Linear and Harmonic Magneto-dielectric Study on Ca$_3$Mn$_2$O$_7$ Layered Perovskite

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Abstract: Dielectric study on Ca$_3$Mn$_2$O$_7$ features relaxor-like segmented dynamics below the antiferromagnetic ordering. Dipolar relaxations associated with rotation and tilt octahedral-distortions are spectrally resolved and their temperature-frequency dispersions exhibit distinct $H$-field alterations. This identifies their allegiance to different magnetic sub-phases and establishes dual coupling of electrical, magnetic, and structural degrees of freedom. Short-range electrical correlations—due to the randomness of structural distortions—collaterally cause measurable harmonic dielectric response in the system. The $\chi''_2$-susceptibility signal yields genuine harmonic magneto-dielectricity, consistent with but exhibiting two orders of magnitude larger $H$-field effect, vis-à-vis that obtained in the fundamental dielectric constant $\varepsilon''$.

Keywords: Layered Perovskite, Magneto-dielectricity, Non-linear Permittivity, Relaxor-like Vitreousity.

INTRODUCTION

Interesting evolution of magnetic and electrical configurations has been realized in layered Ruddlesden-Popper (R-P) compounds. These are pronounced successor of perovskites with inter-coupled structural, magnetic, and electric properties. R-P series compounds are represented as $A_{n+1}B_{n+1}O_{3n+1}$ for $+2$ valence state ‘$A$’ cations and $+4$ valence ‘$B$’ ions, with $C$ usually being oxygen ($-2$ valence) [1]. Structurally, they reveal themselves as integral-$n$ ABO$_3$ perovskite blocks, with inserted AO sheets in-between, along the $c$-axis. La$_{1.4}$Sr$_{1.6}$Mn$_2$O$_7$ has been shown to possess inter-planar tunneling induced low-field magneto-resistance [2]. Development of ferromagnetic clustering in the long range antiferromagnetic (AFM) ordering has been reported in $n=3$ R-P compound La$_{3-x}$Sr$_{x}$Mn$_3$O$_{10}$ [3]. Hybrid improper ferroelectricity (HIF) supported by first-principles calculation has been evident in $n=2$ R-P compound Ca$_3$Ti$_2$O$_7$ [4, 5]. Here, the ferroelectric mechanism is described via combination of two octahedral distortion patterns [6]. These distortions offer scope for magneto-electric (ME) coupling and multiferroicity; since unfulfilled $d$-orbital accommodated in the oxygen octahedra favors (anti)ferromagnetism, which relates profoundly with the metal-oxygen-metal bond angles [7]. Emphasis on $n=2$ R-P system Ca$_3$Mn$_2$O$_7$ has been due its expected candidacy for ME coupling [6]. Ca$_3$Mn$_2$O$_7$ exhibits structural transition from I4/mmm tetragonal phase to Cmc$_2$1 orthorhombic phase, with introduction of octahedral rotation in (001) plane, along with the octahedral tilt about [100] axis [8]. Complementarily, octahedral tilting supports weak ferromagnetism and octahedral rotation induces magneto-electricity [9].

Inversion-symmetry-breaking orthorhombic phase in Ca$_3$Mn$_2$O$_7$ can possess ferroelectricity (FE) [6]. Electric field tunability of octahedral rotation is expected to enhance the ME effect. The structural transition covers a wide (300-600K) temperature range [10], with coexistent tetragonal and orthorhombic phases. In pure orthorhombic phase, relaxor behaviour has been suggested [10] below the room temperature. Because of the high leakage-current at high temperatures in the orthorhombic phase, there have been difficulties in experimentally ascertaining ferroelectricity in the system [7]. Upon cooling, dielectric losses get reduced and ferroelectricity with measurable polarization is detected below 60K [10], which can be further explored at lower temperatures. Moreover, magnetic ordering at 123K is expected to affect the dipolar interactions, via the magneto-electric effect. From first-principles calculations [6], Benedek and Fennie have reported G-type AFM ground state for the system, with a net perpendicular spin-canted moment via spin-orbit (S-O) interactions. Dzyaloshinskii’s criteria explain the canted moment via the oxygen-octahedral tilt distortion. ME effect for Ca$_3$Mn$_2$O$_7$ has been demonstrated by Zhu et. al.

