Electrical behavior of $(Ba_{1-x}Gd_x)$ TiO_3 ceramics

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ABSTRACT

Polycrystalline ceramic samples of $(Ba_{1-x}Gd_x)$ TiO_3 (x = 0.001, 0.002, 0.004 and 0.005) of perovskite structure family have been synthesized by ceramic technique. The electrical conductivities have been investigated over a wide range of temperature and activation energy, PTCR (positive temperature coefficient of resistivity) and NTCR (negative temperature coefficient of resistivity) were calculated. Thermoelectric power of the material changed its sign near the Curie temperature. The tetragonal phase at room temperature exhibited n-type behavior. © 2010 Trade Science Inc. - INDIA

INTRODUCTION

Pure barium titanate $(BaTiO_3)$ is one of the best-known ferroelectric perovskite compound that have been extensively studied by sintering in air, normally exhibit electrical conductivity of $\sim 10^{-13}$ S/cm at room temperature[1,2]. Conventional $BaTiO_3$ materials are manufactured by high-temperature solid-state reaction between $BaCO_3$ and TiO_2 or by calcining chemically derived intermediates. By doping of precisely controlled amounts of rare earth elements, can cause n-type conduction of this composition[3,4]. However, dopants in $BaTiO_3$ lead to interesting and sometimes unexpected properties and makes it semiconductor[2]. Aliovalent dopants have a profound influence on microstructural developments and resultant electrical properties of $BaTiO_3$-based ceramics[5,6]. Even though rare earth doping at Ba-site was studied by large number of researchers, this is an attempt to investigate the electrical behaviour of Gd-doping with little concentration (≤ 0.005) by estimating dc electrical conduc-

tivity, thermoelectric power, activation energy and Seebeck coefficient.

EXPERIMENTAL PROCEDURE

Samples of composition $(Ba_{1-x}Gd_x)$ TiO_3 (BGT) with a range of x=0.001-0.005, (0.001, 0.002, 0.004 and 0.005 here after called as BGT_1, BGT_2, BGT_3 and BGT_4 respectively) were prepared by the conventional ceramic method. High purity (99.99%) chemicals, $BaCO_3$ (Qualigens fine chemicals, Mumbai, INDIA), TiO_2 (HiMedia, Mumbai, India), Gd_2O_3 (HiMedia, Mumbai, India), in their stoichiometric proportions and were weighed, mixed and grounded thoroughly in an agate mortar for 4 hrs. BGT samples were calcined in air media at 950^0C and at 1050^0C for 8 hrs in an alumina crucibles (M/s. ANTS Ceramics, Nashik, India) with intermediate grindings for 2 hrs, in a programmable high temperature muffle furnace (Indfur Electric Furnace, Chennai, India). The finished powder was pressed and plastified using aqueous (5%) polyvinyl alcohol into

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a circularly shaped disc pellets of 10mm diameter and thickness of 1.5mm using tungsten carbide dye and plunger (M/s Sandwick Asia Ltd., Mumbai, India), with hydrostatic pressure of 45 kN/m², applied by hydraulic press machine (AIMIL, New Delhi, India). The pellets were sintered at 1280⁰C and annealed at 1175⁰C for 1hr. The heating and cooling rate for all thermal cycles was 2⁰C/min. The sintered pellets were polished and coated with silver paint and later cured at 400⁰C for 1hr. The dc electrical resistivity (ρ_{dc}) was measured with two-probe technique, employing digital multimeter (DMM 2000, Kethley make, USA) in the temperature range 30⁰C-300⁰C. Thermoelectric power (TEP) was determined by the differential method using standard

set up in the temperature range of 25°C-400°C.

