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PREPARATION OF BT-BIT COMPOSITES AND THEIR CHARACTERIZATION THROUGH IMPEDANCE ANALYSIS AND POLARIZATION

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ABSTRACT

$BaTiO_3$ (BT), $Bi_4Ti_3O_{12}$ (BIT) samples were prepared through Sol-gel method, and both were mixed in weight ratios of 9:1 and 8:2 to prepare BT-BIT Composites. The XRD analysis shows two individual phases with tetragonal and orthorhombic structures in the composites. Surface morphology of the composites was observed using scanning electron microscopy (SEM) images. PE loops measurement was done from room temperature to 200°C. Saturated loops were observed. Impedance studies were done for the samples and grain, grain boundary effects are analyzed.

Keywords: BT-BIT composite, XRD, SEM, Impedance

INTRODUCTION

$BaTiO_3$ (BT) is first ferroelectric material at and above room temperature, and also good piezoelectric material. BT belongs to perovskite family with chemical formula ABO3. BT has tetragonal structure [1]. Structural phase transitions of BT from ferroelectric phase (tetragonal) to paraelectric phase (cubic) takes place at 120oC [2]. Tetragonal structure is stable up to 5oC, and below 5oC, it transforms to orthorhombic structure and remains in orthorhombic structure till -90oC, rhombohedral structure is stable below -90oC.

$Bi_4Ti_3O_{12}$ (BIT) is member of layered structured bismuth compounds, first proposed by Aurivillius hence known as Aurivillius family [3]. BIT is a ferroelectric material, the transition from ferroelectric phase (orthorhombic) to paraelectric phase (tetragonal) occurs at curie temperature Tc= 670oC. Due to its high curie temperature it is useful for applications in high temperature transducer, sensors, and capacitors [4].

In the present paper, We report the results of study on BT-BIT ceramic composite prepared by combining two individual phases, synthesized by Sol-gel chemical route. From these the composites of BT-BIT are prepares. Ferroelectric, AC impedance, DC conductivity studies of BT-BIT ceramic composites are reported.

Experimental methods

BT, BIT were synthesized by sol gel chemical route method. For preparation of BT, $Ba(NO_3)_2$ (SD fine 99.5%), Ti(100mesh,Aldrich 99.7%), H_2O_2 (30%, SD fine) and ammonia solution(25% AR grade, SD fine) were taken. The Ti metal powder is added to a solution containing 70 ml of H2O2 and 30 ml of ammonia at 0oC to form in titanium peroxide (yellow colour viscous solution), Ba(No3)2 was dissolved in water and added to titanium peroxide solution under constant stirring at room temperature. Then the citric acid is added to this solution in the molar ratio 2:1, so that citrate is formed. The pH of the resultant solution adjusted to 7 by adding ammonia and then solution is heated for 24h. After evaporating 1/4th of the solution, ethylene glycol and citric acid are added in the molar ratio 1:1.2. Then the solution is heated at 180°C for 6-7 hours. A black porous solid is obtained. This precursor powder was then ground in an agate mortar and then calcined at 1000oC for 6h. Similar procedure was used for preparation of BIT, the starting compounds were $Bi(NO_3)_3$ (Sd fine 99.5%), Ti metal powder (100 mesh, Aldrich 99.7%), H2O2 (30%, SD fine) and ammonia solution(25% AR grade, SD fine). The calcined powders of BT and BIT were mixed in weight percentage for synthesizing composite materials, and the mixture is ground for 4 hours to obtain a homogeneous mixture. The powders of the mixture were pressed into pellets of 10 mm diameter and about 1.8 mm thickness, using hydraulic press. Polyvinyl alcohol was used as a binder. These pellets were sintered at 900o C for 4h. Silver coating was done on both surfaces of sintered samples for ohmic contacts during all electrical measurements. X-ray diffraction pattern is recorded using PANalytical X'pert plus diffractometer, with Cu Kα (1.54 Å) radiation, at room temperature in the range of 20°≤ 2θ≤ 80°, at a scan speed of 2/min. Densities of the parent and composite ceramics were measured by the Archimedes method using Xylene (density 0.87g/cc) as liquid media. Surface morphology of the parent and composite ceramic samples was observed using scanning electron microscope (ZEISS EVO18). AC impedance measurements were done using AUTOLAB PGSTAT-30 instrument as a function of frequency in the range 100-1M Hz and at different temperature ranging from 25^{o}C to 500^{o}C. DC conductivity measurements were done, using Keithely 617 programmable electrometer and keithely 196 from 25oC to 500oC. P-E loop measurements were performed using custom built P-E loop tracer of Marine India Ltd., working at 50 Hz frequency. The PE measurement was carried out from room temperature to 180oC at an interval of 25^{o}C, with constant heating rate of 5^{o}C/min.