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[11], via measurements of the magnetization under electric field; 6% reduction in magnetization at 4K with the application of $E$-field of 40 kV/m under 100 Oe $H$-field has been reported.

It is well known that octahedral rotations have profound effect on transition metal-oxygen-transition metal (TM-O-TM) bond angle, which further affects the interaction between spins [12, 13]. In Ca$_3$Mn$_2$O$_7$ system, antiferromagnetic transition with Néel temperature 123K, along with the emergence of weak ferromagnetism (WFM) below 110K, have been reported previously [14]. Dzyaloshinskii-Moriya (D-M) interaction favored WFM clusters’ formation in the AFM-matrix, inducing an exchange-bias (EB), was characterized in detail [14, 15], and the magnetic evolution is as summarized in fig.1. In Ca$_3$Mn$_2$O$_7$, structural distortions prompt coupling between spin and charge degrees of freedom [9]. Here, we present the linear/non-linear dielectric properties of Ca$_3$Mn$_2$O$_7$, and their correlation with magnetic-evolution/phase-mixing is compared & distinguished. Magneto-dielectricity is explored under applied magnetic field, across a sufficiently wide temperature range covering the AFM ordering at $T_N = 123$K.

RESULTS

Dielectric Spectroscopy:

Low temperature fundamental dielectric response along with second harmonic measurements have been performed in parallel-plate capacitor configuration, from 200K down to 7.5K in the frequency range of 50 Hz to 300 kHz, using NovoControl Alpha-A Broadband Impedance Analyzer. To study the magneto-dielectricity in the system, dielectric measurements under application of magnetic field ($H$) have also been performed in Oxford NanoSystems Integra 9T magnet-cryostat.

Fig.2(a) presents the dielectric constant $\varepsilon'(T)$ of Ca$_3$Mn$_2$O$_7$ at various frequencies. Here, sharp frequency-dependent step-change in $\varepsilon'(T)$ is observed. At high-$T$'s, relaxation times $\tau(T)$ are small enough that even at higher radio frequencies (RF) condition $2\pi\tau(T) < 1$ applies; resulting in a rather small frequency-dependence of $\varepsilon'(T)$, as observed.
In layered perovskites, FE-instability consists of O6-octahedron rotations, with negligible off-centering of the B-site cation. The associated energy-gain (due to lattice-strain) and energy-loss (due to dipole-dipole interaction) here rather settle in introducing antiferro-distortive (AFD) -like features over a temperature window [16], thereby suppressing the long-range FE-ordering in the system at a sharp transition temperature [17]. In the quantum paraelectric-like AFD systems, chemical substitution, application of electric field, or dimensional-strain can induce the FE [18]. In the layered Ca$_3$Mn$_2$O$_7$, no specific heat anomaly pertaining to a long-range FE transition is observed below the room temperature [11]. At lower temperatures however, magnetic ordering at $T_N = 123$K supports FE in this magneto-electric system [10].

Appearance of orthorhombic phase upon cooling supports the development of ferroelectric correlations between the dipoles; manifest here as step-like (thermally-activated) decrease of the dielectric constant. Thus-increased $\tau(T)$ leads to resonance of the measurement frequency and the response timescale of the correlated dipoles ($2\pi \tau(T) = 1$); which marks maximum slopes (inflexion-points) of $\varepsilon'(T)$, at successively lower frequencies upon cooling. Similar steps in permittivity are discernible in the report by Liu et. al. [10]. Here, the correlations produce size-dispersed dipole-clusters, each responding optimally at different frequency ($\omega_p(T) \sim 1/\text{cluster-size}$), which shows up in thermally activated dielectric spectra. For a given measurement frequency, super-resonance ($2\pi \tau(T) > 1$) condition upon further cooling causes the roll-off of $\varepsilon'(T)$ to lower values, for the same inertial reason as occurs for the $\varepsilon'(f)$-isotherms at high frequencies.

