

Temperature dependent negative differential resistance behavior in multiferroic metal organic framework $(\text{CH}_3)_2\text{NH}_2 \text{Mn} (\text{HCOO})_3$ crystals

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ABSTRACT

We present the temperature dependent negative differential resistance behavior of $(\text{CH}_3)_2\text{NH}_2\text{Mn} (\text{HCOO})_3$ crystals prepared by solvothermal synthesis. The paramagnetic to antiferromagnetic transition temperature, T_N and paraelectric to ferroelectric transition temperature, T_C were at 8 K and 184 K respectively. Above 100 K, negative differential resistance peaks in the low bias voltage region (between -4 V and $+4$ V) of the current-voltage characteristic were observed till 224 K. Fowler Nordheim tunneling mechanism was the dominant current conduction mode in the temperature independent high bias region (± 5 V to ± 10 V). The highest peak to valley ratio of 10 was recorded at 176 K with a peak current, I_{peak} of 2.7×10^{-11} A. The peak V_{peak} and valley V_{valley} were recorded at 1.5 V and 2.7 V respectively. The dielectric transition was found to be accompanied by an electronic transition of the metal to insulator type around 204 K.

1. Introduction

Negative differential resistance (NDR) occurs when the nonlinear nature in the current (I)- voltage (V) characteristic shows a negative slope (differential resistance, dI/dV) in some regions. NDR has tremendous potential as oscillators, low-power memory and logic devices [1,2]. Commonly used materials such as organic crystal [3] and biological molecules [4], semiconductor quantum wells [5], polymer – nanoparticle composites [6], metal-oxide hetero-structures [7], however, suffer from irreproducible and unstable NDR effect [8]. These reliability issues may be caused by the uncertain and complex mechanism at play, such as charge trapping and detrapping [9], filament formation and rupture [10], and redox reaction [11,12]. One of the possible way out, as demonstrated by Fan and Gao et al. [8] is using ferroelectrics materials, which offer a unique mechanism because of their polarization switching-induced charge injection and subsequent charge trapping at the metal/ferroelectric interface. Another reliable mechanism for NDR maybe the electronic transition of the insulator to metal type as has been observed in single crystals of nTTF-TCNQ and their origin has been explained on the basis of some current induced excitation mechanism from an insulating ground state to a higher-conductivity excited state [3]. NDR in organic materials, as compared to conventional inorganic materials, has gained augmented attention over the last few years due to their optical transparency and mechanical flexibility [2,13,14].

It is well known that materials in which magnetic and electric orders

coexist, known as multiferroics, have tremendous potential in applications such as AC/DC magnetic field sensors, multiferroic magnetic recording read heads, multiferroic random access memories with multi-state memories, to name a few [15]. The prospects of controlling the ferroelectric property by magnetic field and vice versa had ensured uninterrupted research for more than a decade [16–18]. An appearance of NDR in such devices could potentially impact the applications mentioned above. Discovered in 1959 by Dzyaloshinskii [16], multiferroic materials were initially all inorganic in nature. However, in 2009, P. Jain et al. [19] first showed the presence of ferroelectric and magnetic property in a special class of material now known as metal organic frameworks (MOFs). These materials with organic and inorganic units form crystalline solid that exhibit ABX_3 type perovskite structure. The A here is an organic cation, B a divalent transition metal ion and X is the organic linker anion; all arranged in a 3D-array of corner sharing BX_6 octahedra with larger A cation occupying the octahedral cavity of the 3D network [19–21]. Thus an individual unit cell of the MOF crystal under study, $[(\text{CH}_3)_2\text{NH}_2] \text{Mn} (\text{HCOO})_3$, is made up of one Mn ion, HCOO^- ion and $[(\text{CH}_3)_2\text{NH}_2]^+$ (to be referred as DMA) ion. In such a unit cell, the metal ion sits inside a MnO_6 octahedron and is linked to six closest metal ions through HCOO^- bridges. This octahedron with six HCOO^- bridges forms a 3 D framework. The DMA ions sits in the cavity of the 3D structure and is connected to the HCOO^- bridge through hydrogen bonds. The nitrogen atom in DMA ion, at room temperature, has three equivalent positions. Upon cooling below the Curie temperature (T_C), the nitrogen atom gets ordered into one of

