Synthetic analogues of Fe(II)–Fe(III) minerals containing a pentagonal 'Cairo' magnetic lattice†

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Versiliaite and apuanite are two minerals containing Fe²⁺ and Fe³⁺ in a low-dimensional structure exhibiting chains of edge-linked FeO₆ octahedra. The chemistry of these minerals has not been fully examined because of their rarity. We demonstrate that chemical synthesis of these minerals is possible to allow measurement of their magnetic properties and a more complete description of their structural features using neutron powder diffraction. We also show that chemical manipulation is possible to provide isostructural phases with different chemical compositions.

The structural formulae can be better represented as [Fe₆]₄⁺[Fe₂,Sb₁₂]₁³⁺O₁₃S₂₉ and [Fe₁₂]₆⁻[Fe₉Sb₁₆]₁²⁻O₄₈S₄₉, respectively (cf. [Fe]⁶⁺[Sb]₁²⁻O₄ for schafarzikite). Since adjacent tetrahedral layers correspond to a 90 degree rotation of the Fe₁–S–Fe₁ links, versiliaite (with an even repeat) has orthorhombic (Pbam) symmetry, while odd-repeating apuanite has tetragonal (P4₃/mnc) symmetry.

The parent mineral schafarzikite, Fe₅Sb₂O₄, shows A-type antiferromagnetic (AFM) order where the Fe magnetic moments align ...+−+−+−... within a given chain and are directed perpendicular to [001] of the tetragonal structure. We have recently shown that partial oxidation of Fe²⁺ to Fe³⁺ by the substitution of Pb²⁺ for Sb³⁺, results in a change in magnetic order to C-type where the magnetic moments within a chain are ferromagnetically (FM) aligned parallel to [001], but neighbouring chains are anti-parallel. In fact, mixed-valence can provide a range of interesting properties in materials such as metal-insulator transitions, structural phase transitions in addition to unusual magnetic properties. Despite the interesting low-dimensional structures of versiliaite and apuanite, and the presence of Fe²⁺/Fe³⁺, their rarity has restricted our knowledge of their chemistry except for their structures. This is unfortunate since a key feature of the structures is the presence of magnetic Fe³⁺ ions substituting for diamagnetic Sb³⁺ ions where interstitial S²⁻ ions occupy channel sites: the resulting Fe–S–Fe would be expected to enhance the interchain magnetic exchange interactions which could result in a more complex range of interactions and possibly frustration. Magnetic frustration is found in many materials, and is of great fundamental interest. It generally originates from triangular (or tetrahedral) arrangements of magnetic ions, such as in the Kagomé lattice, which occurs in a number of structures such as pyrochlores. An alternative route to magnetic frustration is by tessellation of irregular pentagons such as occurs in the so-called ‘Cairo’ lattice. While widely used in art, this packing is
relatively rare in crystallography, the most well-known structure exhibiting this motif being that of mullite (Al₆Si₂O₁₃). The magnetic analogue Bi₂Fe₄O₉ (and related compounds) are currently the nearest examples of a 2D Cairo lattice exhibiting magnetic frustration. A number of theoretical magnetic ground states have been predicted for this 2D lattice, but few have been experimentally realised.

Here we report the first chemical synthesis of apuanite and versiliaite which will now allow the exploration of their properties and their ability to undergo chemical manipulation to target specific features. For the first time, we report the magnetic structures of the minerals and compare with our synthetic analogues. As a result of the Fe–S–Fe links, the structures show a rare, pentagonal lattice of magnetic ions which provides a relatively high temperature antiferromagnetism, and a magnetic structure exhibiting geometric frustration. We also demonstrate that atomic substitution is possible within these materials, by synthesising a Mg-containing versiliaite-like phase, Mg₄Fe₈Sb₁₂O₃₂S₂.

**Experimental**

Samples were synthesised from stoichiometric amounts of Fe₂O₃, Fe metal, MgO, Sb₂O₃ and Sb₂S₃ (all >99%, Aldrich), ground and heated within sealed quartz ampoules between 520 °C and 600 °C for between 48 hours and 1 month, with intermediate grinding. Slow cooling was necessary in order to minimise structural disorder. Phase purity was checked with laboratory X-ray powder diffraction (XRPD) equipment (Bruker D2 [Co Kα] and Bruker D8 [Cu Kα], both with PSD LynxEye detector). Neutron powder diffraction (NPD) data were collected at Institut Laue-Langevin (D2B diffractometer, \( \lambda = 1.594 \) Å), Paul-Scherrer Institute (HRPT instrument, \( \lambda = 1.494 \) Å and 1.886 Å) and the ISIS facility, UK (GEM diffractometer, TOF) at a range of temperatures in He cryostats. Refinements were performed using GSAS with the EXPGUI interface. Mineralogical samples were obtained from Systematic Mineralogy and removed from parent dolomite samples using a mineral drill. XRPD showed a small amount of residual dolomite within the samples.

