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The rich physics of A-site-ordered quadruple perovskite manganites $\text{AMn}_7\text{O}_{12}$

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Perovskite-structure AMnO_3 manganites played an important role in the development of numerous physical concepts such as double exchange, small polarons, electron–phonon coupling, and Jahn–Teller effects, and they host a variety of important properties such as colossal magnetoresistance and spin-induced ferroelectric polarization (multiferroicity). A-site-ordered quadruple perovskite manganites $\text{AMn}_7\text{O}_{12}$ were discovered shortly after, but at that time their exploration was quite limited. Significant progress in their understanding has been reached in recent years after the wider use of high-pressure synthesis techniques needed to prepare such materials. Here we review this progress, and show that the $\text{AMn}_7\text{O}_{12}$ compounds host rich physics beyond the canonical AMnO_3 materials.

1. Introduction

Perovskite-structure manganites have experienced waves of intensive study,¹ starting in the late 1940s with the discovery of conductive and ferromagnetic (FM) properties and metal–insulator transitions in mixed-valence $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (R = trivalent cations and A = divalent cations). A theoretical understanding of these properties was quickly developed, including the theory of double exchange² and Goodenough's one-electron

electronic structures.³ Then followed the discovery of colossal magnetoresistance (CMR),⁴ prompting intensive work on single crystals and thin films, and the proposal of magnetic and electronic phase separation scenarios.⁵ Perovskite manganites also played an important role in the revival of interest in multiferroic and magnetodielectric materials with RMnO_3 (R = Tb and Gd) hosting some of the largest values of spin-induced ferroelectric polarization.⁶ They were also intensively studied as catalysts,⁷ solid mixed-conductive electrolytes, electrode materials, thermoelectric ceramics and sensors. This remarkable diversity in physical properties is rooted in considerable structural and chemical flexibility. As such, the perovskite manganites have become canonical systems for the study of structure–property relationships in strongly correlated electron systems.

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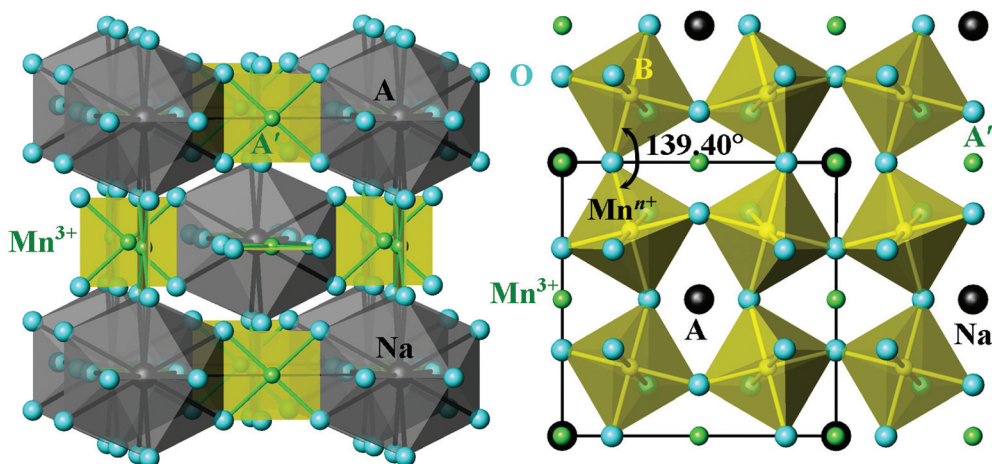


Fig. 1 Crystal structure of the parent cubic modification of A-site-ordered quadruple perovskites $\text{AMn}_7\text{O}_{12}$ and $\text{AA}'_3\text{B}_4\text{O}_{12}$ in space group $Im\bar{3}$ exemplified by the structure of $\text{NaMn}_7\text{O}_{12}$ at RT.¹² An Mn–O–Mn (B–O–B) angle is given. A-site polyhedra are shown on the left, and B-site octahedra – on the right.

$\text{AMn}_7\text{O}_{12}$ manganites (with A = Na, divalent and trivalent cations) are a special subfamily of perovskite-type materials, namely the A-site-ordered quadruple perovskites⁸ with general chemical formula $\text{AA}'_3\text{B}_4\text{O}_{12}$. Three quarters of large A cations are replaced by small Mn^{3+} cations at the A' sites with an effective square-planar coordination (Fig. 1). By heterovalent substitution of the A cations, which have a large 12-fold coordination (Fig. 1), one can obtain mixed-valence states of Mn at the B sites, i.e. $\text{A}^{n+}\text{Mn}^{3+}_3(\text{Mn}^{3+}_{1+n}\text{Mn}^{4+}_{3-n})\text{O}_{12}$, in close analogy to $\text{R}_{1-x}\text{A}_x\text{MnO}_3$. The $\text{AMn}_7\text{O}_{12}$ compounds are stabilized by very large tilts of the $a^+a^+a^+$ type in Glazer's notation,⁹ requiring high-pressure high-temperature treatments for their preparation (except for $\text{CaMn}_7\text{O}_{12}$, which can be synthesised at ambient pressure). Such an 'exotic' synthesis procedure could be the main reason why they did not attract much attention immediately after their discovery despite great interest in the classical mixed-valence $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ perovskites. Only with the widespread use of high-pressure facilities has research on $\text{AMn}_7\text{O}_{12}$ intensified, and significant progress in their under-

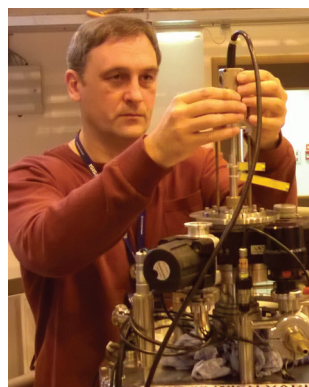
standing has been reached in recent years. In this work, we review the recent progress on $\text{AMn}_7\text{O}_{12}$ manganites.

Because of the space limitations we cannot cite all references, especially those devoted to $\text{CaMn}_7\text{O}_{12}$. Therefore, only foundational references are given that are widely cited in latter works.

2. $\text{NaMn}_7\text{O}_{12}$

$\text{NaMn}_7\text{O}_{12}$ was the first compound of the $\text{AMn}_7\text{O}_{12}$ series to be discovered (in 1973) and was found to crystallize in an $Im\bar{3}$ cubic structure at room temperature (RT) (Fig. 1); now identified as the parent aristotype to all $\text{AMn}_7\text{O}_{12}$.¹⁰ A low-temperature (LT) structural phase transition near $T_{\text{CO}} = 176\text{--}190\text{ K}$ (CO stands for charge order) was soon found (Fig. 2), below which a monoclinic $I2/m$ crystal symmetry with $1\text{Mn}^{3+}:1\text{Mn}^{4+}$ B site charge order was suggested (here, the pattern of charge ordering is analogous to the pattern of orbital ordering associated with the $I2/m$ structure of $\text{LaMn}_7\text{O}_{12}$ (see part 4)).¹¹ Despite clear parallels with the widely studied half-doped $\text{R}_{0.5}\text{A}_{0.5}\text{MnO}_3$ perovskite manganites also containing a $1\text{Mn}^{3+}:1\text{Mn}^{4+}$ mixture at the B sites, $\text{NaMn}_7\text{O}_{12}$ attracted little attention for nearly 30 years.

