Glassy dielectric response in Tb$_2$NiMnO$_6$ double perovskite with similarities to a Griffiths phase

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Abstract – Results of frequency-dependent and temperature-dependent dielectric measurements performed on the double-perovskite Tb$_2$NiMnO$_6$ are presented. The real ($\epsilon_1(f,T)$) and imaginary ($\epsilon_2(f,T)$) parts of dielectric permittivity show three plateaus suggesting dielectric relaxation originating from the bulk, grain boundaries and the sample-electrode interfaces, respectively. The $\epsilon_1(f,T)$ and $\epsilon_2(f,T)$ are successfully simulated by a RC circuit model. The complex plane of impedance, $Z'$-$Z''$, is simulated using a series network with a resistor $R$ and a constant phase element. Through the analysis of $\epsilon(f,T)$ using the modified Debye model, two different relaxation time regimes separated by a characteristic temperature, $T^*$, are identified. The temperature variation of $R$ and $C$ corresponding to the bulk and the parameter $\alpha$ from modified Debye fit lend support to this hypothesis. Interestingly, the $T^*$ compares with the Griffiths temperature for this compound observed in magnetic measurements. Though these results cannot be interpreted as magnetoelectric coupling, the relationship between lattice and magnetism is markedly clear. We assume that the observed features have their origin in the polar nanoregions which originate from the inherent cationic defect structure of double perovskites.

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Introduction. – Double-perovskite compounds $R_2B'B''O_6$ ($R =$ rare earth; $B, B'' =$ transition metal) display a variety of interesting properties such as ferromagnetism [1], magnetocapacitance/magnetoresistance [2] and field-induced changes of dielectric constant [3], all of which make them potential candidates for spintronics applications. Theoretical predictions [4] and experimental observation [5] of multiferroicity have been reported for double perovskites. However, most investigations of this class of compounds were focused on La-based compositions, for example, La$_2$NiMnO$_6$ which has a high ferromagnetic transition temperature of 280K [6,7]. Ceramics of La$_2$NiMnO$_6$ are reported to show relaxor-like dielectric response which is attributed to Ni$^{2+}$-Mn$^{4+}$ charge ordering [7]. Epitaxial thin films of La$_2$NiMnO$_6$ are known for dielectric relaxation and magnetodielectric effect [6]. In the present paper, we report the results of impedance spectroscopy of Tb$_2$NiMnO$_6$. The motivation for this work stems from our previous study that showed a clear correlation between the lattice anomaly observed in the FWHM of the phonon mode and the Griffiths temperature observed through magnetization [8]. Here we address the dielectric response of this system, its interpretation and appraisal based on the previous knowledge. Experimentally observed dielectric data are faithfully reproduced using resistor network models which help to extract intrinsic contributions. A characteristic temperature is identified in the ensuing analyses which is compared with the magnetic and Raman data already reported on this material. It is found that the magnetic Griffiths temperature is reflected in the dielectric data also through this characteristic temperature.

 Experimental details. – Details of synthesis, structure, magnetism and Raman studies of Tb$_2$NiMnO$_6$ were reported earlier [8]. In order to perform dielectric measurements, pellets of approximate thickness 0.8 mm and area 6.8 mm$^2$ were prepared using poly-vinyl alcohol as a...
Fig. 1: (Colour on-line) The real part of dielectric permittivity, $\varepsilon_1$, and the dissipation factor or loss factor, $\varepsilon_2$, as a function of temperature, measured with different applied frequencies in the range 100 Hz–800 Hz ((a), (b)) and 1 kHz–7 MHz ((c), (d)). In the low-frequency region, three different plateaus are observed which can arise from intrinsic, grain boundary and sample-electrode interfaces, respectively.

binder. The density of the pellet is measured to be greater than 95% of the theoretical density. A temperature-dependent dielectric constant was measured using a Janis cryostat in the frequency range from 1 kHz to 10 MHz using a 4294 A precision impedance analyser with an applied ac voltage of 800 mV. Dielectric experiments on these samples were repeated using several electrodes. Initially, silver paste was applied on both sides of the pellet and was baked at 250°C for 3–4 hours before measurement. Afterwards, the measurements were repeated using silver- and gold-plated electrodes. The data obtained with all the three types of electrodes were consistent.

