

High frequency and temperature stable dielectric response of Cr³⁺ doped Sm_{1.5}Sr_{0.5}NiO₄ ceramics

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Abstract: The structural and electrical properties of ceramics Sm_{1.5}Sr_{0.5}NiO₄ with Cr doped in Ni site are evaluated over wide ranges of temperature (303K – 473K) and frequency (50 Hz – 5 MHz) values. The polycrystalline samples of Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO₄ ceramics (x=0.0, 0.075, 0.1) are prepared through the standard solid state reaction method. The refinement of the X-ray diffraction data using the Rietveld method confirmed a single phase compound with orthorhombic structure. Dielectric studies show frequency independent high dielectric constant values (10⁴) up to MHz region and considerable reduction in dielectric loss with increase in frequency. Similar results of dielectric constant are observed with increase in temperature with thermal stability around 303 – 380 K. The impedance spectrum analysis indicates that the colossal dielectric values are contributed by the more resistive grain boundaries.

Keywords: Solid state reaction; Sintering; Grain boundaries; Dielectric properties; Impedance

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I. Introduction

Materials with high dielectric constant values have the potential of yielding major technological development. The discovery of materials with ABO₃ structure like CaCu₃Ti₄O₁₂ (CCTO) has promoted the research for finding new materials with giant dielectric constant [1-14]. Previous experiments have shown that certain materials with K₂NiF₄ type structure, commonly known as nickelates [9-15], can exhibit giant dielectric response. Giant dielectric responses were observed in La_{2-x}A_xNiO₄ (A = Sr, Ca and Ba) up to GHz frequency. However, it showed a step like decrease in dielectric constant towards low temperature region (below 200 K) [13]. Similarly high electrical conductivity in Sm_{1.5}Sr_{0.5}NiO₄ resulted in a considerably high loss factor which made this material less fit for practical applications [14]. This work is a successful attempt to get control over the dielectric loss of Sm_{1.5}Sr_{0.5}NiO₄ nickelates from room temperature onwards by controlling its electrical conductivity by lightly substituting nickel with chromium at the B-site.

II. Material And Methods

Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO₄ (x=0.0, 0.075, 0.1) nickelates were prepared by solid state reaction of stoichiometric amounts of pure Sm₂O₃ (99.9%), SrCO₃ (99%), Cr₂O₃ (99.9%) and NiO (99%), all in powder form. For this, the accurately weighed samples were thoroughly mixed in an agate mortar in an alcohol medium. The dried-up mixture was then calcined at 1423 K for 14 hours to yield the desired material. The crystalline phases of the compounds were studied by powder X-ray diffraction using Cu K_α radiation on a Bruker D8 Advance diffractometer. The calcined powder was pressed into pellets incorporating polyvinyl alcohol (PVA) under a pressure of 5 tonnes for 3 minutes. The pellets were sintered at 1673 K for 16 hours and the flat surfaces were coated uniformly with pure silver paste. The electrical properties of this parallel plate capacitor unit component were studied using a Hioki 3532 LCR HiTester in the frequency range 50 Hz to 5 MHz and temperature range 303 K to 473 K.

III. Results and discussion

The powder XRD data of Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO₄ (x=0.0, 0.075, 0.1) ceramics refined by the Rietveld method are shown in Fig. 1. Assuming the *Bmab* space group of Sm_{1.5}Sr_{0.5}NiO₄ [14], the refinement converged to a single orthorhombic phase and the refined parameters are provided in Table 1.

Table1. The refined parameters from the XRD patterns of $Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO_4$ ($x = 0.0, 0.075, 0.1$) ceramics.

$Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO_4$	$x = 0.00$	$x = 0.075$	$x = 0.1$
Lattice parameters(Å)			
a	5.3166 (2)	5.3283 (3)	5.33959 (15)
b	5.3542 (2)	5.3633 (3)	5.36527 (15)
c	12.3452 (5)	12.3297 (4)	12.3248 (4)
Goodness of fit			
χ^2	3.46	2.83	1.51

