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## Synthesis and characterization of mixed-valence manganese fluorophosphate and analogues with clathrate-like structures: $\text{Mn}^{\text{III}}_6\text{F}_{12}(\text{PO}_3(\text{OH}))_8\text{[Na}_8(\text{K}_x(\text{H}_3\text{O})_{4-x}(\text{H}_2\text{O})_2)\text{M}^{\text{IV}}(\text{OH})_6]$ ( $\text{M}^{\text{IV}} = \text{Mn, Ti, Ge}$ )<sup>†</sup>

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A novel, mixed- and high-valence manganese ( $\text{Mn}^{3+}/\text{Mn}^{4+}$ ) fluorophosphate,  $\text{Mn}^{\text{III}}_6\text{F}_{12}(\text{PO}_3(\text{OH}))_8\text{[Na}_8(\text{K}_x(\text{H}_3\text{O})_{4-x}(\text{H}_2\text{O})_2)\text{Mn}^{\text{IV}}(\text{OH})_6]$  (denoted as **MN**), has been prepared via a water-deficient hydrothermal route with phosphoric acid as the sole solvent. This compound features a cubic three-dimensional open-framework structure built from corner-sharing  $[\text{Mn}^{\text{III}}\text{O}_4\text{F}_2]$  octahedra and  $[\text{HPO}_4]$  groups, which encapsulates a clathrate-like "guest cluster" of  $\text{Na}_8(\text{K}_x(\text{H}_3\text{O})_{4-x}(\text{H}_2\text{O})_2)\text{Mn}^{\text{IV}}(\text{OH})_6$ . The guest cluster is architecturally composed of a  $[\text{Mn}^{\text{IV}}(\text{OH})_6]$  octahedron in a cubic cage of  $\text{Na}^+$  cations, which in turn is surrounded by an octahedral arrangement of  $\text{K}^+/\text{H}_2\text{O}$  ions, resulting in an unprecedented octahedral @ cubic @ octahedral @ cubic arrangement (OCOC). The +4 oxidation state of Mn in the guest cluster has been confirmed by the synthesis of isotopic Ti- and Ge- analogues (denoted as **TI** and **GE**) using  $\text{TiO}_2$  and  $\text{GeO}_2$  as the replacement for  $\text{MnO}_2$  in the starting materials. The compounds **MN**, **TI** and **GE** are not stable in aqueous solution and are peeled off layer-by-layer after the absorption of water. This report provides a new route for the synthesis of mixed- and high-valence manganese phosphates that cannot be produced by conventional hydrothermal methods.

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## 1. Introduction

With the development of novel molecular materials and in-depth studies on the origin and process of life, it is now recognized that many optical,<sup>1</sup> electrical<sup>2</sup> and magnetic properties,<sup>3</sup> as well as superconductivity<sup>4</sup> and electronic transmissions within organisms,<sup>5</sup> are closely related to the mixed-valence phenomenon. Although mixed-valence compounds were produced by chemists a century ago for their unusual color and non-stoichiometric valence, there are only four mixed-valence manganese phosphates among hundreds of inorganic manga-

nese phosphates:  $\text{BiMn}^{\text{II/III}}_6\text{PO}_{12}$ ,<sup>6</sup> bermanite  $\text{Mn}^{\text{II}}(\text{H}_2\text{O})_4\text{[Mn}^{\text{III}}_2(\text{OH})_2(\text{PO}_4)_2]$ ,<sup>7</sup>  $\alpha\beta\alpha\text{-K}_3\text{Na}_{11}[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]\cdot 40\text{H}_2\text{O}$ <sup>8</sup> and  $\text{K}_{14}\text{Na}_{17}[(\text{Mn}^{\text{III}}_{13}\text{Mn}^{\text{II}}\text{O}_{12}(\text{PO}_4)_4(\text{PW}_9\text{O}_{34})_4)\cdot \sim 56\text{H}_2\text{O}]$ .<sup>9</sup> It is also noteworthy that all of these four compounds are the mixtures of  $\text{Mn}^{\text{II}}$  and  $\text{Mn}^{\text{III}}$ , although manganese has diverse valence chemistry:  $\text{Mn}^{\text{II}}$ ,  $\text{Mn}^{\text{III}}$ ,  $\text{Mn}^{\text{IV}}$ ,  $\text{Mn}^{\text{V}}$ ,  $\text{Mn}^{\text{VI}}$ ,  $\text{Mn}^{\text{VII}}$ , etc. High-valence manganese compounds have important applications in oxidation, catalysis and magnetism. However, the instability of high-valence manganese ions in aqueous solution makes the synthesis of these compounds difficult.

