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Complex impedance analysis of layered perovskite structure electroceramics—$NaDyTiO_4$

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A ceramic oxide ($NaDyTiO_4$), having layered perovskite structure, has been prepared by a standard high-temperature solid-state reaction technique. X-ray diffraction (XRD) studies have confirmed material formation under reported condition along with the presence of impurity ($Na_2Dy_2Ti_3O_{10}$) as the minor phase. Complex impedance spectroscopy (CIS) analysis has been carried out to investigate its microstructure and electrical properties as a function of frequency and temperature. CIS analysis has indicated that the electrical behavior of the material sample shows negative temperature coefficient of resistance (NTCR) typical to a semiconductor. Impedance studies have also indicated the presence of temperature dependent relaxation process in the material with a spread of relaxation time. The d.c. conductivity of the material as evaluated from the impedance spectrum has been observed to be $\sim 10^{-9}$ Scm^{-1} at room temperature (RT). It has been observed to increase as a function of temperature with a maximum of $\sim 10^{-5}$ Scm^{-1} at 550°C. The conductivity variation shows a cross over from Mott-type hopping phenomena at lower temperatures to a thermally activated Arrhenius type behavior at high temperature.

1. Introduction

Ceramic oxides having layered perovskite structure are of particular interest in view of their versatile physical [1–3], structural [3–10], electrical properties [3, 5, 7, 9] associated with them. A wide variety of properties exhibited by the family of perovskites have made it a potential structure for innovations in materials development for various types of specific applications. Recent developments [11–13] have indicated that interesting electrical properties in ceramics oxides of a wide variety of structures arise due to ionic and electronic defect structures resulting in electrical behavior ranging from insulating through ionic to electronic conductor or a combination of the two (i.e. mixed conduction). The defect structure/point defects, that includes in a wider sense vacancy sites (for ion mobility)/electronic charge carriers (due to excess electrons) or a site with electron deficiency (holes) play a pivotal role in the electrical transport processes and act as a controlling factor in the function of electroceramics. Local topography/microstructure also play a very significant role in governing the mechanism of electrical conduction.

A complete information on correlation of sample topography/microstrucutre with its electrical properties can be obtained by the technique of Complex impedance spectroscopy (CIS). CIS is a powerful technique, which is used to investigate the electrical processes occurring in a material on applying a.c. signal at the input. An analysis of the impedance data provides unique relaxation frequency describing the relaxation processes occurring within a polycrystalline sample. The relaxation frequency ($\omega_{\max}$) of the material, at a given temperature, is only a unique intrinsic property of the material independent of sample geometrical factors. Consequently, the analysis of the electrical properties (conductivity etc.) carried out using relaxation frequency ($\omega_{\max}$) values give unambiguous results when compared with those obtained at arbitrarily selected fixed frequencies. The relaxation frequency ($f_{\max}$) of the material obeys the condition:

$$\omega_{\max}\tau = \omega_{\max}RC = 1 \quad 2\pi f_{\max}RC = 1$$

In the present paper, we report a ceramic oxide $NaDyTiO_4$ belonging to the layered perovskite structure family with a general formula $AA'BO_4$ (A = monovalent, A′ = trivalent, B = tetravalent) having a typical ordered structure with A-site cations. This class of layered perovskite oxides having the general formula $NaLuTiO_4$ (Lu = Rare earth) has been described in literature primarily in relation to their structural analysis. Literature reveals that a detailed analysis of electrical properties of this class of oxides has received little attention. This factor motivated us to carry out a detailed characterization of the electrical properties

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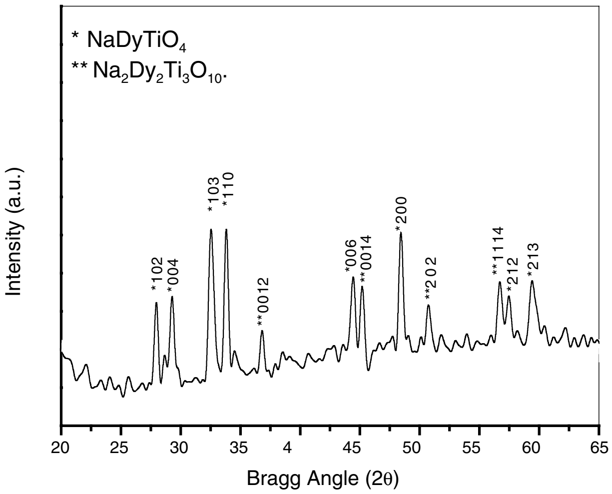


Figure 1 XRD pattern of $NaDyTiO_4$ at room temperature.

of $NaDyTiO_4$ using the impedance spectroscopy technique.

