PVDF Impregnated La$_2$NiMnO$_6$ as a New Form of Magnetoelectric Materials

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Abstract. In the continuation of our recently published work **[Tiwary et al., J. Appl. Phys. 124, 044101 (2018)]** on triphasic La$_2$NiMnO$_6$, here we are reporting the magnetodielectric and magnetoelectric properties of the new form of polymer modified (4H+P) La$_2$NiMnO$_6$ sample. A spectrum of unusual temperature dependent transitions, are spotted in both magnetodielectric and magnetoelectric data in the temperature range of 130 to 290K. Both Positive and negative magnetodielectricity of ~5% and 12% is observed. The positive magnetodielectricity is found in the wide temperature range (130 to 270K) whereas the negative magnetodielectricity is observed nearly at the paramagnetic to ferromagnetic transition temperature of the material. The various transitions found in the Magnetodielectric are seems to be related with the magnetic ordering of the material.

The room temperature x-ray diffraction (XRD) intensity recorded as a function of 2θ is displayed in figure 1(a). The difference line is not perfectly flat because of not including the crystallographic phase of PVDF[11]. The XRD patterns and the corresponding Rietveld refinement of the sample, confirmed the triphasic nature of the sample along with a very small peak ~ 20.2° (marked with star) corresponding to the β phase crystallization of PVDF[11].

A very demonstrative example of how the pores of the La$_2$NiMnO$_6$ sample is filled with polymer is shown in Fig.1 (b), a block (I) consisting of circles (signifies particles) is shown to visualize a matrix of 4H samples. The IInd block represents the PVDF polymer and the IIIrd block illustrates the 4H+P sample, in which all the pores are filled with PVDF. The FESEM of this sample conveying this pictorial representation is given in Ref 11.

