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Synthetic versiliaite and apuanite: investigation by ^{57}Fe Mössbauer spectroscopy

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Abstract The minerals versiliaite and apuanite have been synthesised for the first time. The ^{57}Fe Mössbauer spectra recorded at 298 and 4 K are reported. The results are indicative of a formulation for versiliaite as $\left(Fe_4^{2+}Fe_4^{3+}\right)^{oct}\left[Fe_4^{3+}Sb_{12}^{3+}\right]^{tet}O_{32}S_2$ and of apuanite as $\left(Fe_4^{2+}Fe_8^{3+}\right)^{oct}\left[Fe_8^{3+}Sb_{16}^{3+}\right]^{tet}O_{48}S_4$. The spectra recorded at low temperature are indicative of complex magnetic interactions. The results indicate the potential for the synthesis of further new structurally-related materials with different compositions and new low dimensional physical properties.

Keywords Versiliaite · Apuanite · Mössbauer spectroscopy

1 Introduction

The mineral schafarzikite of composition $FeSb_2O_4$ consists of rutile-related chains of FeO_6 octahedra along the *c*-axis linked by trigonal pyramidal Sb^{3+} cations which, being bound to three oxygen ions, possess a lone pair of electrons which can be envisaged as a fourth ligand [1, 2] (Fig. 1). The Fe-Fe distance within the chains (2.96 Å) is shorter than the nearest Fe-Fe distance within the layers (6.07 Å) and is consistent with some one-dimensional character in
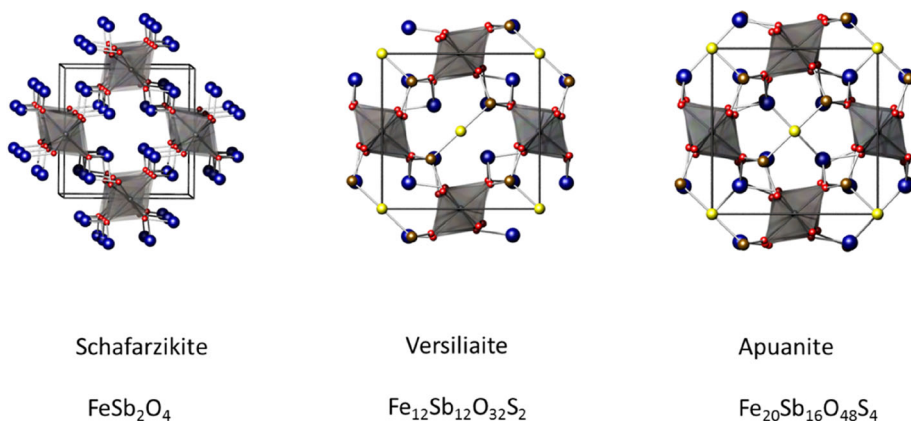
Fig. 1 Representations of the structures of schafarzikite, versiliaite and apuanite. *Grey spheres =* octahedral iron, *gold spheres =* tetrahedral iron, *blue spheres =* antimony, *yellow spheres =*sulphur and *red spheres =* oxygen

$FeSb_2O_4$. As a part of our interest in the synthesis of natural materials and the manipulation of their compositions, structures and physical properties we have previously reported on the synthesis of both $FeSb_2O_4$ and of $FeSb_{2-x}Pb_xO_4$ in which lead substitutes for antimony in the schafarzikite structure [3]. We have also shown [4, 5] how ^{57}Fe- and ^{121}Sb-Mössbauer spectroscopy has elucidated the relative strengths and interplay of electronic quadrupole- and magnetic- interactions of Fe^{2+} and Fe^{3+} in these materials. We are, in these studies, seeking to demonstrate the possibility of functionalising low dimensional structures to allow control of the oxidation states of the transition metals within the octahedral chains and identify opportunities for the synthesis of new compounds with essentially one-dimensional electronic characteristics.

Two minerals with structures closely related to that of schafarzikite and which offer such possibilities are versiliaite of composition $Fe_{12}Sb_{12}O_{32}S_2$ and apuanite of formula $Fe_{20}Sb_{16}O_{48}S_4$ [6, 7] (Fig. 1). In versiliaite and apuanite pairs of antimony ions in the schafarzikite structure are replaced by iron and linked by a sulphur bridge. The S^{2-} ions in versiliaite and apuanite are located in the empty channels of the schafarzikite structure and effectively substitute for some of the lone pairs on the Sb^{3+} ions.