2. Experimental procedures

A standard solid-state reaction method has been used to prepare the ceramic oxide $NaDyTiO_4$. Initially, the precursor materials in an appropriate stoichiometric ratio (AR grade Na_2CO_3, Dy_2O_3, TiO_2) have been mixed mechanically in an agate mortar for 2 h. The physical mixture so obtained was then calcined in an alumina crucible at ~1150°C for 12 h. The process of grinding and calcination was repeated till the formation of the material ($NaDyTiO_4$) was confirmed. Subsequently, the calcined powder was cold pressed into cylindrical pellets of diameter 10 mm and thickness 1–2 mm with polyvinyl alcohol (PVA) as the binder, using a hydraulic press at a pressure of $\sim 2.5 \times 10^7$ Nm^{-2}. The pellet was then sintered in an air atmosphere at a temperature of 1200°C for 12 h. The sintered pellets were finally polished with fine emery paper to make their faces flat and parallel followed by coating with a conducting silver paint for electrical measurements.

X-ray diffraction (XRD) studies have been carried out to confirm compound formation and phase identification using a X-ray powder diffractometer (PHILIPS, Model: PW1710). The XRD pattern of the sample pellet was recorded at room temperature using Cu K_α radiation ($\lambda = 1.5418$ Å) at a scan speed of 3° min^{-1} in the wide range of Bragg angles $2\theta(20 \leq 2\theta\, 65^\circ)$. The surface morphology/microstructure of the material has been studied using a computer-controlled scanning electron microscope, SEM, (JOEL-JSM, model 5800F). The pellet was gold coated prior to being scanned under high-resolution field emission gun scanning electron microscope. The gold coating of thickness ~200 Å was carried out under argon(Ar) gas at a vacuum of $\sim 10^{-2}$ Torr. The impedance measurements were carried out using a computer-controlled impedance analyser (HIOKI LCR Hi TESTER Model: 3532) in the frequency range of 100 Hz to 1 MHz. The impedance spectra of the cells were recorded using ac signal of amplitude 1.5 V up to a temperature of 550°C starting from room temperature. The pellet coated with conducting silver paint was dried by firing it at 150°C for 2 h before carrying out the measurements. The electrical properties of the material evaluated from the a. c. impedance measurement have been observed as a function of frequency and temperature.

3. Results and discussion

Material formation and phases present in the sample under investigation has been confirmed from X-ray diffraction (XRD) analysis carried out at room temperature. The XRD pattern of the material prepared under the reported condition is shown in the Fig. 1. The pattern indicates the presence of standard peaks of $NaLuTiO_4$ (Lu = La, Nd, Sm and Gd) as reported previously [1, 2] together with some new peaks as observed