Magnetic studies were performed in 2004, which showed two magnetic transitions at $T_{\text{N1}} = 125\text{ K}$ and $T_{\text{N2}} = 92\text{ K}$.¹² It was suggested that Mn magnetic moments at the B sites order first at 125 K with an AFM-CE-type structure (AFM stands for antiferromagnetic), which can be described by two propagation vectors; $\mathbf{k} = (1/2, 0, -1/2)$ and $\mathbf{k} = (0, 0, 0)$. Mn moments at the A' sites were reported to order at 92 K with an anti-body-centered arrangements of spins with propagation vector $\mathbf{k} = (0, 1, 0)$.¹² In this study the symmetry of the LT phase was taken to be $I2/m$ (see above) with compressed Jahn–Teller (JT) distortions of the Mn^{3+} B sites. However, a theoretical study in 2014 pointed out inconsistencies between the reported experimental



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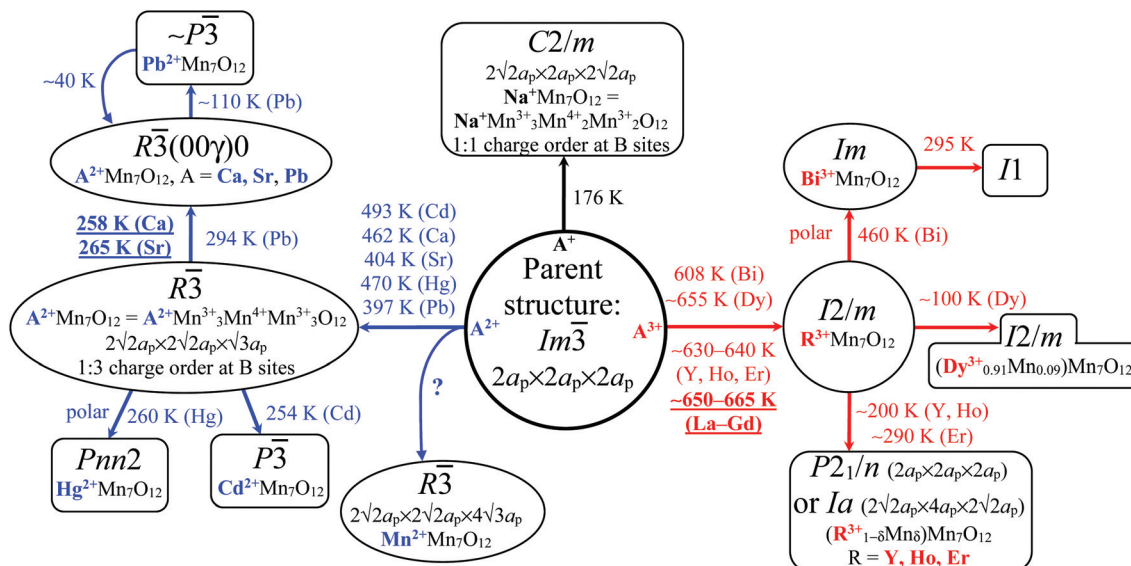


Fig. 2 A diagram of temperature-driven structural distortions in $\text{AMn}_7\text{O}_{12}$ manganites from the parent cubic structure. Transition temperatures are reported on the figure when available. All distortions keep the $2a_p \times 2a_p \times 2a_p$ cell (with $\alpha \approx \beta \approx \gamma \approx 90^\circ$) except trigonal systems (with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$), $C2/m$ (ref. 13 and 14; with $\alpha = \gamma = 90^\circ$ and $\beta \approx 90^\circ$) and Ia (ref. 68; with $\alpha = \gamma = 90^\circ$ and $\beta \approx 90^\circ$). Note that for the $R\bar{3}$ distortion with $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times \sqrt{3}a_p$, the $2a_p \times 2a_p \times 2a_p$ cell (with $\alpha = \beta = \gamma \approx 90^\circ$) can also be constructed (using rhombohedral axes and non-standard setting). For $\text{MnMn}_7\text{O}_{12}$, a $4a_p \times 4a_p \times 4a_p$ cell with $F\bar{1}$ symmetry was also reported at RT.³⁷ $a_p \approx 3.8$ Å is a lattice parameter of the cubic ABO_3 perovskite (space group $Pm\bar{3}m$). For underlined compositions there are no further structural transitions.

crystal and magnetic structures.¹³ The theoretical work¹³ proposed an alternative LT crystal structure, which was soon confirmed experimentally.¹⁴ This correct LT structure has $C2/m$ symmetry, a $2\sqrt{2}a_p \times 2a_p \times 2\sqrt{2}a_p$ superstructure with $\alpha = \gamma = 90^\circ$ and $\beta \approx 90^\circ$ (where a_p is a lattice parameter of an ideal cubic ABO_3 perovskite), full static $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge ordering, and elongated JT distortions of the Mn^{3+} B sites. This LT crystal structure can be described in terms of a commensurate modulation of the parent cubic structure with propagation vector $\mathbf{k} = (1/2, 0, -1/2)$. Importantly, this structural modulation is consistent with the magnetic propagation vectors observed below 125 K.

We believe that the magnetic structures of $\text{NaMn}_7\text{O}_{12}$ need re-investigation considering recent results on the magnetic structures of all other $\text{AMn}_7\text{O}_{12}$ and $\text{RMn}_7\text{O}_{12}$ manganites (see parts 3 and 4), where simultaneous ordering of Mn at the B and A' sites was observed. An additional magnetic anomaly near 34 K was recently reported in $\text{NaMn}_7\text{O}_{12}$,¹⁵ which, in our opinion likely originates in an impurity: MnCO_3 has a magnetic transition with weak FM-like properties at this temperature, and an X-ray diffraction pattern reported in (ref. 16) gave evidence for the presence of an MnCO_3 impurity (a 100% peak of MnCO_3 near 31.5° was observed; note that (ref. 16) incorrectly assigned impurity peaks).

$\text{NaMn}_7\text{O}_{12}$ is a weak insulator with thermally activated charge transport, and resistivity increases by about one order of magnitude below T_{CO} .¹² $\text{NaMn}_7\text{O}_{12}$ ceramics also showed dielectric anomalies at T_{CO} and additional relatively sharp step-like frequency-dependent dielectric anomalies from 50 K (at $f = 1$ kHz) to 80 K (at $f = 1$ MHz).^{15,17} These steps were orig-

inally left without explanation.¹⁷ Similar step-like dielectric behavior was observed in $\text{RMn}_7\text{O}_{12}$ ($R = \text{La, Ce, Sm, Eu}$ and Gd) between 17 and 35 K, which was assigned to extrinsic effects (see part 4). No apparent dielectric anomalies were detected in $\text{NaMn}_7\text{O}_{12}$ at T_{N1} and T_{N2} .¹⁷ Broad and symmetrical pyroelectric current anomalies were observed in $\text{NaMn}_7\text{O}_{12}$ from 20 K to 40 K, which were assigned to a (spin-induced) ferroelectric transition associated with the 34 K magnetic anomaly.¹⁵ Following the results of more recent detailed studies of other $\text{AMn}_7\text{O}_{12}$ compounds (see part 4), we expect that the dielectric and pyroelectric current anomalies in $\text{NaMn}_7\text{O}_{12}$ are most probably caused by extrinsic effects.

A number of works were devoted to the single-crystal growth of $\text{NaMn}_7\text{O}_{12}$.^{16,18} It was found that small amounts of water and Na excess facilitate the crystal growth. The formation of good samples was observed in the pressure range of 2–6 GPa and temperature range of 670–1120 K with the best conditions at 6 GPa and 1100 K. Single-crystal X-ray diffraction studies gave the real chemical composition of the studied crystal as $(\text{Na}_{0.95}\text{Mn}_{0.05})\text{Mn}_7\text{O}_{12}$.¹⁶ No structural phase transitions were found up to 40 GPa (at RT), but some anomalies in resistivity near 18 GPa gave evidence for charge transfer from the B site to the A' site.¹⁹

3. $\text{AMn}_7\text{O}_{12}$ ($A = \text{Mn, Cd, Ca, Sr, Hg}$ and Pb)

