Impedance spectroscopy and permittivity investigation of NdCrO₃ perovskite ceramic nanoparticles

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The NdCrO₃ Perovskite Ceramic Compound has prepared by Sol-gel auto-combustion technique. The X-ray diffraction analysis confirmed that single-phase orthorhombic structure. The average size of the grain has estimated and it has found to be ~50nm. The impedance and permittivity investigations of NdCrO₃ perovskite ceramic nanoparticles have performed in the frequency range 20Hz-1MHz and temperature range 150K-300K. Impedance spectroscopy studies indicate the presence of grain and grain boundary relaxations in the compound. The polarization mechanism suggests for change in the dielectric constant and loss with temperature. The Impedance analysis supports the typical behaviour NTCR of material. The temperature dependent relaxation time for both grain and grain boundary follows the Arrhenius law.

Keywords: Sol-gel auto-combustion; Impedance; Permittivity.

1. Introduction

ABO₃ perovskites show exciting properties like high temperature superconductivity, colossal magneto resistance and multi-ferrocity [1]. The orthochromaties with a common formula RCrO₃ has investigated for their applications in various devices such as solid-oxide fuel cells and catalytic converters [1]. In the recent years, RCrO₃ materials exhibited so-called giant dielectric constant (ε’') [2]. A literature survey of these materials reveals that no detailed work on NdCrO₃ has reported. Therefore, we have studied the frequency and temperature dependence of dielectric and impedance properties of NdCrO₃ perovskite ceramics. In this paper, the results of extensive studies on electrical properties of NdCrO₃ in the temperature range 150K to 300K have presented.

2. Experimental Details
Polycrystalline powder of NdCrO₃ has been prepared by sol-gel auto combustion technique, and detailed procedure has been described in previous publication [3]. Resulting powder was annealed at 750°C for 4 hours. Finally, this powder has been used to pelletize under uniaxial pressing. The pellets have been sintered separately at 900°C temperatures for 4 hours. These sintered pellets have been used for microscopic and dielectric measurements. The dielectric measurements have been carried out using SOLARTRON SI1260 model impedance analyzer.

3. Results and Discussion

The material structural characterization of annealed powders and sintered pellets of NdCrO₃ were presented in our previous paper [3]. The annealed powder showed a single phase with orthorhombic symmetry, Pnma space group. The sintered pellets showed around 94% of theoretical density and the average grain size was estimated using SEM micrograph and found to be in the order of 50 nm.

Figures 1(a) and 1(b) show the frequency dependence of dielectric constant (ε’) and dielectric loss (tanδ) of NdCrO₃ at different temperatures respectively. There exist two plateaus in each curve at lower and higher frequency regions. These are shifting towards the higher frequencies with increasing temperature. The Low frequency plateaus may be due to grain boundary response, whereas the high frequency plateau observed may be due to grain effect [2, 4]. The dielectric constant of this material increases with increase in temperature, suggesting the thermally activated relaxation in the material. The dielectric constant and loss decreases rapidly with increasing frequency. It can explain by polarization mechanism. At low frequencies, the dipoles can follow the alternating electric field, giving rise to higher values of dielectric constant and dielectric loss, whereas at high frequencies the dipoles cannot follow the rapidly changing field, hence the reduction in the value of dielectric constant and loss.
Figure 1. Frequency dependent of (a) dielectric constant ($\varepsilon'$) and (b) loss tangent (tan\(\delta\)) of NdCrO$_3$ at different temperatures.

Figures 2(a) and 2(b) show the frequency dependence of real part of impedance ($Z'$) and imaginary part of impedance ($Z''$) of NdCrO$_3$ at different temperatures respectively. The $Z'$ is more significant in the low frequency region, and it has decreased with increasing frequency and temperature. The value of $Z'$ is high in the low frequency region, and it has gradually decreased with increasing frequency and attains a constant value at higher frequencies irrespective of temperature. This trend is shifting towards the higher frequency with rise in temperature. The decrease of $Z'$ with increasing temperature indicates a possibility of space charge and subsequent lowering of barrier properties in the material [5, 6].

Figure 2(b) shows two relaxation peaks at lower and higher frequencies for all temperatures. The polycrystalline materials generally show grain and grain boundary properties [7]. Hence, these two relaxation peaks occurred may be due to grain and grain boundary properties and is clear proof of temperature and frequency dependent relaxation. The relaxation time (\(\tau\)) of grain and grain boundary was estimated from the $Z''$ Vs frequency curve. Inset Figure 2b showed the variation of grain and grain boundary relaxation time (\(\tau\)) as a function of temperature. The slope of these plots follows the Arrhenius law. This slope indicating the temperature dependent spread of relaxation in the range of $10^{-2}$ to $10^{-7}$ sec suggests the enhancement in the relaxation process of the carrier transport in the material with the rise in temperature [8]. The activation energies of grain and grain boundary relaxations were evaluated, which are found to be $E_{a(gr)}=2.36$eV and $E_{a(gbr)}=1.8$eV.
Figure 2. Frequency dependence of (a) Real part impedance \((Z')\) and (b) Imaginary part of impedance \((Z'')\) of NdCrO\(_3\) at different temperatures. Inset Figure 2(b). Showed the variation of grain and grain boundary relaxation time \((\tau)\) as a function of temperature.

Figure 3(a) Complex impedance (Cole-Cole) plots of NdCrO\(_3\) at different temperature shows two depressed arcs, which are corresponding to the contributions of two separate polarization relaxation processes. The appearance of two arcs or semicircles at a particular temperature shows the electrical properties of the materials arise mainly due to the contribution of the bulk (grain) and grain boundary effects in the higher and lower frequency regions respectively. The formation of full, partial or no semicircles mainly depends on the strength of relaxation, experimentally available frequency range. The electrical process takes place within the materials may be modelled (RC circuit) based on the bricklayer model. The intercept of the semicircle on \(Z'\)-axis gives the value of grain (bulk) resistance \((R_g)\) and grain boundary resistance \((R_{gb})\) at higher and lower frequencies respectively. Both of these resistances have found to be decreasing with increases in temperature seen in figure 3(b). It suggests that material shows the negative temperature coefficient of resistance (NTCR) type behaviour [9-11]. These plots exhibit depressed semicircles having a centre lying below the real axis confirming the presence of non-Debye type of relaxation phenomenon in the materials.
Figure 3. (a) Complex impedance (Cole-Cole) plots of NdCrO$_3$ at different temperature [Inset Fig.3 (a) Zoom view of the same], (b) Temperature dependent resistance of grain and grain boundary of NdCrO$_3$.

4. Conclusion

Polycrystalline perovskite ceramic compound of NdCrO$_3$ has prepared by sol-gel auto-combustion method. Frequency and temperature dependence of dielectric constant analysis suggests that there exist thermally activated relaxation in the material. A polarization mechanism is suggested for change in the dielectric constant and loss with temperature. The Impedance analysis supports the typical behaviour NTCR of material. The temperature dependent relaxation time for both grain and grain boundary follows the Arrhenius law.

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