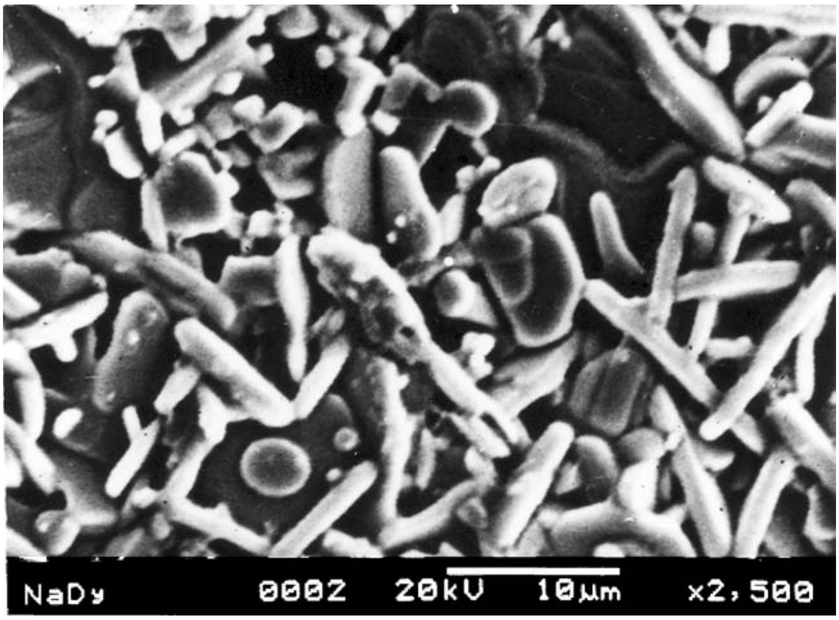
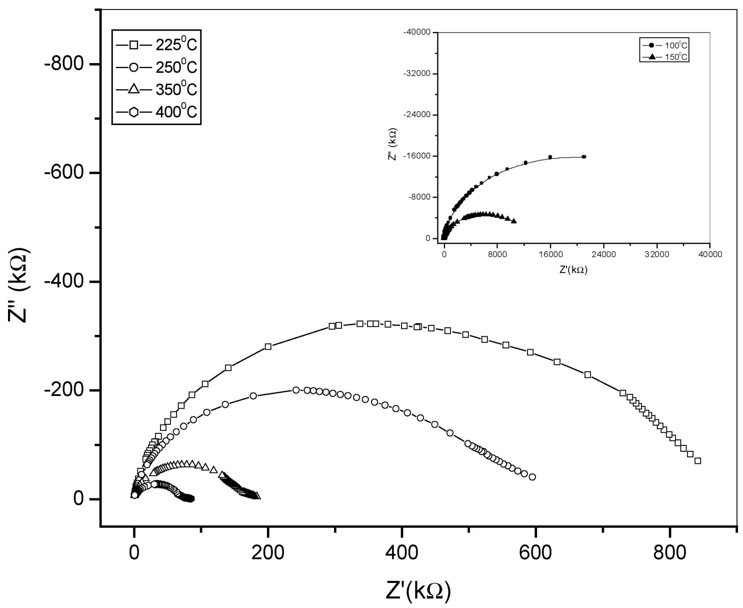
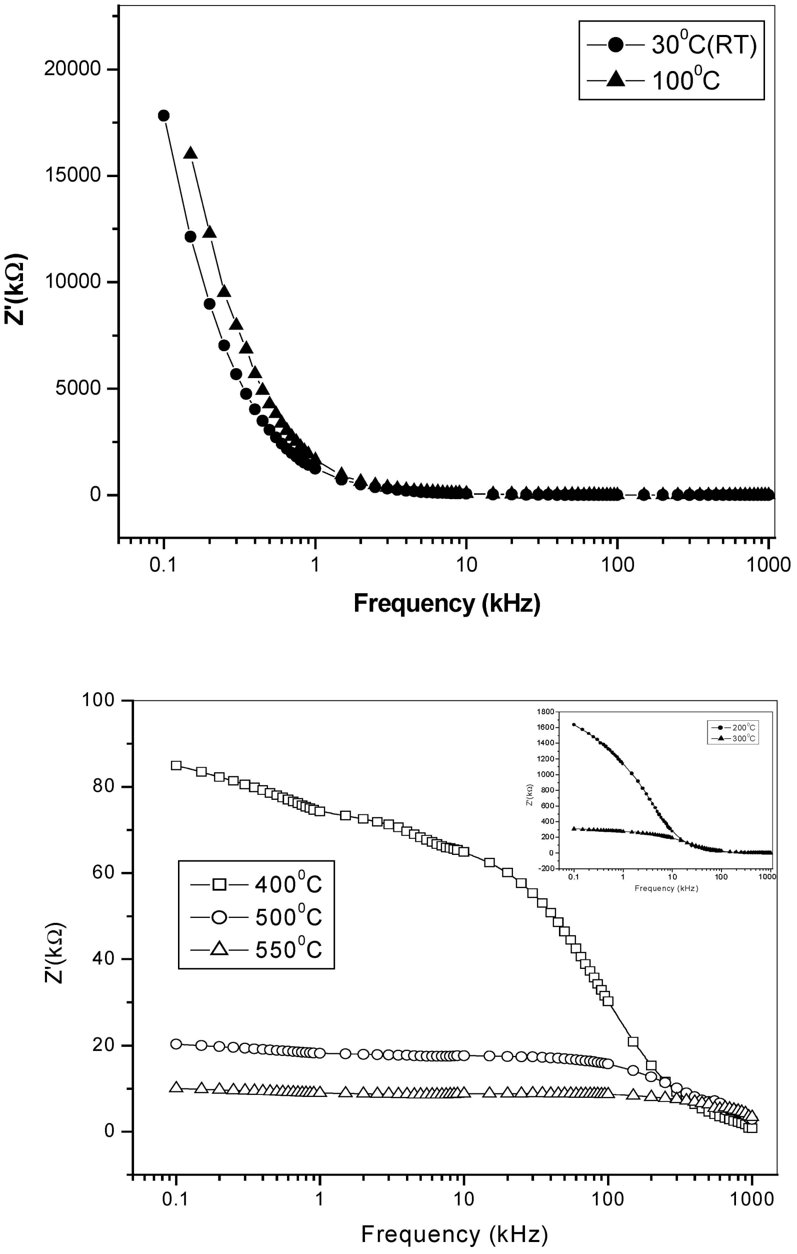


