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Role Rare Earth (Nd^{3+} & La^{3+}) Modified $PbTiO_3$ on Dielectric, Impedance & Conductivity of $NiFe_2O_4$ Based Ceramic Composites

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Ceramic Composites of Rare Earth modified PbTiO3 (Pb0.76Nd0.24TiO3-PNT & Pb0.76La0.24TiO3-PLT) & NiFe2O4 have been successfully synthesized by commonly used mechanical mixing method in required stoichiometric proportion of 0.55PNT-0.45NiFe2O4 & 0.55PLT-0.45NiFe2O4. The temperature dependent dielectric permittivity reveals an increment may result due to increase of Maxwell wanger polarization at higher temperature whereas decrease of real part of impedance reveals decreases in resistive response of prepared ceramic composites. The maxima in imaginary part of impedance reveals presence of dielectric relaxation and disappearing of this maxima with increase of temperature manifest temperature dependent dielectric relaxation. Increase of conductivity with increase in temperature evident for presence of oxygen vacancies which reveals increase of conductivity.

1. Introduction

Most modern electronic equipment relies on semiconductors and magnetic materials. Semiconductors have been employed in production of microprocessors that possess capability to process information swiftly. Conversely, magnetic materials utilized for information storage owing to their inherent capacity to sustain magnetization in a fixed direction of orientation of domains without need of power source. By integrating these benefits of both features into a single material, ongoing information transfer between magnetic materials (memories) and semiconductors (microprocessors) can be eliminated, resulting in devices that are both speedier and more cost-effective. The majority of experimental outcomes raised questions regarding the true origin of magnetism [1,2]. It has been shown that segregation of metallic clusters was responsible for magnetism in certain situations, whereas double exchange was responsible for magnetism in other systems comprising transition elements with distinct valence states [3-5]. Recent and seminal research in this area has demonstrated that magnetic properties significantly influenced by defects and not solely by the presence of magnetic ions [6-9]. For this, $PbTiO_3$ has been selected for ferroelectric component whereas Nickel ferrite as a magnetic component. The modification of $PbTiO_3$ has been carried out using Nd^{3+} & La^{3+} selected as rare earth ions for substitution at Pb^{2+} because rare earth reduces ferroelectric transition temperature reported by Ram et al. [9] and dielectric constant near transition temperature is supposed to be maximum [10].

So In this research report, conventional mechanical mixing approach has been adopted for preparation of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$- $_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$- $_{0.45}(NiFe_2O_4)$ Ceramic Composites. The effect partial replacement of Nd^{3+} & La^{3+} modification of $PbTiO_3$ ($Pb_{0.76}La_{0.24}TiO_3$ & $Pb_{0.76}Nd_{0.24}TiO_3$) with on dielectric, impedance and conductive properties have been thoroughly studied.

2. Experimental

Conventional Mechanical mixing approach has been adopted for synthesis of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites. For this, various metal nitrates as well as oxides of high purity grade have been used. The calcined powders of $Pb_{0.76}La_{0.24}TiO_3$, $Pb_{0.76}Nd_{0.24}TiO_3$ & $NiFe_2O_4$ mixed in above mentioned stoichiometric proportion using plastic bottles & zirconia balls and ball milled using milling machine for 24 hours. After finishing of milling process, mixed powder taken out from bottles and dried. The dry powder was mixed with a 2% weight polyvinyl alcohol binder to create disc shaped of roughly 10 mm in diameter and 0.5 mm thick. The pellets then sintered at 1200 °C for 4 hours in environment of PbO to avoid PbO volatility for densification. Sintered Pellets have been studied for high temperature dielectric, impedance & conductivity properties using complex impedance spectroscopy. The real and imaginary components of electrical impedance as well as dielectric permittivity has been studied using complex impedance spectroscopy. Contribution of grain and grain boundaries to electrical properties through the analysis of Nyquist plots and conduction mechanism from universal johncher's power fitting of conductivity data at different temperatures has been studied using complex impedance spectroscopy (CIS). This is valuable and important characterizing technique in material science. These electrical properties were ascertained using Keysight Technologies (E4990A) using impedance analyzer. All of these characteristics were calculated from empirically acquired Z versus θ at various temperatures using recognized equations.

$$\text{Complex Impedance}, Z^* = Z' - jZ''$$

$$\text{Complex dielectric constant}, \varepsilon^* = \varepsilon' - j\varepsilon''$$

$$\text{Complex electric modulus}, \quad M^* = M' + jM''$$

$$\text{Also}, \tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Where Z',ε', M' and Z'', ε'', M''denote the real and imaginary parts of the impedance, dielectric constant and electric modulus respectively and j = $\sqrt{(-1)}$.

