Interplay of Spin, Lattice, Vibration, and Charge Degrees of Freedom in Ca$_3$Mn$_2$O$_7$

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Abstract: Polycrystalline Ruddlesden-Popper structure Ca$_3$Mn$_2$O$_7$ synthesized using solid state technique has been structurally characterized with Synchrotron powder X-ray diffraction. Thermal evolution of octahedral distortions, responsible for transition to orthorhombic state from the parent tetragonal structure, has been explored down to 37K. Change in Mn-O-Mn bond angle connecting MnO6 octahedra have been established as responsible for the magnetic ordering in the system. This has been further confirmed with Raman spectroscopy, which demonstrates spin-lattice coupling. Dipole-relaxation characteristics revealed from dielectric spectroscopy underlie the inter-related spin, lattice, phonon, and charge degrees of freedom consistently in terms of genuine and intrinsic magneto-electricity of the system.

INTRODUCTION

Ruddlesden-Popper (R-P) compounds (An$_{n+1}$B$_n$O$_{3n+1}$) recognized as layered systems are getting much attention because of their evolved complex magnetic [1,2] and electrical properties [3]. These perovskite-related systems possess structural-distortion coupled range of magnetic phases. Compared to the 3D perovskites, these systems are structured as oxygen-octahedron, consisting B$^{4+}$ ions in single- or multiple-connected perovskite blocks, sandwiched in between A$^{2+}$ cation-oxygen layers [4,5].

Using first principles calculations [5], $n = 2$ R-P compounds have been found to support hybrid improper ferroelectricity (HIF), evident experimentally [6,7]. HIF mechanism describes ferroelectricity with a combination of two inequivalent symmetric octahedral-distortion patterns [8]. Reports on $n = 2$ RP compound Ca$_3$Mn$_2$O$_7$, possessing tetragonal phase (I4/mmm) at high temperatures, have established introduction of two symmetrically different octahedral distortions; which result in the transition to orthorhombic broken-centrosymmetry phase (Cmc21) at lower temperatures [9]. Among these distortions, oxygen octahedral-rotation has been found to enhance magneto-electricity in the system. Along with it, oxygen octahedral-tilt is introduced, which supports canted spin moments in the system at low temperatures, explained with Dzyaloshinskii’s criteria [8].

Depending upon the metal-oxygen-metal bond angle, unfilled Mn$^{4+}$ d-orbitals in oxygen-octahedron environment adopt (anti)ferromagnetism [10]. Crystallographic analysis performed at room temperature for Ca$_3$Mn$_2$O$_7$ by Lobanov et. al. [11] featured the presence of small proportion of tetragonal phase, along with the orthorhombic phase in the system. Furthermore, Mn-O-Mn interatomic distance and octahedral-distortion have been explored with Th-doping at Ca-site and more decisive study on structure has been motivated [12].

Magnetic state predicted in Ca$_3$Mn$_2$O$_7$ using first principles calculations [8] was confirmed by Lobanov et. al via its temperature dependent neutron diffraction study, establishing G-type antiferromagnetic (AFM) state. Symmetry conditions further permitted weak ferromagnetism (WFM) on lowering the temperature. Recently in Ca$_3$Mn$_2$O$_7$ antiferromagnetic transition with Néel temperature 123K, along with the emergence of weak ferromagnetism (WFM) below 110K has been reported [13,14]. The WFM is traced to the canted spin-clusters in the AFM-matrix, rather than to a uniform spin-canting. This is consistent with the observed exchange-bias (EB) effect, characterized in detail for the system. The indirect spin-exchange interactions are profoundly affected by the change in transition metal-oxygen-transition metal bond-length and -angle, which get altered by the octahedral-distortions [15,16]. To examine the inter-coupling of structural distortions with magnetic and electrical properties of the system, it is essential to investigate the changes in the structural environment of Mn$^{4+}$ ions, versus thermal cooling of the CMO system.

