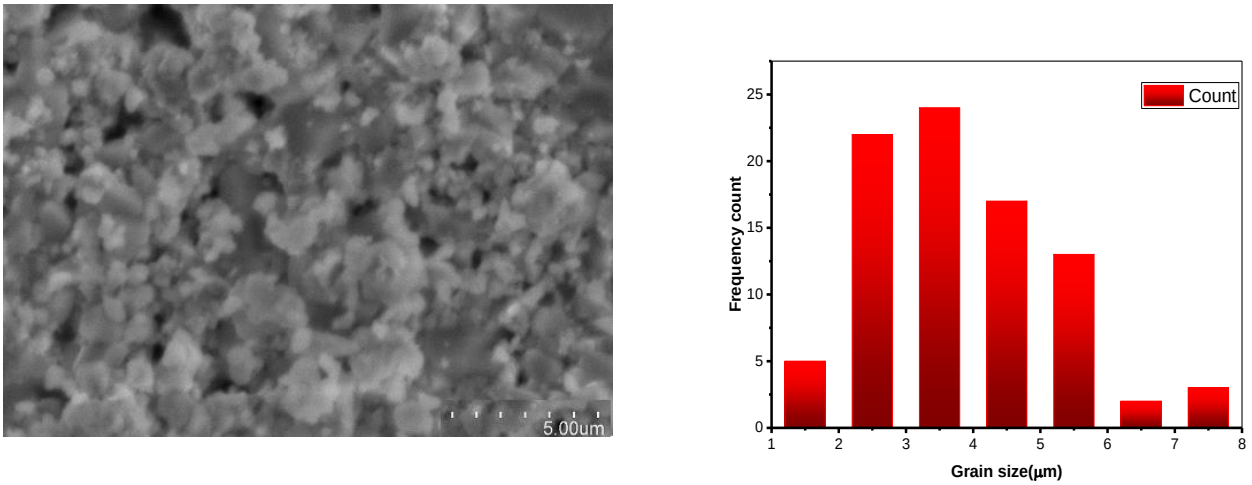


Figure 2 SEM micrograph and Histograms showing the grain size distribution of $BaBi_3SbTi_4O_{15}$

The microstructure of the sample is studied through SEM analysis. The SEM image of samples are given in fig 2 with good magnification. It is found that the microstructure of the compound is dominated by the spherical and irregular clustered like grains. The mean grain size calculated from histogram by gaussian fitting is 3.85μm. Thus, it is clear that a single grain consists of several crystallites.

B. Dielectric study

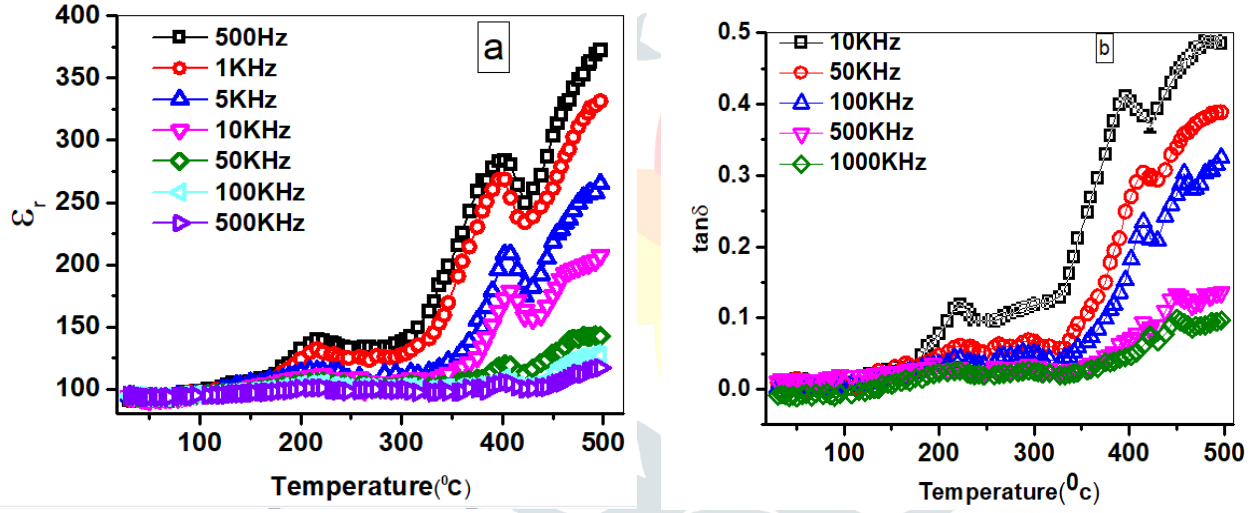


Figure 3 (a)(left) and (b)(right) Temperature variation of relative dielectric constant (ε_r) & loss tangent (tanδ) of $BaBi_3SbTi_4O_{15}$