Results and Discussion

X-ray diffraction:

X-ray diffraction of parent (BT, BIT), and BT-BIT composite ceramics is shown in fig 1. It is observed that at room temperature, parent BT crystallizes in tetragonal phase, whereas parent BIT crystallizes in orthorhombic phase. Both phases are observed in composites XRD pattern. The XRD data of present samples are compared with the reported ICSD data (BT-ICSD Card No.-245944, BIT-ICSD Card No. 59796). The lattice parameters and (h k l) values are calculated using POWD software by least square fitting method using Psudo Vogit method. Densities of the ceramic composites obtained by Archimedes principle are compared with X-ray densities. The lattice parameter and density values are given in table 1.

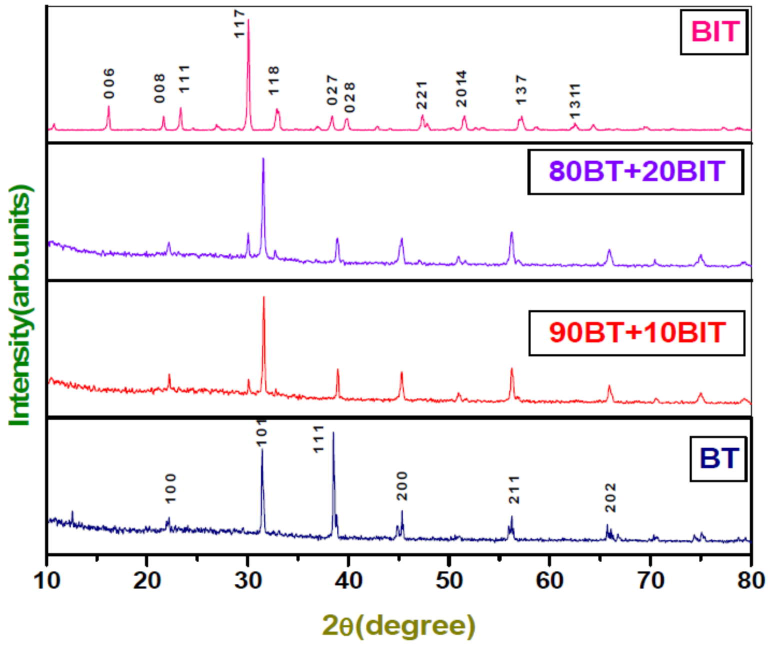

Fig.1 X-ray diffraction pattern of parent BT, BT-BIT composites and parent BIT.