Results and discussion. – The temperature dependence of real and imaginary parts of dielectric permittivity, $\varepsilon_1(f,T)$ and $\varepsilon_2(f,T)$ of Tb$_2$NiMnO$_6$ in the frequency region, 100 Hz–800 Hz, is shown in fig. 1(a), (b) and for the range, 1 kHz–7 MHz in fig. 1(c), (d). Clear frequency dispersion is observed in both plots $\varepsilon_1(f,T)$ and $\varepsilon_2(f,T)$ and a closer examination reveals different plateaus. Schmidt et al. [9] have shown that each relaxation is represented by a dielectric plateau, three of which are indeed seen at low frequencies (fig. 1(a)). At high frequencies (fig. 1(c)) the third plateau is not observed. The low-temperature plateau originates from the intrinsic bulk contribution and the high-temperature plateaus could be due to the grain boundaries and sample-electrode interface [10,11]. Each relaxation can be ideally represented by one RC element [12], where $R$ and $C$ are connected in parallel, and three RC elements in series (upper panel of fig. 2) were used to model the real and imaginary parts of the permittivity vs. $T$ and the frequency dependence.

The complex impedance is given by [13]

$$Z^* = Z' + iZ''$$

(1)

where $Z'$ and $Z''$ are the real and imaginary part of the $Z^*$, respectively.

For a series of three RC elements as shown in fig. 2, the real and imaginary parts of the permittivity are calculated [9] as

$$Z^* = \frac{R_1}{1 + i\omega R_1 C_1} + \frac{R_2}{1 + i\omega R_2 C_2} + \frac{R_3}{1 + i\omega R_3 C_3}$$

(2)

$$\varepsilon_1 = -\frac{Z''}{\omega \varepsilon_0 g (Z'^2 + Z''^2)}$$

(3)

$$\varepsilon_2 = \frac{Z'}{\omega \varepsilon_0 g (Z'^2 + Z''^2)}$$

(4)

where $\omega$ is the angular frequency of the applied ac voltage and $\varepsilon_0$ is the permittivity of free space and $g$ is a geometrical factor ($\propto$ area/ thickness). In eq. (2), $R_1 C_1$ represents the intrinsic contribution, while $R_2 C_2$ and $R_3 C_3$ are the external contributions from the grain boundaries and...
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![Diagram of R-CPE circuit](image)

**Fig. 3:** (Colour on-line) Top: the R-CPE circuit used to model the complex plane of impedance, $Z'$ vs. $Z''$. Bottom: the experimental $Z'$ vs. $Z''$ plot at 300 K shown as circles. A fit to the observed data according to the circuit model shown above is given as solid line. The three different contributions to the total relaxation are marked. The inset shows the temperature dependence of $R_0$ and $L_0$ (in the circuit) extracted from the fit. A clear divergence in slope is seen in both $R_0$ and $L_0$ around 200 K.

The sample-electrode interface, respectively. Initially all capacitances are treated as temperature independent and the resistors obey an Arrhenius-type activated behavior \[ R_n = a_n \exp(20 \text{meV} / k_B T) \]. Assuming $R_3 \gg R_2 \gg R_1$, the pre-exponential constants $a_1$, $a_2$ and $a_3$ are taken as 1, 1000, and 10000, respectively. The capacitance values used for the simulation are calculated from the experimental observed plateaus of $\epsilon_1$ vs. $T$ plots, which yielded $C_1 = 1.76$ pF ($\epsilon_{\text{low}} = 20$), $C_2 = 88.4$ pF ($\epsilon_{\text{med}} = 100$), and $C_3 = 1.326$ nF ($\epsilon_{\text{max}} = 15000$). The simulated plots for the real and imaginary parts of the permittivity are shown in fig. 2(a), (b). The real part, $\epsilon_1$, has three plateaus in accordance with the three types of relaxations: the bulk, grain boundaries and the third from the sample-electrode interface [9,11]. If the temperature is lowered, the intrinsic contribution dominates and at sufficiently low $T$, the extrinsic contributions ceases (fig. 2(c)). The imaginary part $\epsilon_2$ has two peaks, which is similar to the experimental data (fig. 1(b) and (d)). These features are also reflected in the simulated frequency-dependent dielectric constant, fig. 2(c) and (d).

Impedance spectroscopy is a very powerful tool to study the multiple relaxations observed in dielectric materials, where the real ($Z'$) vs. imaginary ($Z''$) part of the complex impedance for different frequencies are plotted together. A subsequent analysis using the RC element model can deconvolute different types of dielectric relaxations present in the material [13]. In the ideal case of a single relaxation, the response is a semi-circle [14]. In real systems, the deviation from the ideal behaviour occurs and in order to account for this non-Debye–type behavior, the ideal capacitor is replaced with a constant phase element (CPE). The complex impedance of a CPE is defined as [9,15]

\[ Z_{\text{CPE}} = \frac{1}{C_{\text{CPE}}(i\omega)^n}, \]