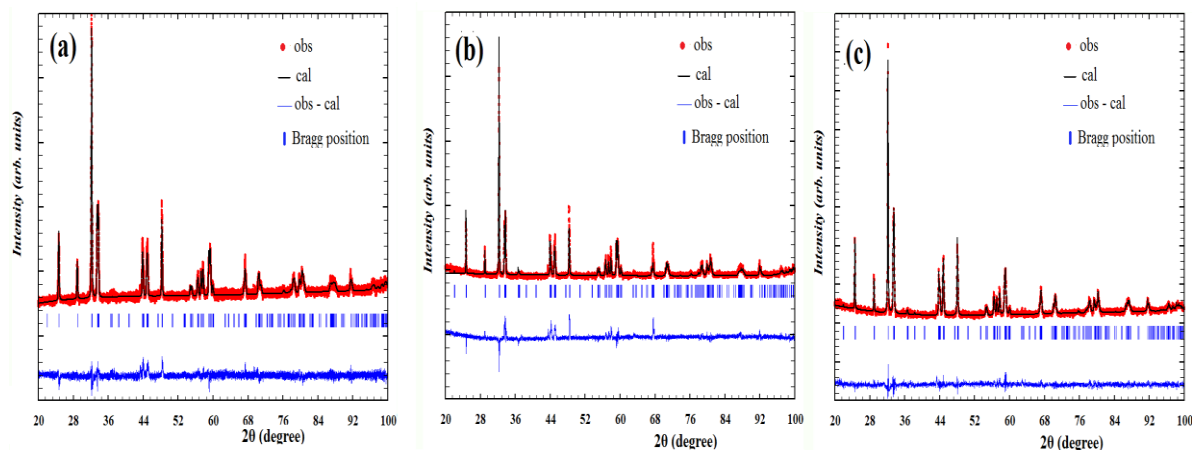


Figure1. The Rietveld refined results for X-ray diffraction patterns of (a) $Sm_{1.5}Sr_{0.5}NiO_4$, (b) $Sm_{1.5}Sr_{0.5}Ni_{0.925}Cr_{0.075}O_4$ and (c) $Sm_{1.5}Sr_{0.5}Ni_{0.9}Cr_{0.1}O_4$ ceramics at room temperature.

In the surface morphological studies as shown in figure 2, the doped samples have smaller grain sizes (4 – 10 μm) as compared to the undoped sample of which the grain size is 12- 15 μm .

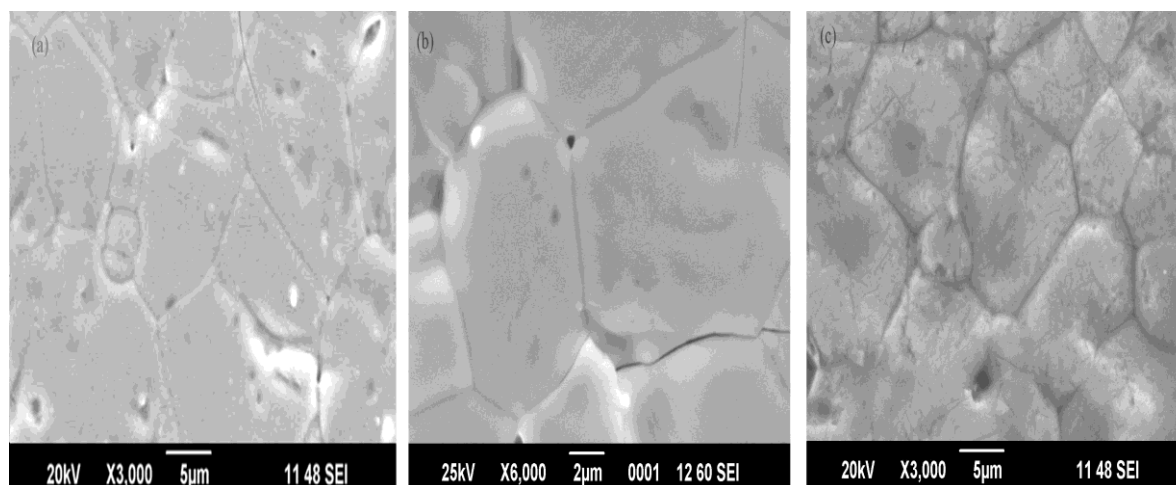


Figure 2. SEM images of $Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO_4$ with (a) $x = 0.0$, (b) $x = 0.075$ and (c) $x = 0.1$.

Figure 3(a) shows the enhanced frequency stability of the colossal dielectric values of all the samples at room temperature. A higher value of dielectric constant ($\epsilon_r \sim 10^4$) is observed in $Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO_4$ ($x = 0.075, 0.1$) ceramics compared to the undoped sample. Also the dielectric constant of the doped samples remains to be almost steady up to the MHz region.

