

Dielectric characterization of the system $\text{Sr}_{1-x}\text{Gd}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.10$) using impedance spectroscopy

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ABSTRACT

The structure of ceramic grain boundaries, boundary composition, the boundary charge and associated space charge controls the dielectric and electrical behavior of ceramics. Various methods were researched and applied to increase the dielectric constant by formation of insulating layers between semi-conducting grains. In this communication, we are reporting the effect of cooling rates from sintering temperature to room temperature on dielectric properties of the resulting ceramics in the system, $\text{Sr}_{1-x}\text{Gd}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.10$. All the samples in this system were prepared by conventional high temperature solid state reaction method. The samples were cooled at different cooling rates from sintering temperature to room temperature. The capacitance and dielectric loss were measured as a function of frequency and temperature using HP 4192A LF impedance analyzer. The samples cooled from different cooling rates from sintering temperature show interesting dielectric properties due to formation of insulating layers between grains. The impedance spectroscopy is used successfully in explaining the dielectric properties of these materials.

Key words: Dielectric characterization, impedance spectroscopy.

INTRODUCTION

The electronic ceramics or electro ceramics are high technology materials whose properties and hence, applications depend on a complex interplay of structural, processing and compositional variables. The particular property of interest may be bulk property of the crystal or grain boundaries in polycrystalline materials i.e. the difference in nature between bulk (grain) and grain boundary regions. For the past few years, various efforts have been made by several groups to increase the dielectric constant by formation of barrier layers between grains or varying the conductivities of grains and grain boundaries of the materials. These include a variety of substitutions or by suitable controlling the processing parameters^{1,2}. Most of the commercially used ceramics have compositions based on the perovskite structure ABO_3 where A is alkali or alkaline earth ion and B is transition metal ion or

rare earth ions. The effect of cationic substitutions in the perovskite lattice on symmetry and physical properties were investigated by several workers³⁻⁵. The alkaline earth titanates doped with rare earth ions have been studied extensively because of their potential applications as thermistors at low doping levels^{6,7}. Strontium titanate doped with rare earth ions exhibit relaxor behavior with increased permittivity⁸. Strontium titanate forms solid solution with lanthanum cobaltite over the entire range of compositions^{9,10}. Compositions with $x \leq 0.50$ have been reported to exhibit relaxor behavior characteristics of barrier layers produced during their processing¹¹ considering the interesting and useful properties of the above system different compositions have been synthesized and studied in an analogous system of the type $\text{Sr}_{1-x}\text{Gd}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ which represents the solid solution between SrTiO_3 and GdCoO_3 . In this system simultaneous substitution of La^{3+} at Ba^{2+} site and Co^{3+} at Ti^{4+} site is expected to maintain the charge neutrality

internally without creation of vacancies in cationic or anionic sub-lattices. In this paper, we are reporting the effect of cooling rates from sintering temperature to room temperature on dielectric properties of the resulting ceramics in the system $\text{Sr}_{1-x}\text{Gd}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.10$.

EXPERIMENTAL

All the samples were prepared by conventional high temperature ceramic method using analytical grade strontium carbonate, gadolinium oxide, titanium dioxide and cobalt oxalate, all having purity better than 99.5%. The stoichiometric amount of starting materials was mixed and grinds using acetone as grinding medium in an agate mortar pestle. The mixed and dried powders were calcined at 1525 K for 12 hours. All these samples were sintered at 1625 K for 12 hours as cylindrical pellets. The intermediate grinding and sintering were repeated to ensure complete homogenization of the product. The sintered pellets were cooled with different cooling rates (5 °C/min. and 20 °C/min.) from the sintering temperature to room temperature. The sintered pellets were powdered and powder x-ray diffraction pattern were recorded using Rigaku Rotoflux x-ray diffractometer employing Cu-K α radiation. Capacitance and dielectric loss were measured on polished pellets coated with silver paint (cured at 975 K for 30 min.) as a function of frequency and temperature using Hewlett Packard 4192A LF impedance analyzer.

