# 6
*Chapter*

# Dielectric and raman investigation of double perovskite

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**Abstract**

Double perovskite was prepared by solid state ceramic heating route. AC conductivity, temperature and frequency dependent dielectric constant, and vibrational Raman spectroscopy investigations have been made to characterizing the crystalline compound $Eu_2NiMnO_6$. Raman spectral analysis showed stretching breathing mode around 651 cm$^{-1}$along with anti-stretching and bending vibration near 507 cm$^{-1}$. An interesting scaling behaviour of the electric modulus and ac conductivity at different temperature was noticed from the deduced master curve with appropriate scaling variables. Strikingly, quite large value of dielectric constant $\sim 10^3$was observed around room temperature with moderate loss ($\sim$ 1.09 at 10 kHz frequency). Debye type relaxation of the dielectric relaxation behaviour was exhibited by this typical double perovskite.

**Keywords:** Dielectrics, Double Perovskite, AC conductivity, Magneto-dielectric

The perovskites type structures display characteristic features having technical as well as fundamental interests. Ferroic displacements in classic and relaxor ferroelectrics, half-metallic ferromagnetism, superconductivity, magnetoelectrics and multiferroics are the long list of properties exhibited by transition metal oxides perovskite [1-3]. Perovskite derived double perovskite compounds $A_2BB'O_6$ (A = alkaline earths/rare earth; B/B'= two dissimilar transition metals) have been the topic of current research interest for their interesting

dielectric, magnetic, magnetoelectricand other properties [3-5]. Mainly, double perovskites are attractive as they are characterized by structural and compositional flexibility which facilitates path of obtaining many substitutional compositions with different type of arrangement of transition metal cations. This is interesting as it opens up a prospect for control of the physical properties. In addition, perovskites form an important class of materials, characterized by subtle structural distortions from the cubic aristo type structure. The distortions are mainly associated with concerted rotations of the $BO_6$ octahedra, and the corresponding displacements of the cations within the space formed by the octahedra. These distortions might also give rise to notable difference in dielectric, magnetic, electrical resistivity and band gap behaviour [1-5].

Double perovskite compound $La_2NiMnO_6$ and $La_2CoMnO_6$ have successfully been synthesized earlier and dielectric, electrical and other properties of these compound have been carried out [3-5]. Europium (Eu) based rare earth perovskite emerges as an interesting compound that show interesting lattice and polarizability mediated spin activity; spin-phonon coupling and magnetoelectric properties etc. Therefore, it is worthwhile to synthesis and investigate double perovskites using this rare earth Eu atom; like $Eu_2NiMnO_6$. Hence, in the present work, we have synthesized $Eu_2NiMnO_6$ compound, and its structural characterization has been made. The dielectric, Raman spectroscopic and ac conductivity measurements of $Eu_2NiMnO_6$ is also made.

## Methodology

Standard solidstate ceramic heating route was taken to prepare polycrystalline $Eu_2NiMnO_6$. The detail of the synthesis condition was reported in [6]. In brief, initially, stoichiometric amounts of high purity (>99%) oxide precursors (EuO, $NiCO_3.2Ni(OH)_2.4H_2O$, and $MnO_2$) were taken and well mixed with intermittent grinding. This well mixed powder was then calcined at specified temperature. After grinding the calcined powder for about hour, pellets were made under a pressure of ~5 ton with the powdered mass. The obtained pellets were then finally sintered at a prescribed temperature. X-ray powder diffraction (XRPD) patterns were recorded at room temperature on a D8 advanced x-ray diffractometer (in Bragg–Brentano geometry with Cu-K$\alpha$radiation, $\lambda$ = 1.541 A). The refinement of the crystal

structure was performed by the Rietveld method using the Material Analysis Using Diffractionsoftware. Like our previous work [7], we measured dielectric permittivity and ac conductivity using a HP 4192 A impedance analyser interfaced with a PC. A good quality silver paste was used for the electrodes in the dielectric measurement. The sample temperature was controlled to a sufficient degree of accuracy by a Lakeshore 332 temperature controller. Room temperature Raman spectrum was taken in a HORIBA JobinYvon Raman spectrometer with an excitation source of an Ar–$F_2$ laser.

## Result and Discussion

X-ray powder diffraction (XPRD) experiment was employed to check the crystallinity and purity of the as prepared target composition $Eu_2NiMnO_6$. The x-ray diffraction pattern was taken at ambient temperature and pressure. The result obtained is shown in figure 1(a).XRPD pattern shown in figure 1 clearly indicate single phase perovskite nature of the prepared compound. No other impurity phases were detected. The XRPD pattern was further analysed by the Rietveld refinement method. Rietveld refinement method is basically fitting of a complete experimental diffraction pattern with calculated profiles and background. We started with the initial choice of space group P2$_1$/n. Experimental x-ray diffraction pattern together with the refined and difference (observed-calculated) x-ray diffraction patterns portrayed in figure 1(a) clearly demonstrated perfect agreement between the observed and the calculated profile of XRPD.
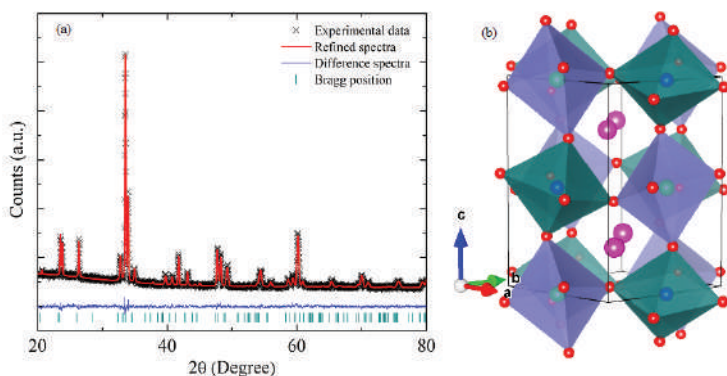