Here, we analyze the crystallographic structure of Ca$_3$Mn$_2$O$_7$ vs. temperature, investigated using Synchrotron powder X-ray diffraction (SPXRD). To further enlighten the spin-lattice-phonon coupling, Raman study across the magnetic ordering is performed. Relaxation characteristics extracted from the magneto-dielectric measurements are correlated with magnetic, structural, and vibrational results. Strong elementary-level coupling found between spin and lattice degrees of freedom, is not fully translated into bulk magneto-electricity, and fails to induce a robust FE. This is traced to the antiferroelectric configuration of the cationic-displacements, within individually polarized layers of the unit cell. The intra-cell vector-cancellations produce a small net dipole moment, which therefore manifests a much reduced magneto-electric effect.
EXPERIMENTAL DETAILS

For temperature dependent structural analysis, Synchrotron powder X-ray diffraction (SPXD) has been performed and analyzed in the temperature range of 37K-340K. SPXD has been performed on area detector (Image Plate Mar-345) using wavelength 0.79866Å. Rietveld analysis was performed using Fullprof program. Raman scattering measurements on Ca$_3$Mn$_2$O$_7$ system have been performed with HR800 Jobin-Yvon spectrometer, in the temperature range of 5K to 300K, using He-Ne laser of wavelength 632.8 nm. Low temperature ac-conductivity measurements were performed using Novocontrol Alpha-A Broadband Impedance Analyzer, under zero and 6T field, using Oxford Nanosystems Integra magnet-cryostat.

RESULTS and DISCUSSION

Structural Characterization

Single phase Ca$_3$Mn$_2$O$_7$ polycrystalline compound has been prepared by solid-state synthesis technique reported elsewhere [13]. The X-ray diffraction profile for the system is refined under Cmc21 orthorhombic symmetry from 300K down to 37K. The model fit for SPXD pattern at 300K is shown in fig.1(a), with acceptable value of goodness of fit ($\chi^2$=1.11). Figure 2(a) shows schematic for the crystal structure obtained from the fitting. Rietveld fit performed gives the thermal evolution of unit-cell parameters in the system. The lattice parameters $a$, $b$, and $c$ (Å) decrease monotonically below 300K, whereupon cooling by 130K, the slopes of their changes effectively degrade, as shown in fig.1(b). Cell volume too shows shrinkage of the unit cell upon cooling.

The (linear) decrease of volume with temperature reduces below 123K. This may enhance the FE-stability to prevail over the antiferrodistortive features present in the system, which has been well established in perovskite structures possessing both these tendencies [17]. Evidence of this has been observed from thermal evolution of the dielectric relaxations, explaining the formation of dipolar nanoregions below 123K, in a previous report [18].

The system has been reported to undergo G-type AFM transition at $T_N$ =123K, with a coexistent WFM nano-phase emergent upon further cooling [13]. Structural distortions related to the oxygen octahedra are expected to play a crucial role in changing the electrical and magnetic properties of the system. Mn-O-Mn bond angles demonstrating the effect of octahedral distortions on the inter-octahedral correlations have been analyzed with temperature, and are shown in fig.2(b). Schematic for crystal structure of Ca$_3$Mn$_2$O$_7$ in fig.2(a) shows the connectivity of MnO6 octahedron in the $bc$-plane via O2 oxygen atom and along the $a$-axis via O1 oxygen atom. Here, change in the bond angles Mn-O2-Mn and Mn-O1-Mn both have been observed with temperature. Profound changes in Mn-O2-Mn and Mn-O1-Mn bond angles upon cooling reflect remarkable octahedral modulation. Increment in Mn-O2-Mn ($bc$-plane) bond angle upon cooling from $\sim$143° (at 300K) to $\sim$146° (at 37K) supports AFM ordering in the $bc$-plane, in accordance with that observed for the system [13, 14]. Mn-O1-Mn (along the $a$-axis) bond angle initially increases on cooling from $\sim$173° (at 300K) to $\sim$176° (at 120K), supporting AFM ordering along the $a$-axis. While on further cooling, Mn-O1-Mn bond angle decreases to $\sim$170°. The effective reduction in
the metal-oxygen-metal bond angles, formed from the interconnected oxygen octahedra in the octahedron layers, signals inclination towards ferromagnetic (FM) feature along the a-axis. Here, these experimental observations enlighten the MnO6-octahedra changes; profoundly affecting the magnetic state in the orthorhombic phase of the system.