Perovskites with $A = \text{Ca, Cd}$ and Sr were first reported by Bochu *et al.*²⁰ and synthesized under high-pressure and high-



hedra has been shown by Khomskii and van den Brink to be unstable due to anharmonic effects which always stabilize elongated octahedra.²³ The transition to the trigonal charge-ordered phase takes place well above RT and is associated with phase coexistence in the temperature range of 409–448 K where the LT trigonal phase coexists with the HT cubic one.²⁴ The LT structural studies^{25–28} revealed another transition at $T_{\text{OO}} = 260$ K (OO stands for orbital order), where the crystal structure of $\text{CaMn}_7\text{O}_{12}$ develops an incommensurate structural modulation with propagation vector $\mathbf{k}_s = (0, 0, \gamma)$ ($\gamma = 0.9215$ at $T = 113$ K,²⁹ in the following discussion we will use the equivalent propagation vector $(0, 0, 3) - \mathbf{k}_s = (0, 0, 2.0785)$ to emphasize its relation with the modulation of the magnetic order). Initially, the modulation was assigned to charge ordering,²⁵ however, subsequent quantitative structure refinement of synchrotron X-ray and neutron powder diffraction data in the $R\bar{3}(0,0,\gamma)0$ superspace group²⁷ did not support this

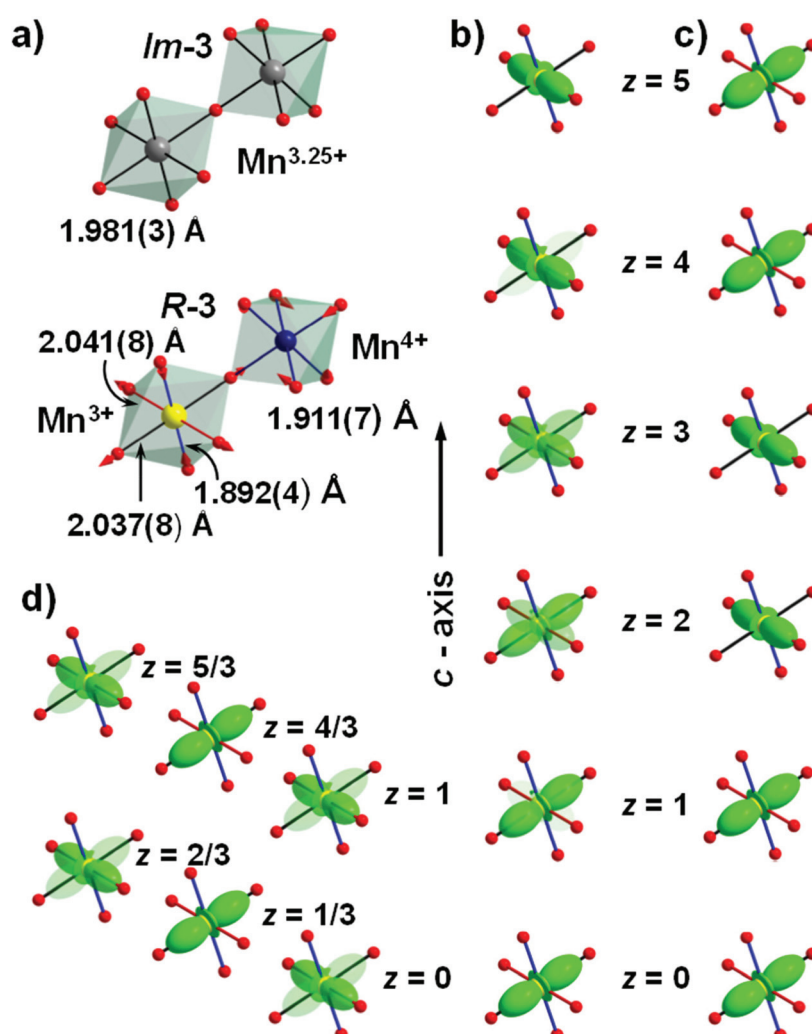


Fig. 3 (a) Compression of Mn^{3+}O_6 octahedra in $\text{CaMn}_7\text{O}_{12}$ at the phase transition from the disordered cubic $Im\bar{3}$ to the charge-ordered trigonal structure (Mn–O bond distances are taken from ref. 24 and 22 for the cubic and trigonal structures, respectively). Orbital density wave in $\text{CaMn}_7\text{O}_{12}$ (b), $\xi_1\text{-Mn}_2\text{O}_3$ (c) and $\text{CdMn}_7\text{O}_{12}$ (d), illustrating the change of orbital state of Mn^{3+} upon propagation along the trigonal axis. In the latter case, the commensurate orbital density wave splits the Mn position into two sites with fully and partially polarised states.

interpretation and instead revealed a complex modulation of Mn–O bond distances. The model was confirmed by Perks *et al.*³⁰ using X-ray single-crystal data, and the modulation was interpreted as an incommensurate orbital ordering (orbital density wave) localised on the B-site Mn^{3+} cations. The density wave implies a periodic change of the $3x^2-r^2$ and $3y^2-r^2$ orbital occupancies passing through the x^2-y^2 state only at the nodal points (Fig. 3b). In other words, in the modulated structure most of the octahedra are locally elongated along one of two axes that alternate periodically within the crystal, giving rise to the apical compression of octahedra on average.

The systematic structural study by Belik *et al.*²⁹ revealed a similar modulation in other members of the family with A = Sr, Cd and Pb, taking place at $T_{\text{OO}} = 265$ K, 254 K and 294 K, respectively (Fig. 2). The propagation vector for the Sr-perovskite is also incommensurate with the magnitude very close to the Ca-counterpart; $\mathbf{k}_s = (0, 0, 2.0765)$ at $T = 113$ K. The modulation was found to be commensurate, $\mathbf{k}_s = (0, 0, 2)$, in the case of $\text{CdMn}_7\text{O}_{12}$, giving rise to the primitive unit cell with $P\bar{3}$ symmetry. The commensurate nature of the orbital density wave was interpreted as an activation of a third-power lock-in term allowed in the Landau free-energy decomposition when the γ -component of the propagation vector takes the commensurate value.³¹ The centrosymmetric space group fixes the global phase of the commensurate orbital density wave and imposes a stacking of fully and partially polarized orbital states (Fig. 3d).

Note that some samples of $\text{CdMn}_7\text{O}_{12}$ showed phase separation below about 60 K,^{31,32} characterised by a mixture of $P\bar{3}$ and $I2/m$ phases and large hysteresis in properties.³³ This coexistence likely reflects small variations in the real chemical compositions of such samples, and the appearance of the $I2/m$ phase needs detailed investigations as it usually appears in $\text{R}^{3+}\text{Mn}_7\text{O}_{12}$ (Fig. 2).

The situation with $\text{PbMn}_7\text{O}_{12}$ has been found to be more complicated.³⁴ Just below the transition at $T_{\text{OO}} = 294$ K the modulation is incommensurate with $\gamma \sim 2.08$. At $T_{\text{OO}2} = 110$ K another structural transition takes place where the propagation vector suddenly drops down to a quasicommensurate value $\mathbf{k}_s = (0, 0, 2.0060(6))$. The quasicommensurate phase is stable in the temperature range of 40–110 K, and below $T_{\text{OO}3} = 40$ K the propagation vector jumps back to the incommensurate value $\mathbf{k}_s = (0, 0, 2.060(6))$. Both the LT structural transitions are strongly first order with large thermal hysteresis. The orbital density wave in the quasicommensurate phase has been found to be substantially suppressed in comparison with the incommensurate phases, and this behaviour was attributed to a competition between the Pb^{2+} lone electron pair and Mn^{3+} JT instabilities. This makes this perovskite particularly attractive as a new playground for various charge doping strategies by analogy with the $\text{BiMn}_7\text{O}_{12}$ system (see section 5, below), where a light hole doping has been shown to stabilize exotic electric dipole and orbital textures due to a fine tuning of the relative strength of these two electronic instabilities.³⁵ Similar to $\text{CaMn}_7\text{O}_{12}$, the perovskites with A = Sr, Cd and Pb exhibit a HT transition to the cubic $Im\bar{3}$ structure at $T_{\text{CO}} = 404$ K, 493 K

and 397 K, respectively, as determined by differential scanning calorimetry.³³ We note that in other studies, T_{CO} for $\text{PbMn}_7\text{O}_{12}$ was reported to be 380 K,³⁶ and for $\text{CaMn}_7\text{O}_{12}$ prepared at high pressure – to be 462 K,³³ suggesting that T_{CO} , and also T_{OO} , are sensitive to the sample quality.