where $C_{\text{CPE}}$ is the CPE-specific capacitance. $\omega$ is the angular frequency and $n$ is a critical exponent with typical values between 0.6 and 1 (for ideal capacitor $n = 1$). Such CPE capacitance can be converted into real capacitance using a standard procedure [16]. Such a circuit model constructed for the present work is illustrated in the top panel of fig. 3. The impedance of the sample is measured at different temperatures and $Z''$ vs. $Z'$ are plotted. The room temperature impedance spectra in the complex plane is shown in fig. 3 as black open circles. The data are fitted using three $R$-$CPE$ units in series corresponding to the bulk, the grain boundary and the sample-electrode contributions. The inductance $L_0$ of the external leads (also related to the magnetic phase) and the resistance, $R_0$, of the leads and electrodes are also taken into account in the circuit model. The curve fit to the experimental data at 300 K using this equivalent circuit is shown in fig. 3 as a solid line. The fit parameters are $R_1 = 6467 \pm 23\%$ ohm, $R_2 = 23625 \pm 9\%$ ohm, $R_3 = 200860 \pm 1.9\%$ ohm, $C_1 = 5.33$ nF $\pm 2.9\%$, $C_2 = 1.62$ nF $\pm 2.6\%$, $C_3 = 2.39$ pF $\pm 2.1\%$, $n_1 = 0.79 \pm 1.1\%$, $n_2 = 0.98 \pm 2.4\%$ and $n_3 = 0.95 \pm 1.8\%$.

The high-frequency response originates normally from the bulk, the intermediate frequency from the grain boundaries and the low-frequency impedance contribution from the sample-electrode interface [12]. Impedance data of magnetic materials are usually modeled by including an inductive element in the equivalent circuit wherein the permeability and magnetic response can be roughly understood from the inductance [17,18]. A combination of
$\epsilon$ is the angular frequency, $\tau$ is the mean relaxation time and $\alpha$ and $\beta$ are the distribution of relaxation times (for ideal Debye relaxation, $\alpha$ is zero). Equation (6) can be separated into the real and imaginary parts of the dielectric permittivity as

$$\epsilon_1 = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + (i\omega\tau)^{1-\alpha}},$$

$$\epsilon_2 = \frac{(\Delta\epsilon/2)\sin(\beta\pi/2)}{\cosh(\beta\pi/2) + \cos(\beta\pi/2)},$$

where $\Delta\epsilon = (\epsilon_0 - \epsilon_\infty)$, $z = \ln(\omega\tau)$ and $\beta = (1 - \alpha)$. The frequency dependence of $\epsilon_1(T)$ for Tb$_2$NiMnO$_6$ at few select temperatures is depicted in fig. 6 along with the curve fits using the modified Debye equation (eq. (7)). Since the bulk contribution will reflect in the high-frequency region, fitting was performed in the high-frequency region. However, the modified Debye model was inadequate to describe the behaviour of $\epsilon_1$ below 120 K (figure not shown) and attempts to fit eq. (7) were not successful. The value extracted for $\alpha$ from the fit falls between 0.18 and 0.27, which is higher than the value reported for La$_2$NiMnO$_6$ [7]. The inset of fig. 6(b) shows the temperature variation of $\alpha$ values extracted from the fit. An anomaly in the behavior is observed in the vicinity of $\sim 200$ K. We denote the temperature at which the deviation occurs as $T^*$, which is close to the temperature where an anomaly in the FWHM of the Raman modes was observed in Tb$_2$NiMnO$_6$ (180 K) [8]. This coincidence gives credence to the correlation between dielectric, Raman and magnetic anomalies in this material.

The frequency dependence of ac conductivity $\sigma$ of Tb$_2$NiMnO$_6$ is shown in fig. 7(a) and (b). This corresponds to two types of conduction behaviour at $T < T^*$ and $T > T^*$. Below 200 K, conductivity decreases with the increase in temperature reflecting an insulating behaviour. A change of slope in the ac conductivity occurs at the temperature at which the dielectric relaxation deviates from

$R$ and $L$ (parallel or series) is generally used for modeling the magnetic phase [17,19]. Using the circuit shown in fig. 3 we tried to extract the temperature dependence of inductance $L_0$ along with $R_0$ and this is shown in the inset of the bottom panel of fig. 3. A clear anomaly is observed around 200 K, which is close to Griffith’s temperature observed in this material [8]. Irvine et al., for example, have observed that the inductance value peaks at the magnetic anomaly transitions in (NiZn)Fe$_2$O$_4$ [17].