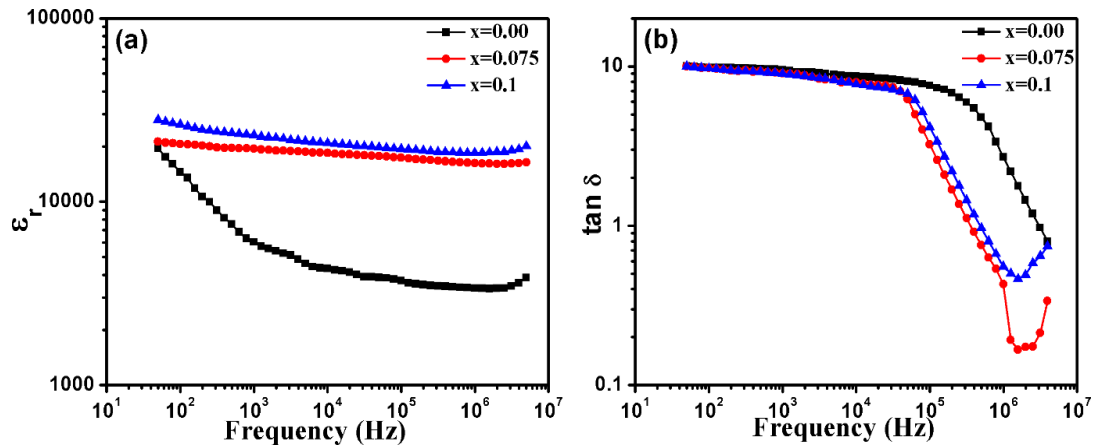


Figure 3. Frequency responses of (a) dielectric constant (ϵ_r) and (b) dielectric loss ($\tan \delta$) of $Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO_4$ ($x = 0.0, 0.075, 0.1$) ceramics at room temperature.

The corresponding dielectric loss values ($\tan \delta$) are shown in Fig. 3(b). It is seen that the loss tangent reduces significantly at higher frequencies, i.e. in the order of 0.1 magnitude in $Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO_4$ ($x=0.075, 0.1$) ceramics as compared to the corresponding decrease in pure $Sm_{1.5}Sr_{0.5}NiO_4$ sample. This can be attributed to the suppression of electrical conductivities in the doped samples since the conductivity is related to the imaginary part of permittivity ϵ'' and hence to the loss factor by the equation

$$\sigma = \omega \epsilon'' \epsilon_0 \tag{1}$$

Because Cr^{3+} is the most stable oxidation state, the presence of free charge carriers is minimal resulting in reduced conductivity and hence low dielectric loss of the doped samples.

The temperature dependence of dielectric constant and their corresponding dielectric loss of the material at selected frequencies are shown in Fig. 4. The dielectric constant of the doped samples is much higher than that of the pure sample and it remains almost stable over a wide temperature range from 303 – 380 K. Beyond this range the dielectric constant increases with the advent of interfacial polarization [16]. The dielectric loss of the doped samples decreases as frequency increases at higher temperatures which makes it suitable of high frequency applications.