Another member of the $\text{A}^{2+}\text{Mn}_7\text{O}_{12}$ family is the ξ -polymorph of Mn_2O_3 . As has been shown by Ovsyannikov *et al.*,³⁷ at high temperature (above 1000 K) and at high-pressure (above 18 GPa), Mn_2O_3 transforms to a perovskite modification which can be quenched into a metastable phase at ambient conditions. This metastable phase exhibits a unique charge disproportionation phenomenon stabilizing the quadruple perovskite structure $\text{Mn}^{2+}\text{Mn}^{3+}_3\text{Mn}^{3.25+}_4\text{O}_{12}$ with an additional $3\text{Mn}^{3+}:1\text{Mn}^{4+}$ charge ordering and commensurate orbital density wave with $\mathbf{k}_s = (0, 0, 9/4)$, localized in the B-site perovskite position. The charge ordered modulated structure possesses $R\bar{3}$ symmetry with a $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4\sqrt{3}a_p$ supercell defined with respect to the pseudocubic simple perovskite structure which is prototype for all families of perovskite materials. Here, the orbital density wave represents a sequence of $3x^2-r^2$ and $3y^2-r^2$ orbital states ordered in a $++--$ fashion (where + and – indicate distinct states) upon propagation along the trigonal axis (Fig. 3c). The commensurate nature of the orbital density wave and the associated structural modulation has been explained by a coupling of the orbital ordering to an independent structural distortion, which improves the poor bonding conditions of Mn^{2+} in the A-site perovskite position.³⁸ The trigonal structure has been reported to be stable at RT,³⁷ but the temperatures at which the B-site charge and orbital ordering onset are yet to be determined.

One more perovskite with a divalent A-site cation, $\text{HgMn}_7\text{O}_{12}$, has been recently reported by Chen *et al.*³⁹ Similar to other members of the family, it exhibits a cubic to trigonal structural transition due to the $3\text{Mn}^{3+}:1\text{Mn}^{4+}$ charge ordering in the B-site manganese position. The transition is first order and takes place *via* phase coexistence in the temperature range of 470–490 K. However, instead of the modulated trigonal ground state, the LT structure of $\text{HgMn}_7\text{O}_{12}$ to a good approximation is commensurate orthorhombic with the polar $Pnn2$ symmetry. The transition to the orthorhombic phase takes place at 240–260 K and is associated with a further charge disproportionation where 1/3 of Mn^{3+} in the A' position become Mn^{2+} , giving rise to $1\text{Mn}^{2+}:2\text{Mn}^{3+}$ charge ordering in the A' square planar position as well as $1\text{Mn}^{3+}:1\text{Mn}^{4+}$ charge and orbital ordering in the B-site position (Fig. 4). The polar symmetry is a result of the common action of two irreducible order parameters. One of them is the charge/orbital order and another serves to improve the coordination environment of the A'-site Mn^{2+} cations by making the environment more regular through shortening the second-nearest-neighbour distances. The charge transfer between the A' and B sites has been suggested as an alternative mechanism to the orbital density wave formation to release the instability associated with the compressed octahedra in the 3:1 charge ordered trigonal phase. The B-site Mn^{3+} in this phase was assumed to exhibit orbital disorder between the $3x^2-r^2/3y^2-r^2$ states. Whether this



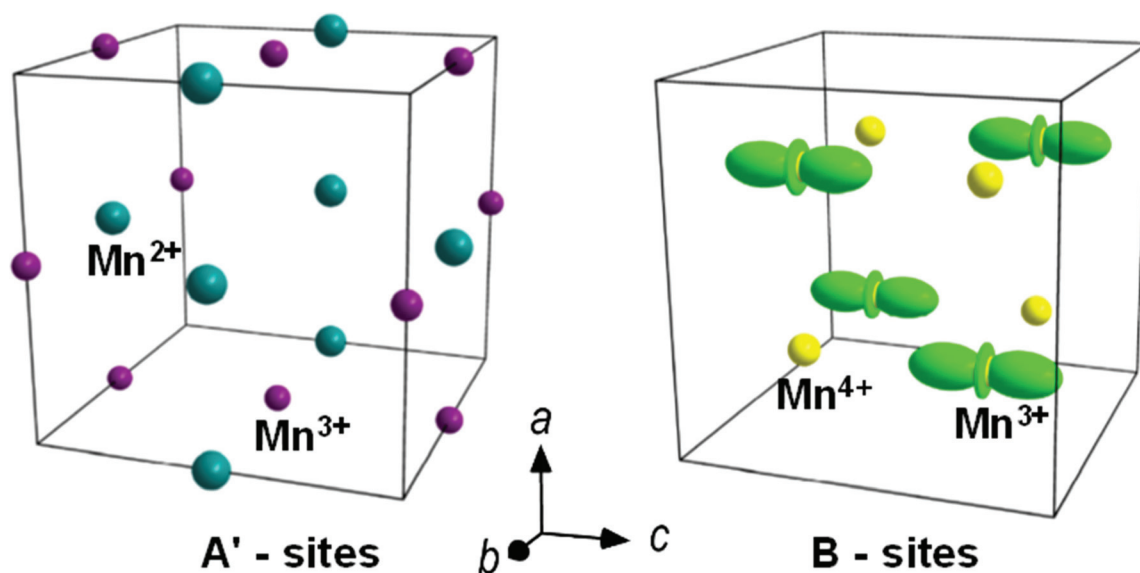


Fig. 4 Charge (left) and orbital (right) ordering in the orthorhombic $Pnn2$ phase of $\text{HgMn}_7\text{O}_{12}$ perovskite.³⁹

is the case, or the x^2-y^2 orbital state is imposed by the bilinear coupling to the atomic displacement mode accompanying the 3 : 1 charge order⁴⁰ is an interesting open question.

The perovskites of the $\text{A}^{2+}\text{Mn}_7\text{O}_{12}$ family attracted great attention after the discovery of prominent multiferroic properties in $\text{CaMn}_7\text{O}_{12}$.^{41,42} Long-range magnetic ordering in this material takes place at $T_{\text{N}1} \sim 90$ K with the incommensurate propagation vector, \mathbf{k}_0 , locked to the structural modulation such that $\mathbf{k}_0 = \mathbf{k}_s/2$.^{26–28} Below $T_{\text{N}2} \sim 48$ K, the magnetic subsystem delocks from the structural modulation giving rise to a complex multi- \mathbf{k} magnetic ground state.⁴³ The initially reported giant spin-driven polarization was found to onset at $T_{\text{N}1}$. Later studies⁴⁴ confirmed the multiferroic properties of $\text{CaMn}_7\text{O}_{12}$ but the electrical polarization was found only below the second magnetic transition at $T_{\text{N}2}$ with substantially lower magnitude. The corresponding ground state magnetic structure was quantitatively determined using high-resolution neutron powder and single crystal diffraction data⁴³ and was found to represent an unprecedented example of helical order with modulated spin chirality (Fig. 5). Unlike usual helical structures with a constant magnetic phase between spins related by a lattice translation along the propagation vector, the magnetic phase of the spins in the ground state of $\text{CaMn}_7\text{O}_{12}$ is incommensurately modulated with the periodicity of the orbital density wave. The magnetic structure decomposes into a set of magnetic order parameters with distinct propagation vectors, \mathbf{k}_{\pm} , along the trigonal axis. A symmetry based phenomenological approach⁴³ revealed that this exotic ground state is a result of coupling between the primary magnetic order, stabilized by competing exchange interactions and referred to as the fundamental component $\mathbf{k}_0 = (0, 0, 1.12354(8))$, and the orbital density wave $\mathbf{k}_s = (0, 0, 2.0775(1))$ at $T = 1.5$ K (magneto-orbital coupling). By symmetry, the fundamental helical order alone cannot lock to the structural