To analyse the modulation in dielectric polarization for the system, the net displacement-vector for Ca(2)O(4) layer in the bc-plane has been evaluated. In Ruddlesdon-Popper materials, polarization has been stated as proportional to the displacement of A-cation in AO-layer at the interface [5]. Figure 2(c) shows this displacement vector for Ca(2)O(4) layer versus temperature, with abrupt enhancement across 127K.

Plot of the bond angles Ca-O-Ca in the bc-plane, shown in fig.2(c)-inset again emphasizes the behavioral change in electrical properties with magnetic ordering. Thus, magnetic ordering in the system conjointly influences its electrical properties via substructural changes, as has been observed in dielectric studies of the system [18].

Figure 3 presents SPXRD patterns at and above the room temperature, up to 340K. Above room-temperature diffraction patterns exhibit weak reflections, indexed as (0 0 10) for I-centered tetragonal symmetry (I4/mmm). This indicates the presence of mixed phase above room temperature. Peaks for both the mixed phases are clearly resolved and the refinement resulted in the structure as an amalgamation of the orthorhombic Cmc21 (majority) phase with weight fraction of 98.48% and tetragonal I4/mmm (minority) phase with weight fraction of 1.52%. The amalgamation of orthorhombic and tetragonal phases was observed even at 340K, indicating the presence of coexistent crystal structures at higher temperatures, which is consistent with the previous reports. [19].

Raman Spectroscopy

Temperature-dependent study of the crystal structure establishes thermal evolution of the octahedral distortion, which has been said to influence the magnetic ordering in the Ca₃Mn₂O₇ system. To confirm this spin-lattice coupling in the system via study of vibrational modes, Raman scattering measurements have been performed. Predicted Raman active optical modes for the system with Cmc21 space group are 18A₁+17A₂+16B₁+18B₂. The Raman spectrum depicting phonon modes for the sample are shown in fig.4 (a), in the temperature range of 5K to
300K. The two most prominent phonon modes have been recognized as $A^{(15)}_1$ and $A^{(17)}_1$ for the Cmc21 phase (=A21ma structure with ‘c’-long axis) [20]. Lorentzian peak-fit analysis has been carried out for the respective modes, to obtain thermal evolution of the phonon modes. Peak-characteristics follow the classical behaviour; frequency-shifts decrease and line-widths broaden with increase in temperature. This is accompanied by sharp changes in the frequency-shifts at ~105K; shown in fig.5.(b) (left-axis) for $A^{(15)}_1$ mode and in fig.5.(c) (left-axis) for $A^{(17)}_1$ mode, which independently confirm the spin-lattice coupling in the system. Line-widths of the respective modes have also been studied, which relates to the decay/lifetime of the phonons involved. Concurrent kinks in the line-widths again at ~105K, shown in fig.5.(b) (right-axis) and fig.5.(c) (right-axis) for $A^{(15)}_1$ and $A^{(17)}_1$ modes respectively, establish the spin-lattice coupling.

Signals corresponding to the co-existing WFM-nanophase (below $T_w$ =110K) in the AFM-matrix phase ($T_N$ =123K) are thus clearly revealed in the Raman study. Here, $A^{(15)}_1$ phonon mode mainly involves atomic motion of O1(z)-, O3(z), and O4(z), along the z-axis (being the a-axis here) with in phase motion of O3 and O4. $A^{(17)}_1$ phonon mode characterizes in phase motion of O3(z), and stretching-type motion of O1(z) atom. The change in the phonon modes across $T_w$ further establishes the effective contribution from O1-atomic motion along the a-axis, in concurrence with the decrease in Mn-O1-Mn bond angle, obtained in the SXRD data analysis. This explains that the Mn-O6 octahedra-distortion related changes in the Mn-O-Mn bond angles-- as shown in SXRD-- induce changes in the magnetic configuration. SXRD and Raman study here establish that the WFM is associated with the inter-octahedral changes connected via O1-atom along the a-axis. This suggests low dimensionality of the WFM-nanophase in this system.

