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MIXED TCR BEHAVIOUR OF GD-DOPED $BaTiO_3$ CERAMICS WITH SINTERING AIDS

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Abstract- Polycrystalline perovskite ceramics of composition $(Ba_{1-x}Gd_x)TiO_3$, $(0.001 \leq x \leq 0.005)$ with sintering aids were prepared by solid state reaction technique. Temperature coefficient of resistivity (TCR) behaviour was studied in the temperature range 30^0C to 300^0C. It is observed that, inclusion of sintering aids lowered the sintering temperature and the room temperature resistivity (ρ_{RT}) and also enhances the positive TCR (PTCR) at the ferroelectric Curie temperature, T_c. PTCR property begins from room temperature and remains up to T_c, thereafter show NTCR behaviour, with nearly same range of TCR values for all the samples, which shows the improved TCR properties due to sintering aids in the Gd-doped $BaTiO_3$ ceramics.

1. INTRODUCTION

Pure barium titanate ceramics are normally insulating materials with high resistance at room temperature 10^9-$10^{13}\Omega$ cm. With a small amount of donor dopants, such as La^{3+} or other rare-earth ions at Ba^2-site or with Nb^{5+} at Ti^{4+}-site, the material becomes semiconductor at room temperature [1]. Barium titanate ceramics when doped with a small proportion of donors can be converted to a semiconducting material [2] and exhibits an anomalous increase in resistivity near the ferroelectric Curie point. This behavior is commonly known as positive temperature coefficient of resistance (PTCR) [3]. The PTCR performance is an effect of grain boundary. The main composition of a grain boundary is sintering aids and acceptors. Acceptors play an important role in the PTCR performance when they are well distributed in a grain boundary [4, 5]. In particular, this is achieved when rare-earth ions are partially substituted for Ba^{2+} ions and grain boundaries are oxidized during sintering of the ceramic samples in air. Rare earth oxides, e.g. Gd_2O_3 and Dy_2O_3, inhibit grain growth in $BaTiO_3$ ceramics; moreover addition of such oxides alters the crystal chemistry [6], because of the difference between the ionic radii of the trivalent rare-earth ions and those of Ba^{2+} and Ti^{4+} ions [7]. The

$BaTiO_3$ sintered in air are semi-conductive for Gd-concentration of 0.05 to 0.1 at%. For air sintered $BaTiO_3$, more than 0.2 to 0.4 at% Gd, grain growth inhibition begins, lattice parameters changes and electrical conductivity begins to decrease [8].
Normally, donor-doped $BaTiO_3$ ceramics can be prepared by the mixed oxides solid state reaction method. SiO_2 or a eutectic mixture like Al_2O_3-SiO_2-TiO_2 (AST) or Y_2O_3-SiO_2-TiO_2 (YST) is added

as the sintering aids, which results in the formation of liquid phase in between 1240^0C-1260^0C, thereby lowers the sintering temperature [9]. Usually, the microstructure of such ceramics is a result of liquid phase sintering. The required liquid phase is formed by a reaction between a suitable additive and the $BaTiO_3$ matrix powder. Addition of SiO_2 promotes anomalous grain growth and lowers the sintering temperature of $BaTiO_3$ ceramics. Chen et al [10] studied the effect of YST sintering aids on PTCR properties of $(Pb_{0.6}Sr_{0.3}Ba_{0.1})TiO_3$, revealed incorporation of sintering aids. SiO_2 has lowered the sintering temperature necessary from 1250^oC (10 min) to 1140^oC (10 min). The materials were stabilized only when they contained more than 7.5mol% SiO_2 and were sintered at 1120^oC (10 min) and higher temperature. Here, an attempt has been done to study the PTCR of Gd-doped $BaTiO_3$ with sintering aids prepared at temperature 1120^0C.