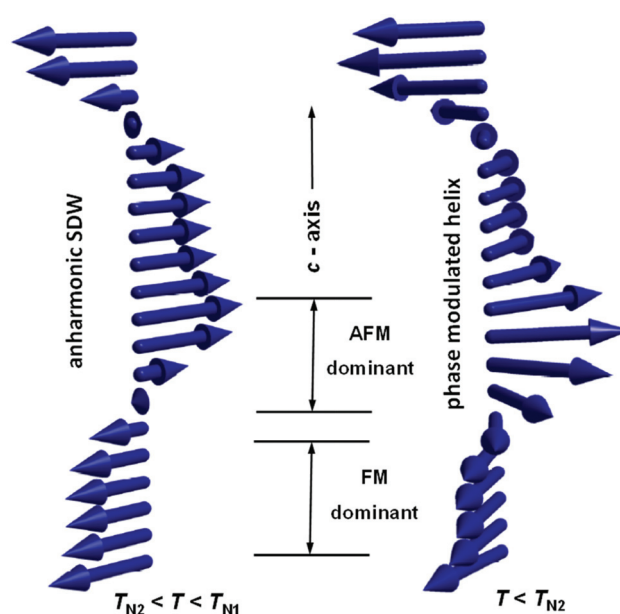


Fig. 5 Schematic representation of the anharmonic spin density wave (SDW) and the phase modulated helix, corresponding to the high-temperature lock-in phase and the ground state of $\text{A}^{2+}\text{Mn}_7\text{O}_{12}$ manganites.⁴³

modulation, and hence the coupling introduces additional magnetic components with $\mathbf{k}_{\pm} = \mathbf{k}_0 \pm n\mathbf{k}_s$ propagation vectors. Experimentally, the components up to $n = 2$ have been confirmed.⁴³ Microscopically, the magneto-orbital coupling implies that the orbital density wave modulates the competing exchange interactions and local anisotropies resulting in faster and slower rotations of spins upon propagation along the trigonal axis.



Unlike the helical order, a spin density wave can be locked to the structural modulation associated with the orbital density wave.⁴³ This type of ordering therefore is the prime candidate for the magnetic structure of $\text{CaMn}_7\text{O}_{12}$ in the temperature range of $T_{\text{N}2} < T < T_{\text{N}1}$, where the magnetic and structural modulations are commensurate with each other, holding the $\mathbf{k}_0 = \mathbf{k}_s/2$ ratio (Fig. 5). The magneto-orbital coupling is expected to yield additional magnetic components making the spin density wave anharmonic, which was confirmed experimentally through the observation of higher order satellites (in particular the $3\mathbf{k}_0$ propagation vector).^{27,43} It has to be pointed out that experimentally it is challenging to distinguish the spin-density wave with the spins confined within the (ab) -plane of the trigonal structure and the helical order. However, the commensurate relation between the magnetic and structural modulations and the absence of electrical polarization in the lock-in phase⁴⁴ strongly support the existence of a spin density wave above $T_{\text{N}2}$. Another argument in favour of this scenario comes from the precise magnetic structure determination in the ξ -polymorph of Mn_2O_3 .^{38,47} Similar to $\text{CaMn}_7\text{O}_{12}$, this perovskite also exhibits two magnetic transitions at $T_{\text{N}1} = 100$ K and $T_{\text{N}2} = 50$ K, and multiferroic properties below $T_{\text{N}2}$. The HT magnetic phase has been found to be commensurate and locked to the structural modulation. The spins in this phase are polarized along the c -axis forming an anharmonic longitudinal spin density wave. The magnetic structure is only partially ordered and contains 1/4 of the A-site Mn^{2+} cations with zero ordered moment. Below $T_{\text{N}2}$, the magnetic propagation vector becomes incommensurate ($\mathbf{k}_0 = (0, 0, 1.2439(3))$) at $T = 1.5$ K) and the magnetic structure turns into a phase modulated constant moment cycloid with only a small admixture of a helical component. Thus, the magnetic behaviour of $\text{CaMn}_7\text{O}_{12}$ and $\xi\text{-Mn}_2\text{O}_3$ is very similar apart from the different magnetic anisotropy which is an easy-plane type in the former case and easy axis (along the trigonal axis) in the latter. The longitudinal spin density wave can be unambiguously distinguished from any other solution and therefore the sequence paramagnetic – spin density wave – constant moment mag-

Thus, the magnetic properties of the divalent A-site quadruple perovskites reveal a universal interplay between magnetic and orbital degrees of freedom, leading to the concept of magneto-orbital coupling. In the HT ordered state the periodicities of the magnetic and orbital subsystems lock together *via* commensurate magneto-orbital coupling. On cooling, these periodicities delock, allowing the system to evolve towards a multi- k magnetic ground state in which incommensurate magneto-orbital coupling gives rise to a modulation of the spin helicity. The stability of the locked and delocked magnetic phases is controlled by the balance between the entropy term (promoting a partially ordered state at higher temperatures), lock-in term, and magnetic exchange interaction requiring a propagation vector different from the orbital modulation.^{31,43} While T_{N1} remains approximately constant across the series (apart from $\xi\text{-Mn}_2\text{O}_3$ which has the additional A-site magnetic sublattice and therefore a noticeably higher T_{N1}), the periodicity of the ground state magnetic structure and the LT transition T_{N2} both monotonically increase with increasing A^{2+} ionic radius. The only member of the family whose magnetic properties might differ significantly from that described above is $\text{HgMn}_7\text{O}_{12}$. Although, the magnetic structure is yet to be reported for this perovskite, there is no reason to believe that it should obey the common scenario where the lock-in phase is followed by the delocked phase-modulated

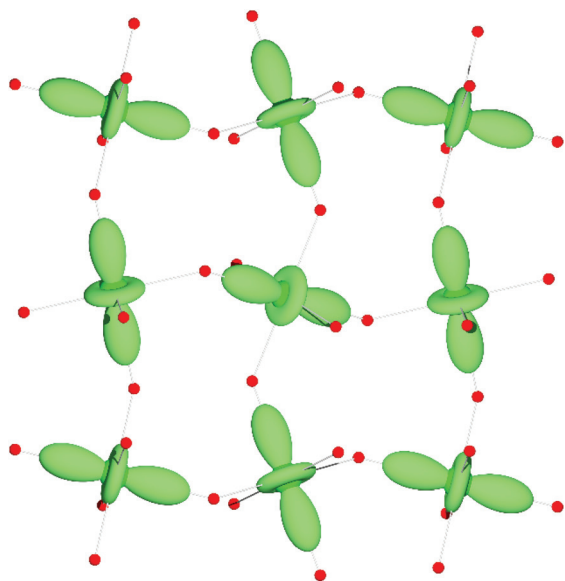


Fig. 6 LaMnO₃-type orbital order spanning the B site Mn³⁺ ions in any given *ac*-plane in monoclinic R³⁺Mn₇O₁₂. The orbital order is co-aligned on moving along *b* (perpendicular to this figure) from one layer to the next.