In an extension of our previous work on synthetic scahafarzikite-related phases we have now synthesised for the first time samples of versiliaite and apuanite and are engaged in an examination of their structural and magnetic properties before seeking to manipulate their compositions and properties. As a part of these initial investigation we have recorded ^{57}Fe Mössbauer spectra from synthetic versiliaite and apuanite and we report on these spectra here.

2 Experimental

Versiliaite and apuanite were synthesised from stoichiometric amounts of Fe_2O_3, Fe metal, Sb_2O_3 and SbS_3 which were ground and heated within sealed quartz ampoules between 520 and 600 °C for between 48 h and 1 month with intermediate grinding. All products were slowly cooled to room temperature. The purity of the phases was determined by
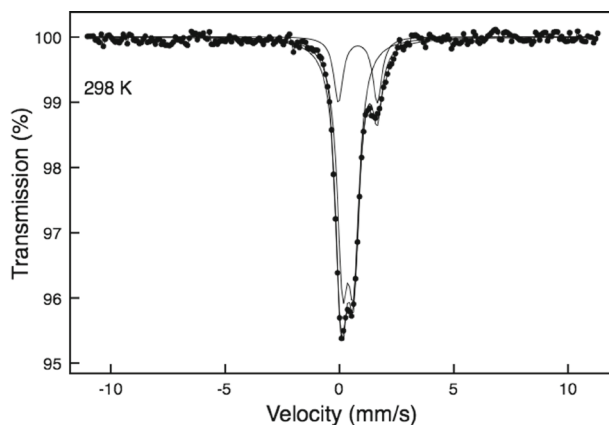
Fig. 2 ^{57}Fe Mössbauer spectrum recorded at 298 K from synthetic versiliaite

X-ray powder diffraction at 298 K with a Bruker D8 diffractometer using Cu K$_{\alpha 1}$ radiation and a Bruker D2 diffractometer using Co K$_\alpha$ radiation. Neutron powder diffraction data were collected at Institut Laue-Langevin (D25 diffractometer), Paul-Scherrer Institute (HRPT instrument) and the ISIS facility (GEM diffractometer). ^{57}Fe Mössbauer spectra were recorded at 298 and 4 K in constant acceleration mode using *ca.*25 mCi ^{57}Co/Rh sources. The spectrum recorded from the sample at 4 K used a helium gas-flow cryostat. All spectra were computer fitted and all chemical isomer shift data are quoted relative to metallic iron at room temperature.

3 Results and discussion

Neutron powder diffraction showed that the synthesised versiliaite and apuanite samples contained a small amount of Fe_3O_4 impurity (1.27(4) wt% and 1.55(4) wt% respectively) whilst apuanite also contained a small (2.23(6) wt%) Fe_2O_3 impurity.

3.1 Versiliaite

The ^{57}Fe Mössbauer spectrum which we recorded here at 298 K from synthetic versiliaite is shown in Fig. 2. The ^{57}Fe Mössbauer parameters are collected in Table 1. The spectrum recorded from synthetic versiliaite is very similar to that recorded previously from a mineral sample [8] and was best fitted to two components characteristic of Fe^{2+} (21 %) and Fe^{3+}(79 %) (Table 1). The Fe^{3+} doublet may be assigned to Fe^{3+} substituting onto the pyramidal Sb^{3+} sites of the schafarzikite structure forming FeO_3S tetrahedral units together with additional Fe^{3+} which arise from the oxidation of some Fe^{2+} ions in the octahedral sites of the rutile-related chains which is necessary to maintain charge balance caused by the insertion of the S^{2-} ions. The Fe^{2+} doublet relates to the unoxidised Fe^{2+} in the six coordinate sites. The concentrations of Fe^{2+} and Fe^{3+}recorded in the spectrum from the mineral sample were 32 and 68 % respectively which are more in line with the expected distribution of these cations in versiliaite of 33.3 and 66.6 %. The difference may indicate that, despite long heating and slow cooling regimes, the synthetic anologue does not exactly replicate the mineral formed over many years on a geological time scale. However, taken together