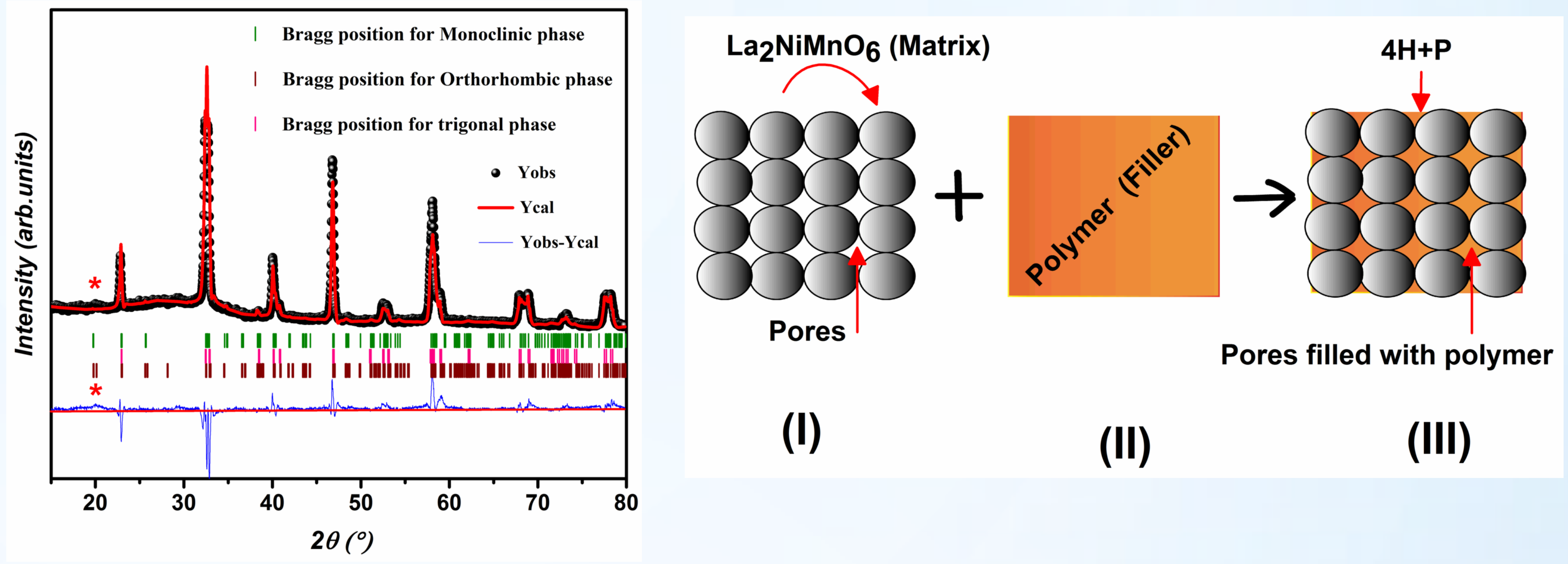

FIGURE 1 Rietveld refined XRD patterns of (a) 4H+P sample (b) Schematic representation of theencapsulation of PVDF filler into the 4H sample matrix is shown.