**Figure 1:** *(a) X-ray powder diffraction and Rietvelt refinement. (b)Schematic crystal structure ofEu$_2$NiMnO$_6$.*

The estimated lattice parameters are a = 5.332 Å, b = 5.523 Å, c = 7.595 Å, and $\beta$ = 90.06°. The goodness of fit indicators of refinement was $R_{wp}$ = 4.8, $R_p$ = 3.85, and $\sigma$ = 1.09 which again support high quality fitting of the XRPD. From the Rietveld refinement result, a schematic of the crystal structure is also drawn and shown in figure 1(b). From figure 1(b), it is clearly visible that the alternating $MnO_6$ and $NiO_6$ corner sharing octahedra are tilted in anti-phase order in the basal plane, and also perpendicular to the basal plane.

Result of room temperature Raman vibrational spectroscopy is shown in Figure 2. The Raman spectrum are dominated by broad peaks around 507, 1120, 1291 and 651 cm$^{-1}$. All the observed modes denote representative band pattern characteristic of the disordered double perovskite structure. From the lattice dynamical calculations for double perovskite; the band around 651 cm$^{-1}$ may readily be assigned to stretching (breathing) vibrations. The modes near 507 cm$^{-1}$ involving both anti-stretching and bending motions are of mixed type [8]. The Raman active modes are quite broad. This indicates the possible role of anti-site disorder. Anti-site disorder results in different contributions to the Ni-O or Mn-O stretching bands, i.e., the disorder Ni and Mn sites contribute different Ni(/Mn) – O stretching vibrations. The peaks around 1120 and 1291 cm$^{-1}$ are relatively weak, and are well correlated to combination and overtone modes of fundamental modes.
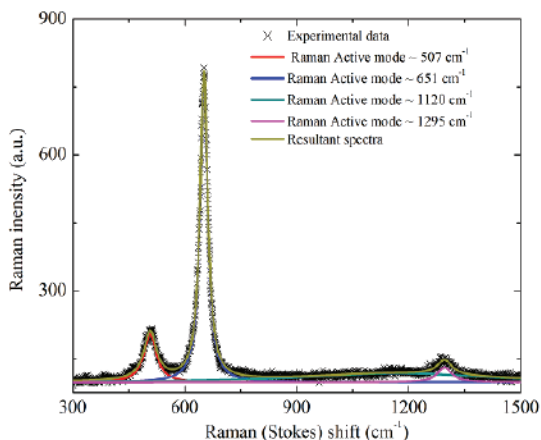


**Fig. 2:** *Room temperature Raman vibrational spectrum.*

In order to extract the dielectric properties of the compound under investigation we measured dielectric constant both as a function of temperatures and frequencies. The frequency dependent dielectric constant measured at different fixed temperature is shown in figure 3(a). At low frequency, the dielectric constant is almost constant and with increasing frequency the dielectric constant reduces to a lower constant value. At 280 K, the relative dielectric constant is ~2400 at 1 kHz, and this high value of dielectric constant after relaxation reduces to ~55 at 1 MHz frequency. Similar trends are also observed at other temperature is well as evident from figure 3(a). The relaxation frequency is observed to shift at higher frequencies with increasing temperature as shown by the green arrow in figure 3(a). We also measured the thermal variation of dielectric constant with temperature. The result obtained is shown in figure 3(b). Here also, thermally activated dielectric relaxation is evident as shown by the green arrow in figure 3(b). Relaxation temperature shifted to lower temperature with lowering frequency. At very low temperature all the frequency dielectric constant merges to a constant value. Most noteworthy feature of the dielectric spectra is the quite large value of dielectric constant $\sim 10^3$ around the ambient temperature associated with moderate loss ($\sim$ 1.09 at 10 kHz frequency). In order to understand the observed dielectric relaxations, it is to be remembered that in the frequency range of our present investigation, dielectric relaxations can arise from two independent mechanisms.
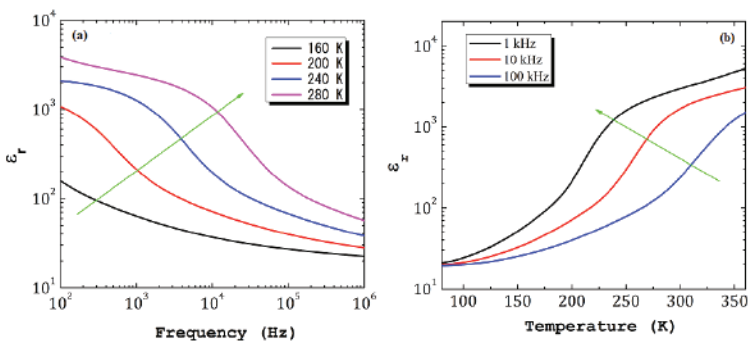