To the best of our knowledge, only a few dozen inorganic trivalent manganese phosphates<sup>10</sup> have been reported and there are no tetravalent or higher-valence manganese phosphates, with one exception being polyoxometalate.<sup>11</sup> Thus, in an attempt to enrich the structural chemistry of mixed-valence compounds and obtain high valence manganese compounds, we initiated a comprehensive synthesis program to explore manganese phosphates. The results reported herein demonstrate that we have succeeded in the synthesis of the first-ever, inorganic, mixed- and high-valence manganese phosphate with both  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{IV}}$ . Mixed  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{IV}}$  organic com-

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<sup>†</sup>Electronic supplementary information (ESI) available: The figures of experimental and simulated powder X-ray diffraction patterns, EDS/SEM images, TG-DTA, FT-IR and XPS. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00646e



pounds are not uncommon.<sup>12</sup> This mixed- and high-valence manganese phosphate  $\text{Mn}^{\text{III}}_6\text{F}_{12}(\text{PO}_3(\text{OH}))_8[\text{Na}_8(\text{K}_{3.74}(\text{H}_3\text{O})_{0.26}(\text{H}_2\text{O})_2)\text{Mn}^{\text{IV}}(\text{OH})_6]$  (denoted as **MN** hereafter) has been synthesized by using a water-deficient hydrothermal method and exhibits a three-dimensional (3D) open-framework structure containing clathrate-like  $\text{Na}_8(\text{K}_{3.74}(\text{H}_3\text{O})_{0.26}(\text{H}_2\text{O})_2)\text{Mn}^{\text{IV}}(\text{OH})_6$  guest clusters.

Of particular interest, the structure of the new mixed- and high-valence manganese phosphate resembles that of the clathrate compounds. Clathrates have been known for over two hundred years and are of growing interests for diverse applications from hydrogen storage<sup>13</sup> to superconductivity<sup>14</sup> and semiconductivity,<sup>15</sup> *etc.* These materials possess open framework structures with large cages in the crystal lattice, which can incorporate guest molecules. Previous studies showed that clathrate structures are commonly cubic.<sup>16</sup> The structure of the title compound **MN** is also cubic and is assembled by guest clusters residing in a 3D open framework. The +4 oxidation state of Mn in the guest cluster has been confirmed by the formation of isotopic Ti- and Ge-analogues,  $\text{Mn}^{\text{III}}_6\text{F}_{12}(\text{PO}_3(\text{OH}))_8[\text{Na}_8(\text{K}_{2.97}(\text{H}_3\text{O})_{1.03}(\text{H}_2\text{O})_2)\text{Ti}(\text{OH})_6]$  and  $\text{Mn}^{\text{III}}_6\text{F}_{12}(\text{PO}_3(\text{OH}))_8[\text{Na}_8(\text{K}_{2.79}(\text{H}_3\text{O})_{1.21}(\text{H}_2\text{O})_2)\text{Ge}(\text{OH})_6]$  (denoted as **TI** and **GE**), in synthesis experiments using  $\text{TiO}_2$  or  $\text{GeO}_2$  as starting materials as the replacement for  $\text{MnO}_2$ . All three isotopic fluorophosphates have been characterized by single X-ray diffraction (XRD) analysis, Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and magnetic studies.

## 2. Experimental section

### 2.1. Synthesis

Reactions of a transition metal fluoride with a phosphate source in a low-water containing, high-fluoride system have been proven to be a powerful route for synthesizing new fluorophosphate compounds.<sup>10,17–19</sup> Here we have synthesized the title compounds *via* a similar water-deficient hydrothermal route with phosphoric acid as the sole solvent. For **MN**, in a typical synthesis procedure, the starting materials of NaF (0.4 g, 9.5 mmol),  $\text{KPF}_6$  (0.8 g, 4.3 mmol) and  $\text{KMnO}_4$  (0.5 g, 3.2 mmol) were dissolved in  $\text{H}_3\text{PO}_4$  (85%, 1 mL, 14.6 mmol) without adding any water. The resulting mixture with the molar ratio of  $\text{NaF}:\text{KPF}_6:\text{KMnO}_4:\text{H}_3\text{PO}_4 = 3:1.3:1:4.6$  was transferred into a 25 mL Teflon-lined stainless-steel autoclave and heated at 240 °C for 3 days under static conditions. The resultant product is composed of crystals in highly viscous gel-like materials. Rosy-red truncated-octahedral crystals in high yields (above 90%, based on Mn, but poor quality) were isolated by filtering after the viscous materials were dissolved in deionized water for a few minutes.

Manganese ions of high oxidation states are well known to be unstable in acidic hydrothermal conditions, *e.g.*  $\text{KMnO}_4$  spontaneously decomposes to  $\text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$ . Consequently, the high valence  $\text{Mn}^{7+}$  ions are readily reduced to low valence ions such as  $\text{Mn}^{4+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$ . In contrast, low-

valence manganese ions (*i.e.*,  $\text{Mn}^{2+}$  or  $\text{Mn}^{3+}$ ) are relatively stable in hydrothermal conditions, and cannot be spontaneously oxidized to high valence ions. It is not possible to synthesize high valence manganese compounds using low valence manganese reactants as starting materials without the addition of high oxidant reagents. In other words, manganese in the starting materials must be tetravalent or higher in valence state in order to synthesize **MN** that contains both trivalent and tetravalent manganese.