EXPERIMENTAL PROCEDURE

The ceramic sample having composition $(Ba_{1-x}Gd_x)TiO_3$ (BGT) with x=0.001-0.005 by solid-state reaction method. High purity (99.99%) chemicals, $BaCO_3$, TiO_2, Gd_2O_3, $Y2O_3$ and SiO_2 in their stoichiometric proportions SBGT samples were labeled as $SBGT_1$ for x=0.001, $SBGT_2$ for x=0.002, $SBGT_3$ for x=0.004, and $SBGT_4$ for x=0.005 with sintering aids YST (1mol% Y_2O_3, 7.5 mol% SiO_2 and 3 mol% of excess TiO_2) were weighed, mixed and grounded thoroughly in an agate mortar for 4 hrs. SBGT samples were calcined in air media at 950^0C and at 1000^0C for 8 hrs in an alumina crucibles, with intermediate grindings for 2 hrs, in a programmable high temperature muffle The finished powder was pressed and plastified using aqueous (5%) polyvinyl alcohol into a circularly shaped disc pellets of 10mm diameter and thickness of 1.5mm using tungsten carbide dye and plunger with hydrostatic pressure of 45 kN/m^2, The pellets were sintered at 1120^0C and annealed at 1050^0C for 1hr. The heating and cooling rate for all thermal cycles was 2^0C/min. The sintered pellets were polished and coated with silver paint and later cured at 400^0C for 1hr. The DC electrical conductivity was estimated by measuring the resistivity with two-probe employing a digital multimeter (Keithley, Model 2000) in the temperature range 30^0C-300^0C.

RESULTS AND DESCUSSION

The SBGT ceramic samples were prepared by solid state reaction method. Figure 1 shows the resistivity vs. temperature characteristics for SBGT samples ($SBGT_1$, $SBGT_2$, $SBGT_3$ and $SBGT_4$). The dc resistivity (ρ_{dc}) was evaluated from the measured resistance 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 resistivity of $SBGT_1$ samples at room temperature is less than that of $SBGT_2$, $SBGT_3$ and $SBGT_4$ samples and the magnitude of the PTCR jump and PTCR coefficient of $SBGT_1$ samples decreases for the higher Gd content. The room temperature resistivity (ρ_{RT}), maximum resistivity (ρ_{max}), resistivity jump (ρ_{max}/ρ_{RT}), TCR and E_a values are shown in Table 1.

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

$$\alpha = 2.303\{\log[R_a/R_b]/[T_a-T_b]x100(\%/^0C)$$

where R_a is the resistivity at temperature T_a and Rb is the resistivity at temperature T_b [11]. The obtained α_{PTCR} value is ≈ 2-15 %/^{0}C and α_{NTCR} value is ≈ 1.5-12 %/^{0}C. Like Al_2O_3, the inclusion of Y_2O_3 sintering aid, raises the room-temperature resistivity slightly, which possibly arises from the formation of incompletely compensated surface states [12-14], due to the segregation of Y^{3+} at grain boundary regions. The grain-boundary Schottky barrier is not

completely suppressed below the Curie point [15, 16]. Similarly, the addition of SiO_2 moderately lowers the room-temperature resistivity. The high-temperature resistivity of all the samples is changed. Since the high-temperature resistivity is known to be due to the formation of the Schottky barrier at the grain boundaries, it is thus inferred that the liquid phase resulted from YST sintering aids will accumulate gradually at junctions of grains such that the grain boundaries are almost free from the YST phase. These ions act as electron trap, which increase the Schottky barrier height and in turn, raises the T_c of the samples [17].

All our samples demonstrated mixed TCR effect i.e., PTCR as well as Negative TCR (NTCR) behaviour. Here, Gd^{3+} act as electron donor and charge compensation results in variation of electrical conductivity. It was reported that the doped-$BaTiO_3$ ceramic sintered in air at 1280ºC is semiconductive only at Gd content of 0.05-0.1 at%. For air-sintered specimens of $BaTiO_3$ containing Gd>0.2-0.4 at%, grain growth inhibition begins, hence lattice parameters changes, and electrical conductivity begins to decrease [18].

The activation energy (E_a) is obtained from the inclinations of log conductivity vs. reciprocal of absolute temperature curve. It is found to be 0.215eV to 0.985eV in the PTC region and 0.107 eV to 0.204 in the NTC region.

CONCLUSION

The synthesized Gd^{3+}-doped $BaTiO_3$ with YST sintering aids exhibited mixed TCR behaviour. PTCR property begins from room temperature and remains up to T_c and further show NTCR behaviour, with nearly same range of TCR values for all the samples, which shows the improved TCR properties due to YST aids. High temperature resistance is due to grain-growth inhibition and electrical charge compensation. Improved TCR coefficient is due to incorporation of YST aids, which lowered the sintering temperature from the reported 1280ºC to 1140ºC.