**Fig. 3:** *(a) Frequency variation of dielectric permittivity at different temperature. (b) Thermal variation of dielectric constant for different fixed frequencies.*

Firstly, the dielectric relaxation can originate either from dipolar contributions originating from asymmetric hopping of charge carriers

(between $Ni^{2+}$ and $Mn^{4+}$ sites). This in presence of an ac electric field give rise to Debye type relaxation [5]. Secondly, it can also arise from the Maxwell-Wagner relaxation due to the presence of accumulated charge carriers between regions in the sample having different conductivities such as near the grain boundaries [7]. The magnetization studied reported in [6] clearly indicated magnetic ordering below 150 K. Therefore, at low temperature (<150 K), the permittivity is almost constant; however, with increasing temperature, the contribution of hopping polarization between transition metal sites contributes above the magnetic transition temperature. As a result, the permittivity gradually increases. Remarkably, an appreciable magnetodielectric response ~10 %under an external applied magnetic field of ~1 T and at a frequency ~11.6 kHz was also noticed and reported in [6].

From the measured dielectric constant, information of electric modulus [9] was also extracted. The complex electric modulus showed thermally activated relaxation peak [6]. An attempt was also given to study the scaling behaviour of the complex electric modulus spectra. Remarkably, the scaling behaviour of the electric modulus at different temperature can be represented by a master curve as shown in figure 4(a). Suitable scaling parameters $M''_{max}$ and $f_{max}$ were used as the scaling parameters for $M''$ and f, respectively. As can be seen from the figure 4(a), all the modulus spectra can be seen to completely overlap and are scaled to a single master curve. The observed scaling of complex electric modulus indicates the shape of the modulus relaxation function is independent of temperature.
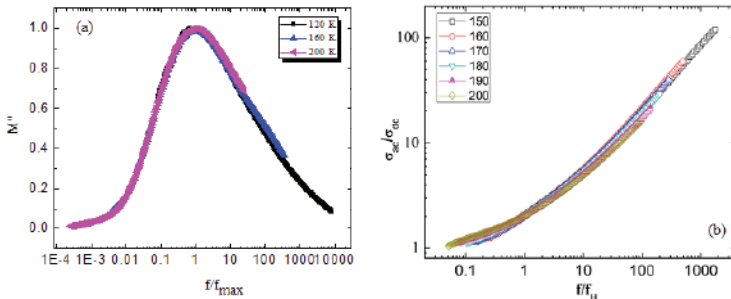


**Fig. 4:** *Scaling of complex electric modulus (a) and ac conductivity (b).*

Figure 4(b) shows the master curve for frequency dependence of ac conductivity [σ(f)] of $Eu_2NiMnO_6$ presented at selected temperatures. The real part of the σ(f) increases with frequency, at

high frequencies the conductivity follows an apparent power law, and at low frequencies there is a gradual transition to frequency independent conductivity. $\sigma(f)$ as a function of frequency obeyed power law (not shown) behaviour ; $\sigma(f)= \sigma_0 + A\omega^n$ where $\sigma_0$ is the dc conductivity, A and n ($<1$) are constant [8]. In figure 4(b), the normalized ac conductivity (by $\sigma_0$) is attempted to scale with normalized frequency (by hopping frequency $f_H$) as shown in the master curve in figure 4(b). Usually, the master curve indicates the independence of the relaxation function on varying temperatures. The lack of a coherent master curve in the present case indicates the dynamics of conductivity are not the same in this frequency and temperature ranges of investigation [10].

## Conclusion

A thorough structural investigation of the double perovskite $Eu_2NiMnO_6$ prepared by solid state chemistry is made. The compound mostly contained two crystallographically independent sites for Ni and Mn cations. Structural analysis also revealed that the effect of rare-earth Eu in the present compound, namely $Eu_2NiMnO_6$, was to noticeably reduce the cell dimensions in comparison to iso-structural double perovskite $La_2NiMnO_6$. Further studies of the structural, dielectric, Raman and conductivity properties confirmed partially ordered nature of the sample. It is possible that during crystal growth an ordered region of Ni and Mn cations meet another ordered region where centre of the consecutive octahedra is occupied by Ni and Mn cation alternately. At the boundary of two ordered region, atomic disorder or anti-site disorder of transition metal cation might be developed. At around room temperature, the dielectric constant showed high values with relatively low loss. High dielectric constant associated with a moderately low loss of the present magnetodielectric system $Eu_2NiMnO_6$ might be suitable for some technological applications. A coherent master curve is obtained for the modulus spectra, however, the same was not apparent from ac conductivity scaling. This gives indication of dominance of different conductivity contribution in modulus and conductivity representation.

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