As an alternative route for the synthesis of **MN**, we adopted a similar experimental method as above but used  $\text{MnO}_2$  (0.278 g, 3.2 mmol) instead of  $\text{KMnO}_4$  and with the addition of KCl (0.239 g, 3.2 mmol). This method did not produce a single phase but a mixture of high-quality single crystals of **MN** with minor amounts of  $\text{KMnF}_2(\text{PO}_3\text{F})$ .<sup>10</sup> The high-quality crystals of **MN** produced *via* this route are suitable for single crystal XRD analysis (see below). Further synthesis investigation shows that  $\text{Mn}_2\text{O}_3$  or  $\text{MnCl}_2$  instead of  $\text{MnO}_2$  resulted in water-soluble, highly viscous gel-like materials without **MN**. Runs using Mn-metal powder as a starting material produced a new compound  $(\text{K}_{0.59}(\text{H}_3\text{O})_{0.41}\text{Mn}^{\text{II}}(\text{P}(\text{O}_{0.5}\text{F}_{0.5})_3\text{OH})_2\text{Cl}_2)$ , to be reported elsewhere, supporting the above discussion that the synthesis of the title compound requires high-valence Mn in the starting materials. Hand-picked crystals used for further characterization were first confirmed by a powder X-ray diffraction (PXRD) analysis, which also indicated **MN** to be a new phase and is consistent with the calculated pattern from the single-crystal structure analysis below (Fig. S1†).

Additional synthesis experiments with Ti and Ge have been carried out to confirm that the title compound contains  $\text{Mn}^{\text{IV}}$  as suggested by the single-crystal structure analysis. It is interesting to note that synthesis experiments using the same ingredients and conditions as described above, plus additional  $\text{TiO}_2$  or  $\text{GeO}_2$  in the stoichiometric proportion, resulted in only the compound **MN** owing to the existence of  $\text{Mn}^{\text{IV}}$ . The Ti and Ge analogues of the title compound (denoted as **TI** and **GE** hereafter) were synthesized by using  $\text{Mn}_2\text{O}_3$  instead of  $\text{MnO}_2$ . In a typical synthesis experiment for the compound **TI**, NaF (0.4 g, 9.5 mmol),  $\text{KPF}_6$  (0.8 g, 4.3 mmol), KCl (0.239 g, 3.2 mmol),  $\text{Mn}_2\text{O}_3$  (0.216 g, 1.37 mmol) and  $\text{TiO}_2$  (0.036 g, 0.46 mmol) were dissolved in  $\text{H}_3\text{PO}_4$  (85%, 1 mL, 14.6 mmol). The molar ratio of  $\text{NaF}:\text{KPF}_6:\text{KCl}:\text{Mn}_2\text{O}_3:\text{TiO}_2:\text{H}_3\text{PO}_4$  was about 20.7:9.3:7.0:3.0:1.0:31.7. Finally, rosy-red truncated-octahedral crystals in high yields (about 90%, based on Ti) were obtained as a pure phase. For the compound **GE**, a similar recipe was used, except that  $\text{GeO}_2$  (0.048 g, 0.46 mmol) was added. Rosy-red truncated-octahedral crystals in high yields (about 90%, based on Ge) were also obtained. The PXRD patterns of both **TI** and **GE** are consistent with the calculated ones from the single-crystal X-ray diffraction analyses shown below, and confirm that they are isostructural with **MN** (Fig. S2 and S3†).

### 2.2. Characterization methodologies

The existence of the Na, K, Mn/Ti/Ge, P, O and F atoms in the title compounds was confirmed by the use of an Energy



**Table 1** Crystallographic data and single-crystal X-ray structure refinement results for the compounds **MN**, **TI** and **GE**

	<b>MN</b>	<b>TI</b>	<b>GE</b>
Formula sum, weight (g mol <sup>-1</sup> )	F <sub>12</sub> H <sub>18.78</sub> K <sub>3.74</sub> Mn <sub>7</sub> Na <sub>8</sub> O <sub>40.26</sub> P <sub>8</sub> , 1853.58	F <sub>12</sub> H <sub>21.10</sub> K <sub>2.97</sub> Mn <sub>6</sub> Na <sub>8</sub> O <sub>41.03</sub> P <sub>8</sub> Ti, 1831.03	F <sub>12</sub> GeH <sub>21.62</sub> K <sub>2.79</sub> Mn <sub>6</sub> Na <sub>8</sub> O <sub>41.21</sub> P <sub>8</sub> , 1852.21
Crystal size (mm <sup>3</sup> ), color	0.27 × 0.27 × 0.27, rosy-red	0.32 × 0.32 × 0.32, rosy-red	0.30 × 0.30 × 0.30, rosy-red
Crystal system, space-group	Cubic, <i>Fm</i> $\bar{3}$ (no. 202)	Cubic, <i>Fm</i> $\bar{3}$ (no. 202)	Cubic, <i>Fm</i> $\bar{3}$ (no. 202)
Cell parameters (Å)	<i>a</i> = 15.968(2)	<i>a</i> = 16.0001(2)	<i>a</i> = 15.981(7)
Cell volume (Å <sup>3</sup> ), <i>Z</i> , Calc. density (g cm <sup>-3</sup> )	4071.5, 4, 3.024	4096.05, 4, 2.969	4082, 4, 3.014
Rad., wavelength (Å), temp. (K)	MoK $\alpha$ , 0.71073, 173(2)	MoK $\alpha$ , 0.71073, 173(2)	MoK $\alpha$ , 0.71073, 173(2)
$\mu$ (mm <sup>-1</sup> ), <i>F</i> (000)	3.067, 3612	2.858, 3575	3.392, 3609
$2\theta_{\max}$ (°), <i>N</i> <sub>para</sub>	55.86, 43	59.49, 55	57.51, 55
Miller-index	$-20 \leq h \leq 13$ , $-21 \leq k \leq 20$ , $-17 \leq l \leq 20$	$-21 \leq h \leq 22$ , $-20 \leq k \leq 15$ , $-21 \leq l \leq 8$	$-21 \leq h \leq 21$ , $-21 \leq k \leq 9$ , $-20 \leq l \leq 20$
<i>R</i> <sub>int</sub> , <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.025, 0.033, 0.106	0.042, 0.036, 0.112	0.048, 0.042, 0.121
<i>S</i> , <i>N</i> , <i>N</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	1.184, 462, 394	1.144, 495, 409	1.100, 493, 424
Weight parameters ( <i>W</i> <sub>1</sub> , <i>W</i> <sub>2</sub> ) <sup>a</sup>	0.0597, 19.4949	0.0535, 8.1128	0.0648, 45.4995
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.780, -0.742	0.955, -0.495	1.317, -0.949