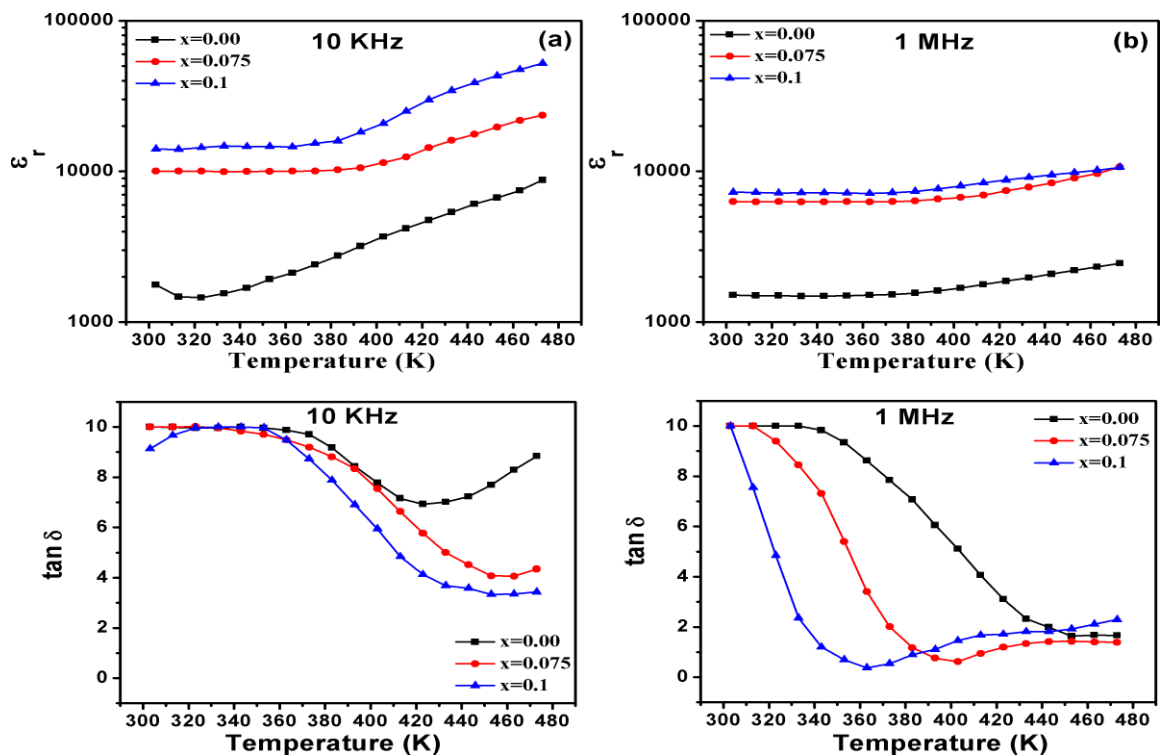


Figure 4. Temperature dependence of dielectric constant for different frequencies of $Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO_4$ ($x = 0.0, 0.075, 0.1$) ceramics.

In order to understand the origin of high dielectric constant values in these samples, one needs to analyse the contributions of the bulk and boundaries of the grains [17-18] along with the overall electrical conductivity of the sample. Figure 5(a) shows the Nyquist plots (Z'' vs Z') at room temperature. Since only one arc is observed, the dielectric response arises due to the polarisation at the grain boundaries [19]. The semi-circular arcs observed with non-zero intercepts at high frequencies (toward lower Z' values) indicate the electrical heterogeneity of the samples. From Fig. 5(a), it is observed that the radius of the frequency arcs increases with increase in Cr³⁺ dopant concentration which is due to the increased resistivity of the doped samples.

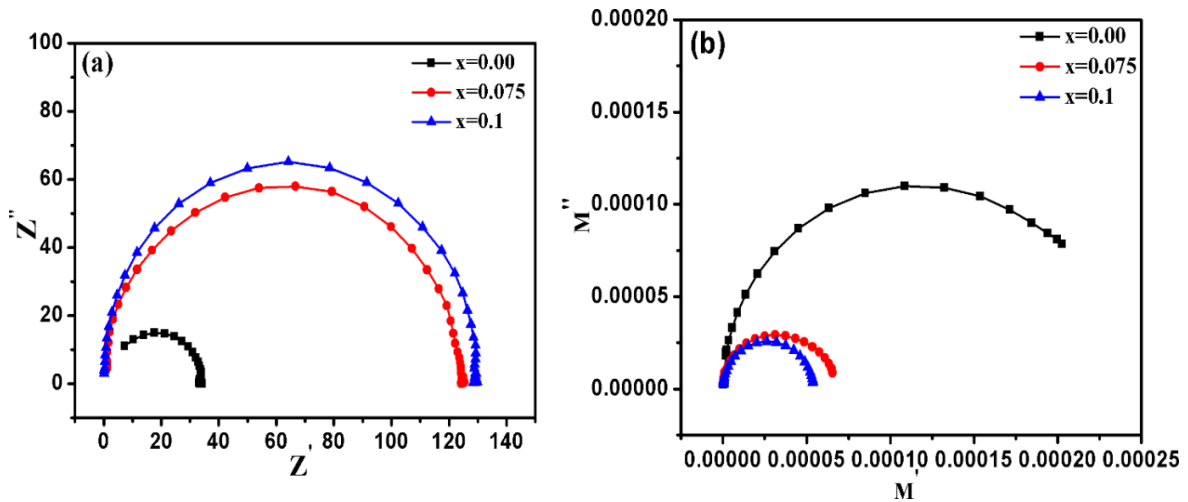


Figure 5. (a) Complex impedance spectra and (b) modulus spectroscopy plot at 303 K.