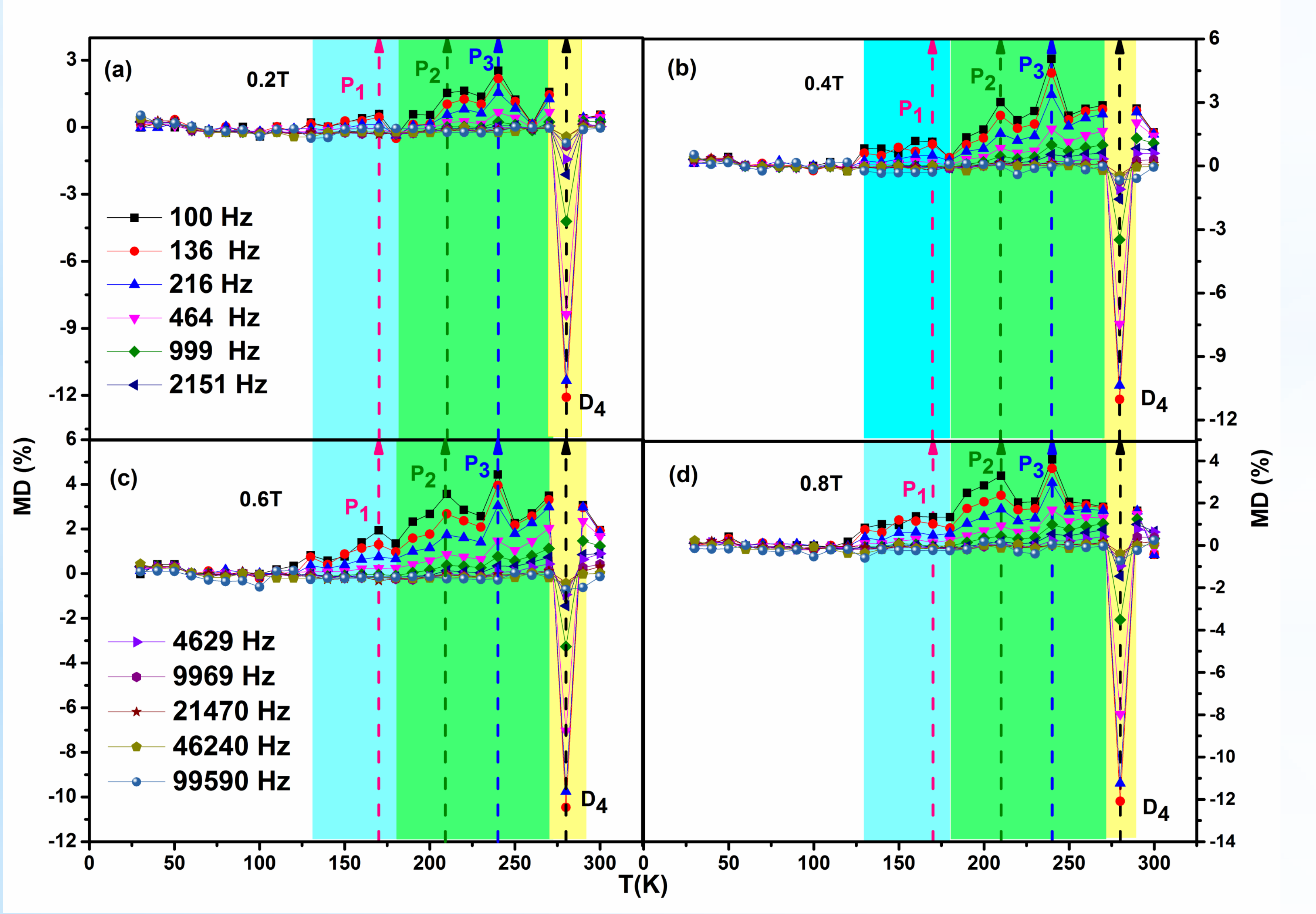

FIGURE 2 Temperature dependent MD (%) for 4H+P sample at, (a)0.2T (b) 0.4T (c) 0.6T and (d) 0.8T field at several frequencies. The solid lines are guide to eye.

The temperature and field variation of magnetodielectric (MD) in percentage at various frequencies are shown in Fig.2. The MD percent is obtained by using the equation as follows.

$$\text{MD}(\%) = \frac{\varepsilon(H) - \varepsilon(0)}{\varepsilon(0)} \times 100 \qquad 1)$$

where, ε(H) and ε(0) are the dielectric permittivity in 1.3T and 0T magnetic field. The data are taken isothermally, first without field and then at four different fields namely 0.2T, 0.4T, 0.6T and 0.8T. Both the positive and negative MD behavior is seen in the respective temperature ranges. A small temperature range near ferromagnetic T_C (290 >T > 270 K) shows negative MD (region 3 shown by yellow color). Positive MD is observed for T < 270 K, which is further divided into two regions namely (1) 130 – 180K (highlighted by cyan color), (2) 180 – 270K (marked with green color), depending on the extent of various peaks observed.

In the first two regions, numerous peaks are seen at various temperatures i.e. 170, 210, 240 and 280K. The peaks at respective temperatures are designated as P_1, P_2, P_3 whereas in region 3 one dip is observed, designated as D_4. The positions of these peaks are not changing with applied magnetic field but its magnitudes are changing. 5% of maximum positive magnetodielectricity and 12% of maximum negative magnetodielectricity is observed at 240K (when applied field is 0.4T) and 280K (observed in both the fields 0.2T and 0.8T, while the magnitude is decreased when the field is 0.4 and 0.8T) respectively. Both the temperatures where the maximum positive and negative MD is observed are marked as a magnetic ordering temperature in various reports[8].