Magnetic susceptibility measurements were obtained using a Quantum Design MPMS under field-cooled (FC) and zero-field-cooled (ZFC) conditions, with an applied magnetic field of 500 Oe. Powdered sample was loaded into a gelatin capsule, and sample movement was suppressed using a small amount of PTFE tape. No diamagnetic correction was applied to the data.

**Results and discussion**

The synthesised products were analysed initially using XRPD data, which revealed close agreement with data from mineral samples, although the latter were found to be contaminated with small amounts of dolomite. Fig. 2 compares synthetic and naturally-occurring apuanite and highlights the main peak from dolomite. Rietveld refinement profiles against XRPD data are given in Fig. S1 and S2, ESI† Refinement against NPD data (Fig. 3 and S3 in ESI†) revealed only small impurities: both versiliaite and apuanite samples contained a small amount of Fe₃O₄ impurity (1.27(4) wt% and 1.55(4) wt%, respectively) whilst apuanite also showed a small α-Fe₂O₃
impurity (2.23(6) wt%). Structure refinement was based on the reported mineral structures.\textsuperscript{1,2} Incomplete order of the sulfide ions was suggested by a degree of broadening of some diffraction peaks, anisotropic peak broadening and some weakened reflections. This effect has previously been observed in mineralogical samples.\textsuperscript{3} The bond valence sums for the Fe sites are also consistent with such partial disorder (vide infra); the order is enhanced by long reaction times. The structural data presented here were from a sample that was heated for ca. 30 days at 530 °C. The disorder was modelled in the refinements using anisotropic peak broadening for high-resolution diffraction data. Correction for anisotropic peak broadening was found to be necessary for HRPT (PSI) and D2B (ILL) data, but not for GEM (ISIS) data.

Refinements show similar results to previous single crystal diffraction studies from mineral samples; slight differences are expected due to the dispersion of impurities in the natural samples. Table 1 shows the unit cell sizes for 298 K data [Tables of coordinates are available in ESI\textsuperscript{†}].

Bond valence sums (BVS)\textsuperscript{11} (Table 2) clearly show that the tetrahedral iron site (Fe1) is trivalent, as expected. The valences of the other two sites are less clear, but are consistent with local charge-balance considerations: a fully ordered structure has divalent Fe2 and trivalent Fe3 since the latter site is closer to the FeO\textsubscript{3}S-containing layers. Deviations from ideal BVS values for the Fe2 and Fe3 sites reflect a small degree of disorder with respect to the sulfide ions.

Magnetic susceptibility for synthetic compounds is dominated by the Verwey transition in Fe\textsubscript{3}O\textsubscript{4} due to the substantial moment change at this 120 K transition compared to the overall magnetic moment of the main phase (Fig. 4). This is observed despite the rather small level of contamination and

\begin{table}[h]
\centering
\caption{Unit cell parameters from NPD data}  
\begin{tabular}{l c c c c c c c}
\hline
 & Versiliaite [ref. 2] & Apuanite [ref. 2] \\
\hline
$\alpha$/Å & 8.4460(4) [8.492(5)] & 8.3825(3) [8.372(5)] \\
b/Å & 8.3155(3) [8.326(5)] & — \\
c/Å & 11.9281(3) [11.938(7)] & 17.9787(7) [17.97(1)] \\
$x^2$, $R_p$ & 2.986, 3.39% & 1.858, 3.69% \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{BVS for synthetic and mineral data (interpolation of 2+ and 3+ values). Mineral data derived from XRD data in ref. 2}  
\begin{tabular}{l c c c c c c}
\hline
 & Versiliaite & Site & 298 K & 5 K & Mineral (298 K) \\
\hline
Fe1 & 3.109 & 3.131 & 2.705 \\
Fe2 & 2.450 & 2.494 & 2.235 \\
Fe3 & 2.811 & 2.813 & 3.107 \\
\hline
 & Apuanite & Site & 1.5 K & \\
\hline
Fe1 & 2.910 & 3.030 & 2.772 \\
Fe2 & 2.375 & 2.332 & 2.196 \\
Fe3 & 2.937 & 2.906 & 3.114 \\
\hline
\end{tabular}
\end{table}
conditions. Susceptibility of mineralogical samples (Fig. 4c) show a weak transition at a slightly higher temperature than this, as well as a significant deviation from the Curie-Weiss fit occurring at ca. 170 K and 190 K for versiliaite and apuanite, respectively; these temperatures correspond to the onset of long-range magnetic order from NPD (vide infra). All transitions occur over a broad temperature range, suggesting low-dimensional behaviour. The low-temperature upturn in both mineral samples can be attributed to paramagnetic impurities within the geological material. Curie-Weiss fits to the paramagnetic region give high-temperature effective moments of 5.69μB and 5.13μB per Fe for versiliaite and apuanite, in reasonable agreement with the expected spin-only values (5.58μB and 5.71μB, respectively). Weiss constants of −160 K and −217 K demonstrate dominant antiferromagnetic (AFM) exchange at high temperature.