Change in $\varepsilon'(T)$ produced under $H$-field is zoomed-on in fig.2(b), shown at selected frequencies for clarity. At temperatures above the $\varepsilon'(T)$-step, $H$-field enhances correlations between the dipoles, evident from $\varepsilon'(6T) < \varepsilon'(0T)$ (fig.2b). Also, for frequencies $f \geq 11.5$ kHz, at all temperatures $\varepsilon'(T)$ simply reduces under the field. At lower frequencies however, $H$-field alters the dielectric constant in both +ve and -ve sense over different temperature ranges, depending upon the extent of the dipolar interactions. At probing frequencies $f < 11.5$kHz, $H$-field mobilizes the larger/frozen dipolar clusters ($2\pi f \tau_{cl} > 1$; $\varepsilon'(6T) > \varepsilon'(0T)$ over 80-130K) and consolidates/freezes the smaller ones ($2\pi f \tau_{cl} < 1$; $\varepsilon'(6T) < \varepsilon'(0T)$ below 80K).

Associated with the step-like change in $\varepsilon'(T)$, relaxation peaks in loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) are observed, as shown in fig.3(a). Our high-frequency loss-tangent results agree fairly with that presented by Liu et. al. [10]. Increase in the peak temperature of $\tan\delta(T)$ isochrones at higher frequency depicts thermally activated character.
Neither the dielectric constant nor the loss-tangent indicate any explicit anomalies across the AFM-T_N. For further insight, dielectric modulus ($M''(T)$) is analyzed, which reveals two sets of localized dipole-relaxations in the system [19]. Figure 3(b) shows imaginary modulus $M''(T)$ at selected frequencies over 90-150K, under zero- (inset) and 6T (main panel) magnetic field. $M''(T)$ isochrones here reveal two relaxation processes in the system; one ($R_1$) well-developed at lower frequencies with higher modulus— persisting to higher frequencies with increase in temperature— and another ($R_2$) with comparatively low modulus well-formed at relatively higher frequencies, approximately above 110K.

Frequencies vs. peak-temperature of $M''(T)$ has been analyzed to get insight on the interaction among dipoles. ($f-T_p$) dispersion corresponding to $R_1$-relaxations (fig.4(a), zoomed-in over low-$T$'s) features Arrhenic kinetics [20] at higher temperatures, described by

$$f = f_0 \exp\left[-E_a/k_B T_p\right]$$

Here $T_p$ is the temperature corresponding to the $M''$-peak at frequency $f$, $E_a$ is the activation energy for relaxations, $f_0$ is the approach frequency, and $k_B$ is the Boltzmann constant. However, as our Havrilak-Negami [21] analysis of $M''(f)$ spectra has revealed, these peaks are not Lorentzian (broadening parameters $\alpha, \beta < 1$ [9]); Arrhenic kinetics manifest here camouflage non-Debyean/liquid-like nature of the dipole-relaxations. For these quasi-independent dipoles, we nominally obtained $E_a^{1A}(0T) \sim O(600K)$ and $f_0^{1A}(R_1) \sim O(200 kHz)$. Enhanced interactions upon cooling manifest Vogel-Fulcher (VFT) dispersion kinetics [22], signifying dipolar-segmentation and their eventual dynamical freezing;