The dielectric study of $BaBi_3SbTi_4O_{15}$ compound is analyzed as temperature verses relative permittivity (ε_r) graph which is as in figure 3 (a). The relative permittivity (ε_r) rises with rise in temperature for all studied frequencies. At a temperature of 216°C a small transition peak is found indicated by high ε_r value. This peak occurs due to structural phase transition from tetragonal to orthorhombic structure [6]. Then ε_r decreases followed by a rise in its value up to 402°C, where another peak is observed. This peak is due to the ferro to paraelectric phase transition with maximum dielectric constant 284.21. This type of successive phase transition is observed in other Sb modified compounds of ferroelectric materials [6]. The materials with large dielectric constant and high curie temperature are found to be extensively used in the perovskite solar cell and storage devices [9]. No such double peaks are found in pure BBT compound as studied in literature survey [9] but when Sb is substituted at A site successive peaks are noticed.

The tanδ verses temperature graph shown in figure 3 (b) exhibits two peaks with a low value of loss with temperature. The low value of tanδ suggests good quality of ferroelectric material for application purpose as storage devices as well as high efficiency perovskite solar cell. The tanδ value increases slowly with the rise in temperature up to some transition value in the high temperature for different frequencies.

C. Modified Curie Wiess Law & diffusivity

The response towards the Curie Weiss (C-W) law in ferroelectric material is better understood from figure 4 (a) which is temperature dependent reciprocal of permittivity ($1/\varepsilon = (T_m-T_{cw})/C$.) For the compound showing diffuse phase transition, a deviation from C-W behavior is observed. It is observed that the parameter ($1/\varepsilon_r$) deviates from the Curie-Weiss law within a certain range of temperature which is called as Curie-Weiss range and in this range the crystal exhibit unusual dielectric and ferroelectric properties [6]. The reciprocal of dielectric constant is a linear function of temperature on both sides of T_c except within the range of ± 6°C. The difference between T_m and T_{CW}, (i.e., ΔT_{cm}) (calculated manually) is found to be ~6°C. Thus, the deviation from normal C-W law is observed.

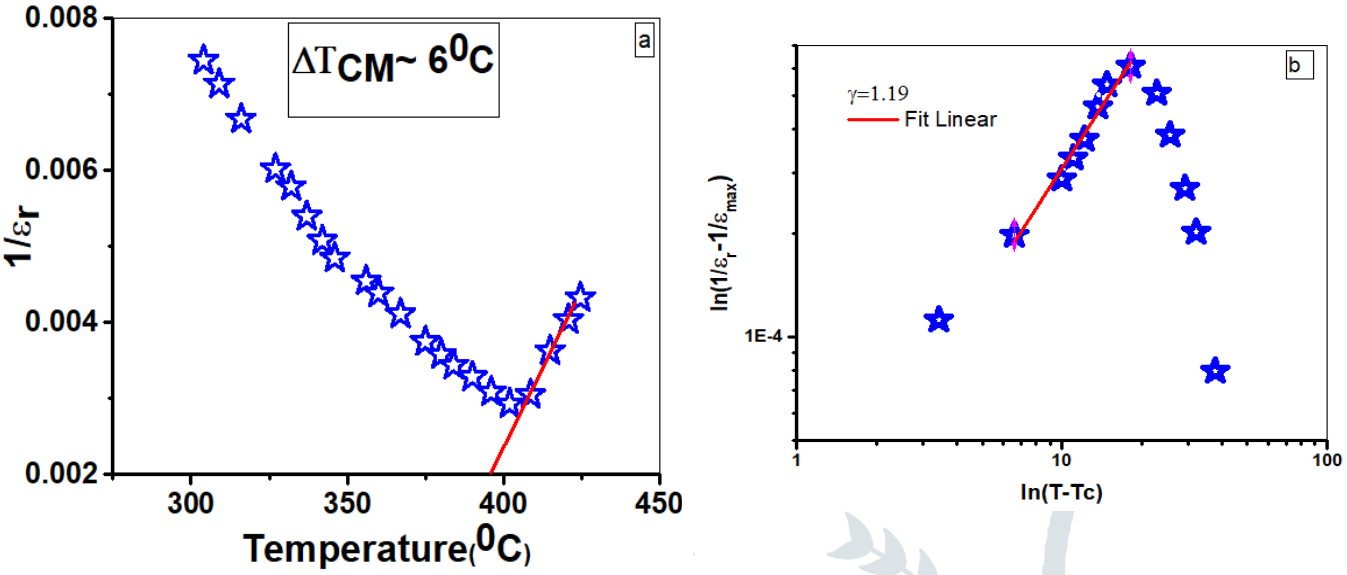


Figure 4. (a) and (b) $1/\varepsilon_r$ ~ temperature graph (left) & ln $(1/\varepsilon_r - 1/\varepsilon_{max})$ ~ γln(T-T_C) graph (right) of $BaBi_3SbTi_4O_{15}$ at 500Hz frequency of $BaBi_3SbTi_4O_{15}$ at 500 Hz frequency