The intrinsic bulk contribution is analyzed using a single $R$-$C$-$CPE$ unit by considering the intermediate- and low-frequency region as extrinsic. The data is fitted faithfully up to 110 K. Figure 4 shows the fit at 250 K (inset (a)) and 150 K (inset (b)). At low temperature the bulk contribution dominates and the extrinsic contribution decreases. By a progressive procedure of fitting, the intrinsic response to the dielectric relaxation was extracted. The resistance ($R$) and the capacitance ($C$) estimated from the fit are plotted against temperature, in fig. 5. A slope change is visible in the temperature region around 200 K which coincides with the experimentally observed Griffith’s temperature in this compound [8]. The spin-lattice coupling also shows a marked change at this point. Although one cannot claim this to be magneto-electric coupling, it certainly indicate a connection between the various degrees of freedom. For ideal Debye relaxation of non-interacting dipoles, the plot of $\epsilon_1(T)$ vs. $\epsilon_2(T)$ follows the Cole-Cole behaviour displaying a perfect semi-circular arc [20]. Like in many complex oxides and those with defects, deviations from the ideal Cole-Cole plot are observed here; these may be accounted for by using the modified Debye equation,

$$\epsilon = \epsilon_1 + i\epsilon_2 = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + (i\omega\tau)^{1-\alpha}},$$
Debye-like behaviour. According to the universal dielectric response (UDR) [15], the relation between conductivity $\sigma'(f)$ and dielectric constant $\epsilon_1$ is given by

$$\sigma'(f) = \sigma_{dc} + \sigma_0 f^s$$

and

$$\epsilon_1 = \tan(s\pi/2)\sigma_0 f^{s-1}/\epsilon_0,$$

where $f$ is the experimental frequency, $\sigma_0$ and $s$ are temperature-dependent constants. A stepwise increase in the background of the loss factor reveals the contribution from dc conductivity (fig. 1(b) and (d)). Equation (10) can be written as

$$f\epsilon_1 = A(T)f^s,$$

where $A(T) = \tan(\pi T/2\Delta T)$, a plot of $\log(f\epsilon_1)$ vs. $\log(f)$ results in a straight line with slope equal to $s$. This is presented in fig. 7(c) where a clear straight line is observed at low temperatures. However, it deviates from linearity as temperature increases above $T^* \approx 200$ K, when charge carriers contribute to polarization. In order to find the dc contribution, the low-frequency ac conductivity was extrapolated to zero frequency. The dc conductivity of Tb$_2$NiMnO$_6$ relates to semiconducting-like behaviour above 200 K but deviates from thermally activated behaviour. The variation of the dc conductivity, $\sigma_{dc}$, with temperature is shown in the inset of fig. 7(c) where the change in slope is clearly visible close to 200 K. Again, the characteristic temperature $T^* \sim 200$ K compares well with the reported anomaly in the FWHM of Raman modes [8]. Figure 7(d) shows the electrical resistivity of Tb$_2$NiMnO$_6$ plotted in log scale against 1000/$T$. The resistivity data fits reasonably well to the Arrhenius law up to $\sim 200$ K. This supports the dc conductivity data derived from the ac conductivity and yields the activation energy, $E_a = 0.192(1)$ eV.

In our previous work concerning the magnetic properties of Tb$_2$NiMnO$_6$, an inhomogeneous magnetic state resembling the Griffiths phase was observed along with clear indications of spin-lattice coupling through Raman studies [8]. We were able to extract a characteristic temperature $T^* \approx 200$ K where magnetic and Raman anomalies coincided. The present dielectric response study validated by the dielectric relaxation and the ensuing impedance and conductivity behavior reflect the same characteristic temperature $T^*$ in this compound. Diffuse dielectric behaviour has been observed in nanoparticle samples of the double-perovskite La$_2$NiMnO$_6$ where disorder leads to local polar nanoregions [21] and also in La$_2$CoMnO$_6$ ceramics [22] where the charge order of Co$^{2+}$ and Mn$^{4+}$ was the origin of relaxation. It could be assumed, in the present case, that clusters that posses local polarization (polar nanoregions) are formed around Ni$^{2+}$ or Mn$^{4+}$ due to the cationic antisite disorder and bring about dielectric relaxation through their mutual interaction. This is also supported by the fact that the frequency dependence of the peak temperature in dielectric data is not explained by thermally activated behaviour. Similar to the magnetic Griffiths phase where the non-analyticity of magnetization extends above the transition temperature (in the present case, $T_c \approx 110$ K), the dielectric relaxation also identifies the characteristic temperature above $T_c$. In this context, it would be interesting to perform experimental investigations using local probes like electron paramagnetic resonance which can give clear signatures about the Griffiths phase [23]. Combining this with the fact that the Griffiths phase can indeed make itself manifested in disordered dielectrics [24] makes this double perovskite an interesting candidate to carry out microscopic measurements, for example using neutrons, to understand the magnetic and dielectric properties in more detail. Impedance spectroscopy and modified Debye model are used to analyse the dielectric response and identified a characteristic temperature that separates two regions of dielectric relaxation. This allows us to postulate a close correlation among magnetic, electronic and dielectric properties in this compound.

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