Supplementary Information

Dielectric and electro-optical properties of Mn₁₂-acetate and ferroelectric liquid crystal composite

Shilpi Verma,^a Amit Choudhary,^{*b} Priti Singh,^{*c} Ashok M. Biradar,^c Surinder P. Singh^c

^a*Academy of Scientific and Innovative Research (AcSIR), National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi-110012, India.*

^b*Physics Department, Deshbandhu College (University of Delhi, Delhi), Kalkaji, New Delhi-110019, India.*

^c*CSIR - National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi-110012, India.*

*E-mail: amitnpl2005@gmail.com * E-mail: pritchem@gmail.com

Preparation of Mn₁₂-acetate: All synthesis based experiments were performed under aerobic conditions using the required chemicals. Mn(II) acetate tetrahydrate [Mn(O₂CCH₃)₂·4H₂O] and acetic acid (CH₃COOH) were purchased from Sigma Aldrich while potassium permanganate (KMnO₄) was purchased from Merck. The solvents and chemicals were used as received. Mn₁₂-acetate was synthesized using the method reported by Lis [1] with slight modifications. Briefly, Mn(O₂CCH₃)₂·4H₂O (16 mmol) was taken in 40 mL of 60% acetic acid and stirred until complete dissolution. Then finely powdered KMnO₄ (6.3 mmol) was added to it in lots in one minute duration followed by stirring of contents for another one minute. The resultant brown colored solution was allowed to stand undisturbed for 4 days in water bath at room temperature.

The black crystals so formed were filtered, washed with acetone, dried and refrigerated. The yield was typically 76%. (Found: C, 20.93; Mn, 32.05. Calc. for $C_{36}H_{72}Mn_{12}O_{56}$: C, 21.02; Mn, 32.99%).

Characterization Techniques used for Mn_{12} -acetate: Mn_{12} -acetate has been characterized using Fourier Transform Infrared (FT-IR) spectroscopy (Agilent Cary 360 FTIR spectrometer in the range of 3600 to 400 cm^{-1} on ATR), UV-visible spectroscopy (Agilent Carry 5000 UV-Vis-NIR in the range 200 to 800 nm) and Single Crystal X-ray diffraction (Bruker AXS KAPPA APEX II). Scanning Electron Microscopy images were collected using Zeiss Evo MA10 electron microscope. Mn% was determined using Atomic Absorption Spectrometer (AAS Vario 6) and C% was determined using Elemental Analyzer (Vario PYRO Cube). The magnetization properties have been measured using Quantum Design USA SQUID magnetometer. The temperature dependence of magnetization is measured using ZFC (zero-field cooled) and FC (field cooled) techniques for Mn_{12} -acetate.

Characterization of Mn_{12} -acetate: The FT-IR spectrum of Mn_{12} -acetate (Figure S1) shows the presence of Mn-O stretches of manganese-oxo cluster in the region 450-700 cm^{-1} . The region around 1500 cm^{-1} and 1400 cm^{-1} exhibits the asymmetric and symmetric (O-C-O) stretches from the coordinated acetate, respectively. Peak at 1708 cm^{-1} is observed due to C=O stretch of free acetic acid present in the crystal. O-H stretches due to associated and coordinated water are seen in the region 3600-3200 cm^{-1} . [2]

Figure S1. FT-IR spectrum of powdered sample of Mn₁₂-acetate.

UV-Vis spectrum (Figure S2) of Mn₁₂-acetate shows an overall diffused character as reported previously.[3] The low-contrast spectral feature in optical response of Mn₁₂-acetate is due to high density of states (DOS) throughout the visible range. Oppenheimer *et al.* have assigned some spectral features by comparing with transitions predicted by theoretical calculations. The lower energy absorption around 510 nm is attributed to charge transfer from Mn⁴⁺ ions in the inner core to the Mn³⁺ ions in the outer core whereas the higher energy absorption around 250 nm is attributed to the ligand to metal charge transfer.[3]

Figure S2. UV-Vis spectrum of Mn₁₂-acetate in acetonitrile.

The structural and morphological features of the compound were investigated using Single Crystal X-Ray Diffraction and Scanning Electron Microscopy (SEM). Single crystal XRD analysis revealed tetragonal structure of Mn₁₂-acetate with lattice parameters ($a = b = 17.28 \text{ \AA}$, $c = 12.34 \text{ \AA}$) in well agreement with the reported data.[1] SEM images of the powdered sample as well as crystal of Mn₁₂-acetate are shown in Figure S3 that clearly illustrate rod shaped features with length in the range 55-60 μm . The sharp edges and clear facets of the rod-like structures signify uniform crystalline growth of the complex.

Figure S3. (a) SEM image of finely powdered sample of Mn_{12} -acetate and (b) SEM image of crystal of Mn_{12} -acetate.

Magnetic Studies of Mn_{12} -acetate: Magnetization studies performed on SQUID magnetometer confirmed the SMM behavior in Mn_{12} -acetate. The graph of magnetization versus applied dc magnetic field at three different temperatures was plotted (Figure S4). The slow reversal of magnetization orientation at low temperatures (below 5.0 K) gives rise to prominent hysteresis curves in Mn_{12} -acetate with significant coercive field which decreases with increasing temperature. This property has been attributed to the superparamagnetic behavior of the SMM.[4,5] However, the hysteresis curve obtained is not even or smooth, steps are seen at periodic field values which has been ascribed to Quantum Tunneling of Magnetization Vector.[5] The temperature dependence of magnetization was explored using zero-field cooled (ZFC) and field cooled (FC) data for Mn_{12} -acetate (Figure S5). As reported earlier, the large difference in FC and ZFC plot is observed due to the slow magnetization relaxation of the compound at low temperatures.[6]

Figure S4. Magnetic hysteresis loop of Mn₁₂-acetate at temperatures 1.8, 2.5 and 5.0 K showing decreasing coercivity with increasing temperature.