RESULTS AND DISCUSSION

It is found from the x-ray diffraction data that the composition prepared in the system $\text{Sr}_{1-x}\text{Gd}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.10$ shows the formation of single phase solid solution. XRD pattern did not contain any other lines characteristic of the constituent oxides or any other compound between them. XRD data for this composition could index on the basis of simple cubic unit cell similar to SrTiO_3 ^{2,12,13}.

The variation of dielectric constant as a function of temperature for the composition $\text{Sr}_{1-x}\text{Gd}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.10$ with cooling rates 5 °C/min. and 20 °C/min. at three frequencies 1, 10 and 100 KHz are shown in Fig. 1-2. These plots indicate that dielectric constant remains constant up to a particular temperature thereafter it decreases rapidly with increase in temperature. This particular temperature increases with increase in frequency.

Plots of dielectric loss as a function of log of frequency are given in Figs. 3-4 for different cooling rates, peak at a particular frequency, which increases with increase in temperature. In this system, peak value of loss at particular temperature increase with increase in temperature. A peak in loss versus log f plot is characteristics of relaxation process in which a peak is observed when $\omega\tau = 1$ where $\omega = 2\pi f$ and τ is the relaxation time. Since

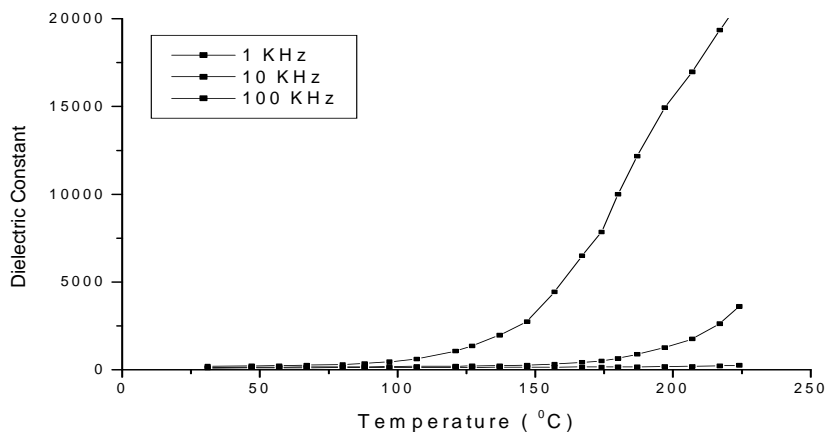


Fig. 1: Dielectric constant as a function temperature for $\text{Sr}_{1-x}\text{Gd}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.10$ with cooling rate 5 °C/min

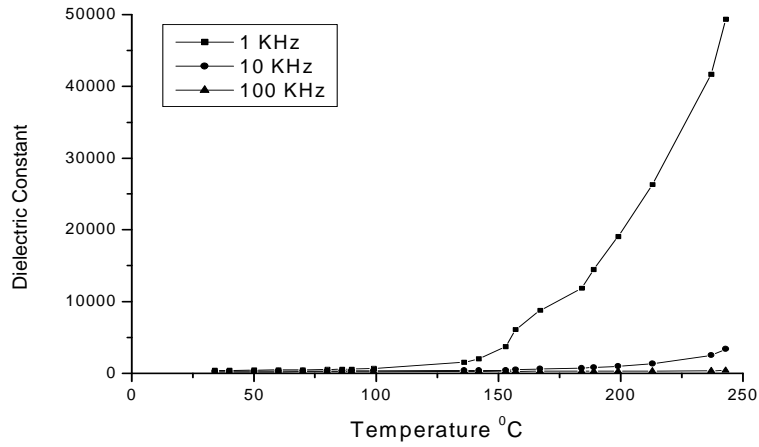


Fig. 2: Dielectric constant as a function temperature for $Sr_{1-x}Gd_xTi_{1-x}Co_xO_3$ with $x = 0.10$ with cooling rate $20\text{ }^\circ\text{C}/\text{min}$