**Magneto-electricity**

To explore the coupling between electrical and magnetic properties in the system, low temperature dielectric measurements were performed. Dielectric relaxations are observed in the imaginary dielectric modulus ($M''$), which is fitted with empirical Havriliak-Negami (H-N) function (WinFit, NovoControl). The model expresses the relaxation function $M''$ in the following form [21]:

$$\frac{M'' - M_\infty}{M_0 - M_\infty} = \frac{1}{(1 + (i\omega\tau)^\alpha)^\beta}$$
Here, \( \omega = 2\pi f; f = \) frequency of the applied electric-field) with \( \omega_{\text{max}} = 1; \omega_{\text{max}} \) denoting the maximum-relaxation frequency, marking the transition from the high-frequency/unrelaxed modulus \( M_0 \) to the low-frequency/relaxed modulus level \( M_0 \). Exponent \( \alpha \) measures the coupling between multiple dipoles \( (\alpha < 1 \) denotes extra-Lorentzian spectral peak-width) and \( \beta \) is the asymmetry parameter of the relaxation peak. H-N fit incorporates the Jonscher power-law frequency-dependence of ac-conductivity, as explained later.

No signal of long range electrical ordering is observed from the dielectric modulus function. Imaginary part of the modulus shows two relaxation processes for the system; at low-frequencies \( (R_1) \) and at high-frequencies \( (R_2), \) fig.5(a). The H-N fitting performed over the temperature regime of 90K to 140K for the \( M''(f) \) yields non-trivial \( (\alpha, \beta < 1) \) exponents’ values for both \( R_1 \) and \( R_2 \)-relaxations, revealing the presence of correlations among the dipoles.

Conductivity parameters obtained from the H-N fit are also studied. In Mott insulators, conductivity is explained using Pollak’s theories [22, 23]; well described by its dc- and ac-components, which correspond respectively to pinned- and free-dipoles’ relaxations [24, 25]. Jonscher power law \( \sigma_{dc} = A\omega^n \) [26] provides the empirical power-law exponent \( n \), whose temperature dependence characterizing the short-timescale current response, is used to divulge the particulate conduction mechanism pursued by the system. “Universal law of dielectrics” [27] well describes the total electrical conductivity for the system:

\[
\sigma(\omega) = \sigma_{dc} + A\omega^n = \sigma_{dc}[1+(\omega/\omega_h)^n]
\]

Here, \( \omega_h \) defines the hopping frequency at the crossover from dc- to ac-conduction \( (\sigma(\omega_h) = 2\sigma_{dc}) \), which shifts to higher values with increase in temperature. For the correlated electron system in \( \text{Ca}_x\text{Mn}_y\text{O}_2 \), multiple hopping mechanism [28, 29] between the charge-carrier sites explains the ac-conductivity.
In the present context, conductivity-signatures of magnetic evolution in the system are best illustrated by contrasting its dc/pinned-dipole and ac/free-dipole relaxation-characteristics. For this purpose, we show in fig.5(b) the Jonscher-exponent n(t) vs. $\sigma_{dc}(T)$, both determined from H-N fits on the $M'_T(\omega)$ isotherms at zero and 6T H-fields. Both n and $\sigma_{dc}$ decrease upon cooling; though n($\sigma_{dc}$)$_{H=0}$ is marked by a sharp step across the AFM transition. Upon further cooling, another sharp step follows-- concurrent with the emergence of the WFM-nanophase within the AFM matrix. Nearly-vertical steepness of these steps signifies that magneto-electricity is manifest exclusively in the fast/ac electrical transport. The two successive steps observed under $H=0$ merge to a single step across $T^{*} \sim 115K$ at 6 Tesla field. This is consistent with the ‘merging’ of suppressed-$T_N$ and enhanced-$T_w$ under high $H$-fields, reported previously [14]; as also in Gd$_3$Sb$_5$ [30]. Both in the paramagnetic ($>T_N$) and the well-established AFM(+WFM) ($<T_w$) phases, absence of magnetoelectric effect renders the 0T/6T-adjointed n($\sigma_{dc}$) co-regressions featureless.