RESULTS AND DISCUSSION

Figure 1 shows curves for BGT samples plotted ρ_{dc} vs temperature. ρ_{dc} was evaluated from the measured resistance (R), multiplied by a geometrical factor, A/t, where A and t are the area and thickness of the testing sample respectively. It is observed that the magnitude of resistivity jump and positive temperature coefficient of resistivity (PTCR) coefficient for BGT$_1$ sample is larger than that of BGT$_2$ and BGT$_3$ samples, whereas it is suppressed in BGT$_4$ ceramics. Room temperature resistivity (ρ_{RT}), maximum resistivity (ρ_{max}), re-
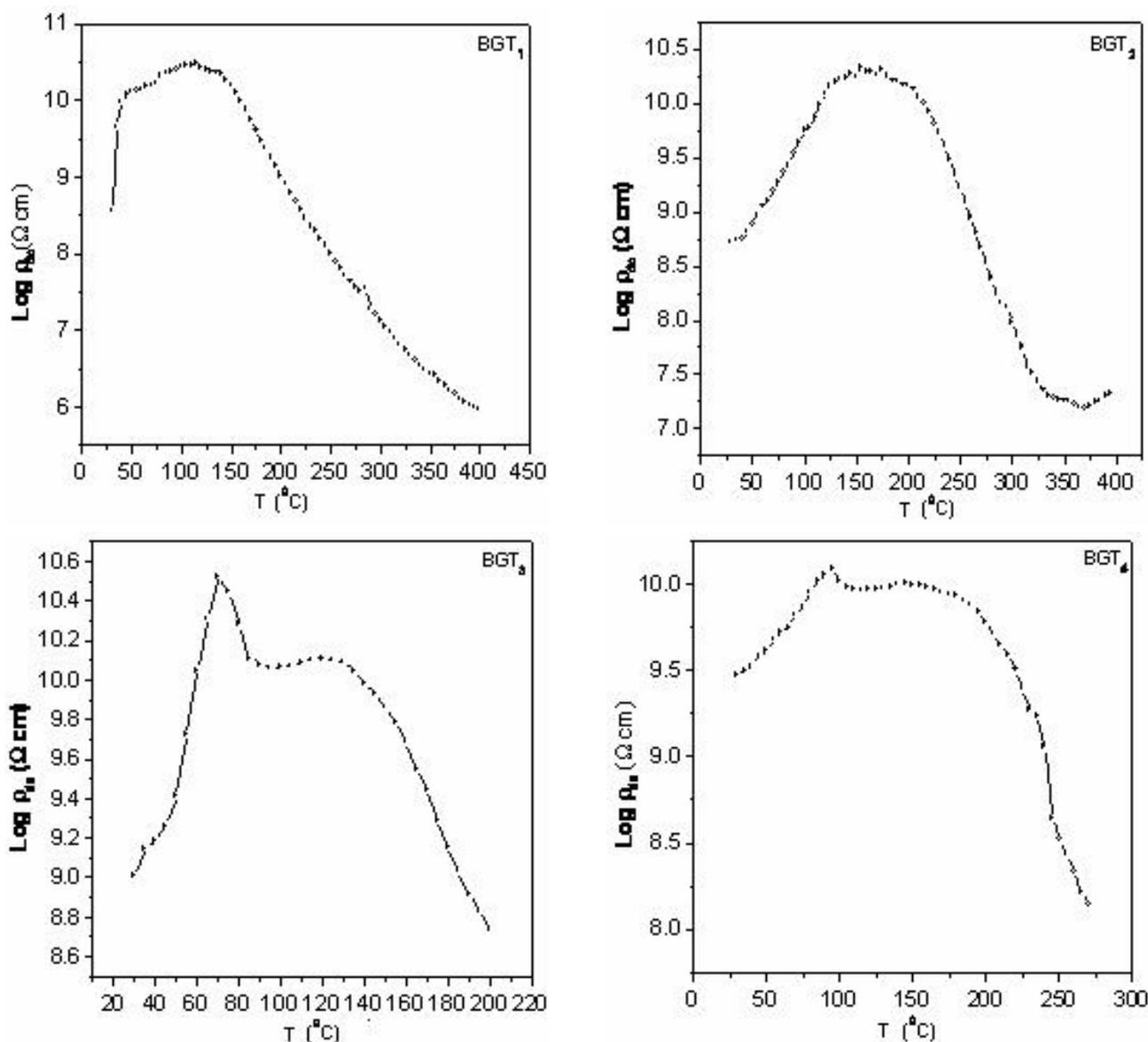

Figure 1 : Temperature dependence of resistivity behaviour of BGT ceramics

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sistivity jump (ρ_{max}/ρ_{RT}), TCR (PTCR and NTCR) and E_a values are given in TABLE 1.

The temperature coefficient of resistivity, α (TCR) is defined as

$$\alpha = 2.303\{\log [R_1/R_2] / [T_1−T_2]\} \times 100 \ (\%/^0C) \qquad (1)$$

where R_1 and R_2 are the resistivity at temperature T_1 and T_2 respectively. The obtained α_{PTCR} value is in

TABLE 1 : Electrical data of BGT samples

Sample code → Electrical Parameters ↓		BGT_1	BGT_2	BGT_3	BGT_4
ρ_{RT} x10^8 (Ω.Cm)		5.31	3.62	10.21	29.6
ρ_{max} x 10^{10} (Ω.Cm)		1.90	3.08	3.35	1.19
ρ_{max}/ρ_{RT}		35.8	85	32.8	4.0
T_C (^{0}C)		115	155	70	100
TCR (%/^{0}C)	PTCR	2 to 7.8	1.9 to 3.7	4.6 to 12.8	1.76 to 9.5
	NTCR	-4.2 to -2.5	-3.7 to -6.5	-2.3 to -6.1	-2.2 to -8.9
Activation energy (eV)	+E_a	0.27	0.18	0.22	0.11
	-E_a	0.99	0.18	0.20	0.30

the range +2 to +12%/^{0}C and α_{NTCR} value in the range −2 to −8.6 %/^{0}C. The little rise in ρ_{RT} is due to the formation of incompletely compensated surface states and also due to the grain-boundary Schottky barrier that is not completely suppressed below the Curie point[7]. Hence, all our samples demonstrated mixed TCR effect i.e., PTCR and NTCR behaviour. Here, Gd^{3+} ion act as an electron donor and electrical charge compensation results in variation of electrical conductivity. Our results are in good agreement with the reported work by T. Murakami *et al*[8]. Gd-ion occupies Ba^{2+} site yield donors. This has influenced the change of structural parameters and also decrease in electrical conductivity.