<sup>a</sup> Weight parameters ( $w = 1/[\sigma^2(F_o^2) + (W_1P)^2 + W_2P]$  where  $P = (F_o^2 + 2F_c^2)/3$ ) were used.

Dispersive X-ray Spectrometer (Oxford Instruments) (Fig. S4–6†). The powder samples checked by PXRD were used for thermal investigations, FTIR and XPS analyses and magnetic measurements. Thermal investigations were performed on a TG-209F1 thermogravimetric/differential thermal analyzer (TG-DTA) in a N<sub>2</sub> atmosphere with a heating rate of 10 K min<sup>-1</sup>. The FTIR spectra recorded were of powder samples mixed with KBr in pressed pellets on a Nicolet 330 FTIR spectrometer in the range of 400–4000 cm<sup>-1</sup>. XPS analyses were performed using a Physical Electronics Quantum 2000 scanning ESCA microprobe equipped with a standard focused monochromatic Al K $\alpha$  (1486.7 eV) X-ray source. Magnetic susceptibility was measured in the temperature range from 2 to 300 K, using a Quantum Design MPMS XL-7 SQUID magnetometer.

### 2.3. Crystal structure determination

Single crystals of the compounds **MN**, **TI** and **GE** were carefully selected on the basis of clarity and uniformity under a petrographic microscope and were glued onto a thin glass capillary for single-crystal X-ray diffraction analysis. Data collection was performed at 173(2) K, using a Bruker Apex CCD diffractometer or an Oxford Diffraction Xcalibur Sapphire 3 CCD diffractometer, equipped with a graphite-monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). A total of 6146 observed reflections were collected from  $2.21^\circ < \theta < 27.93^\circ$ , yielding 462 unique reflections (*R*<sub>int</sub> = 0.025) with 394 *I* > 2 $\sigma$ (*I*) for the compound **MN**. 2364 observed reflections were collected from  $3.60^\circ < \theta < 29.75^\circ$ , yielding 495 unique reflections (*R*<sub>int</sub> = 0.042) with 409 *I* > 2 $\sigma$ (*I*) for the compound **TI**. 6452 observed reflections were collected from  $2.21^\circ < \theta < 28.75^\circ$ , yielding 493 unique reflections (*R*<sub>int</sub> = 0.048) with 424 *I* > 2 $\sigma$ (*I*) for the compound **GE**.

The crystal structures of the compounds **MN**, **TI** and **GE** were solved in a cubic space group of *Fm* $\bar{3}$  by direct methods

and refined by the full-matrix least-squares method using the SHELXS-2014 and SHELXL-2014 software packages.<sup>20</sup> The final refinements converged at *R*<sub>1</sub> [*I* > 2 $\sigma$ (*I*)] = 0.033, 0.036 and 0.042, as well as *wR*<sub>2</sub> (for all) = 0.106, 0.112 and 0.121 for the compounds **MN**, **TI** and **GE**, respectively. Experimental details for the structure determinations are summarized in Table 1. Detailed information may be found in the ICSD (no. 429030–429032).