CeMn₇O₁₂, SmMn₇O₁₂ and EuMn₇O₁₂ undergo a single magnetic phase transition at $T_{N1} = 80$, 87 and 87 K, respectively.^{59,62,64} Both A' and B site Mn³⁺ magnetic moments adopt long range order below T_{N1} with propagation vector $\mathbf{k} = (0, 0, 0)$. The A'-sites form a collinear ferrimagnetic structure, with magnetic moments lying in the *ac* plane and rotated away from the *c*-axis towards $-a$ by 38.7(3)°, 34.7(4)°, and 32.1(5)° for R = Ce, Sm and Eu, respectively.⁵⁹ One in every three A' site moments is uncompensated, giving a net ferrimagnetic moment as observed in magnetometry measurements. The B site Mn³⁺ magnetic moments form a C-type AFM structure (following the notation of Bertaut),⁷⁰ in which nearest neighbour moments are antiferromagnetically aligned in the *ac* plane, and coupled ferromagnetically along the *b* axis. B site spin canting is allowed by symmetry but could not be detected in

neutron powder diffraction experiments. Hence, a minimal model with B site moments collinear with the A' site moments was proposed (Fig. 7).⁵⁹ Importantly, the magnetic structures on both sublattices transform by the same irreducible representation (Γ_2^+ , defined w.r.t. the *I2/m* paramagnetic parent), hence the two are directly coupled and can develop together below a single phase transition. Based upon the Goodenough–Kanamori–Anderson rules³ taken in the limit of 180° Mn–O–Mn bonds, the LaMnO₃ type orbital order should stabilise an A-type magnetic structure on the B sites (FM layers stacked AFM). This magnetic structure was indeed observed in LaMnO₃,⁷¹ but it is the exact opposite of what is found in the above RMn₇O₁₂ compounds. The octahedral tilting in RMn₇O₁₂ is large compared to that of the RMnO₃ perovskites, leading to a more significant departure from 180° Mn–O–Mn bonds that may weaken or even change the sign of the superexchange interaction. In addition, the RMn₇O₁₂ compounds host strong d–d superexchange between A' and B sublattices. Such A'–B exchange may compete with B–B exchange and play a key role in stabilising the C-type structure. We note that a B site A-type structure transforms by a different $\mathbf{k} = (0, 1, 0)$ irreducible representation to the observed $\mathbf{k} = (0, 0, 0)$ C-type structure, hence the energy gain through A'–B interactions would average to zero in this case.

Magnetic susceptibility and heat capacity measurements of GdMn₇O₁₂ and TbMn₇O₁₂ show anomalous behaviour at $T_{N1} = 86$ and 82 K, respectively, qualitatively similar to the behaviour of the R = Ce, Sm and Eu samples; hence consistent with a phase transition to the same ferrimagnetic ground state.⁶⁴ However, the microscopic nature of the long range magnetic order is yet to be confirmed, for example, by neutron powder diffraction experiments. Measurements of the isothermal magnetisation at 5 K indicate a sizeable uncompensated ferrimagnetic moment in both GdMn₇O₁₂ and TbMn₇O₁₂, which is enhanced compared to the R = Ce, Sm and Eu compounds likely due to the large moments carried by Gd and Tb. For all five samples discussed above, no direct evidence has been provided for long-range magnetic order of the rare-earth ions. However, a Schottky-like anomaly was observed in the specific

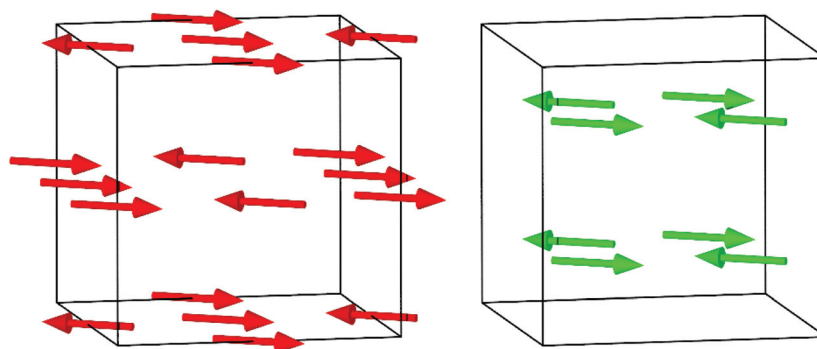


Fig. 7 The A' site ferrimagnetic structure (red, left) and B site C-type antiferromagnetic structure (green, right) observed for R = La, Ce, Nd, Sm, Eu, Dy and Y, and likely common to all R³⁺Mn₇O₁₂ compounds below T_{N1} .^{59,65,67} The cubes represent the unit cell. The monoclinic *b*-axis points up the page, and the *c*-axis to the right.



heat of $\text{GdMn}_7\text{O}_{12}$ below ~ 10 K that was largely suppressed by a 9 T magnetic field.⁶⁴ This result may point towards Gd ions playing a significant role in the ground state. In addition, magnetic and specific heat measurements gave evidence that a second LT magnetic transition could emerge under magnetic fields in $\text{R} = \text{Sm}$ and Eu .⁶⁴

The dielectric constant of the $\text{R} = \text{Ce}, \text{Sm}, \text{Eu}, \text{Gd}$ and Tb compounds has been reported,^{62,64} measured as a function of both temperature and excitation frequency. In all cases a small kink-like anomaly was observed at $T_{\text{N}1}$, with the LT behaviour (frequency-dependent sharp steps between 18 and 35 K) otherwise dominated by extrinsic relaxation processes typical of these and related material systems. As such, there exists no evidence for dipolar or ferroelectric properties in these five compounds. N.B. Sharp steps in dielectric constant near 30 K were also reported in $\text{LaMn}_7\text{O}_{12}$, discussed below.⁶⁰

$\text{PrMn}_7\text{O}_{12}$ is the only member of the $\text{RMn}_7\text{O}_{12}$ family that has two polymorphs at RT.⁶³ The $I2/m$ phase supports the same orbital order and ferrimagnetic magnetization below a single phase transition ($T_{\text{N}1} = 70$ K) as is characteristic of the compounds with $\text{R} = \text{Ce}, \text{Sm}, \text{Eu}, \text{Gd}$ and Tb . Again, one might therefore speculate that the $I2/m$ polymorph of $\text{PrMn}_7\text{O}_{12}$ adopts the same ferrimagnetic structure below $T_{\text{N}1}$, but this is yet to be confirmed. The $R\bar{3}$ polymorph was reported to have the same crystal structure as $\text{CaMn}_7\text{O}_{12}$, implying a 3 : 1 splitting of B sites. In $\text{CaMn}_7\text{O}_{12}$ this splitting can be understood in terms of a 3 : 1 charge ordering of Mn^{3+} and Mn^{4+} ions from an average valence of $\text{Mn}^{3.25+}$ imposed by the divalent Ca cation. It is therefore somewhat surprising to find this polymorph in the $\text{RMn}_7\text{O}_{12}$ family (Fig. 2). Nonetheless, this $R\bar{3}$ phase displays altogether different magnetic behaviour with $T_{\text{N}1} = 44$ K,⁶³ and it has been proposed that in the $R\bar{3}$ symmetry the B-site Mn^{3+} ions split into three high spin and one low spin per formula unit, with the low spin ion at the undistorted octahedral site occupied by Mn^{4+} in $\text{CaMn}_7\text{O}_{12}$.

$\text{LaMn}_7\text{O}_{12}$ is arguably the most studied of all $\text{RMn}_7\text{O}_{12}$ compounds. Unlike the above, $\text{LaMn}_7\text{O}_{12}$ displays two magnetic phase transitions at $T_{\text{N}1} = 79.5$ and $T_{\text{N}2} = 22.5$ K.⁵² The HT transition was first assigned to the onset of the same B site C-type AFM structure described above, but independent of A' site Mn order which was instead assigned to the LT transition – an observation akin to the behaviour of $\text{NaMn}_7\text{O}_{12}$.¹² The proposed LT A' site order had propagation vector $\mathbf{k} = (0, 1, 0)$, with FM layers in the ac plane, stacked AFM along b . Owing to the different symmetries, the A' sites could naturally order independently of the B sites. Both A' and B sublattice magnetic structures refined against neutron powder diffraction experiments⁵² did not have a net ferrimagnetic moment – a result inconsistent with magnetometry measurements showing a net magnetisation similar to that measured for $\text{R} = \text{Ce}, \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}$ and Tb . It was therefore proposed that the net moment in $\text{LaMn}_7\text{O}_{12}$ arose through an exceptionally large canting of the B site magnetic structure induced by the Dzyaloshinskii–Moriya interaction.⁵² The application of the same model to $\text{YMn}_7\text{O}_{12}$ led to the suggestion that the A' Mn sublattice remains disordered as only one magnetic transition was

found.⁶⁶ More recently, analysis of high resolution neutron powder diffraction data has shown that both A' and B Mn moments order together at the HT transition with the same magnetic structure found for $\text{R} = \text{Ce}, \text{Sm}$ and Eu , hence providing a more natural explanation for the sizeable ferrimagnetic moment.⁵⁹ We note that these two different scenarios manifest in remarkably subtle changes in the neutron powder diffraction pattern.⁵⁹ The latter scenario requires a more complex explanation for the LT transition, and it was proposed that $\text{LaMn}_7\text{O}_{12}$ enters into a ground state in which B site moments adopt a canted magnetic structure characterised by an admixture of commensurate C-type and A-type modes.⁵⁹ Intriguingly, such a ground state points towards an underlying instability towards the A-type structure expected in the presence of LaMnO_3 -type orbital order – perhaps acting in competition A'–B superexchange.