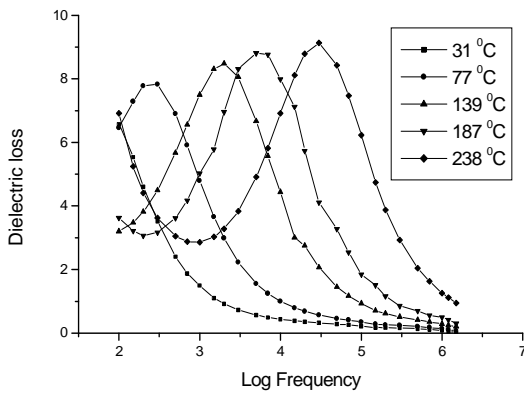


Fig. 3: Dielectric loss as a function temperature for $Sr_{1-x}Gd_xTi_{1-x}Co_xO_3$ with $x = 0.10$ with cooling rate $20\text{ }^\circ\text{C}/\text{min}$

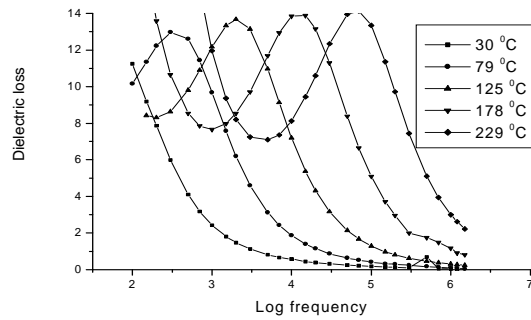


Fig. 4: Dielectric loss as a function temperature for $Sr_{1-x}Gd_xTi_{1-x}Co_xO_3$ with $x = 0.10$ with cooling rate $5\text{ }^\circ\text{C}/\text{min}$

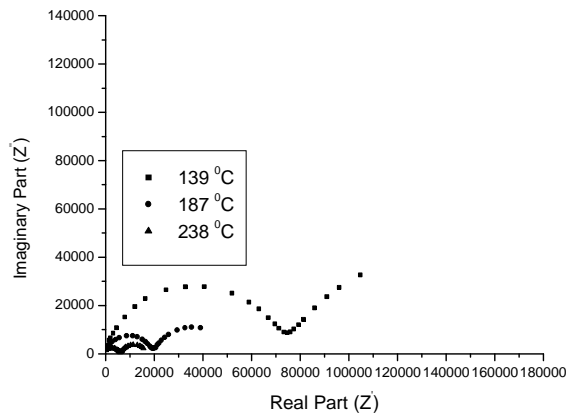


Fig. 5: Z' versus Z'' plots $Sr_{1-x}Gd_xTi_{1-x}Co_xO_3$ ($x = 0.10$) with cooling rate $20\text{ }^\circ\text{C}/\text{min}$. at three different temperatures

peak frequency is increasing with increase in temperature, the relation $\omega\tau = 1$ will be satisfied for higher values of ω with increase in temperature.

The samples cooled with cooling rate 20 °C/min. possesses high value of grain boundary resistance which increases the dielectric constant of the material as compared to samples with cooling rate 5 °C/min. Dielectric loss also decrease substantially for the samples with higher cooling rates. Dielectric properties of this composition can be explained by considering the nature of grain and grain boundaries. For the last few years, impedance spectroscopy is used as tool to reveal the nature of grain and grain boundaries. Usually three different processes take place during charge transport

through a polycrystalline ceramic (i) bulk conduction (ii) grain boundary conduction and (iii) conduction across the electrode – specimen interface. Each of these processes may be represented as an R-C parallel combination. The overall specimen then corresponds to circuit comprising of three R-C parallel combinations connected in series. In impedance spectroscopy, the imaginary part (Z'') of the total impedance (Z^*) is plotted against the real part (Z') over a range of frequencies. The three transport processes have single but significant by different values of the relaxation times ($t = 1/RC$), then one gets three distinct semicircular arc with their centers on the real axis, the arc with highest frequency range represents the bulk conduction, the arc with intermediate frequency range