The dielectric relaxation has been verified by theoretically fitting dielectric data with the Debye and non-Debye formulas. The semi-circle in Nyquist plots provides information about the role of grain and grain boundaries in electrical properties. Using Jonscher's power law [11] to study conduction process

$$\sigma_{ac} = \sigma_{dc} + A\omega^{n}$$

"A" denotes the dispersion parameter describing the strength of Polarizability; "dc" denotes "dc conductivity," "ac" denotes "ac conductivity," and so on. "n" is a dimensionless quantity that gives information on the interaction between mobile ions and the lattice in which they interact.

3. Results & Discussion

Temperature dependent profile of ε' & ε" vs. Frequency (Hz) in temperature range varied from 100 °C-200 °C of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites have been shown in Figure 1 & 2. It has been clearly predicted from graphs real and imaginary a part of dielectric permittivity exhibits maximum value in lower frequency and later on decreases constantly with growing frequency towards higher values predicts normal dielectrics response of prepared ceramic composites. The maximum value of both ε' & ε" consequences because of participation of all polarizations (Ionic, Dipolar, Electronic and Space Charge Polarization) in dielectric response and whereas almost linear variant may be results because of removal a few polarizations at higher in higher frequency regime gets eliminated. The graphs clearly show that the dielectric permittivity values (both ε' & ε") first rise to a particular temperature before declining and such trend can be explained by dope theory that initial increase may result due to behavior of dipoles which being easily oriented with respect to applied field. Temperature-dependent dielectric relaxation occurs when a dipole is unable to respond appropriately applied field beyond certain temperature range. The experimental data has been matched with established theoretical models of Debye and non-Debye relaxation in order to investigate more in detail whether it is a Debye or non-Debye relaxation [11-13]. The dielectric permittivity value decreases with temperature, increasing first to a point before beginning to decline. This kind of behavior can be explained by thermal energy that provides sufficient energy to dipoles. This makes it easier for dipoles to respond to an applied field, which increases the dielectric permittivity (real and imaginary component). Therefore, dipoles became relaxed as the temperature increased that they were unable to react to applied signals, which further reduced the dielectric permittivity value (real and imaginary parts).

Further, detailed information about dielectric relaxation has been concluded from fitting of experimentally collected dielectric data using dielectric relaxation model, either Cole-Cole or Cole-Davison termed as modified variant of Debye relaxation model used to explain the relaxation phenomena [15-18]. According to this model, as follows:

$$\varepsilon'(\omega) = \varepsilon_{\infty} + (\varepsilon_s - \varepsilon_{\infty}) \frac{1 + (\omega\tau_0)^{1-\alpha} \sin\frac{1}{2}\alpha\pi}{1 + 2(\omega\tau_0)^{1-\alpha} \sin\frac{1}{2}\alpha\pi + (\omega\tau_0)^{2(1-\alpha)}}$$

$$\varepsilon''(\omega) = (\varepsilon_s - \varepsilon_\infty)\frac{(\omega\tau_0)^{1-\alpha}\cos\frac{1}{2}\alpha\pi}{1+2(\omega\tau_0)^{1-\alpha}\sin\frac{1}{2}\alpha\pi+(\omega\tau_0)^{2(1-\alpha)}}$$

Where is the dielectric constant measured at high frequency, s is the dielectric constant measured at low frequency, and is the typical relaxation period of the medium. 2f is the angular frequency of the applied field. The shape of spectral curves is described by the exponent parameter, which normally falls between 0 and 1. It should be noted that when = 0, the Cole-Cole model transforms into the Debye model.

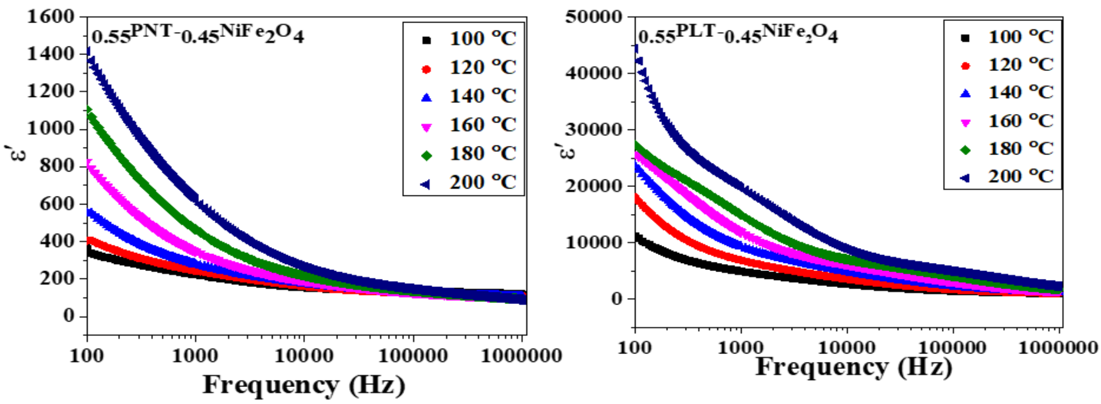

Figure 1: ε' vs. Frequency (Hz) in temperature range varied from 100 °C-200 °C of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites

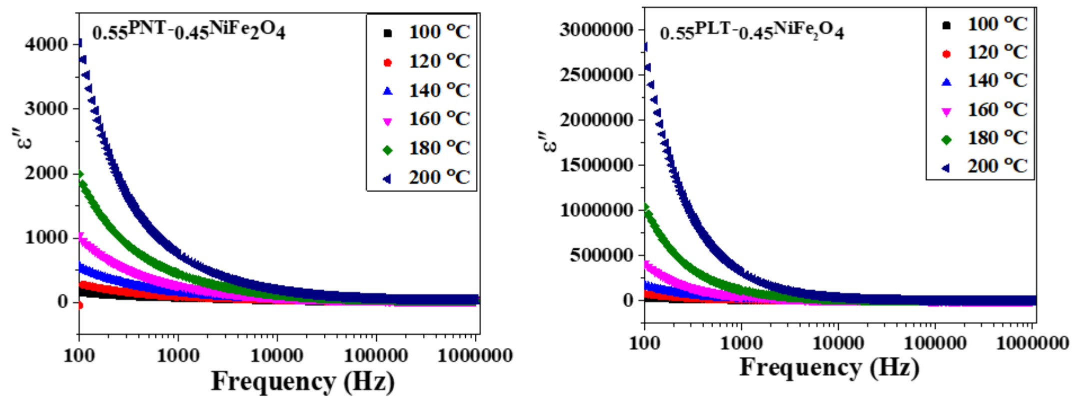

Figure 2: ε'' vs. Frequency (Hz) in temperature range varied from 100°C-200 °C of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites

Figure 3 illustrates Z´ vs. Frequency (Hz) in temperature range varied from 100 °C-200 °C of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites. The prepared samples have negative temperature coefficient of resistance (NTCR) confirmed from drops in value of Z´ when frequency and temperature increase simultaneously, as demonstrated by the clearly defined graphs [13]. The inverse relationship between temperature and Z′ indicates that as ferrite concentration increases in prepared ceramic composites, resistive qualities drop and conductive behavior increases. The temperature-dependent conductivity profile also provides justification for the reduced resistive behavior or barrier. An increase in concentration may be the cause of the conductivity's temperature increase. The increase in conductivity with temperature may results due to increase in concentration of oxygen vacancies with increasing temperature. [14-15].

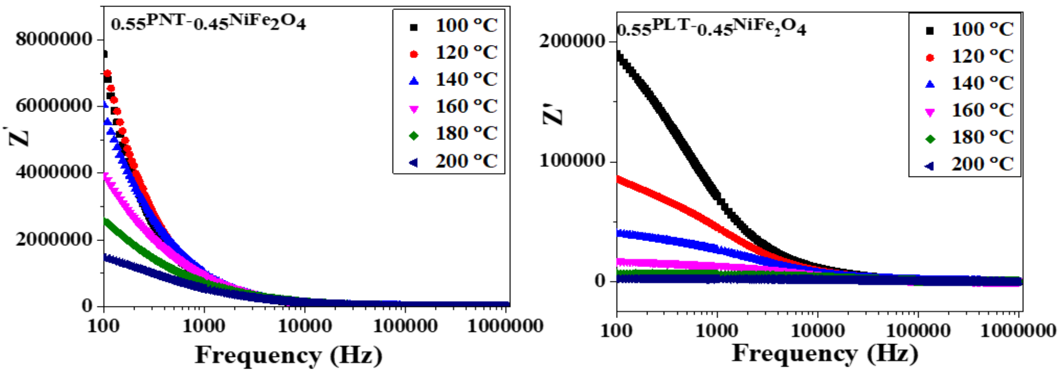

Figure 3: Z′ vs. Frequency (Hz) in temperature range varied from 100 °C-200 °C of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites

Z″ vs. Frequency (Hz) in temperature range varied from 100 °C-200 °C of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites in whole range of frequency (up to 1 MHz) has been shown in figure 4. The graphs clearly delineated that Z″ increases first continuously with increasing upto certain value frequency and then starts decreases with further increase of frequency clearly overted the presence dielectric relaxations. The continuous shift in maxima of Z″ vs. Frequency directly evident for presence of temperature dependent dielectric relaxation [13-15] and merging at higher temperatures reveals for elimination of space charge polarization [17-18].