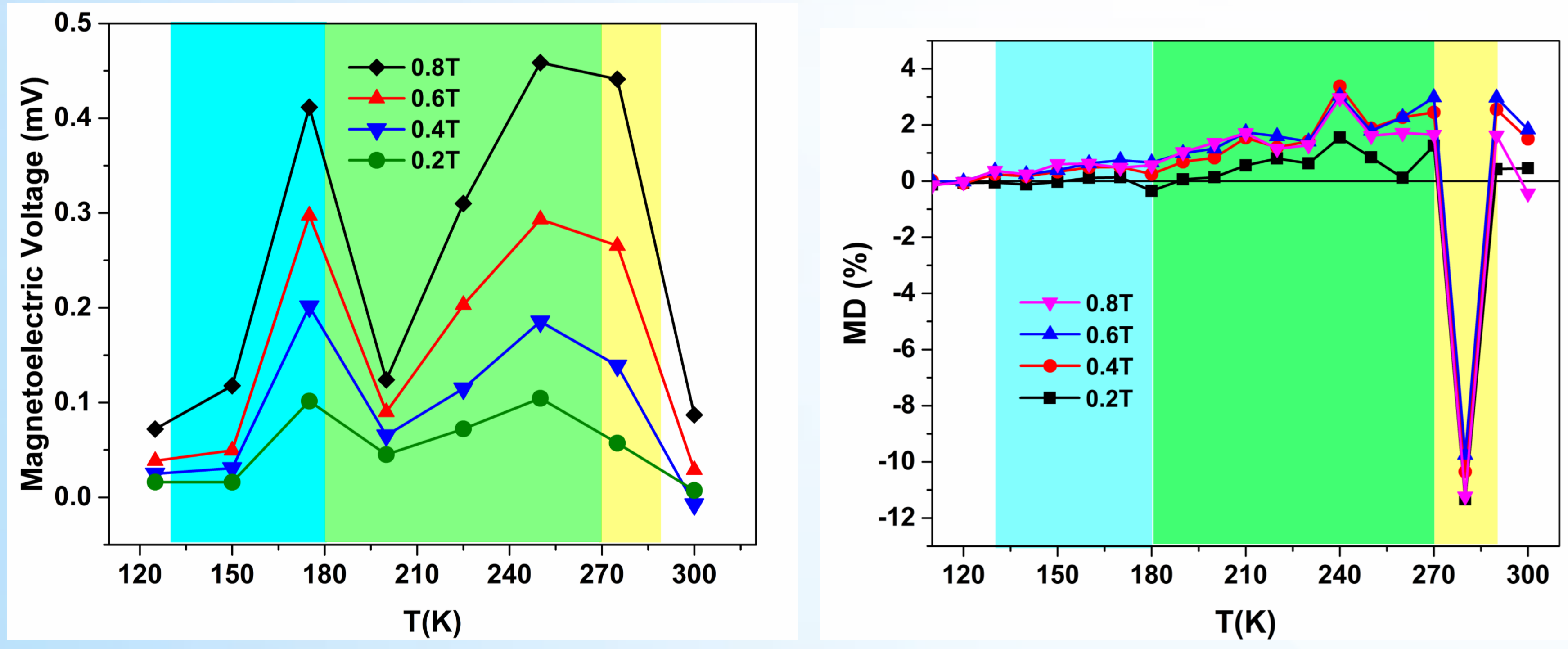

FIGURE 3 (a) Magnetoelectric voltages verses temperature (b) magnetodielectric (in %) verses temperature, at various fields (0.2, 0.4, 0.6 and 0.8T) at 216Hz frequency is shown, the three different color showing different regions.

Temperature dependence of both magnetoelectric (ME) and magnetodielectric data taken at frequency (216 Hz) at various fields is shown in Fig.3. For the sake of comparison, all the three regions discussed in the magnetodielectric section are shown here in the respective background color. In ME, two peaks are seen: 1st peak is very sharp ~ at 180K and the 2nd peak is very broad in the temperature range 290-200K. Interestingly this is the same temperature range where various small peaks are spotted in MD (see Fig 3(b)). According to magnetization behavior, at T ~170K, the Pbnm phase of La$_2$NiMnO$_6$ starts ordering[6] whereas ~280K is the transition temperature of both P2$_1$/n and R-3c phases[10,11]. This indicates that the magnetoelectric peaks may be related to the building up of magnetic ordering in the material. A large magnetodielectricity was earlier reported in this temperature range[10] but not with sharp features as it is here.

CONCLUSION: In conclusion, impregnated 4H+P sample is synthesized and studied for magnetoelectricity. Various peaks are seen in the temperature range of 130 to 300K, whose magnitudes are first increased with increase of applied magnetic field upto 0.6T and then decreased upon increasing magnetic field. In the same temperature range significant magnetoelectric voltage is also observed. Earlier various magnetic transitions were reported in this temperature range[5-10]. The 5% of maximum positive magnetodielectricity and 12% of maximum negative magnetodielectricity is observed at 240 and 280K respectively. The ME plot suggests involvement of magnetic ordering process in the contribution of magnetoelectricity.

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