Table 1 ^{57}Fe Mössbauer parameters recorded from synthetic versiliaite and apuanite

Temperature K		$\delta \pm 0.04$ mms^{-1}	Δ or $e^2qQ/2 \pm 0.02$ mms^{-1}	$H \pm 0.5$ T	Area ± 5 %
Versilaite					
298	Fe^{2+}	0.80	1.70		21
	Fe^{3+}	0.38	0.49		79
4	Fe^{2+}	1.30	0.00	13.0	17
	Fe^{3+} tet	0.37	−0.03	44.3	40
	Fe^{3+} oct	0.53	−0.07	51.0	43
Apuanite					
298	Fe^{2+}	0.88	1.97		23
	Fe^{3+} tet	0.25	0.45		30
	Fe^{3+} oct	0.45	0.44		47
4	Fe^{2+}	1.50	−0.08	32.8	16
	Fe^{3+} tet	0.32	−0.08	43.2	32
	Fe^{3+} oct	0.46	−0.04	50.1	52
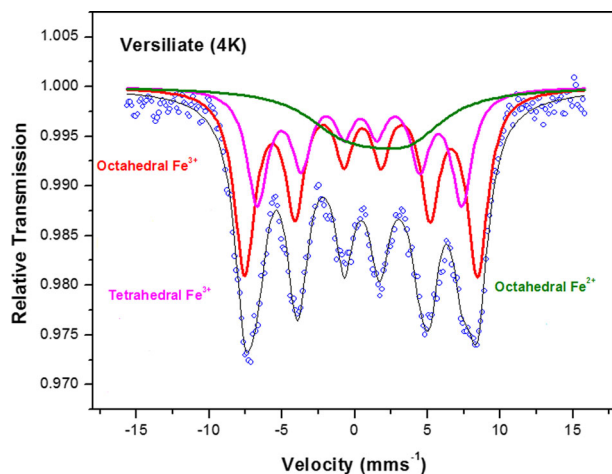
Fig. 3 ^{57}Fe Mössbauer spectrum recorded at 4 K from synthetic versiliaite

the results are consistent with the structural description of versiliaite involving the substitution of every fourth Sb^{3+} cation in the pyramidal chains of the scahfarzikite structure by an Fe^{3+} ion and the insertion of sulphide anions with corresponding oxidation of Fe^{2+} and is consistent with the formulation of versiliaite as $Fe_4^{2+}Fe_8^{3+}Sb_{12}^{3+}O_{32}S_2$.

The ^{57}Fe Mössbauer spectrum recorded from synthetic versiliaite at 4 K is shown in Fig. 3 and the fitted parameters are contained in Table 1. The spectrum was best interpreted in terms of three magnetically split components. The component with magnetic hyperfine field $H \sim 44.3$ T is associated with Fe^{3+} in the tetrahedral sites and that with magnetic
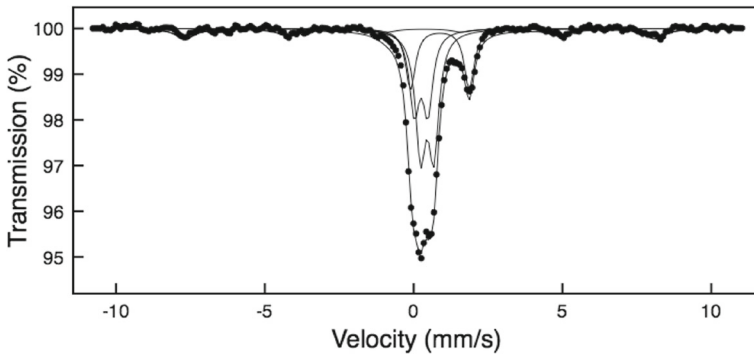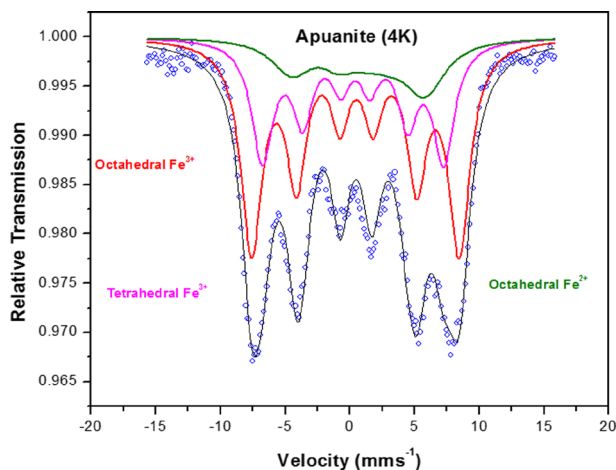
Fig. 4 ^{57}Fe Mössbauer spectrum recorded at 298 K from synthetic apuanite