Evolution of the dipolar-correlations upon cooling is obtained from the temperature dependent $\alpha(T)$ and $\beta(T)$. However, it is their physically more relevant product $\left\{\beta_{KWW} = \alpha \beta; \Phi(t) \sim \Phi(0) \exp[-(t/t)\beta_{KWW}]\right\}$, which describes stretched-exponential time-domain behavior of the Kohlrausch-Williams-Watts (KWW) relaxations, vis-à-vis the generic exponential time-decay of independent-dipoles’ Debyean ($\alpha$, $\beta =$1) relaxation. Moreover, it implies that a distribution of relaxation time ($\beta_{KWW} < 1 \equiv P(t) \neq \delta(t-t_0)$) determines the dipolar dynamics [31], in the KWW correlated relaxations. The stretched-exponent parameter $\beta_{KWW}(T)$ for the R$_1$-relaxations clearly marks the antiferromagnetic (AFM) transition (~120K), whereas the abrupt drop at ~110K in that for the R$_2$-relaxations registers the emergence of WFM-nanophase in the AFM-matrix, shown in fig.5(c). Abrupt drop in $\beta_{KWW}(R_1)$ across the AFM transition-- implying magneto-electric enhancement in dipolar-correlations-- clearly evidences spin-dipole coupling.

To further understand this coupling, dielectric measurements performed under 6T magnetic field were similarly analyzed with the H-N fits. From thus obtained H-N parameters, percentage magneto-exponents $M_{\beta_{KWW}}$=$100 \times (|\beta_{KWW}(6T)|/\beta_{KWW}(0T)-1)$ are evaluated. Fig.5(d) shows that under the applied $H$-field $\beta_{KWW}(R_{1,2})$ decrease below 130K ($>T_N$) itself (-ve $M_{\beta_{KWW}}$). While the drop of $\beta_{KWW}(R_1)$ slows down (minimum at 120K $\leq T_N$), that of $\beta_{KWW}(R_2)$ speeds up below 115K ($<T_N$ in 6T field). These trends further corroborate our earlier inferences [18]; that in the spin-disordered state ($>T_N$), antiferrodistortive-correlations amongst both the R$_1$-$\phi$-type dipoles are enhanced by the applied $H$-field. Moreover, in the AFM state, the FE-correlations between R$_1$-type dipoles (hosted in the bulk-AFM phase) are field-diluted, whereas those between R$_2$-type dipoles are further field-enhanced (especially below $T_w$, upon the WFM nanophase emergence). This dual ME character observed too is in conciliation with the field-suppression (-enhancement) of Néel ($T_N$) and WFM ($T_w$) temperatures [14]. The temperature dependence of magneto-exponent $M_{\beta_{KWW}}$ is found to be consistent with that of the magneto-dielectricity MD(%) =100($\varepsilon$’(6T)/$\varepsilon$’(0T)-1) reported earlier [18]. All-frequency -ve MD above ~$T_N$ relates to the field-enhancement of (both R$_{1&2}$-relaxing) antiferrodistortive dipole-correlations. Positive MD at low-frequencies (R$_1$-relaxations) over 80-125K results from the field-suppressed relaxor-FE correlations of dipoles in the bulk AFM-matrix. Negative MD below ~$T_N$ at higher frequencies (R$_2$-relaxations) is due to the field-actuation of relaxor-FE dipole-correlations, with their allegiance to WFM-nanophase. Therefore, both MD and $M_{\beta_{KWW}}$ consistently reveal the intricate dual nature of magneto-electricity in the system.