$\text{NdMn}_7\text{O}_{12}$ was found to undergo three magnetic phase transitions, one at $T_{\text{N}1} = 85$ K, and a further two at low temperature ($T_{\text{N}2} = 12$ and $T_{\text{N}3} = 8.5$ K). Both A' and B sublattices were found to order below $T_{\text{N}1}$ with ferrimagnetic and C-type magnetic structures, respectively – in common with all of the above $\text{RMn}_7\text{O}_{12}$ compounds.⁵⁹ It was reported that below the second transition there developed an incommensurate modulation of the B-site magnetic structure with $\mathbf{k} = (0.248(2), 1, 0.064(3))$, which corresponds to an admixture of commensurate C-type and incommensurate A-type modes. In comparison with $\text{LaMn}_7\text{O}_{12}$, the incommensurate modulation of $\text{NdMn}_7\text{O}_{12}$ can be thought of as a spatially varying unidirectional canting (addition of an orthogonal spin density wave) or as a conical rotation of moments (addition of an orthogonal cycloid). These two scenarios could not be differentiated by neutron powder diffraction, but both support the argument for competing magnetic instabilities in both $\text{R} = \text{La}$ and Nd compounds (it is well established that incommensurate structures can be stabilised by competing interactions). Below the third transition the incommensurate propagation vector was found to jump to $\mathbf{k} = (0.3231(7), 1, 0.0069(7))$, accompanied by a finite ordered moment appearing on the Nd ions.

It is apparent that the additional LT magnetic transitions occur for compounds with rare earth ions of largest ionic radii, with the exceptions of $\text{CeMn}_7\text{O}_{12}$ and $\text{PrMn}_7\text{O}_{12}$. It was suggested that this discrepancy may arise due to $\text{Ce}_{1-x}\text{Mn}_{7+x}\text{O}_{12}$ or $\text{PrMn}_7\text{O}_{12+d}$ off-stoichiometry of the measured samples. Indeed, the second transition was found to be suppressed in non-stoichiometric $\text{La}_{0.9}\text{Mn}_{7.1}\text{O}_{12}$.^{59,62} The experimental results published to date indicate complex behaviour at low temperatures, and we suggest future studies, both experimental and theoretical, are required to establish the full microscopic details of the ground state magnetic structures of $\text{LaMn}_7\text{O}_{12}$ and $\text{NdMn}_7\text{O}_{12}$, and the underlying competing interactions in the $\text{RMn}_7\text{O}_{12}$ family.

Unpublished dielectric measurements of $\text{LaMn}_7\text{O}_{12}$ and $\text{NdMn}_7\text{O}_{12}$ indicate qualitatively similar behaviour to the non-polar compounds with $\text{R} = \text{Ce}, \text{Sm}, \text{Eu}, \text{Gd}$ and Tb . Recently, however, a large electric polarisation of up to $0.56 \mu\text{C cm}^{-2}$ has



been suggested for $\text{LaMn}_7\text{O}_{12}$ developing below T_{N1} ,⁶⁰ based on the observation of very strong, broad and symmetrical pyroelectric-current peaks. Following the reported giant ferroelectric polarisation in $\text{CaMn}_7\text{O}_{12}$ (ref. 41) some debate ensued regarding the intrinsic nature of the polarisation in these systems. Indeed, other works have assigned such pyroelectric-current peaks to extrinsic effects.^{44,48,62,64} In light of this, we suggest that it is important for extrinsic effects, for example those due to thermally stimulated currents, to be ruled out in the case of $\text{LaMn}_7\text{O}_{12}$.

Specific heat and magnetometry measurements showed that $\text{YMn}_7\text{O}_{12}$ supports a single ferrimagnetic phase transition at $T_{\text{N1}} = 108 \text{ K}$,⁶⁶ approximately 20–30 K higher than the $\text{RMn}_7\text{O}_{12}$ compounds discussed above. Unlike the other $\text{RMn}_7\text{O}_{12}$ compounds, $\text{YMn}_7\text{O}_{12}$ was found to undergo a structural phase transition at $T_{\text{s}} = 200 \text{ K}$ that was clearly marked by anomalous behaviour in the temperature dependence of the specific heat and spontaneous negative thermal expansion of the lattice.⁶⁶ The microscopic details of both phase transitions were established in a later publication, in which the same ferrimagnetic structure discussed above was reported to occur below T_{N1} , apparently independent of the structural transition at T_{s} .⁶⁷ The ground state crystal structure was characterised by an ordered pattern of atomic displacements that lowered the crystal symmetry to $P2_1/n$, accompanied by disordered displacements of yttrium ions forming a so-called dipolar glass that naturally explained the observed negative thermal expansion.⁶⁷ A recent publication based on single crystal diffraction measurements showed that the yttrium ions can form partial antiferroelectric order out of the dipolar glass state,⁶⁸ the extent of which is likely sample dependent. The structural modifications below T_{s} could in principle occur independent of one another, but they all improve the bonding conditions of the yttrium ions that were shown to be somewhat underbonded above T_{s} .⁶⁷ Hence, $\text{YMn}_7\text{O}_{12}$ has a *pseudo*-JT instability associated with A site cations – phenomena usually associated with B site cations in perovskite-derived materials – that can drive unusual LT structural phase transitions. We note that, compared to the RMnO_3 systems, the quadruple perovskites may be prone to underbonding of R cations as the octahedral tilts primarily generate square planar coordinations for the majority A' site Mn^{3+} ions, perhaps at the expense of the minority A site R ions. Pyroelectric current measurements similar to those reported for $\text{LaMn}_7\text{O}_{12}$ have also led to the suggestion of a large ferroelectric polarisation developing in $\text{YMn}_7\text{O}_{12}$ at low temperature.⁶⁸ As before, we stress a similar level of caution when interpreting the results of these measurements.

Finally, the reported phenomenology of $\text{DyMn}_7\text{O}_{12}$ is similar to that of $\text{YMn}_7\text{O}_{12}$ but with one key difference; the structural and magnetic transitions come together (T_{N1} and T_{s} are merged) to create a single, first order magneto-structural phase transition at $T_{\text{N1}} \sim 95 \text{ K}$.⁶⁵ Below T_{N1} the Dy dipolar glass and ferrimagnetic order parameters were found to be cross-coupled (note that in $\text{DyMn}_7\text{O}_{12}$ ordered atomic displacements were not observed below T_{N1}),⁶⁵ as demonstrated by temperature and field dependent dielectric constant measurements

(Fig. 8) (N.B. when T_{N1} and T_{s} are separated as in $\text{YMn}_7\text{O}_{12}$ no dielectric anomalies were found at the both temperatures).⁶⁵ In addition, long-range FM ordering of Dy magnetic moments was found below 5.5 K.⁶⁵

In summary, all $\text{RMn}_7\text{O}_{12}$ compounds host a common magnetic structure composed of a ferrimagnetic A' site Mn^{3+} sublattice with one uncompensated Mn^{3+} moment per unit cell, and a C-type AFM B site sublattice (Fig. 7). In addition, $\text{LaMn}_7\text{O}_{12}$ and $\text{NdMn}_7\text{O}_{12}$ show LT magnetic phase transitions likely associated with the competition between A'–B and B–B exchange. For compounds with small R ionic radius ($R = \text{Dy}$ and Y), the R cations adopt a *pseudo*-JT instability that leads to exotic LT phases characterised by cross-coupled magnetic and electric degrees of freedom.