Table 1 Lattice parameters (a,b&c), density (theoretical and experimental), and percentage of relative densities of parent and composite ceramics

Sample ID	BT		BIT			ρX-ray	ρexp	Relative
	a(Å)	c (Å)	a(Å)	b(Å)	c(Å)	g/cc	g/cc	density(%)
BT	3.9996	4.0404	-	-	-	5.99	5.82	97
90BT+10BIT	3.9954	4.0428	5.4420	5.4247	32.9514	6.39	5.64	88
80BT+20BIT	3.9984	4.0416	5.4430	5.4206	32.8613	6.193	6.015	97
BIT	-	-	5.4356	5.4247	32.7128	8.06	6.48	80

Scanning Electron Microscopy:

Fig 2 shows the scanning Electron microscopy (SEM) images of parent compounds and composites. From sample morphology, it is observed that irregular polygonal grains appear in the parent BT, plate like grains are observed in the parent BIT and the samples have good density and small porosity. Decreasing grain size is observed for composites compared to parent ceramics.

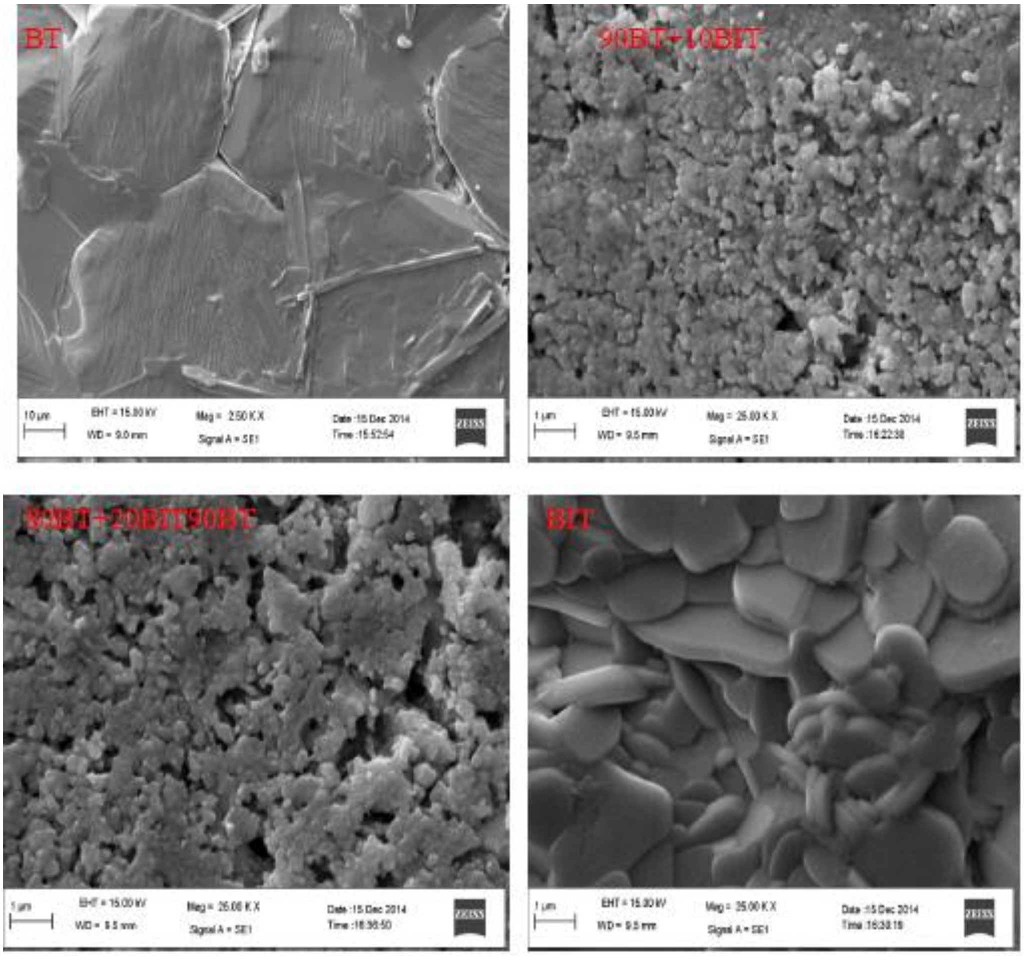

Fig 2.SEM pictures of parent BT, BT-BIT composites and parent BIT.