Figure 2 Scanning electron micrographs of the material $NaDyTiO_4$.

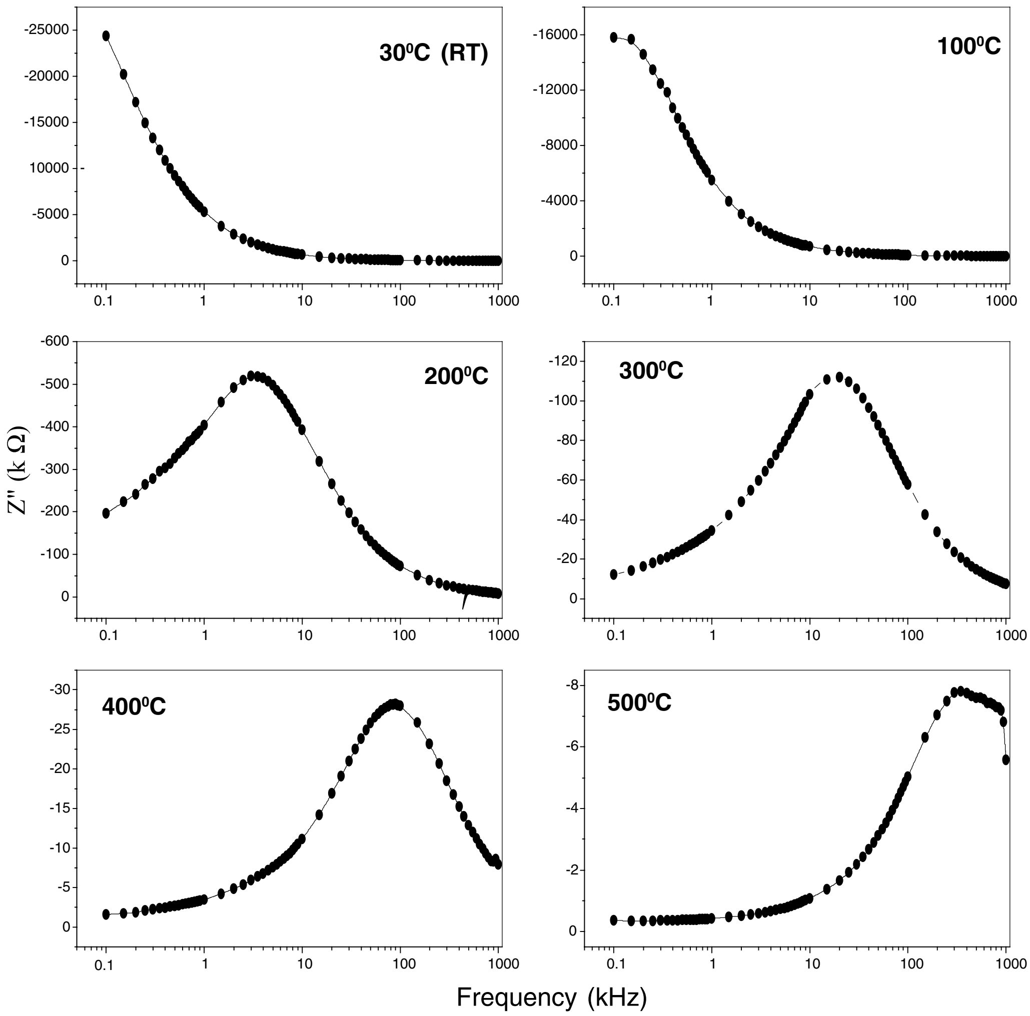


(a)