5. $\text{BiMn}_7\text{O}_{12}$

Compared with $\text{RMn}_7\text{O}_{12}$, $\text{BiMn}_7\text{O}_{12}$ has an electronic instability originating from the presence of the lone-electron pair of Bi^{3+} cations. As a result, it exhibits distinct structural, magnetic and dielectric properties. $\text{BiMn}_7\text{O}_{12}$ was first reported in 2008,⁷² and its RT crystal structure was often described using a centrosymmetric $I2/m$ model derived from powder diffraction experiments.^{53,58,73,74} On the other hand, more sensitive single-crystal structural investigations gave evidence for polar Im symmetry at RT.^{58,75} A number of additional structural phase transitions were later found,^{58,76} and the sequence of phase transitions is now well established (on cooling) as $Im\bar{3} \Rightarrow I2/m \Rightarrow [R\bar{1}(\alpha\beta\gamma)0] \Rightarrow Im \Rightarrow I1$ with transitions at about 608 K, 460 K, and 295 K, respectively, where $[R\bar{1}(\alpha\beta\gamma)0]$ denotes an incipient phase, which appears only as diffuse scattering in undoped $\text{BiMn}_7\text{O}_{12}$ between the $I2/m$ and Im phases.⁵⁸ The proper stabilisation of the $R\bar{1}(\alpha\beta\gamma)0$ phase can be triggered by small Cu^{2+} or Fe^{3+} doping.³⁵ The $Im\bar{3} \Rightarrow I2/m$ transition is related to orbital ordering of Mn^{3+} similar to $\text{RMn}_7\text{O}_{12}$, and the $I2/m \Rightarrow Im$ transition – to the development of a ferroelectric polarization associated with the Bi^{3+} lone pair electrons. However, no direct confirmation of ferroelectricity (such as P – E loops) has been obtained to date.

Two magnetic transitions were widely reported in $\text{BiMn}_7\text{O}_{12}$ at about $T_{\text{N1}} = 59 \text{ K}$ and $T_{\text{N2}} = 21 \text{ K}$ in analogy with $\text{LaMn}_7\text{O}_{12}$,^{72,74,75,77} despite the first paper (ref. 72) reporting evidence for three magnetic transitions from specific heat measurements. In comparison with $\text{RMn}_7\text{O}_{12}$, frequency-independent peaks in the dielectric constant of $\text{BiMn}_7\text{O}_{12}$ were observed at all (three) magnetic transition temperatures without any extrinsic steps,^{72,75,78} but no pyroelectric current anomalies have been detected. Therefore, the origin of dielectric peaks remains unclear and needs further investigation.

The only neutron diffraction study of the magnetic structures assumed that Mn at the B sites are ordered at T_{N1} , and Mn at the A' sites are ordered at T_{N2} , in analogy with $\text{LaMn}_7\text{O}_{12}$.⁷⁴ In addition, the total zero moment was assumed for both A' and B sites despite the observation of large uncompensated moments on M versus H curves (e.g., about $1\mu_{\text{B}}$ at 2 K



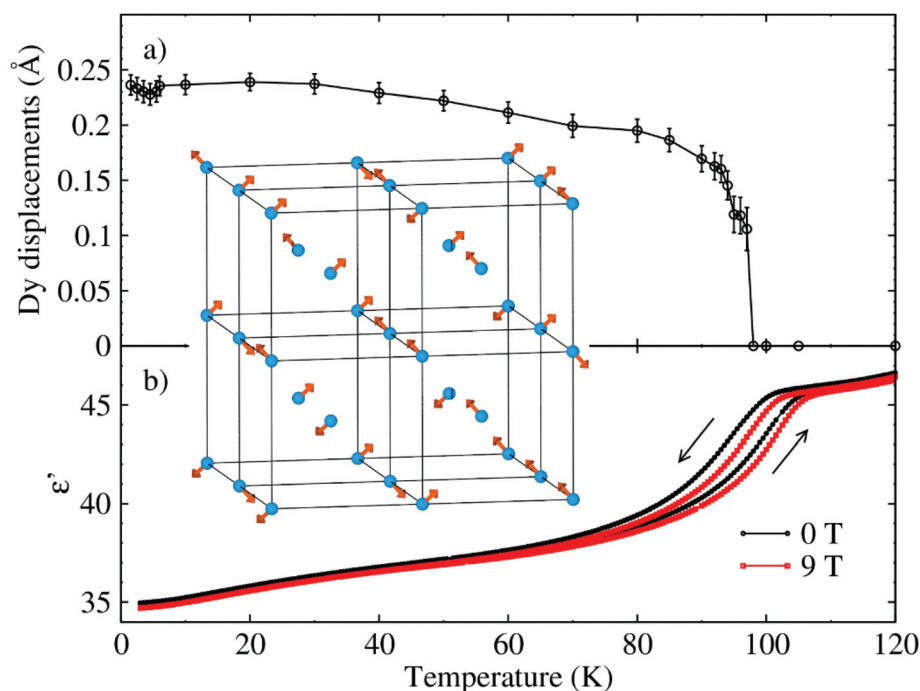


Fig. 8 The magnetostructural dipolar glass found in $(\text{Dy}_{0.91}\text{Mn}_{0.09})\text{Mn}_7\text{O}_{12}$: (a) The temperature dependence of the disordered Dy atomic displacement amplitudes established through structural refinements against neutron powder diffraction data,⁶⁵ and (b) the temperature dependence of the real dielectric constant measured in 0 T (black) and 9 T (red) applied magnetic fields.⁶⁵ The inset illustrates the disordered Dy dipolar glass (circles are ideal positions of Dy atoms at the (0,0,0) site; arrows show displacements).

and $0.8\mu_B$ at 40 K).^{72,77} Furthermore, in the analysis of the magnetic structures the (crystal) symmetry was considered to be Im ,⁷⁴ while the real ground-state symmetry is $I1$. Hence, we suggest that the magnetic structures of $\text{BiMn}_7\text{O}_{12}$ need careful re-investigation.

Similar to $\text{PrMn}_7\text{O}_{12}$, several modifications of $\text{BiMn}_7\text{O}_{12}$ were reported at RT (monoclinic, rhombohedral and cubic).^{73,77–79} However, in this case, the polymorphism was assigned to cation non-stoichiometry ($\text{Bi}_{1-x/3}(\text{Mn}^{3+}_3)$ ($\text{Mn}^{3+}_{4-x}\text{Mn}^{4+}_x$) O_{12} and $\text{Bi}_{0.94}\text{Mn}_{6.91}\text{O}_{12}$) and the appearance of Mn^{4+} at the B sites. We believe the same should be true for $\text{PrMn}_7\text{O}_{12}$. Magnetic properties of non-stoichiometric $\text{BiMn}_7\text{O}_{12}$ were noticeably different from stoichiometric $\text{BiMn}_7\text{O}_{12}$.

6. Conclusions

We have reviewed the current state of research on $\text{AMn}_7\text{O}_{12}$ quadruple perovskite manganites and identified some future directions, such as the re-investigation of magnetic structures of $\text{NaMn}_7\text{O}_{12}$ and $\text{BiMn}_7\text{O}_{12}$ and understanding dielectric behavior of all members, in particular, $\text{BiMn}_7\text{O}_{12}$. Investigations of different solid solutions^{35,80–82} may also yield fascinating results, as it allows continuous variations of Mn oxidation states at the B sites, while keeping nearly the same B-site Mn–O–Mn bond angles,⁸² as was extensively studied in the mixed-valence $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ perovskites.

Conflicts of interest

There are no conflicts to declare.

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