The single arcs of the samples can be attributed to the parallel combination of the capacitance C_{gb} and resistance R_{gb} of the grain boundary regions [20]. Hence the total impedance from the equivalent circuit can be written as

$$Z^* = \frac{R_{gb}}{1 + (i\omega R_{gb} C_{gb})} \quad (2)$$

The conductivity ($\ln \sigma$) values drawn from this equation is plotted against $1000/T$ in Fig. 6. The linear graphs are suggestive of the Arrhenius type conduction mechanism given by the equation

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (3)$$

where k_B is the Boltzmann constant and T is the absolute temperature. The activation energies E_a calculated from the slope of $\ln \sigma$ vs $1000/T$ are 100 meV for Sm_{1.5}Sr_{0.5}NiO₄ sample and for Cr³⁺ doped Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO₄ samples the values are 107 meV and 114 meV for $x=0.075$ and $x=0.1$ respectively. These higher values of activation energy for the doped samples result in their higher dielectric constant values.

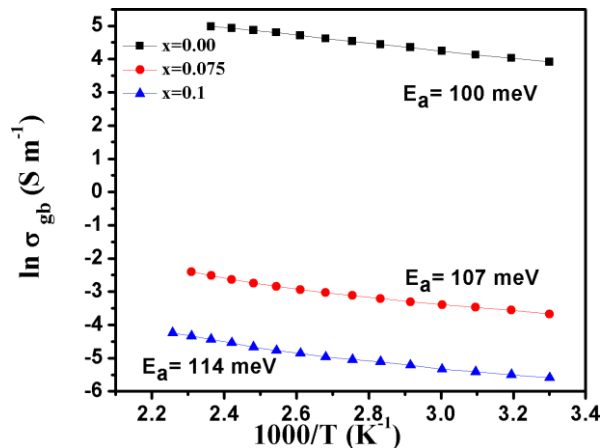


Figure 6. Arrhenius plots of conductivity corresponding to grain boundary.

In order to confirm the dielectric behaviour of the samples, the modulus spectrum may be analysed as it is linked to the capacitance and also more arcs may appear in the modulus spectrum which reveals the contribution of different factors [18]. In the room temperature modulus spectrum of the samples shown in Fig. 5(b) we observe only one arc which is also due to the contribution of grain boundaries.

The combined plots of M'' and Z'' vs. frequency may be used to provide information on long range or short range movement of the charge carriers [21]. In Fig. 7, the separation of the peak frequencies between M'' and Z'' corresponding to the $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{Ni}_{1-x}\text{Cr}_x\text{O}_4$ ($x=0.075, 0.1$) samples suggest a thermally activated hopping process in which the short range movement of the charge carrier dominates as compared to the long range movement in the undoped sample. The dielectric relaxation time, τ is calculated using the relation

$$\tau_z = 1/2\pi f_{(max)} \quad (4)$$

where $f_{(max)}$ is the peak frequency of M'' . This relaxation time plotted against the function of temperature is shown in Fig. 7.