Hysteresis loops:

Fig 3 shows the ferroelectric hysteresis loops of parent BT, BIT and BT-BIT composites pellets. The measurement is taken by placing the samples in silicon oil bath and heating the samples from room temperature to 200^{o}C. The hysteresis loop of parent BT is well saturated whereas parent BIT shows lossy loops indicating the conductivity nature of the BIT samples, because of migration of oxygen vacancies created during the sintering [5]. The hysteresis loops of composites are slightly deformed and saturation destroyed with addition of BIT percentage and coercive field is also increasing. Coercive field and remnant polarisation values of parent and composite ceramics are given in table 2.

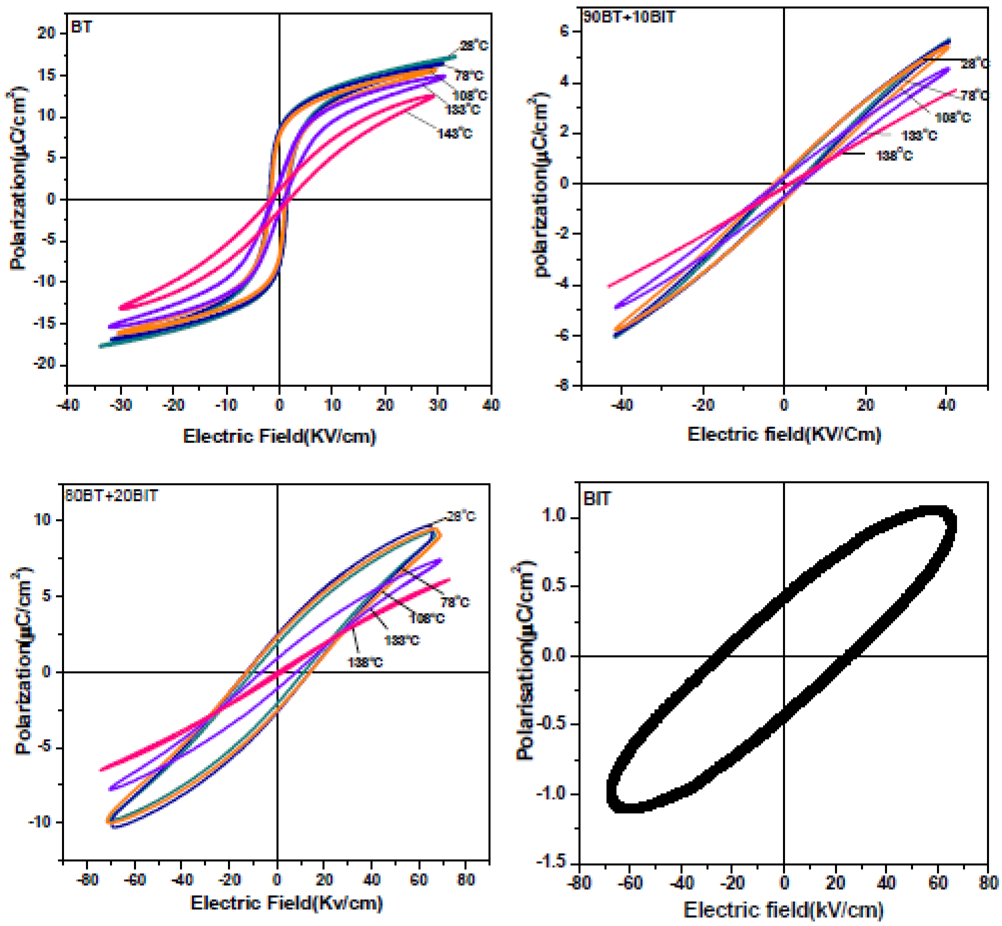

Fig.3. P-E loop of the parent BT, BIT, BT-BIT composites

Table2 remnant polarization and coercive field values for the BT and composites.