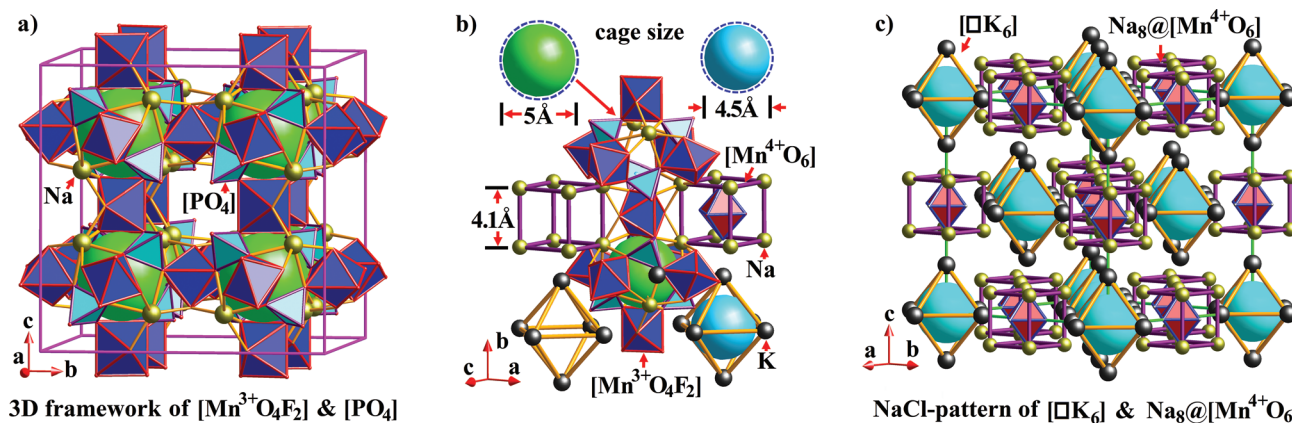
## 3. Results and discussion

### 3.1. Crystal structure description

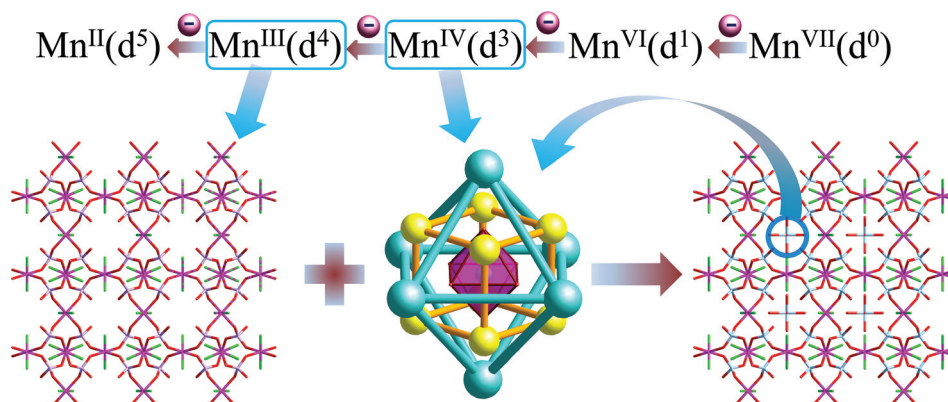
The crystal structures of the three compounds, **MN**, **TI** and **GE**, are isotypic and are characterized by [Mn<sup>III</sup>O<sub>4</sub>F<sub>2</sub>] octahedra sharing O-corners with [HPO<sub>4</sub>] tetrahedra to form a three-dimensional open-framework of {Mn<sup>III</sup><sub>6</sub>F<sub>12</sub>(PO<sub>3</sub>(OH))<sub>8</sub>}<sup>10-</sup> with an eight-membered ring channel running along the direction of <100>, in which the {Na<sub>8</sub>(K<sub>x</sub>(H<sub>3</sub>O)<sub>4-x</sub>(H<sub>2</sub>O)<sub>2</sub>)M<sup>IV</sup>(OH)<sub>6</sub>}<sup>10+</sup> (M = Mn, Ti, Ge) clusters are encapsulated.

In the crystal structure of **MN**, Mn ions of two different valences (BVS: 3.05 and 4.02 vu).<sup>21</sup> occur separately at two crystallographically distinct positions: Mn(1)<sup>3+</sup> and Mn(2)<sup>4+</sup> at Wyckoff 24d and 4b sites, respectively. Each Mn(1)<sup>3+</sup> ion is coordinated to four oxygen atoms at 2.066(2) Å and two fluorine atoms at 1.818(2) Å to form a compressed [Mn(1)<sup>3+</sup>O<sub>4</sub>F<sub>2</sub>] octahedron, whereas the Mn(2)<sup>4+</sup> ion is surrounded by six hydroxyl groups (OH) at 1.901(5) Å in a regular octahedron. The compressed [Mn(1)<sup>III</sup>O<sub>4</sub>F<sub>2</sub>] octahedron may suggest that the Mn<sup>3+</sup> ion adopts the high-spin electronic configuration of four unpaired 3d electrons with one electron in one e<sub>g</sub> (*i.e.*, dx<sup>2</sup> - y<sup>2</sup>) orbital. Each [Mn(1)<sup>III</sup>O<sub>4</sub>F<sub>2</sub>] octahedron links to four [HPO<sub>4</sub>] groups *via* the sharing of equatorial O-corners, and four bidentate Na<sup>+</sup> ions in the axial sides. The [HPO<sub>4</sub>] tetrahedron shares





**Fig. 1** The crystal structure of MN. (a) The framework composed of corner-sharing  $[\text{Mn}^{\text{III}}\text{O}_4\text{F}_2]$  and  $[\text{PO}_4]$ , with encapsulated cages that are located at the centers of the 8-minicubes of the cubic cell, as F in the fluorite ( $\text{CaF}_2$ ) structure; (b) illustration of the relationship of the framework, cages and guest clusters (the green spheres represent the encapsulated cages in the framework; and the cyan spheres denote the spaces surrounded by six K ( $\text{H}_3\text{O}$ )/ $\text{H}_2\text{O}$  ions); (c) guest clusters and potassium ions in channels arranged in a NaCl-type pattern.



