DIELECTRIC PROPERTIES OF GD-DDOPED BaTiO$_3$
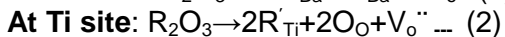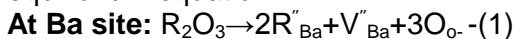
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Abstract- Ferroelectric $(Ba_{1-x}Gd_x)TiO_3$ (x=0.001, 0.002, 0.004 and 0.005) (BGT) ceramic samples were prepared by employing a solid-state reaction technique. Dielectric properties were investigated by measuring the capacitance measurement in the temperature range 30^0C-400^0C. for x=0.002 sample, large value of dielectric constant was obtained at room temperature, maximum dielectric constant (ε_{max}) of 4523 was observed at T_c, and further increase of Gd content lowered the ε_r. It was also observed that the phase transition peak was broadened with the increase of Gd-concentration.

1. INTRODUCTION

BaTiO$_3$ is a well-known ferroelectric ABO$_3$–based perovskite with high permittivity (>1000) at room temperature and one of the most widely used ceramic materials in electronic industry [1]. A more effective way to use BaTiO$_3$-based ceramic materials is with high dielectric properties as the capacitor when doped with some rare-earth oxides. The relative permittivity (ε_r) was increased up to 5000 in polycrystalline BaTiO$_3$ of 1.1µm-grain size [2, 3]. At high temperature, the rare-earth elements dissolve in both the A-and B-sites, depending on the A/B ratio in BaTiO$_3$. Hiroshi Kishi et al [4] reported that rare earth elements are believed to act as a donor in the Ba-site or as an acceptor when they dissolve in the Ti-site, as represented by the chemical equilibrium equation:

At Ba site: $R_2O_3 \rightarrow 2R^{''}_{Ba} + V^{''}_{Ba} + 3O_o$ -(1)

At Ti site: $R_2O_3 \rightarrow 2R^{'}_{Ti} + 2O_O + V_o^{\cdot\cdot}$ --- (2)

Aliovalent dopants have a profound influence on micro-structural developments and the resultant electrical properties of BaTiO$_3$-based ceramics [5].

This paper reports on substitution of Gd at Ba-site of BaTiO$_3$ and studies to reveal its effect on the dielectric properties.

2. 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$_2$O$_3$, in their stoichiometric proportions BGT samples were labeled as BGT$_1$ for x=0.001, BGT$_2$ for x=0.002, BGT$_3$ for x=0.004, and BGT$_4$ for x=0.005 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, with intermediate grindings for 2 hrs, in a programmable high temperature muffle The finished powder was pressed and plasticized 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 1280^{0}C and annealed at 1175^{0}C for 1hr. The heating and cooling rate for all thermal cycles was 2^{0}C/min. These sintered pellets were polished and coated with silver paint and later cured at 400^{0}C for 1hr. Dielectric measurements were obtained by employing a capacitance measurement in the temperature range 30^{0}C-400^{0}C.

3. RESULTS AND DISCUSSION

When Gd substitutes at Ba^{2+} and Ti^{4+}-sites, it leads to variance in the vacancy concentration in the crystals. Solubility at different lattice site is decisively influenced by the energy needed to form compensating defects. However, no energy is needed for dopants to concentrate at grain boundaries. Hence, Gd^{3+} is rich at or near grain boundaries to restrain abnormal grain growth during sintering, as it promotes the formation of fine grains and high density in BaTiO$_3$. This suggests that all defect concentrations are the lowest. Gd could retard the abnormal grain growth during sintering, which caused the average grain size, about 1μm when x≤0.002, the substitution mechanism reaction can be, xGd^{3+}+BaTiO$_3$→(Ba$^{2+}_{1-x}$Gd$^{3+}_{x}$)[Ti$^{4+}_{1-x}$(Ti^{4+}e)]O$_3$+xBa^{2+} --------------------(3)

When Gd occupies Ba-site, Ti^{4+} reduces to Ti^{3+} and in order to keep charge neutrality, conduction electron (Ti^{4+}e) is formed. Subsequently, at the critical dopant concentration, i.e., at 0.2at% resistivity (ρ_{dc}) and dielectric constant (ϵ_r) decreases sharply. When Gd substitutes both at Ti^{4+} and Ba^{2+}, with a higher dopant level, i.e., ≥ 0.2 at %, the charge is compensated, results into high resistivity.

A compensation mechanism reaction [6] is, xGd^{3+}+BaTiO$_3$→Ba$^{2+}_{1-x/2}$ Gd$^{3+}_{x}$(Ti$^{4+}_{1-x/2}$)O$_3$ +x/2Ba^{2+}+x/2Ti^{4+}-- (4)

The permittivity (ϵ_r) as a function of temperature for BaTiO$_3$ doped with different concentrations of Gd$_2$O$_3$ is shown in Figure 1 and Table 1 shows the estimated dielectric parameters.

For BGT$_2$ sample, ϵ_r is of the order of 1323 at room temperature. At the Curie point near 120°C, ϵ_r rises sharply to about 4523, and above this temperature then it decreases obeying Curie-Weiss law. This ferroelectric behavior was observed in all the samples exhibiting a pronounced Curie peak for x=0.004 and x=0.005 samples.