Thermally activated behavior of dc-conductivity [32] conveys increase in its activation-barrier (W) with the modification of system’s magnetic configuration [14].

$$\sigma_{dc}(T) = \sigma_0e^{-W/k_BT}$$

From the Jonscher-fit $\sigma_{dc}$, we have evaluated magneto-

![Figure 6. Temperature dependence of MD at 434 Hz and 11.5 kHz](image-url)

(Left-axis), featuring behaviors uncoupled with the MR (Right-axis).
resistivity (MR = $\sigma_{dc}(0)/\sigma_{dc}(H)$-1)). MR is seen to increase upon cooling, and is anomalously impervious to magnetic ordering & evolution (fig.6: right-axis); consistent with the nearly-vertical steps in $n(\sigma_{dc})$, fig.5(b). Figure 6 also shows MD(T) [18] at 434 Hz and 11.5 kHz, mainly contributed to by the dipolar organizations undergoing R1- and R2- relaxations respectively. MD(T) clearly illustrate magneto-electric evolution of the system, and lack an algebraic co-variation with the feature-free MR(T), which registers an order of magnitude larger and essentially monotonic change ($\Delta$MR =55%) over the ME-relevant temperature range 80-130K. This evidences that the (ac-) magneto-electricity in the system is exclusive of the (dc-) magneto-resistance, as e.g. reported previously for another system [33]. Comparatively low MD magnitude (~1% max.) obtained vis-à-vis rather dramatic changes in the relevant sub-structural attributes (fig.2(c)) are understood as follows. In the n =2 Ruddlesden-Popper (RP) compounds, because of mutually ‘antiferroelectric’ displacements of A-cations in seven AO-layers within a unit cell, there results only a small net dipole moment from the ‘uncancelled’ AO-layer [5]. For Ca$_3$Mn$_2$O$_7$ system, lack of long range electrical order plus cancellation of A-cations’ vector-displacements therefore account for the low MD. Note that for the most part, both |MD| and MR increase upon cooling. Extending the analysis by Catalan [34]-- carried out for negative MR systems-- to the present case; |MD| would be expected to anti-regress with the +ve MR, if magneto-capacitance featured without any magneto-electric coupling. Therefore, the +ve regression observed here between |MD| and MR again discounts the magneto-resistive origins of genuine magneto-electricity in the system.

CONCLUSIONS

Prominent spin-lattice coupling has been established in Ca$_3$Mn$_2$O$_7$ by analyzing its Synchrotron-based structural data and Raman spectra, over common temperature range. Appreciable decrease observed in particulate bond-angle coincides with the emergence of WFM-nanophase. Upon cooling across the AFM transition, slower decrease of the unit cell volume alongwith rise in the displacement vector defining net dipole moment, are observed. These structural changes signify spin-lattice coupling and its enhancement upon the formation of interacting-dipoles nano-regions. This also shows up in clear change of characteristics of the relevant phonon modes. Spectral analysis of dipole relaxations corroborates the dual (±ve) nature of magneto-dielectricity in the system, besides marking its magnetic evolution, consistent with the structural and vibrational signatures obtained. Magneto-electricity as the convoluted manifestation of coupled spin, lattice, vibration, and charge degrees of freedom is confirmed to be genuine, independent of the magneto-resistance. As outlook, the issue of rather small magneto-electricity, despite a strong spin-lattice coupling, could be addressed by partly replacing the AO-layers by A’O-layers within the unit cell; thus realizing the (ABO$_3$)$_2$A’O structure. Further substitution of A’-cation may reduce the antiferroelectric-cancellation of intra-cell layer-polarizations. Another approach to introduce strain in the system is dimensional reduction— e.g., nanostructuring, thin-film, and nanofiber synthesis. Tuning down the antiferrodistortive energetics in the system, to enhance the unit cell polarization, therefore seems the key to robust ferroelectricity prospects, alongwith its realization at ambient temperatures, for functional magneto-electricity.

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