Neutron diffraction from synthetic samples shows development of long range magnetic order below approximately 160 K for versiliaite, while for apuanite, broad magnetic peaks (corresponding to short-range ordering) are observed up to 210 K (Fig. 5). Both of these temperatures are similar in magnitude to the Weiss constants obtained from magnetic susceptibility data in the minerals. This is somewhat surprising given the presence of Cairo linkages highlighted in Fig. 1e. However, the direct exchange between the Fe centres within the chains appears very strong which may reduce the impact of the inherent frustration caused by the Fe–S–Fe linkages. The magnetic structures of both synthetic compounds can be indexed with a propagation vector \( k = [0.5, 0.5, 0] \), with all magnetic moments oriented in the \( ab \)-plane. The complex magnetic order is shown in Fig. 6. The Fe1–S–Fe1 linkages show AFM alignment in accordance with simple superexchange arguments; however, the best fit was obtained with adjacent linkages in a given \( ab \)-plane arranged at 90° to each other (Fig. S4 and S5, ESI†). In versiliaite, the Fe1 moments point along the nuclear \( a \)- or \( b \)-axes; in apuanite, the exact orientation is unknown due to the metrically tetragonal symmetry observed from neutron diffraction. During refinement, the Fe1 moments were therefore constrained to align in the same directions as versiliaite. In both structures, adjacent sulfur-containing layers along the \( c \)-axis exhibit parallel spins, such that any two Fe1 sites linking the same two octahedral chains are parallel. In both structures, moments within each octahedral chain display ferromagnetic (FM) alignment, directed approximately along an Fe1–S–Fe1 linkage direction. In the refined model, nearest-neighbour octahedral chains show FM order along the nuclear [110]\(_{\text{nuc}}\) direction, but AFM order along [110]\(_{\text{nuc}}\). The results (Table 3) were obtained using a single constrained moment for both Fe2 and Fe3 sites; without this constraint, the refined moments remained identical within error, but produced a less stable refinement.

The refined magnetic model is very similar to that found in Bi\(_2\)Fe\(_4\)O\(_9\) (ref. 7) and recently in Bi\(_2\)Fe\(_3\)–Cr\(_2\)O\(_6\). However, the moments in the latter are canted away from the \( ab \) plane and the chain moments in the former are modulated along both [110]\(_{\text{nuc}}\) and [110]\(_{\text{nuc}}\) directions. A similar model applied to the materials studied here does not fit as well, although the primary difference from powder diffraction would be in the
magnetic peak, which unfortunately coincides with the Fe$_3$O$_4$ (001) peak. However, the deduced magnetic model corresponds closely with the magnetic order theoretically predicted if the coupling between the Fe1 (tetrahedral) sites is stronger than between Fe1 and Fe3.\(^\text{12}\)

In addition to synthetic analogues of versiliaite and apuanite discussed above, we have also demonstrated that chemical modification, e.g. cation substitutions, are possible. For example, the versiliaite analogue Mg$_4$Fe$_8$Sb$_{12}$O$_{32}$S$_2$, where Mg$^{2+}$ ions replace all Fe$^{2+}$ ions, has been successfully syn-

**Fig. 5** Development of magnetic reflection intensity (measured on warming) in (a) synthetic versiliaite measured at 298 K, 150 K, 50 K, 20 K and 1.5 K, and (b) synthetic apuanite measured at 298 K, 210 K, 170 K, 150 K, 130 K, 120 K, 100 K, 80 K, 40 K and 5 K.