For more confirmation of degree of diffusivity of Sb substituted compound modified Curie Weiss law is utilized which is given by

$$\ln (1/\varepsilon_r - 1/\varepsilon_{max}) = \gamma \ln(T-T_C) + \ln K$$

where T is the temperature, K is a constant, and γ diffusivity of phase transition. If the value of γ varies between 0 to 1 then the material is classical ferroelectric in nature and for the value in between 2, it is of disorder type material [11, 12].The value of γ is calculated from the slop of the graph represented in Figure 4 (b).The value of γ is found to be $1 \leq \gamma \leq 2$. Thus, a deviation from normal ferroelectric behavior is observed which indicates occurrence of diffused phase transition [14]. The diffuse phase transition occurs due to the disordering of the substituted ion at cation site of the host compound which is also found in the barium bismuth family.

D. Polarisation Study

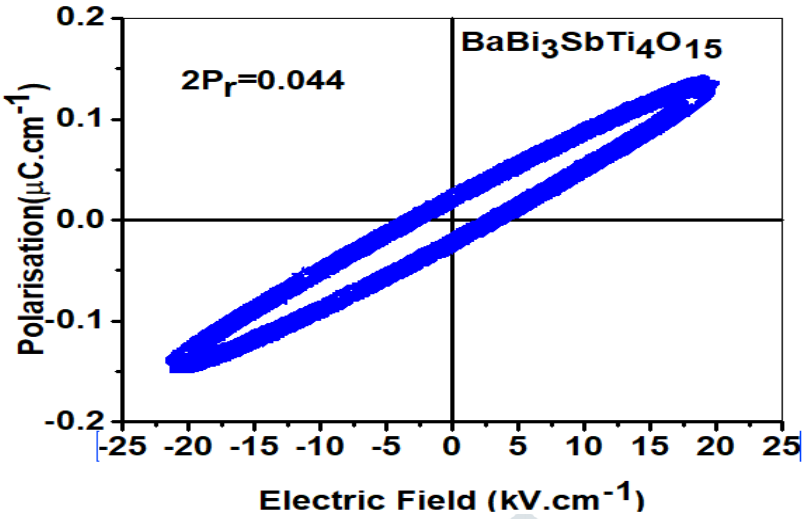


Figure 5 Room temperature P-E loop of $BaBi_3SbTi_4O_{15}$

The polarization (P) ~ electric field (E) plot is as shown in figure 5. Presence of hysteresis loop with remanent polarization ($2P_r$) 0.044μCcm^{-2} & coercivity ($2E_c$) 026kVcm^{-1} confirms the presence of ferroelectricity in the material. The proper ferroelectric polarization loop is not found due some lossy characteristics of the materials [14].

E. Conductivity study

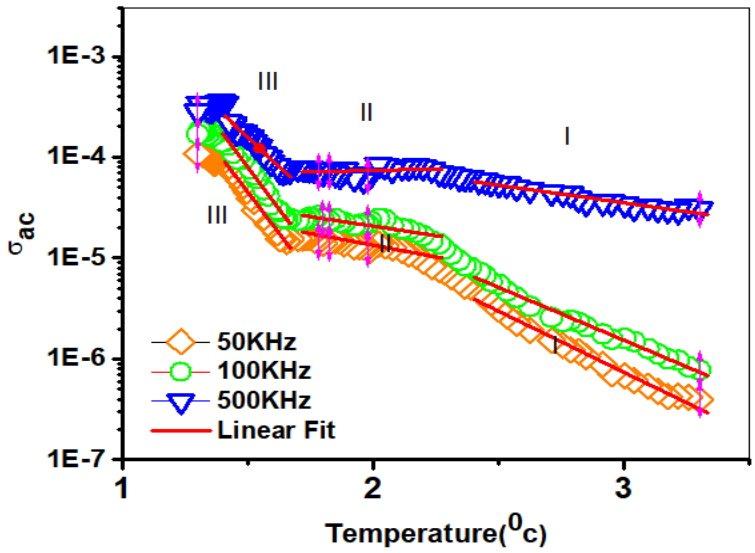


Figure 6: Variation of ac conductivity with temperature of $BaBi_3SbTi_4O_{15}$

The conduction mechanism is a very important study in the electrical analysis. The temperature dependent conductivity σ_{ac} at different frequencies is shown in fig 6. From the plot it is clear that σ_{ac} rises when temperature rises up to some temperature 350^o C and then remains independent of temperature i.e parallel to the temperature axis. On other word this type variation of curve obeys the Arrhenius relation i.e $\sigma_{ac} = \sigma_0 \exp(-E_a/K_BT)$,where E_a is the activation energy, K_B is Boltzmann constant and T absolute temperature. Two distinct regions are taken as per the variation of slopes at low and high temperature for the different frequencies. The value of activation energy is estimated utilizing above equation. The change in slopes informs different mechanism involved in conduction process. The change in slope occurs at phase transition temperatures (402^{o}C). Thus, ferro to paraelectric phase transition is, confirmed at that temperature