$$f = f_0 \exp\left[-E_a/k_B (T_p-T_0)\right]$$

VFT-fit here gives $E_a^{1V}(0T) =163.5K$, $f_0^{1V}(0T) =9.64 kHz$, and freezing temperature $T_0^1(0T) =51.5K$. Under H-field; $E_a^{1V}(6T) =281.8K$, with $f_0^{1W}(6T) =19.1 kHz$ and freezing temperature $T_0^1(6T) =38.1K$. Speedup of approach frequencies $\{f_0^{1V}(6T) > f_0^{1W}(0T)\}$ and reduction of VFT freezing temperature $\{T_0^{1}(6T) < T_0^{1}(0T)\}$ both signify field-suppression of dipole-correlations. This is consistent with magneto-enhancement of the activation-energy barrier $\{E_a^{1V}(6T) > E_a^{1V}(0T)\}$, which also accompanies thermal fading of dipole-interactions upon warming $\{E_a^{1A} > E_a^{1W}\}$. Magneto-kinetics of $R_1$-relaxations thus explains the observed positive magneto-dielectric (MD) effect at lower frequencies.
R$_2$-relaxations in $M''(T)$ replicate those observed in $\tan\delta(T)$; only the peaks occur at slightly higher temperatures [23]. Dispersion kinetics ($f$-$T_p$) for these relaxations too is Arrhenic at higher temperatures; here also, weakly-interacting ($\alpha$, $\beta < 1$ [9]) liquid-like degrees of freedom relax quasi-independently, with $E^A_2 \sim O(1100K)$ and $f^A_0 \sim O(100$ MHz). Upon field application, R$_2$-relaxation peaks show up down to lower temperatures. Now, the lower-$T$/field-emergent segmental dynamics (Vogel-Fulcher kinetics) yields $E^{2V}_a$ ($6T$) =348.6K, with $f^{2V}_0$ ($6T$) =1.14 MHz and freezing temperature $T^*_f$ ($6T$) =36.5K. Induction of canted-spin WFM-clusters prompts & strengthens local interaction of the site-dipoles undergoing R$_2$-relaxations. Emergence of a freezing temperature (otherwise, no $T^*_f$ ($0T$) here!) signifies purely magneto-actuated consolidation of R$_2$-relaxing dipoles, onto which WFM-nanophase gets pinned. In contrast to the R$_1$-relaxations, emergence of a finite $T^*_f$ ($6T$) vs. no $T^*_f$ ($0T$) reconciles with all-negative magneto-dielectricity at higher frequencies— over which the R$_2$-relaxations are observed— as discussed later.

Full width at half maxima (FWHM) have been obtained for the $M''(f)$ spectral peaks. FWHM’s excess over the constant Debye width is normalized to yield scaled extra-Debyean index $\text{SEDI} = \left(\frac{\text{FWHM}}{1.14 - 1}\right) \times 100$ of relaxations, marking magnetic evolution at $\sim T_{N,W}$.
R₂ (R₁) is recognized to be associated with octahedral-tilts (-rotations), which require higher (lower) activation-energy for the polarization flipping [6]. R₂-relaxations characterize correlated dipoles which consolidate in wake of the emergent/coupled WFM-nanophase. These field-actuated PNR-segments exhibit dynamical freezing upon further cooling. Observed all -ve MD at higher frequencies is thus entirely traced to the R₂-relaxations. On the other hand, R₁-relaxations at lower frequencies (≤3.8 kHz) are attributed to the PNR-segments formed in the bulk/AFM-matrix. These larger (slower-responding) entities are somewhat de-correlated under the H-field, accounting for the +ve MD at low-frequencies, over certain temperature window. Thus, the electrical, magnetic, and structural properties in the system are intricately coupled to each other [9].

**Magneto-dielectric and Second-harmonic Measurements:**

![Graphs showing temperature dependence of magneto-dielectricity and second harmonic signals](image)

Fig.5(a): Temperature dependence of Magneto-dielectricity MD(%). (b): Temperature dependence of second harmonic (ε₃') signal at 434 Hz, under zero and 6T-magnetic field. Top-right inset: Temperature dependence of ε₃' signal at mentioned frequencies in the absence of H-field; Bottom-right inset: Temperature dependence of ε₃' signal under the application of 6T magnetic field; Left inset: Harmonic magneto-dielectricity MD₃(%) from the second harmonic signal.

To further correlate electric and magnetic properties of the system, change in dielectric properties with application of 6 Tesla magnetic field has been studied. Figure 5(a) demonstrates temperature dependence of magneto-dielectricity MD(%) = [ε(H)/ε(0)-1]×100, depicting all -ve MD at temperatures above 130K, while at lower temperatures, both negative (high-f's) and positive (low-f's) MD can be seen. This is already evident in the zero- and 6T-field ε₃'(T)-plots (fig.2(b)) at selected frequencies. Over 80-130K temperature-window, magnetic field suppresses dipole-interactions in larger clusters (c.f., thermal activation), thereby reducing (increasing) the local polarization (polarizability ε'), whereas outside this window, H-field consolidates the growth of smaller-sized dipolar clusters (c.f., thermal de-activation), thereby enhancing (reducing) the local polarization (ε'). The dual (±ve) nature of MD shows up over the temperature region where consolidating dipolar clusters evolve. The exclusive orientational-liquid at high-T's however features only -ve MD (i.e., field-enhanced dynamical correlations), as indeed expected.