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Table 1- Electrical data of synthesized samples

Sample code → Electrical Parameters↓		$SBGT_1$	$SBGT_2$	$SBGT_3$	$SBGT_4$
ρ_{RT} x10^8 (Ω.Cm)		2.10x10^5	2.75x10^8	3.14x10^8	2.75x10^8
ρ_{max} x 10^{10} (Ω.Cm)		8.00x10^8	0.18x10^{10}	0.38x10^{10}	0.51x10^{10}
ρ_{max}/ρ_{RT}		3.92x10^3	0.68x10	1.22x10	1.85x10
T_C (^{0}C)		130	50	80	100
TCR (%/^{0}C)	PTCR	2 to 15.62	3.1 to 7.44	5.75 to 6.37	3.0 to 12.0
	NTCR	-1.4 to -4.9	-2.3 to -36.7	-1 to -12.7	-1.5 to -3.07
Activation energy (eV)	$+E_a$	0.9845	0.3019	0.1481	0.2156
	$-E_a$	0.2042	0.1258	0.1306	0.1078

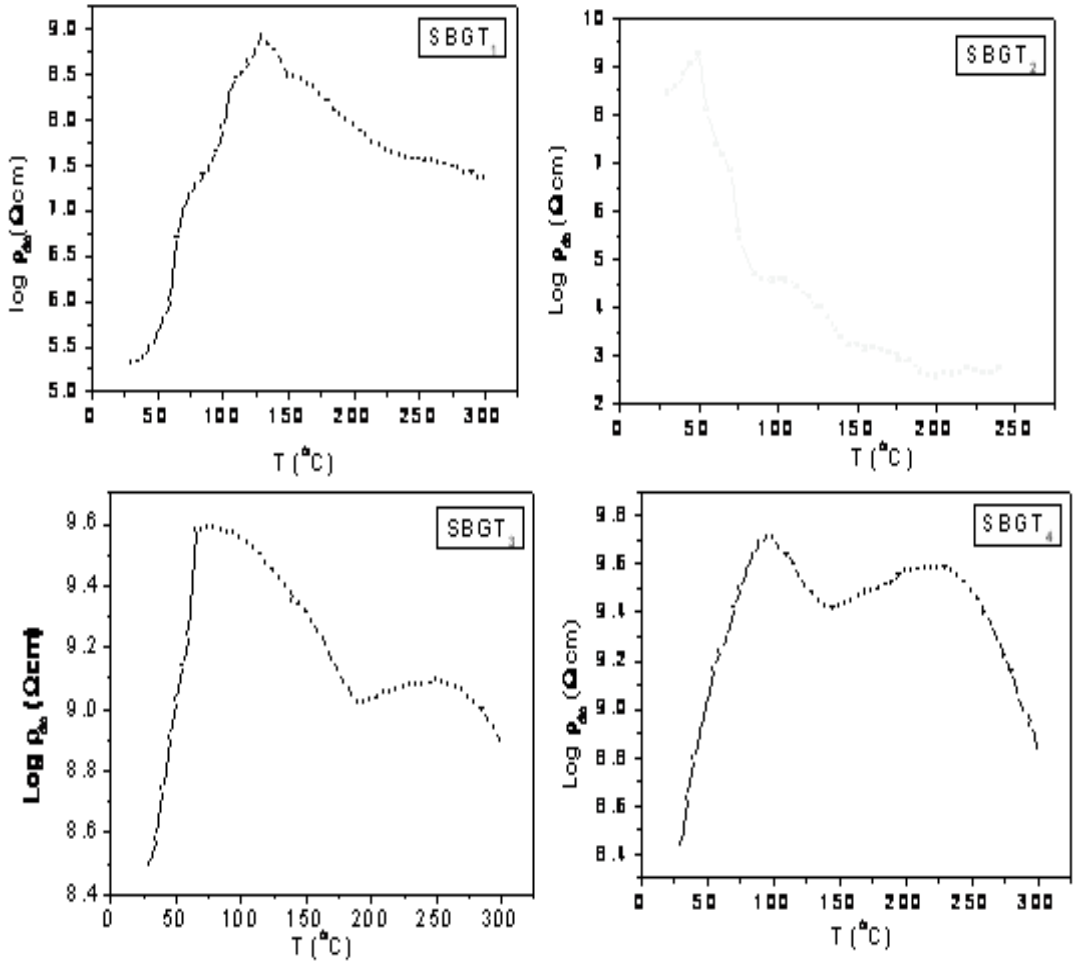

Fig. 1- Resistivity-Temperature characteristics of SBGT samples