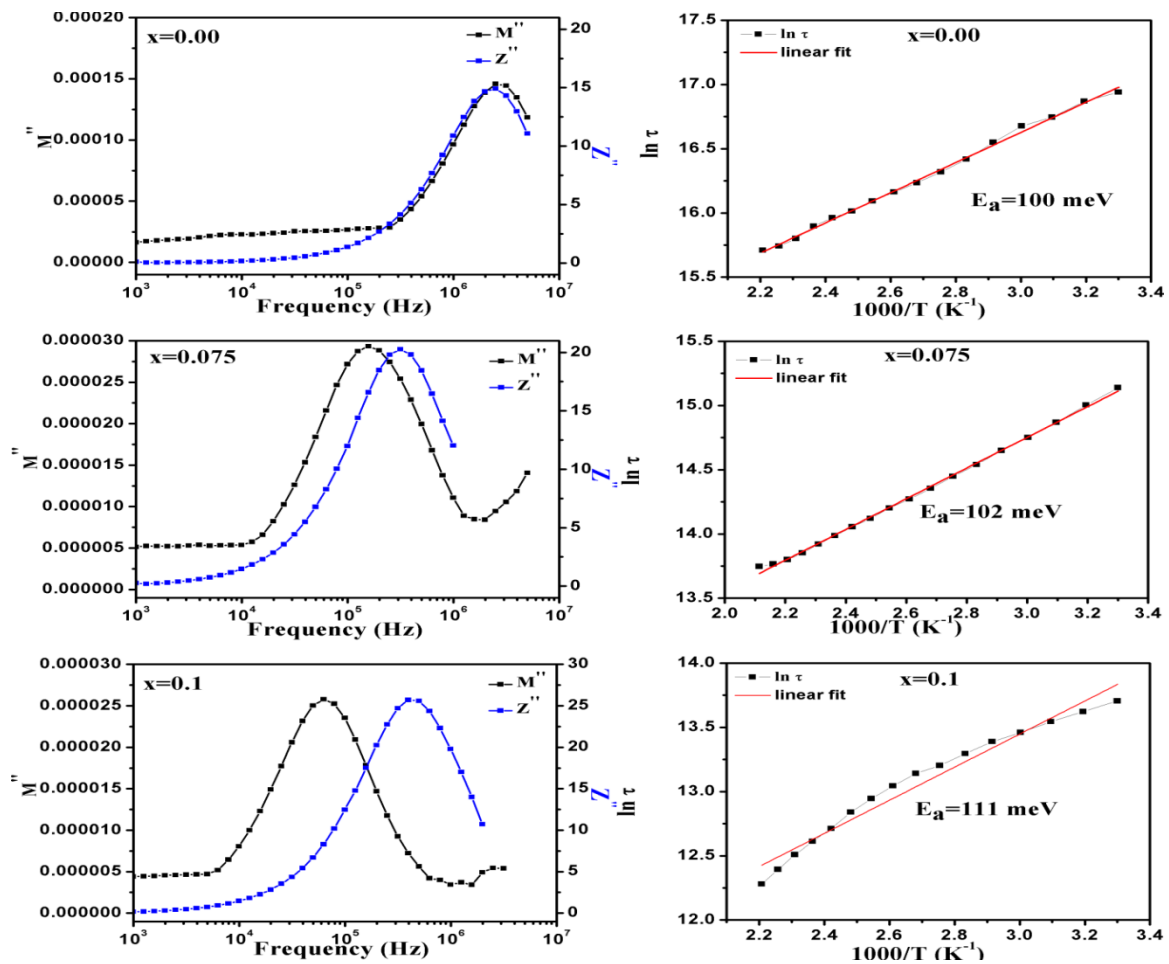


Figure 7. M'' and Z'' plotted against frequency for $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{Ni}_{1-x}\text{Cr}_x\text{O}_4$ ($x = 0.0, 0.075, 0.1$) ceramics and their corresponding dielectric relaxation τ plotted against temperature.

The linear variation of dielectric relaxation, $\ln \tau$ with $1000/T$ (Fig. 7) is indicative of the Arrhenius relation

$$\tau = \tau_0 \exp(-E_a/k_B T) \quad (5)$$

Here the activation energies, E_a of each samples calculated from the slope of the graph are 100meV, 102meV and 111 meV for $x=0.00, 0.075$ and 0.1 respectively in good agreement with the results obtained earlier. The higher values of activation energy for the doped samples indicate that the grain boundary resistance is higher for the Cr^{3+} doped $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{Ni}_{1-x}\text{Cr}_x\text{O}_4$ samples as compared to $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ sample.

In short the experimental results show that the origin of giant dielectric constant in $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{Ni}_{1-x}\text{Cr}_x\text{O}_4$ ($x = 0.075, 0.1$) is due to the highly resistive grain boundaries of the samples. The loss reduction especially at high frequencies of the doped samples is attributed mainly to the suppression of electrical conductivities at the boundaries by Cr^{3+} ions at Ni^{2+} sites as evident from the low values of activation energies.

IV. Conclusion

Following the solid state reaction method, ceramic samples of orthorhombic Sm_{1.5}Sr_{0.5}Ni_{1-x}Cr_xO₄ (x=0.0, 0.075, 0.1) were yielded. The doped samples possess significantly larger dielectric constant values, which remain almost stable up to MHz frequencies. The loss factor decreases sharply with increase in frequency and reaches the order of 0.1 magnitude at very high frequencies around the MHz region. This is achieved by the reduction in electrical conductivities with partial Cr³⁺ doping at the Ni sites. The high activation energies for the doped samples prove that the higher dielectric values of the doped samples are contributed by the insulating grain boundary regions. Also the peak frequencies separation between the plots of M'' and Z'' vs. frequency points out that the short range movement of the charge carrier dominates in the case of doped samples. These low loss samples with appreciably stable dielectric values up to MHz frequencies have the potential of finding applications in energy storage devices.

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