**Fig. 2** Illustration of the relationship of the framework and guest clusters. Heptavalent  $\text{Mn}^{\text{VII}}(\text{d}^0)$  ions of the starting materials were reduced to low-valence ions: with tetravalent  $\text{Mn}^{\text{IV}}(\text{d}^3)$  ions in the guest clusters and trivalent  $\text{Mn}^{\text{III}}(\text{d}^4)$  ions forming the framework.

three O-corners, each with a different  $[\text{Mn}^{\text{III}}\text{O}_4\text{F}_2]$  octahedron, and has a terminal OH group. Each bidentate  $\text{Na}^+$  ion also links to three  $[\text{Mn}^{3+}\text{O}_4\text{F}_2]$  octahedra. Six neighboring  $[\text{Mn}^{\text{III}}\text{O}_4\text{F}_2]$  octahedra in octahedral distribution enclose a minicube cage, where four involved  $[\text{HPO}_4]$  groups and four bidentate  $\text{Na}^+$  alternately locate at the mini-cube corners in tetrahedral patterns. The mini-cube cage has a diameter of 5.0 Å (Fig. 1). By viewing along the direction of  $\langle 100 \rangle$ , three-dimensional (3D) interconnected channels contain a narrow 8-membered ring neck consisting of alternating four  $[\text{Mn}^{\text{III}}\text{O}_4\text{F}_2]$  octahedra and four  $[\text{HPO}_4]$  groups. The octahedrally distributed K/ $\text{H}_3\text{O}$  ions and water molecules (denoted as  $[\text{K}_6]$ ) and the  $[\text{Mn}^{\text{IV}}(\text{OH})_6]@[\text{Na}_8]$  clusters locate within the channels and are arranged in the positions of the NaCl-type structure (Fig. 1). Interestingly, the  $[\text{Mn}^{\text{IV}}(\text{OH})_6]@[\text{Na}_8]$  cluster is octahedrally surrounded by six potassium or water molecules to form a new  $[\text{MnO}_6]@[\text{Na}_8]@[\text{K}/\text{H}_2\text{O}]$  cluster in the channels. The  $[\text{Mn}^{\text{IV}}(\text{OH})_6]$  octahedra are not involved in the construction of the 3D open

framework structure, and are separated from the framework by  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{H}_2\text{O}$ . As such, the  $[\text{Mn}^{\text{IV}}(\text{OH})_6]$  octahedra and surrounding  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{H}_2\text{O}$  form a clathrate-like “guest cluster” of  $\text{Na}_8(\text{K}_x(\text{H}_3\text{O})_{4-x}(\text{H}_2\text{O})_2)\text{Mn}^{\text{IV}}(\text{OH})_6$  (Fig. 2).

### 3.2. Thermal properties

Thermal analysis of the compound **MN** shows that the first-step weight-loss of 2.32% at the temperature range of 250–450 °C in the TG curve (Fig. S7†) can be ascribed to the removal of  $2.39 \times \text{H}_2\text{O}$  per formula unit (calcd, 2.40%). The powder X-ray diffraction analysis shows that the solid residue of **MN** after annealing at 477 °C for 2 hours mainly consists of  $\text{Na}_2\text{MnPO}_4\text{F}$  with a minor amount of  $\text{KMnF}_3$  and an unidentified phase<sup>22,23</sup> (Fig. S8†).

### 3.3. Infrared spectroscopy

The FTIR spectra of the compounds **MN** and **TI** show similar absorption bands (see Fig. S9†). The peaks at 3439/3437  $\text{cm}^{-1}$





(medium, broad) can be attributed to the asymmetric O–H stretching, while the peaks at 1620/1640  $\text{cm}^{-1}$  (weak, broad) and 3599/3597  $\text{cm}^{-1}$  (sharp, weak) are assigned to the H–O–H bending mode. The free  $\text{PO}_4^{3-}$  ion with the perfect  $T_d$  symmetry has four normal modes:  $\nu_1(A_1)$ , the symmetric stretching mode,  $\nu_2(E)$ , the OPO symmetric bending mode, and  $\nu_3(F_2)$  and  $\nu_4(F_2)$ , the asymmetric stretching and bending modes, respectively (all Raman allowed, but only  $\nu_3$  and  $\nu_4$  IR allowed). The bands at 1151/1157 and 1023/1030  $\text{cm}^{-1}$  are attributable to the antisymmetric stretching mode ( $\nu_3$ ) of  $[\text{HPO}_4]$ , and those at 585/592 and 517/522  $\text{cm}^{-1}$  are ascribed to the antisymmetric bending mode ( $\nu_4$ ). Two inactive IR modes (*i.e.*,  $\nu_1$  &  $\nu_2$ ) are not observed, suggesting that the IR forbidden modes are not lifted, and this consistent with the high symmetry of the lattice. The band at 793/826  $\text{cm}^{-1}$ , which is beyond the ranges of occurrences for the four normal modes of  $[\text{HPO}_4]$ , may be attributed to the water librations.<sup>24</sup>