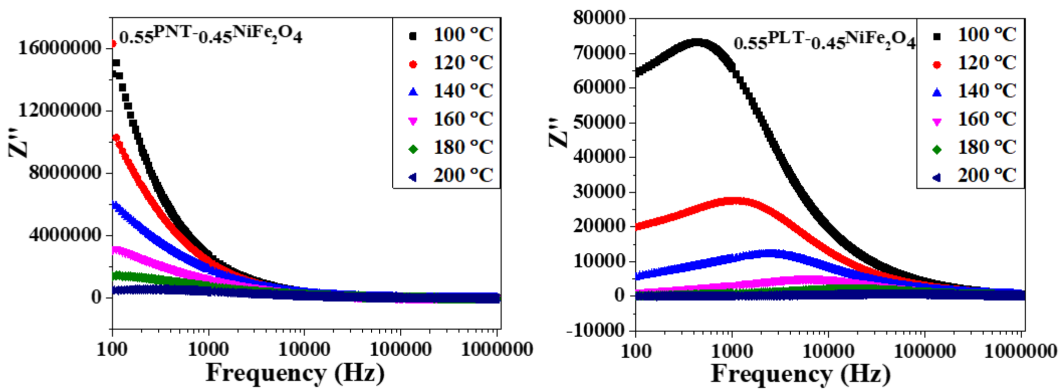

Figure 4: Z′ vs. Frequency (Hz) in temperature range varied from 100 °C-200 °C of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites

□$_{ac}$ vs. Frequency (Hz) in temperature range varied from 100 °C-200 °C of

$_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites in whole range of frequency (up to 1 MHz) has been shown in figure 5. It has been clearly seen in graphs that graphs divided into two parts (a) frequency independence represents to dc conductivity (σ_{dc}) & (b) varied w.r.t. frequency in higher frequency regime termed as ac conductivity (σ_{ac}). The universal johncher's power law has been used to study conduction mechanism from ac conductivity given as follow

$$\sigma_{ac} = \sigma_{dc} + A\omega^n$$

Where σ_{ac} = ac conductivity, σ_{dc} = dc conductivity, A = dispersion parameter representing the strength of Polarizibilty & "n" is dimensionless parameter.

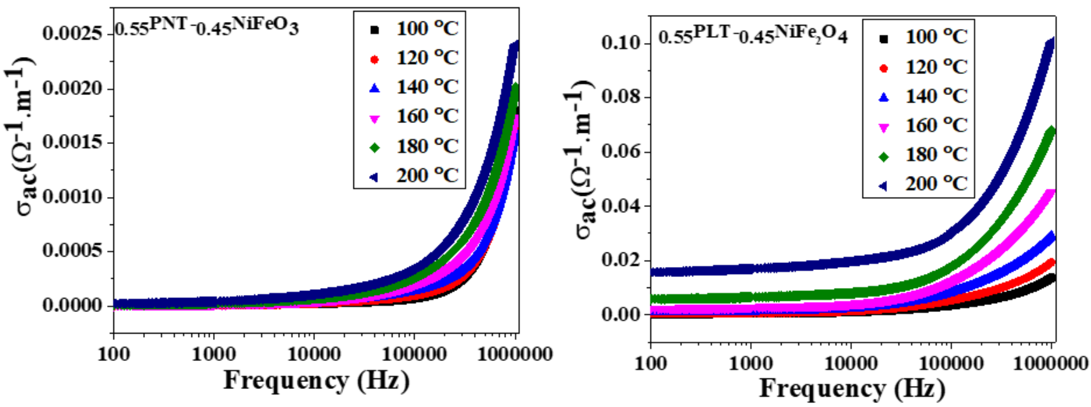

Figure 5: $\square_{ac}$ vs. Frequency (Hz) in temperature range varied from 100 °C-200 °C of $_{0.55}(Pb_{0.76}La_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ & $_{0.55}(Pb_{0.76}Nd_{0.24}TiO_3)$-$_{0.45}(NiFe_2O_4)$ Ceramic Composites

It has been clearly perceived from graphs that conductivity increases with increasing temperature. The increase of oxygen vacancies due to temperature may results for uninterrupted increase in electrical conductivity. [21-22]. Figure 10 shows that electrical conductivity σ_{ac} vs. frequency in increases. The increase in value of electrical conductivity may be due to increase of oxygen vacancies created due to increase in temperature.

4. Conclusion:

Ceramic Composites of Rare Earth modified $PbTiO_3$ ($Pb_{0.76}Nd_{0.24}TiO_3$-PNT & $Pb_{0.76}La_{0.24}TiO_3$-PLT) & $NiFe_2O_4$ have been successfully synthesized by commonly used mechanical mixing method. It has been clearly reveals that modification of $PbTiO_3$ with La^{3+} increases conductive response in prepared ceramic composites as compare to Nd^{3+} modification. The dielectric spectroscopy directly evident for improvement in dielectric as well as conductive properties which also confirmed from decrease in value of real part of impedance.

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