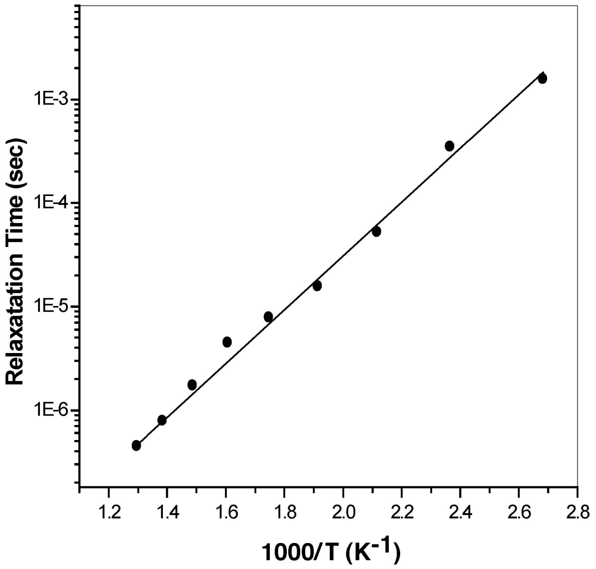


(b)

Figure 3 Complex Impedance Spectrum: (a) Complex impedance (Nyquist) plot with equivalent circuit, (b) Real impedance (Z'') as a function of frequency, (c) Imaginary impedance (Z'') as a function of frequency, (d) Relaxation time (τ) as a function of temperature. (*Continue on next page*).



(c)



(d)

Figure 3 Continued.

in the XRD pattern. These additional peaks, which are of smaller intensity and only a few in numbers, have been identified with that of $Na_2Nd_2Ti_3O_{10}$ [15]. It may be attributed to the presence of small impurity phase in the material sample. These observations indicate that the formation of such impurity phases, although of minor in nature could not be eliminated under the reported conditions of calcinations. This finding is in agreement, so far as the synthesis conditions reported in this study is concerned, with a few previous reports [1, 2]. An estimation of lattice parameters for both the phases have indicated that they correspond to tetragonal unit cells in agreement with that reported in literature [1, 15] and compare well with the patterns of similar systems [1, 2, 14]. The matching of peaks with their standard data confirms the formation of $NaDyTiO_4$ as the major component with $Na_2Dy_2Ti_3O_{10}$ as the minor impurity phase contribution in the sample.

Fig. 2 presents the scanning electron micrograph of the material sample. The micrograph indicates the existence of polycrystalline microstructure with a certain degree of porosity. The material microstructure typically comprises of fibrous grains with shape anisotropy. The grains of unequal sizes ($\sim 4^{-10}$m) possibly appear to be distributed inhomogeneously throughout the matrix of the material.

The complex impedance spectrum (Nyquist-plot) of the material measured at different temperatures is shown in Fig. 3a. The complex impedance plot typically comprises of a single semicircular arc that becomes gradually resolved with rise in temperature. The presence of a single arc in the impedance spectrum indicates that the electrical processes in the material arise only due to the contribution of bulk material [17, 18]. The bulk resistance (d. c. resistance) decreases with rise in temperature as indicated by the corresponding reduction in the diameter of the semicircles with increase in temperature. This type of d. c. resistance variation with rise in temperature indicates an increase in the bulk conductivity of the material with increasing temperature, a material behavior analogous to the negative temperature coefficient of resistance (NTCR) property normally observed in semiconductors.

Fig. 3b shows the variation of real part of impedance (Z') with frequency at different temperatures. Z' has higher values at lower frequencies and it decreases monotonically with rise in frequency and attains a constant value at higher frequencies for almost all the temperatures. This trend (attainment of constancy of Z' value) appears to be shifting gradually towards higher frequency side with rise in temperature. The magnitude of Z' decreases with rise in temperature and merge in the higher frequency domain for all the temperatures. The decrease in the real part of impedance (Z') with rise in the value of temperature and frequency indicates a possibility of increase in a. c. conductivity with increase in temperature and frequency. The merger of real part of impedance (Z') in the higher frequency domain for all temperatures indicates a possibility of the release of space charge as a result of lowering in the barrier properties of the material [11, 12].