### 3.4. XPS analysis

X-ray photoelectron spectroscopic analysis (Fig. S10†) was performed to identify the oxidation states of manganese and confirm the existence of other elements (*i.e.*, Na, K, F, O, and P) in the compound **MN**. Fig. S10 shows that the XPS spectrum of **MN** exhibits two strong peaks at 642.5 and 653.9 eV in the energy region of Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub>, respectively. The distance between the two main peaks is about 11.4 eV, which may suggest that the manganese mainly has an oxidation state at +3.<sup>25,26</sup> It is noteworthy that the BVS calculations suggest only one Mn<sup>4+</sup> ion but six Mn<sup>3+</sup> ions per formula unit in the compound **MN**, and thus the signal of the former in the XPS spectrum is probably overshadowed by the much more abundant Mn<sup>3+</sup>.

### 3.5. Magnetic properties

Compounds **MN** and **TI** show linear Curie–Weiss behavior in the  $\chi^{-1}$  vs.  $T$  data in the entire 2–300 K temperature range, yielding  $C_1 = 20.33 \text{ emu K mol}^{-1}$ ,  $\theta_{C_1} = -2.2 \text{ K}$  and  $C_2 = 18.35 \text{ emu K mol}^{-1}$ ,  $\theta_{C_2} = -2.7 \text{ K}$ , respectively (Fig. 3). The observed effective moment  $\mu_{\text{eff}1} = 12.75\mu_B$  for the compound **MN** is in excellent agreement with the predicted value of  $12.61\mu_B$ , assuming a spin-only  $J$  value for one Mn<sup>4+</sup> and six high-spin Mn<sup>3+</sup> ions. Considering the d<sup>0</sup> state of Ti<sup>4+</sup>, the observed effective moment  $\mu_{\text{eff}2} = 12.11\mu_B$  for the compound **TI** is also in good agreement with the predicted value of  $12.00\mu_B$ , assuming a spin-only  $J$  value for six high-spin Mn<sup>3+</sup> ions. Weak anti-ferromagnetic (AF) Mn–Mn interactions are expected to predominate in both compounds, which explains the small negative Weiss temperatures, as observed. The gradual increase in the  $\chi T$  product *versus* temperature also conforms to the AF couplings.

### 3.6. Structural flexibilities and stabilities

The ideal phosphate ion,  $\text{PO}_4^{3-}$ , has four O<sup>2-</sup> ions arranged at the corners of a regular tetrahedron. In the compound **MN**, however, each phosphorus atom is split into two positions, and correspondingly, one of the oxygen atoms is also distribu-

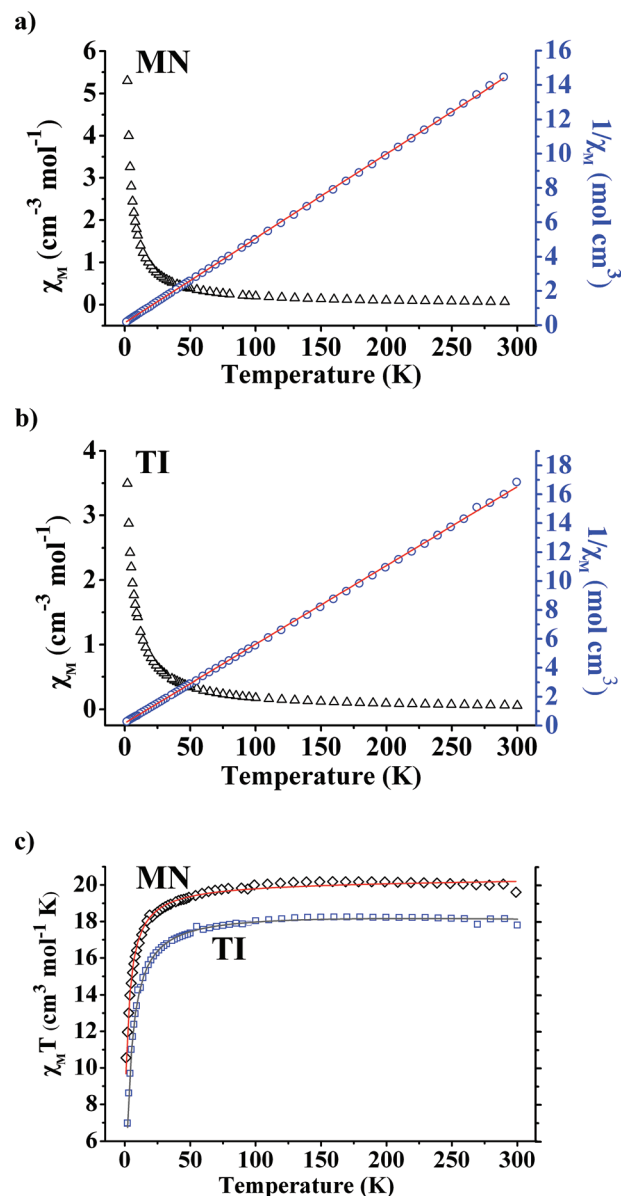


Fig. 3 Magnetic properties of the compounds **MN** and **TI**. Magnetic susceptibility ( $\chi_M$ ) and reciprocal susceptibility ( $\chi^{-1}$ ) vs. temperature at 1000 Oe for **MN** (a) and **TI** (b), respectively; their  $\chi_M T$  product vs. temperature (c).