Table 1: Dielectric data of BGT samples

Sample Label	Dielectric parameters		T$_c$ (^{0}C)
	ϵ_{RT}	ϵ_{max}	
BGT$_1$	1020	2422	110
BGT$_2$	1323	4523	110
BGT$_3$	1089	1861	115
BGT$_4$	145	265	115

The room temperature ϵ_{RT} values for samples x=0.001, and x= 0.002 was found to be increased with respect to undoped BaTiO$_3$. This increase in the maximum permittivity at the Curie peak (ϵ_{max} = 2422 and 4523) in BGT$_1$ and BGT$_2$ samples may be explained in the light of the type of solid solution. The addition of Gd$_2$O$_3$ to BaTiO$_3$ does not show any noticeable change shift in the Curie temperature up to 0.2 at %, which is in agreement with the reports for BaTiO$_3$ doped with rare earths [2,3, 7].

Thus, as a result of formation of this solid solution, an increase in the polarization arises from these charge carriers, which tends to trap and accumulate lattice defects (Barium vacancies) and hence there is an apparent increase in the ϵ_r. J P Bonsack [8] and Mazdiasni et al [9] have explained an increase in the permittivity of BaTiO$_3$ with additives and attributed them mainly to density and grain size. Further according to M. A. Issa et al [10], grain size effects do not play the major role in permittivity.

In our case, this behavior would indicate that the density is not the dominant

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factor in increasing ϵ_r. Here, the value of ϵ_{max} and ϵ_{RT} increases for BGT_1 and BGT_2 and decreases for BGT_3 and BGT_4 samples.
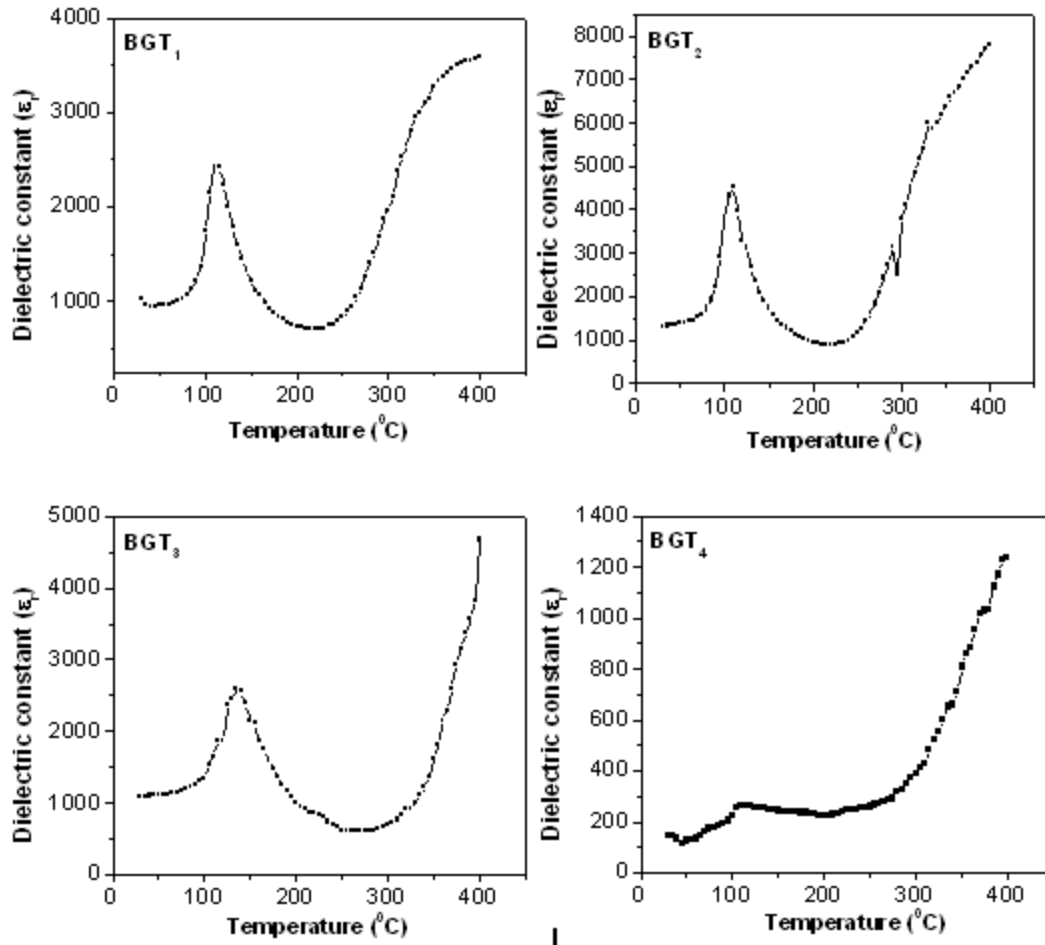

Fig. 1- Variation of ϵ_r as a function of temperature in BGT samples

4. CONCLUSIONS

The introduction of Gd as a donor dopant affects the dielectric properties at the room temperature as well as the transition temperature. BGT_2 has shown the most profound effect in dielectric behaviour. The large difference in ϵ_r is due to lattice distortions and grain boundaries.

ACKNOWLEDGEMENTS

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