The counterintuitive ‘de-correlating effect’ of the applied magnetic field in the intermediate temperature range is driven by the same free-energy considerations, that favor the emergence of isolated WFM nanophase (coexistent with the AFM-matrix) versus phase-separated or uniformly spin-canted configurations. In M"₃'(T) (fig.3(b)), R₂-relaxation peaks observed without field only above 110K, get extended under 6T
field down to 95K. Evidently, the $H$-field magneto-electrically enhances the correlations, causing segmentation of the orientational-liquid undergoing the $R_2$-relaxations. Thus, $100\times$ faster $R_2$-relaxations reasonably admit to a 2-D extent of WFM nano-phase pinned onto the $R_2$-relaxations site, vs. the 3-D character of the PNRs in the bulk-AFM, undergoing the slower $R_1$-relaxations. Negative-MD from locally more conducting WFM-regions versus the positive-MD traced to the evidently less-conductive AFM-matrix therefore endows a topological attribute to magneto-electricity in this layered compound. Finite MD $\neq 0$ below the VFT $T_0$'s signifies the existence of MER-actuated intra-cluster dipole-dynamics. Dual character of magneto-dielectric coupling observed here, associated with the AFM (mostly $+$ve MD) and WFM (all $-$ve MD) magnetic sub-phases, duly correlates with the field-suppression of AFM-order ($T_N(6T) < T_N(0T)$) and field-enhancement of WFM ($T_w(6T) > T_w(0T)$) [15].

The magneto-electric effect coupled through structural distortions collaterally manifests in the second-harmonic ($\varepsilon'_{3}$) measurements. Negative-definite $\varepsilon'_{3}(T)$-signal has been observed, undergoing through an extremum at $\sim 100K$, and vanishing near $\sim 50K$, as shown in fig.5(b). This is in agreement with theoretical modeling for relaxor-like ferroelectrics, exhibiting frequency-dispersive relaxation [24, 25]. The low strength of $\varepsilon'_{3}$-signal indicates its major contribution from the term $\sim \chi_4^{1}$, denoting cluster-induced relaxor-like FE, and not from the bulk polarization term $\sim P_2^{X1}$ [25, 26]. Well-measurable second-harmonic signal precisely registers the dynamical transit from the weakly-interacting orientational liquid (Arrhenic dispersion; manifest as the higher-$T$ tail in the $\varepsilon'_{3}$-signal) to the segmented ones (Vogel-Fulcher kinetics; sharp reduction in the $\varepsilon'_{3}$-signal below $\sim 100K$). The segmented dipolar interactions evolve upon further cooling and freeze by $\sim 50K$, below which the harmonic signal $\varepsilon'_{3}$ too vanishes. Dispersive $\varepsilon(T)$ vs. relatively dispersion-free $\varepsilon'_{3}(T)$ refer their origins to different (voluminous and aerial, say) topologies, harboring distinct electrical organizations (usual & hyper polarizations, [25]). Specifically, linear (harmonic) signals here likely arise from within (outside) the bulk of the correlated PNR-segments. The extremum in $\varepsilon'_{3}$ around $\sim 100K$ signifies optimum electrical non-linearity.

Increase of harmonic signal upon cooling is expected to diverge critically, with power-law $T$-dependence [27, 28]

$$|\varepsilon'_{3}| \propto (T - T_g)^{\gamma}$$

(3)