ted in two sites. This disordered distribution of the  $[\text{HPO}_4]$  tetrahedron is supposedly caused by self-adjusting of the fundamental building units for fitting the whole structure. As described above, the “guest cluster” of  $[\text{Mn}^{\text{IV}}(\text{OH})_6]$  in the channel can be substituted by  $[\text{Ge}(\text{OH})_6]$  or  $[\text{Ti}(\text{OH})_6]$  to form the isotypic compounds of **TI** and **GE**. In both compounds **TI** and **GE**, there is a small residue peak observed around the P-positions, suggesting that a slight disorder of the  $[\text{HPO}_4]$  tetrahedra also occurs in **TI** and **GE**. However, the occupancies of the disordered P atoms are less than 5% in those compounds; they can be considered to be in an almost fully ordered arrangement. In contrast to **MN**, the P atoms in **TI** and **GE** are



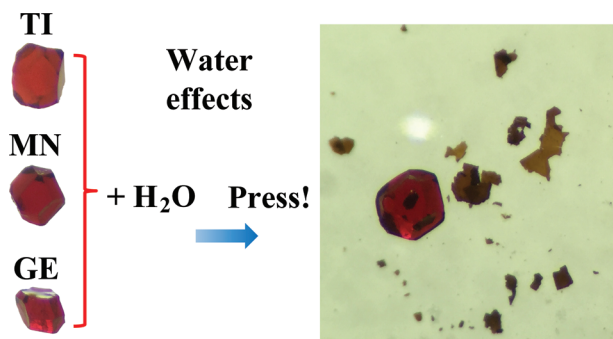


Fig. 4 Illustration of the decomposition of the title compounds in water. All crystals of MN, TI and GE peeled off layer-by-layer after soaking in aqueous solution for 1 hour.

nearly fully ordered in the framework, but the “guest clusters” in the channel are disordered. Every oxygen atom (24e) in the  $[\text{Ti}^{\text{IV}}(\text{OH})_6]$  or  $[\text{Ge}^{\text{IV}}(\text{OH})_6]$  octahedron is split into three positions: at Wyckoff 24e, 48h and 48h sites, respectively. So the crystal structures of the title compounds have high structural flexibilities, which are tuned by order and disorder alteration.

It is interesting to note that the crystals of MN, TI and GE are highly unstable in aqueous solution. When the crystals were soaked in water for one hour, they were peeled off layer-by-layer along  $\{100\}$  and  $\{111\}$  after being pressed slightly (Fig. 4). This pattern of dissolution is observed in all three title compounds, MN, TI and GE, and suggests a preferential removal of the channel constituent oriented along  $\{100\}$ . This suggestion is further supported by the presence of minor crystalline  $\text{Na}(\text{OH})$  and  $\text{K}_2\text{SiF}_6$  in the dissolved glassware, although the majority of the solid dissolution products from the title compounds are amorphous (Fig. S11†). Such instability of the title compounds in aqueous solution is not unexpected and is consistent with the fact that high-valence manganese phosphates cannot be synthesized under normal hydrothermal conditions. The successful syntheses of the title compounds in the present study are attributable to our usage of phosphoric acid as the sole solvent under water-deficient hydrothermal conditions. Our previous works have shown that the water content is a crucial factor in the synthesis of other chloride,<sup>27</sup> phosphate<sup>28</sup> and borate<sup>29</sup> compounds.

## 4. Conclusions

In this paper, we have demonstrated three isotypic new compounds:  $\text{Mn}^{\text{III}}\text{F}_{12}(\text{PO}_3(\text{OH}))_8[\text{Na}_8(\text{K}_x(\text{H}_3\text{O})_{4-x}(\text{H}_2\text{O})_2)\text{M}^{\text{IV}}(\text{OH})_6]$  ( $\text{M}^{\text{IV}} = \text{Mn}, \text{Ti}, \text{Ge}$ ). The first-ever, mixed- and high-valence manganese fluorophosphate with both  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  has been synthesized by a water-deficient hydrothermal method with phosphoric acid as the sole solvent. This compound features a clathrate-like structure with a cubic three-dimensional open-framework structure encapsulating the unprecedented  $\text{Na}_8(\text{K}_{3.74}(\text{H}_3\text{O})_{0.26}(\text{H}_2\text{O})_2)\text{Mn}^{\text{IV}}(\text{OH})_6$  guest clusters in the channels. Successful syntheses of the isotypic compounds TI and

GE confirm the presence of  $\text{Mn}^{4+}$  in the guest clusters. This report provides a new hydrothermal route for the synthesis of mixed- and high-valence manganese compounds.

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