**Fig. 6** Refined magnetic structures for (a) versiliaite, (b,c,d) apuanite. (c) and (d) show magnetic moment alignment in sulfur-containing layers at $z = 0$ and $z = 0.5$, respectively. The nuclear unit cell is marked in red in (a).
Table 3  Refined magnetic moments from NPD: components along the magnetic unit cell axes \( (M_x, M_y) \) and total moment \( (M_{\text{tot}}) \)

|       | Versiliaite \( (5 \text{ K}) \) | Apuanite \( (1.5 \text{ K}) \) | \( \text{Mg}_2\text{Fe}_2\text{Sb}_{12}\text{O}_{32}\text{S}_2 \) \( (5 \text{ K}) \) |
|-------|-------------------------------|----------------------------|-------------------------------------------------|
| Fe1   | \( M_x, M_y \) (\( \mu_B \)) | 2.8(1), 2.68(9)            | 1.70(3), 1.70(3)                                |
|       | \( M_{\text{tot}} \) (\( \mu_B \)) | 3.89(7)                    | 2.41(5), 3.4(4)                                 |
| Fe2/3 | \( M_x, M_y \) (\( \mu_B \)) | 2.13(2), 2.13(3), 3.39(2), 3.20(1), 3.03(1) |
|       | \( M_{\text{tot}} \) (\( \mu_B \)) | 3.57(4)                    | 4.36(3), 3.7(1)                                 |

Fig. 7 Magnetic susceptibility for Mg-substituted versiliaite, \( \text{Mg}_2\text{Fe}_2\text{Sb}_{12}\text{O}_{32}\text{S}_2 \), showing ZFC (red squares) and FC (black circles) data.

Conclusions

We have shown that the rare minerals versiliaite and apuanite can be synthesised using a simple sealed-tube approach. The crystal structures are in close agreement with mineralogical samples. Moreover the successful synthesis of a Mg-substituted versiliaite confirms that the synthetic method will facilitate chemical manipulations in order to explore how the interesting low-dimensional structure may be utilised to provide specific functional properties. Magnetically, the materials studied here exhibit AFM order at relatively high temperatures, although they show magnetic development over a broad temperature range. The arrangement of magnetic ions represents a new class of compounds containing a Cairo-lattice motif, and orders as expected from theoretical models. The significant difference between these compounds and existing Cairo lattices (such as for \( \text{Bi}_2\text{Fe}_3\text{O}_9 \)) is that the Cairo layers are much more isolated in versiliaite and apuanite, with interlayer distances of \( \sim 12 \) Å and \( \sim 9 \) Å, respectively (compared to \( \sim 3 \) Å in \( \text{Bi}_2\text{Fe}_3\text{O}_9 \)). Chemical substitutions may result in greater magnetic isolation between Cairo layers, and a useful route to study frustrated magnetism on a non-triangular lattice.

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References

1. M. Mellini, S. Merlino and P. Orlandi, *Am. Mineral.*, 1979, 64, 1230.
2. M. Mellini and S. Merlino, *Am. Mineral.*, 1979, 64, 1235.
3. M. Mellini, *Am. Mineral.*, 1981, 66, 1073.
4. J. R. Gavarrì, J. P. Vigouroux, G. Calvarin and A. W. Hewat, *J. Solid State Chem.*, 1996, 138, 210.
5. M. J. Whitaker, R. D. Bayliss, F. J. Berry and C. Greaves, *J. Mater. Chem.*, 2011, 21, 14523.
6. R. Moessner and A. P. Ramirez, *Phys. Today*, 2006, 59, 24.
7. E. Ressouche, V. Simonet, B. Canals, M. Gospodinov and V. Skumryev, *Phys. Rev. Lett.*, 2009, 103, 267204.
8. M. G. Rozova, V. V. Grigoriev, I. A. Bobrikov, D. S. Filimonov, K. V. Zakharov, O. S. Volkova, A. N. Vasiliev, A. A. Tsirlin and A. M. Abakumov, *Dalton Trans.*, 2016, 45, 1192.
9. C. Larson and R. B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, 2000.
10. H. Toby, *J. Appl. Crystallogr.*, 2001, 34, 210.
11. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, 41, 244.
12. I. Rousochatzakis, A. M. Lauchli and R. Moessner, *Phys. Rev. B: Condens. Matter*, 2012, 85, 104415.
13. R. D. Shannon, *Acta Crystallogr.*, 1976, A32, 751.