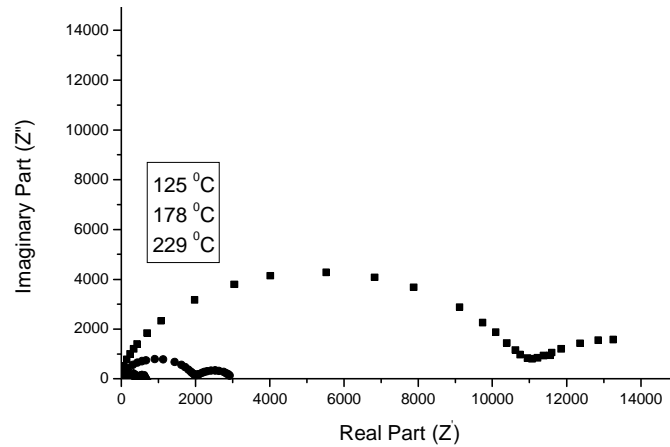


Fig. 6: Z'' versus Z' plots for $\text{Sr}_{1-x}\text{Gd}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.10$) with cooling rate 5 °C/min. at three different temperatures

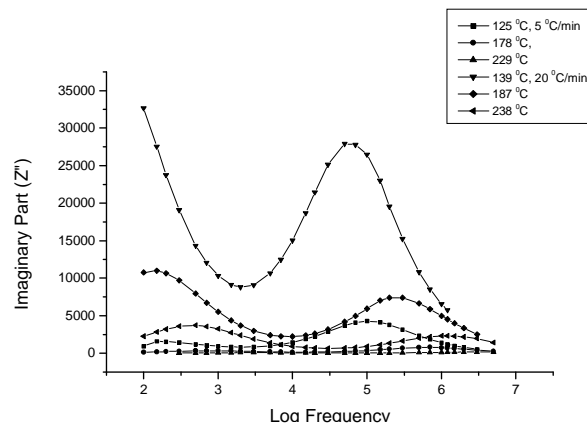


Fig. 7: Z'' versus $\log f$ plots for $\text{Sr}_{1-x}\text{Gd}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.10$) with cooling rate 5 °C/min. and 20 °C/min at three different temperatures

represents the grain boundary conduction and the arc with lowest frequency range represents contribution of the electrode conduction. If any of the process has a distribution of relaxation times, a depressed semi-circular arc with centre below the real axis is obtained corresponding to that process in complex impedance plot. The resistance contribution to the total observed resistance due to any of the above process is given by the intercept on the real axis and corresponding capacitance is given by the highest point of the arc where $\omega RC = 1$ and ω is applied angular frequency^{2, 14-16}.

The variation of Z'' with Z' at three selected temperatures for samples with cooling rates 5 °C/min. and 20 °C/min. are shown in Figs. 5 -6. These impedance plots give rise to two semi-circular arcs. The arc in higher frequency region shows bulk resistance whereas lower frequency arc shows grain boundaries contribution. The corresponding intercepts on a-axis will give the values of grain and grain boundaries resistances of the samples. It is observed from these figures that the resistance of grain boundary increases with increase in cooling rate from 5 °C/min. to 20 °C/min. These high resistance grain boundaries envelopes the grains having comparatively low resistance. These grain boundaries are source of heterogeneities, which occur in polycrystalline ceramics. The difference in electrical conductivity of grains and grain boundaries give rise to interfacial polarization in the present materials^{16,17}. The grain boundaries with high resistance compared to grains impeded the movement of dipoles or transport of charge carriers

between grains. This charge accumulation and hence interfacial polarization is responsible for high dielectric constant in lower frequency range. A wide dispersion in dielectric parameters observed in these materials can also be explained considering the role of interfacial polarization. The presence of interfacial or space charge polarization can also be confirmed by nature of impedance pattern. Fig. 5 shows the variation of imaginary part of total impedance (Z'') as a function of frequency at few selected temperatures.

It shows appearance of peaks at a particular frequency dependent on temperature and can be related to the type and strength of the electrical relaxation phenomenon in the material. The peak appears to shift towards high frequency region with increase in temperature due to increasing relaxation in the sample. The magnitude of Z'' maxima decrease with temperature indicating increasing loss in the resistive property of the material due to presence of space charge in the materials^{18,19}. Hence is concluded from this study that by varying and controlling the different processing parameters, dielectric properties can tailored for various technological applications.

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