Fig. 3c shows the variation of the imaginary part of impedance (Z'') with frequency at different temperatures. The typical variation indicates that Z'' attains a maximum value at a particular frequency which is different at different temperatures. The variation shows a considerable decrease in the magnitude of Z'' and a clear shift in the frequency peak towards the higher frequency side with rise in temperature. This feature becomes noticeable on and above 100°C. The trend of variation of Z'' with frequency is typical of the presence of electrical relaxation phenomena in the material and it indicates that the relaxation is temperature dependent. A similar observation has been seen in the variation of Z' as a function of temperature for different frequency. At lower temperatures, the relaxation process may attributed to orientational effects of the immobile species as indicated by monotonous fall of Z'' with frequency. The decrease in the magnitude of Z'' with a shift in the peak frequency towards the higher side with rise in temperature arises possibly due to the presence of "space charge" in the material and is in agreement with the observations of complex impedance data [11, 12].

Fig. 3d shows the variation of relaxation time (evaluated from impedance data) as a function of temperature. The relaxation time (τ) has been computed from the peak position of Z'' vs. frequency plot in accordance with the relation $\omega\tau = 1$. The τ vs. 10^3/T plot shows that relaxation time vary linearly with inverse of temperature and can be approximated to the Arrhenius type relation:

$$\tau = \tau_o e^{-E/kT}$$

where E is the activation energy and k is the Boltzmann constant. The result shows a substantial variation of relaxation time with temperature from 10^{-3} to 10^{-7} second suggesting electrical process in the material with a spread of relaxation time in agreement with the observation from Fig. 3d. The value of activation energy obtained from the plot works out to be ~0.51 eV.

The bulk conductivity of the material has been evaluated from the complex impedance spectrum (Fig. 3a) measured at different temperatures. The d. c. conductivity estimated from the bulk response of the material has been observed as a function of temperature as shown in the Fig. 4a. An inspection of the Fig. 4a indicates two different types of electrical conduction process in the material over two different regions of temperatures. At higher temperatures, the conductivity behavior appears to be a thermally activated transport of Arrhenius type governed by the relation:

$$\sigma_{\text{dc}} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

where σ, E_a and k represent the pre-exponential factor, the activation energy of the mobile charge carriers and Boltzmann constant respectively. In the low temperature region, there is a small departure from the linear behavior. This departure in electrical behavior from linearity in electrical conduction behavior cannot be attributed to structure, thermal phase transition. This result appears to be consistent with the observation from detail structural analysis reported previously. The change in conduction behavior is purely a function of temperature and may be related to insulator-conductor transition. The trend of electrical conduction in this temperature zone has been observed to follow Mott's hopping type phenomena characterized by a steady decrease in conductivity, with gradual change of slope in the low temperature region [19, 20]. The activation energy evaluated from d. c. conductivity vs. temperature pattern in different temperature regions work out to be ~0.66, 0.34, 0.65 and 0.13 eV in the temperature ranges 350 to 550°C, 200 to 350°C, 125 to 200°C and below 125°C respectively. The average value of the calculated activation energy is nearly close to the activation energy evaluated from the τ vs. 10^3/T plot. This analogy possibly indicates that the species responsible