Figure S5. ZFC and FC field plot of magnetization versus temperature of Mn₁₂-acetate at $H = 1000$ G.

DSC Measurements of FLC and Mn₁₂-acetate/FLC composite: The shift of about 3.5 °C in SmC*-SmA phase transition has been shown in DSC measurement during heating cycle. The SmA to nematic phase has also been found shifted towards the higher temperature with the same ratio. No shrinkage has been found in any of the two phases (SmC* and SmA).

Figure S6. Differential Scanning Calorimetry (DSC) of the pure FLC and Mn₁₂-acetate/FLC composite showing the shift of about 3.5 °C in the SmC* to SmA phase transition of the Mn₁₂-acetate/FLC composite.

Viscosity and spontaneous measurement: The change in rotational viscosity at room temperature has been measured and found to be about 460 mPa.s for Mn₁₂-acetate/FLC composite

sample and 380.4 mPa.s for pure FLC. The rotational viscosity of pure FLC in its catalogue is 380 mPa.s at 20 °C. On the other hand the spontaneous polarization 30.86 nC/cm² for Mn₁₂-acetate/FLC composite and 27.67 nC/cm² for pure FLC. The spontaneous polarization of pure FLC is 29 nC/cm² at 20 °C temperature (provided by manufacturer). These results corroborate our observations in dielectric relaxation and memory effect.

Table 1a: Dielectric parameters used to fit the real part of complex dielectric permittivity of FLC ZLI 3654 using Eq. 1.

Temp. (°C)	ϵ_{∞} (High frequency permittivity)	ϵ_0 (Low frequency permittivity)	τ (relaxation time)	ν (Frequency from fitting)	ν (Frequency from experiment)	α (Distribution parameter)
32	5.2	170	0.0014	113.7397634	102	0.063
35	5.5	180	0.0013	122.488976	114	0.059
45	5.3	170	0.00098	162.4853763	149	0.059
50	5.2	165	0.00095	167.6164935	134	0.025
55	5.2	145	0.00097	164.1604833	134	0.006
60	5.3	115	0.00096	165.8704883	134	0.06
62	5.3	15	0.00095	167.6164935	149	0.086
64	5.125	5.98	4.50E-06	35385.70418	40442	0.04
65	5.125	5.612	2.50E-06	63694.26752	77659	0.01
65.5	5.11	5.416	1.60E-06	99522.29299	101000	0.005
66	5.1	5.4	1.58E-06	100782.0689	115000	0.005
67	5.081	5.326	1.10E-06	144759.6989	145000	0.005

Table 1b: Dielectric parameters used to fit the real part of the complex dielectric permittivity of Mn₁₂-acetate/FLC composite using Eq. 1.

Temp. (°C)	ϵ_{∞} (High frequency permittivity)	ϵ_0 (Low frequency permittivity)	τ (relaxation time)	ν (Frequency from fitting)	ν (Frequency from experiment)	α (Distribution parameter)
32	4.95	90	0.0015	106.15	95	0.067
35	4.93	100	0.0014	113.73	97	0.06
45	4.86	82	0.00115	138.46	114	0.04
50	4.827	70	0.00102	156.11	82	0.045
55	4.84	55	0.00092	173.08	113	0.081
60	4.768	27	0.0009	176.93	114	0.1
62	4.75	15	0.00088	180.95	127	0.15
64	4.76	8	0.00085	187.34	142	0.4
65	4.75	6	0.00072	221.16	157	0.5
65.5	4.72	5.8	0.00053	300.44	320	0.171
66	4.71	5.69	0.000006	26539.27	27700	0.171
67	4.7	4.996	0.0000016	99522.29	99351	0.2

References

- [1] Lis T. Preparation, Structure, and Magnetic Properties of a Dodecanuclear Mixed-Valenced Manganese Carboxylate. *Acta Cryst.* 1980;B36:2042-2046.
- [2] Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B, Applications in Coordination, Organometallic and Bioinorganic Chemistry*: John Wiley & Sons, Inc.; 2009.
- [3] Oppenheimer SM, Sushkov AB, Musfeldt JL, Achey RM, Dalal NS. Diffuse optical excitations in Mn_{12} -acetate. *Phys Rev B*, 2002;65:054419. doi: 10.1103/PhysRevB.65.054419.
- [4] Christou G, Gatteschi D, Hendrickson DN, Sessoli R. Single-Molecule Magnets. *MRS Bull.* 2000;55:66-71.
- [5] Bagai R, Christou G. The Drosophila of single-molecule magnetism: $[\text{Mn}_{12}\text{O}_{12}(\text{RCOO})_{16}(\text{H}_2\text{O})_4]$. *Chem Soc Rev.* 2009;38:1011-1026. doi: 10.1039/b811963e.
- [6] Sessoli R, Gatteschi D, Caneschi A, Novak MA. Magnetic bistability in a metal-ion cluster. *Nature*, 1993;365:141-143. doi: 10.1038/365141a0.