From the fits of $\varepsilon'_{3}(T, H)$-signals over 115-160K with eq.(3) (solid curves in fig.5(b) main panel), we obtain $T_g(0T) = 53.63K$ as the freezing temperature with divergence exponent $\gamma(0T) = 1.21$ at zero-field—comparing well with $\gamma = 1.25$ found for BTZ35 by Kleemann et. al. [29]— and $T_g(6T) = 40.66K$ with $\gamma(6T) = 0.79$ at 6T-field. The agreement (up to $\sim 5\%$) between the $T_g$'s and the Vogel-Fulcher $T_0$'s for the $R_1$-relaxations is rather excellent. Together with $T_g(0T, 6T) \approx T_0^3(0T, 6T)$, concurrency of the finite & $-$ve harmonic MD$_g$(%) =$\{\varepsilon'_{3}(H)/\varepsilon'_{3}(0)-1\} \times 100$ over roughly the same temperature-window with the $+$ve fundamental MD, associates them both to the PNR-segments undergoing $R_1$-relaxations; allied with octahedral-rotations, in the bulk/AFM-matrix. Cluster-glassy/power-law critical-divergence of $\varepsilon'_{3}(T)$ versus the relaxor-like/VFT $\eta(T)$-divergence obtained from $M''(T)$ complementarily corroborate the inter-/intra-PNR origins of the harmonic/fundamental responses, as characterized. Higher $e$-moments (say, quadru- & octu-poles) can emerge from the vortex-configuration of the dipole-orientations, in the spatially-separated interstices formed by the surrounding PNRs; providing the required non-linear susceptibility in the $e$-disordered/zero-$P$ phase of the system, apparently responsible for the observed harmonic $\varepsilon'_{3}$-signal.
Harmonic signal is $H$-dependent and exists ($\varepsilon_3^\prime(T, H) \neq 0$) only down to the freezing temperature $\approx 50$K of the segmented dynamics; yielding $\text{MD}_3 \neq 0$ over the $T$-window hosting dynamically-activated dipoles. Over 80-160K, $\varepsilon_3^\prime(T)$-signal decreases under the applied $H$-field, giving -ve $\text{MD}_3$. Expectedly, under-field decorrelation of dipoles relaxing at low-frequencies (yielding $\text{MD} > 0$) also thermally randomizes the ‘higher-moments’ in the PNR-interstices; thereby decreasing the harmonic response. This is complemented by the magnitude-crossing of the zero-field and in-field $\varepsilon_3^\prime$-signals at 434Hz roughly across $\approx 160$K, above which +ve $\text{MD}_1$ (fig.5(b)-left inset) now concurs with the -ve $\text{MD}$ (fig.5(a)). Vis-à-vis observed $\text{MD}(<T_0) \neq 0$ from the ‘frozen’ PNRs, both $\varepsilon_3^\prime(<T_0)$ & $\text{MD}_3(<T_0) = 0$ ($\equiv$ data-scatter) further corroborate the (magneto-)harmonic response being exterior to the PNR-segments, besides non-contributed to by (even local) $P^2\chi_1^5$-terms. Under-field enhancement of $T_W$ and actuation of (R$_2$-relaxing) PNR-segments also suggests the localization of WFM-nanophase at the PNR-interstices; although further work and supportive observations are mandated to rigorously establish the circumstance.

CONCLUSIONS

Magneto-dielectric coupling in Ca$_3$Mn$_2$O$_7$ has been established in reference to two structural distortions—octahedral-tilt and octahedral-rotation. We have analyzed the signatures of interacting-dipole structures, featuring vitreous relaxation kinetics upon cooling below the AFM transition and with the emergence of weak ferromagnetic nano-phase at $T_W \approx 110$K, in the AFM matrix ($T_N = 123$K). Alterations of dipoles’ correlation-status are allied with the system’s magnetic evolution and reflect in the magneto-dielectric signals, upon magnetic field application. Observed second-harmonic magneto-dielectricity is some two orders of magnitude larger, vis-à-vis that obtained in the fundamental response. Vortex-configuration of dipoles’ orientation in the PNR-interstices is invoked as the source of the harmonic electrical response, consistent with its observed characteristics. Structural, magnetic, and electrical coupling in this Ruddlesden-Popper compound is the consequence of its layered structure, which is found to exhibit a topological character. Hence, the ME-coupling can be tailored in its thin-film or nano-fiber formations, where the exclusive features can be enhanced/suppressed by dimensional reduction and intrinsic strain. Furthermore, chemically-doped variants may be investigated to tune the magneto-electric functionality.

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