The activation energy (E_a) obtained from the inclinations of log conductivity (log σ_{dc}) vs reciprocal of absolute temperature (1/T) curve. E_a is found to be about 0.11 eV to 0.27 eV in the positive temperature coefficient (PTC) region, which is in fine conformity with the reported values by Tennery and Cook[9], whereas in the NTC region, it is about 0.18 eV to 0.98 eV.

Thermoelectric power of these materials relatively high in the tetragonal phase i.e.−4000μV/^{0}C to −5000μV/^{0}C. Transition to cubic phase 3000μV/^{0}C to +500μV/^{0}C is accompanied by the change in sign of the thermoelectric power. The temperature dependence of the Seebeck coefficient (S) for BGT_1, BGT_2 and

BGT_3 is shown in Figure 2. S is negative for all the samples at room temperature and transforms its sign at its transition temperature. This validates the sign of the majority carriers in these ceramics in the tetragonal phase and p-type nature in the cubic phase.
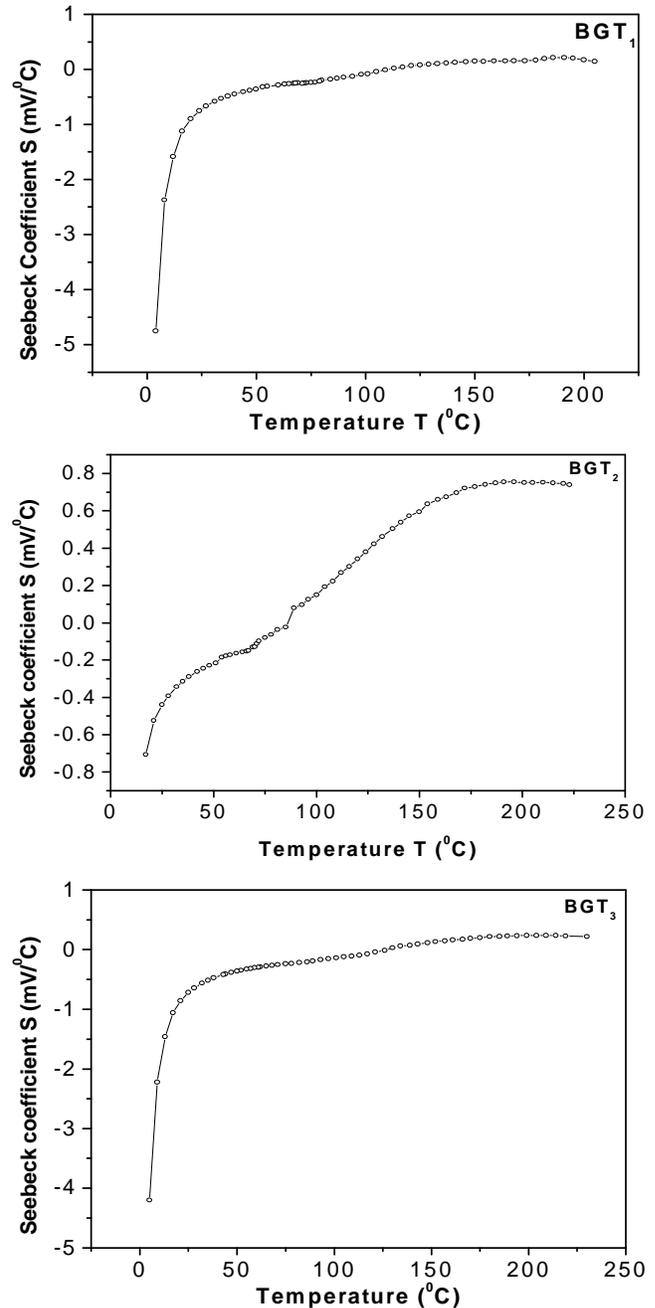

Figure 2 : Thermoelectric characteristics of BGT ceramics

CONCLUSIONS

BGT ceramics with ≤0.005 Gd-concentration exhibit PTCR property from room temperature up to T_c

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and then NTCR behavior, with nearly same range of temperature coefficient of resistivity (TCR) values. The room temperature resistivity is high due to amphoteric behavior of Gd^{3+}. Grain-growth inhibition and electrical charge compensation is observed for higher concentration of Gd. Thermoelectric power of these materials is relatively high in the tetragonal phase. Transition to cubic phase is accompanied by the change in sign of the thermoelectric power.

ACKNOWLEDGEMENTS

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