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the equivalent crystallographic sites, lowering the crystal symmetry and ultimately leading to a paraelectric to ferroelectric phase transition [19,22]. The possibility of an electronic transition accompanying this paraelectric to ferroelectric phase transition is yet to be investigated. Thus multiferroic MOFs present a strong case for observing reproducible and stable NDR. Multiferroic MOFs are predominantly synthesized by either solvothermal method or solution evaporation methods [19,23].

In our work, millimeter sized $[(\text{CH}_3)_2\text{NH}_2][\text{Mn}(\text{CHOO})_3]$ (to be referred as DMAMnF) crystals were synthesized by solvothermal route and their dielectric, magnetic and temperature dependent NDR properties were investigated. With paramagnetic to antiferromagnetic transition temperature, T_N and paraelectric to ferroelectric transition temperature, T_c at 8 K and 184 K respectively, the multiferroic nature of these crystals were established, as reported in literature [19]. A negative differential resistance type behavior has been obtained, for the first time, with a maximum peak to valley ratio (PVR) of 10:1 at 176 K. The conduction mechanism behind the temperature dependent NDR of these crystals could be understood using the Hubbard model and Fowler–Nordheim (FN) tunneling has been found to be the dominant conduction mechanism in high bias low temperature region (below 180 K). An electronic transition was found to accompany the dielectric transition in our DMAMnF crystal.

2. Experimental

DMAMnF crystals were grown in an autoclave according to the procedure given by Jain et al. [19] albeit with slight modification. A typical reaction starts with the dissolution of commercially available MnCl_2 (99%, Aldrich) in 50:50 v/v solution of N,N dimethylformamide (DMF) (99.8%, Aldrich) and deionized water. The mixture was placed under solvothermal conditions at 140 °C for 3 days. At the end of the solvothermal reaction, the chamber was allowed to cool undisturbed for four more days. Large colorless crystals were collected after filtration, washed three times in absolute ethanol and air dried. Reproducible X-ray diffraction spectra were obtained even after prolonged (more than six months) exposure to ambient atmosphere. Powder diffraction pattern were used to establish the composition and phase purity of the crystals obtained. Powder X-ray diffraction pattern were obtained from Philips XPERT PRO (Cu K_α) instrument at room temperature. Magnetic properties were analyzed as a function of magnetic field and temperature in a Superconducting Quantum Interference Device (SQUID). Temperature dependent dielectric measurements were carried out in the range of 40–300 K in a closed cycle refrigerator using Agilent 4294A precision impedance analyser. Polarization vs electric field (P-E) loop measurement was carried out in Radiant Technology Precision Premier II. Current voltage (I-V) characteristics were measured using Keithley 4200-SCS between temperatures 100 K and 294 K using Lakeshore temperature controllers. I-V plots were recorded while the sample was heated from 100 K to room temperature in steps of 4 K.

3. Result and discussion

Fig. 1 shows the powder diffraction pattern of crushed DMAMnF crystals at room temperature. The intensity ratios and the peak positions matches well with earlier reports [21]. The single crystal structure of DMAMnF is very well studied and it has been consistently found that at room temperature, the crystal belongs to trigonal system R-3c [19,20].