sample	BT		90BT+10BiT		80BT+20BiT	
T(°C)	P_r ($\mu C/cm^2$)	E_c (kV/cm)	P_r ($\mu C/cm^2$)	E_c (kV/cm)	P_r ($\mu C/cm^2$)	E_c (kV/cm)
28	7.302	2.114	0.389	2.216	1.996	39.570
78	8.010	5.339	0.465	2.761	2.554	13.390
108	7.275	15.570	0.546	3.355	2.412	13.398
133	1.791	1.036	0.363	2.874	0.992	7.308
138	1.264	6.460	0.019	0.158	0.109	1.030
158	1.723	4.339	0.003	0.024	0.099	0.979

AC Impedance studies:

The impedance spectroscopic studies of samples BT,BIT, 90BT+10BIT and 80BT+20BIT are shown in Fig 4. The plots are drawn between the real and imaginary parts of impedance. These plots are distorted semicircles and indicate the presence of non Debye type relaxing species in the samples of BT, BIT. But for composite samples (90BT+10BIT and 80BT+20BIT) more complex behavior is observed and has high resistive nature with increasing of BIT in BT sample.

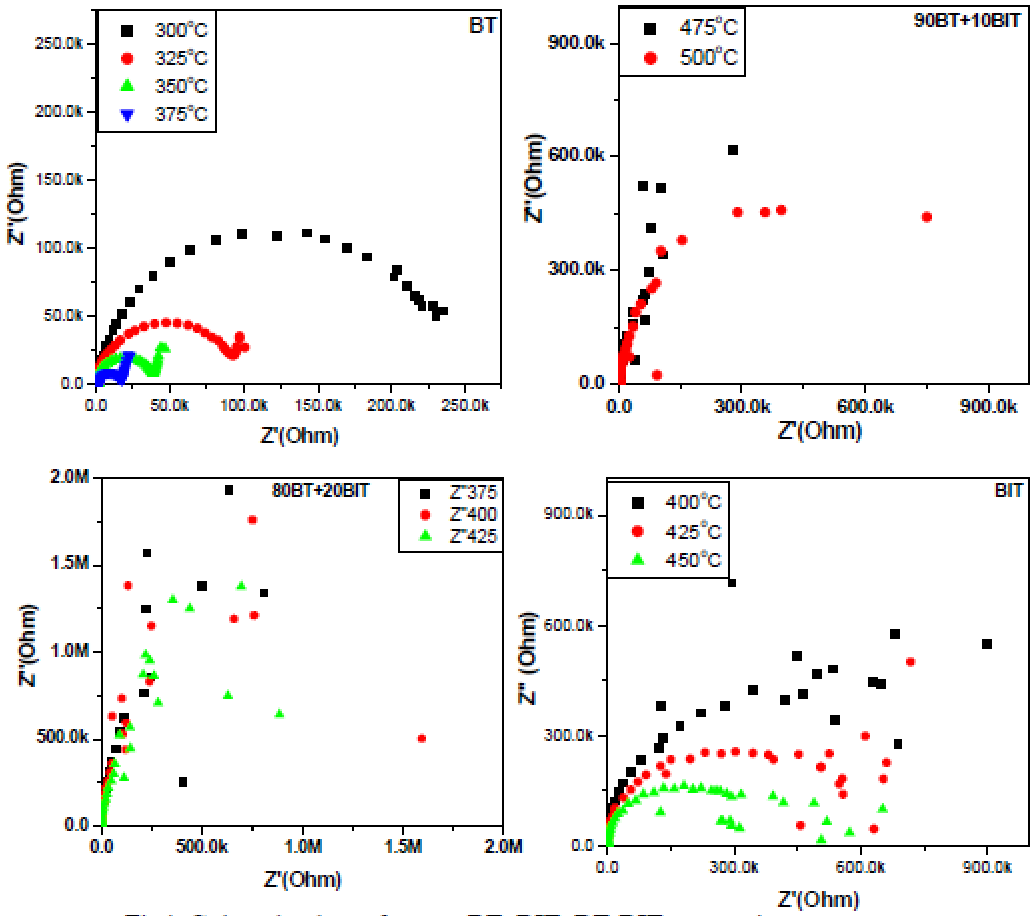

Fig4. Cole cole plots of parent BT, BIT, BT-BIT composites

DC conductivity studies

Variation of DC conductivity with temperature in the range 25 -500°C of parent and composite ceramics is shown in fig 5 there are two regions indicating different types of conduction mechanism. Conduction in the first region at low temperature is due