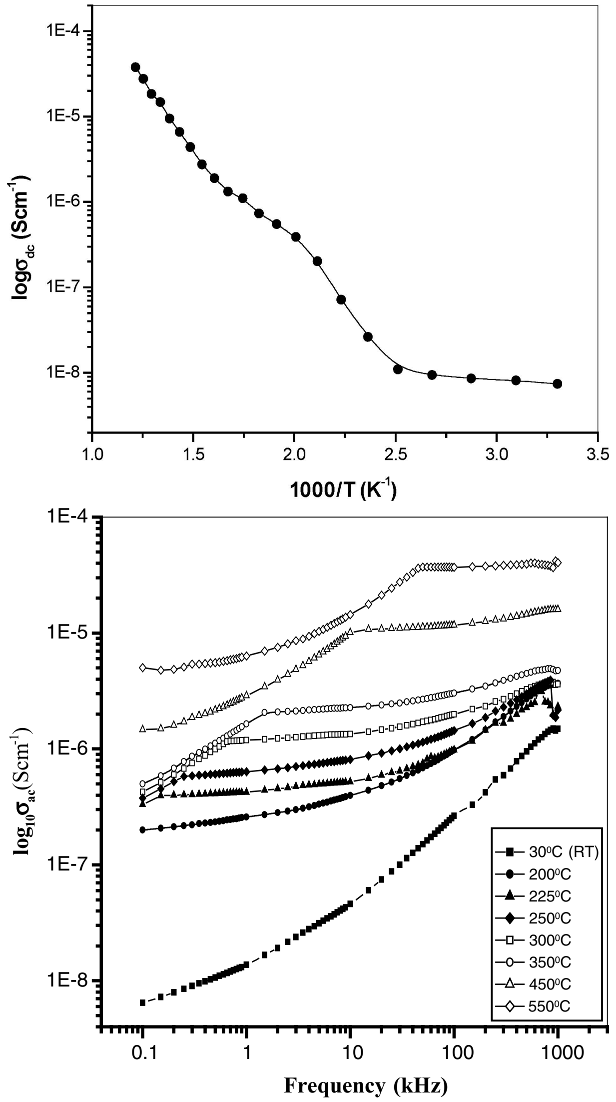


Figure 4 Electrical conductivity: (a) Variation of electrical conductivity (σ_{dc}) as a function of temperature, (b) Variation of electrical conductivity (σ_{ac}) as a function of frequency.

for both conductivity and relaxation phenomena are the same [18]. Further, it has been noticed that the conductivity of the material at 550°C is 3.76×10^{-5} Scm^{-1}, which is substantially higher than room temperature conductivity ($\sim 10^{-9}$ Scm^{-1}). It may be interpreted to be due to the creation of vacancies/defects (disorders) at higher temperatures.

Fig. 4b shows typical variation of electrical conductivity (σ_{ac}) of the materials as a function of frequency at different temperatures. The pattern of variation indicates characteristic dispersion phenomena of conductivity in both the low and high frequency region at room temperature. This frequency dependence of conductivity obeys Jonscher's power law equation [16, 18]:

$$\sigma(\omega) = \sigma_{dc} + A\omega^n \qquad 0 < n < 1.$$

where σ_{dc} is the frequency independent conductivity, A is the temperature dependent pre-factor and n is the frequency exponent. It has been observed that low frequency dispersion obeying the power law feature $\sigma(\omega) \propto \omega^n$ changes its slope governed by n. The frequency at which change in slope takes place is known as "hopping frequency (ω_p)" and it appears to be temperature dependent with characteristic shift towards higher frequency side with rise in temperature. In lower frequency region, the increasing trend of σ_{ac} with increase in frequency may be attributed to the disordering of cations between neighboring sites [21]. Further, the variation of σ_{ac} as a function of frequency is very much significant at lower temperatures when compared with the results at higher temperature. This indicates the presence of space charge in the material that vanishes at higher temperatures and frequencies. This observation is in agreement with our observations from impedance result.

4. Conclusion

A ceramic oxide, $NaDyTiO_4$, with layered perovskite structure has been synthesized by a standard solid-state reaction technique. The X-ray diffraction studies have confirmed the formation of polycrystalline material $NaDyTiO_4$ as major phase and $Na_2Dy_2Ti_3O_{10}$ as the minor phase. Morphological study by scanning electron microscopy has indicated the polycrystalline nature of the material. The complex impedance studies of the material have indicated that the electrical processes in the material: (i) exhibit the negative temperature coefficient of resistance, a behavior typical to a normal semiconductor, (ii) comprises of a relaxation process dependent on temperature with spread of relaxation time, (iii) relaxation process is governed by the presence of space charge at high temperatures. The electrical conductivity of the material has been explained on the basis of Mott-type hopping phenomena in the low temperature region and Arrhenius-type thermally activated process in the higher temperature region. The material has a high conductivity ($\sim 10^{-5}$ Scm^{-1}) at 550°C as compared to the room temperature conductivity ($\sim 10^{-9}$ Scm^{-1}).

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