The dielectric phase transition temperature and the nature of the phase transition can be understood from the temperature dependent complex dielectric measurement carried out during the heating and cooling cycle. Fig. 2 shows the temperature dependent real dielectric constant (ϵ') plot from a crystal of dimension 3 mm × 2 mm × 4 mm. Variation of ϵ' with temperature plot at 90 KHz shows a fairly broad peak spanning between 180 K and 224 K and a $d\epsilon'/dT$ plot was used to

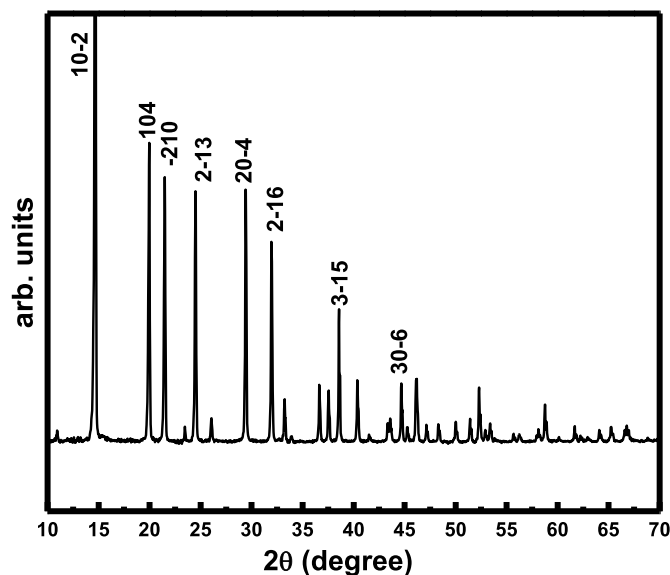


Fig. 1. Room temperature XRD pattern of as-prepared DMAMnF powder.

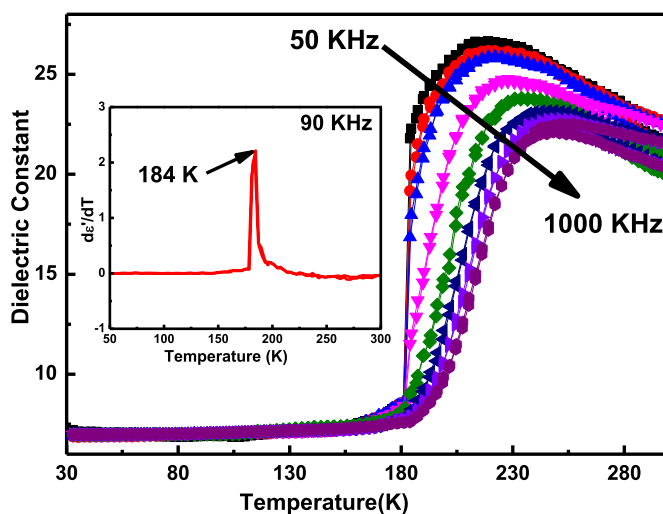


Fig. 2. Temperature dependent dielectric constant at different frequencies. The inset shows the derivative peak at 184 K.

elucidate the exact peak position at 184 K (inset of Fig. 2). The broadness of the peak has been explained to occur due to the slow movement of the fairly large DMA cation [24]. The nature of the dielectric transition was confirmed by tracing a P-E loop from an unsintered pressed pellet at 77 K at various maximum voltage V_{max} as shown Fig. 3. Hysteresis loops were obtained for all voltages applied, indicating the ferroelectric nature of the sample [25]. The P-E loop moved towards saturation as the applied voltage was increased to 700 V. The saturation polarization of the DMAMnF sample for 700 V V_{max} was nearly $0.3 \mu\text{C cm}^{-2}$.

The magnetic properties of DMAMnF crystals were investigated and the results are presented in Fig. 4. The magnetization versus temperature plot measured under standard zero field cooled (ZFC) and field cooled (FC) protocols reveal a transition temperature T_N and a blocking temperature T_B occurring at 9 K and 7 K respectively. The separation between the ZFC and FC below 8 K plot indicates the material has spin canted antiferromagnetic behavior [21]. A plot of susceptibility (χ)* temperature vs temperature (inset Fig. 4) shows a single sharp peak at 8.5 K signaling that the transition is from a paramagnetic to an antiferromagnetic phase [26].

The electrical transport properties of the DMAMnF crystals were

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