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

Sweta Tiwary$^1$, S. Kukta$^1$, M. R. Saheoa$^1$, A. Barik$^1$, P. D. Babu$^2$, and P. N. Vishwakarma$^*$

$^1$Department of Physics & Astronomy, National Institute of Technology, Rourkela-769008, Odisha INDIA
$^2$UGC DAE Consortium for Scientific Research, Mumbai Centre, BARC, Mumbai 400085, India

Corresponding author:*E-mail: prakashn@nitrkl.ac.in and pnvissc@gmail.com

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 magnetoelectric 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 magnetoelectric and magnetoelectric data in the temperature range of 130 to 290K. Both Positive and negative magnetoelectricity of ~5% and 12% is observed. The positive magnetoelectricity is found in the wide temperature range (130 to 270K) whereas the negative magnetoelectricity is observed nearly at the paramagnetic to ferromagnetic transition temperature of the material. The various transitions found in the Magnetoelectric 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 at 20.2° (marked with star) corresponding to the β phase crystallization of PVDF$^{12}$. A very demonstrative example of how the pores of the La$_2$NiMnO$_6$ sample is filled with polymer is shown in figure 1(b), a block (I) consisting of circles (signifies particles) is shown to visualize a matrix of 4H samples. The II$^*$ block represents the PVDF polymer and the III$^*$ 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 thencapsulation of PVDF filler into the 4H sample matrix is shown.](image1)

Temperature dependence of both magnetoelectric (ME) and magnetoelectric data taken at frequency $\omega$ = 1.3T and at 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 Tc (200 to 270K) 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 (i) 130 – 180K (highlighted by cyan color), (ii) 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$_0$. The positions of these peaks are not changing with applied magnetic field but its magnitudes are changing. 5% of maximum positive magnetoelectricity and 12% of maximum negative magnetoelectricity 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 an ordering temperature in various reports$^{12}$. The field and temperature variation of magnetoelectric (MD) in percentage at various temperatures are shown in figure 2. The MD percent is obtained by using the equation as follows.

$$MD(%) = \frac{c(H) - c(0)}{E(0)} \times 100$$

where, c(H) and c(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 Tc (200 to 270K) 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 (i) 130 – 180K (highlighted by cyan color), (ii) 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$_0$. The positions of these peaks are not changing with applied magnetic field but its magnitudes are changing. 5% of maximum positive magnetoelectricity and 12% of maximum negative magnetoelectricity 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 an ordering temperature in various reports$^{12}$.

CONCLUSION: In conclusion, unimpregnated 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 up to 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$^{11}$. The 5% of maximum positive magnetoelectricity and 12% of maximum negative magnetoelectricity is observed at 240 and 280K respectively. The ME plot suggests involvement of magnetic ordering process in the contribution of magnetoelectricity.

REFERENCES
P. Kumar et al., 184, 47 (2014).

ACKNOWLEDGMENTS: The authors are thankful to DST, New Delhi and UGC DAE CSR, Mumbai for their support in the form of projects “EMR-2014/000341” and “CRS-M-223/2016/6724” respectively. Dr. V. Sirguri is also acknowledged for his support and time to time valuable suggestions. The author Sweta Tiwary would also like to thank CSIR, India, for CSIR-SRF fellowship and financial assistance.