Table-1 Values of activation energy calculated from above figure 6

Frequencies	E_a (eV)		
	Region-I	Region-II	Region-III
50KHz	0.2399	0.0920	0.6459
100KHz	0.2080	0.0746	0.6582
500KHz	0.0693	0.01149	0.4430

IV. CONCLUSIONS

Mixed oxide process is used to synthesize $BaBi_3SbTi_4O_{15}$ compound at a calcination temperature 850°C for 12 hrs and then corresponding compound is sintered at 875° C for 12 hrs. Orthorhombic crystal structure is confirmed from XRD analysis with particle size ~19.38 nm . The effect of antimony substitution on BBT compound is clearly visualized in dielectric analysis, with occurrence of double peaks at temperature 216°C and 402°C as analyzed from the ε_r- temperature curve. The law value of tan δ indicates good ferroelectric nature of the compound. The presence of P~E loop suggests presence of ferroelectricity in the material. Thus, the compound can have potential used in solar cell devices. Different activation energy in different regions confirms different conduction mechanism in the compound.

Acknowledgements

One of the authors L.K Mishra is thankful to NOU, Takatpur, Baripada, Mayurbhanj, Odisha for allowing him to do his research work as a Research scholar and to Professor R.N.P Choudhary, Department of Physics ITER ,SOA, Bhubaneswar for his assistance and allowing to perform some of the experimental work in his laboratory.

Conflict of interest: The authors declare that they have no conflict of interest.

References

1 Jelena D.Bobic,Mirjana M. Vijatovic, Tadej Rojac , Biljana D.Stojanovic, Characterization and properties of barium bismuth titanate “Processing and application of ceramics 7(3)(2013)97-11048(2013)(3766-3772) DOI;10.2298/PAC1303097B

2 Wikipedia;Application of Perovskite

3 Parveen Kumar, Sangeeta Singh, Manjula Spah, J.K Juneja, Chandra Prakash,K.K Raina “Synthesis and dielectric properties of substiyuted barium titanate ceramics.”Journal of Alloys and compounds 489(2010)59-63

4 M.M Vijatovic, J.D Bobic, J.Banys, B.D Stojanovic “Electrical properties of antimony doped barium bismuth titnate” Materials research Bulletin 48(2013) 3766-3772

5 B. Aurivillius,” Mixed bismuth oxides with layer lattices,III structure of $BaBi_4Ti_4O_{15}$”Ark Kemi 1(1950)519-527

6 Sunil Kumar and and KBR Verma Journal of physic ;Applied physics volume-42 no-07 12 march 2009

7 Jelena D.Bobic, Mirjana M. Vijatovic, Tadej Rojac , Biljana D.Stojanovic Ceramic International volume39,issue 7 sept 2013, pages 8049-8057

8 PS sahoo ,B. Mohanty,J panda RNP Choudhury “Synthesis and analysis of electrical properties of lead free Ba3Sr2LaTi3V7O30” Reasearch Inventry International Journal of Engineering and science vol-4 issue12 dec 2014 pp38-42,

9 B.B Mohanty, PS Sahoo, Mahapatra P.K Sahoo, RNP Choudhary”Synthesis and electrical analysis of $Ba_5GdTi_3V_7O_{30}$ ceramics “ Materials science and application 2013,3,173-178,doi; 10.4236/msa.2012.33027

10 G. Nalini,T.N Guru Row,"Structure determination at room temperature and phase transition studies above Tc in $ABi_4Ti_4O_{15}$ (A=Ba,Sror Pb) "Bull.Mater Sci.25(2002) 275-281

11 H.Irie,M.Miyayama,T.Kudo," Structure dependence of ferroelectric properties of bismuth layered structured ferroelectric single crystal", JAppl.Phys.90[8](2001)4089-4094

12 I.Rivera,A.Kumar, N.Ortega,R.S Katiyar,S.Lushnikov,Solidstate Commun.149(2009)172-176

13 P.S Sahoo,A.Panigrahi,S.K Patri and R.N.P Choudhary," Ferroelectric phase transition in $Ba_4SrSmTi_3V_7O_{30}$ " Materials Letter,Vol.63 No.11.2009.PP864-866 doi;10.2016/j.matlet.2009.01.053