to ionic hopping while second region is due to electron hopping and oxygen vacancies [6,7]. Ionic conduction is predominating in BT and 90BT+10BIT, whereas electronic conduction mechanism is predominating in 80BT+20BIT, BIT. The activation energies of parent and composite ceramics are given in table 3

Table 3 activation energies of parent and composite ceramics

Sample	Activation Energy	
	Region I	Region II
BT	0.62±0.03	1.19±0.02
90BT+10BIT	1.29±0.019	1.61±0.02
80BT+20BIT	1.22±0.01	0.65±0.02
BIT	1.45±0.01	0.93±0.006

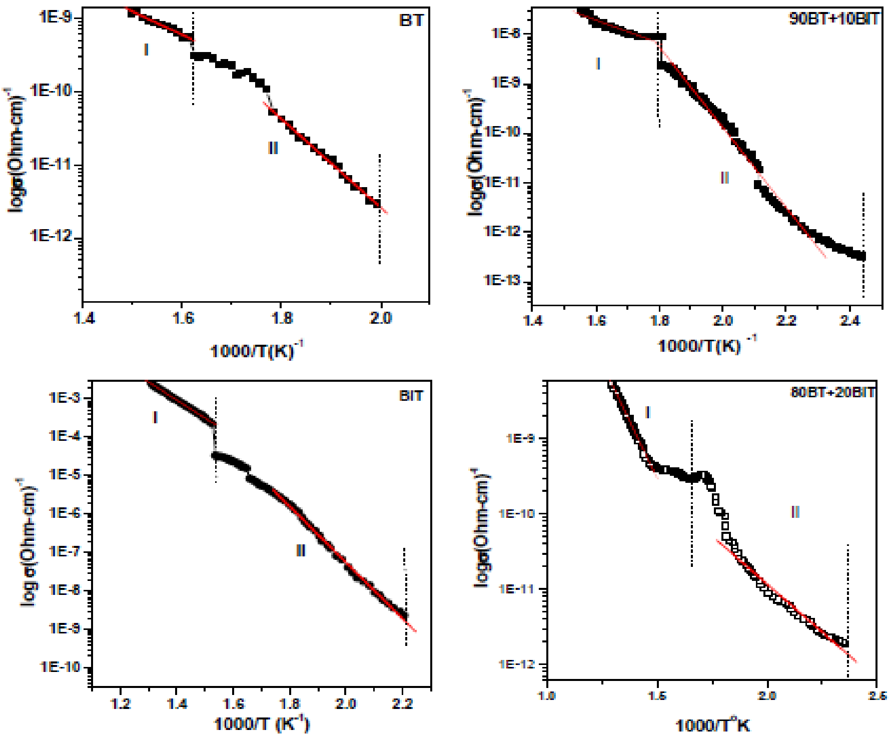

Fig 5. DC conductivity of parent BT,BIT, and BT-BIT composites

Conclusions

Parent compounds were prepared through Sol gel method and composites were prepared by using conventional solid state method. XRD of composites shows the presence of two individual phases, cubic phase of BT and orthorhombic phase of BIT. SEM images shows smaller grains for composites and densified grains for BT and BIT. Remnant polarization of the samples decreased with increasing temperature, and order parameter of the samples becomes zero beyond transition temperature. Bulk response of the samples analyzed by Cole-Cole plots.

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