hyperfine field $H \sim 51.0$ T with Fe^{3+} in the octahedral sites within the chains. The broad component with smallest magnetic hyperfine field ($H \sim 13$ T) is associated with Fe^{2+} in the octahedral sites of the rutile-related chains. The dominance of the quadrupole interaction over the magnetic interaction in Fe^{2+} [9] precluded accurate fitting of this component and the spectral area is probably an underestimation of the Fe^{2+} content. Indeed, the expected Fe^{3+}_{tet} Fe^{3+}_{oct} Fe^{2+} contents of 33.3 %, 33.3 %, 33.3 % are distorted by the difficulty in fitting the Fe^{2+} component and , given the errors, the results are in reasonable agreement with a composition for versiliaite of $\left(Fe^{2+}_4 Fe^{3+}_4\right)^{oct} \left[Fe^{3+}_4 Sb^{3+}_{12}\right]^{tet} O_{32}S_2$. Further interpretation of the magnetic hyperfine interactions must await examination of the magnetic properties of versiliaite.

3.2 Apuanite

The ^{57}Fe Mössbauer spectrum which we recorded at 298 K from synthetic apuanite is shown in Fig. 4 and the ^{57}Fe Mössbauer parameters are collected in Table 1. The spectrum recorded from synthetic apuanite clearly showed the presence of an iron oxide impurity phase and, although the paramagnetic component of the spectrum was not significantly different from that recorded previously from a mineral sample [8], was best fitted to two components characteristic of Fe^{3+} (77 %) and to one doublet characteristic of Fe^{2+}(23 %)(Table 1). The result is consistent with the formulation of apuanite as $Fe^{2+}_4 Fe^{3+}_{16} Sb^{3+}_{16} O_{48}S_4$ and with the structural description of apuanite involving the substitution of every third antimony cation in the pyramidal Sb^{3+} sites of the schafarzikite structure by an Fe^{3+} ion to form FeO_3S tetrahedral units with pairs of these Fe^{3+} ions being linked by sulphide anions and with charge balance being achieved by oxidation of some Fe^{2+} to Fe^{3+} in the octahedral sites within the chains. The Fe^{3+} doublet with smaller chemical isomer shift is associated with Fe^{3+} in the tetrahedral sites whilst that with larger chemical isomer is assigned to Fe^{3+}in the octahedral sites within the chains. The Fe^{2+} doublet is representative of the unoxidised Fe^{2+} ions in octahedral sites within the rutile-related chains.

The ^{57}Fe Mössbauer spectrum recorded from synthetic apuanite at 4 K is shown in Fig. 5 and the fitted parameters are contained in Table 1. As for synthetic versiliaite, the spectrum was best fitted to three magnetically split components which we assign in an analogous fashion to octahedral Fe^{2+}, octahedral Fe^{3+} and tetrahedral Fe^{3+}. Again, the difficulty in fitting the broad magnetic Fe^{2+} component inhibited accurate association of peak

Fig. 5 ^{57}Fe Mössbauer spectrum recorded at 4 K from synthetic apuanite

areas with site occupancy. The expected Fe_{tet}^{3+} $Fe_{oct}^{3+}Fe^{2+}$ contents in apuanite are 40 %, 40 %, and 20 % but, given the data recorded at 298 K where the combined quadrupole- and magnetic-interaction is absent, the results are in reasonable agreement with a formulation for apuanite as $\left(Fe_4^{2+}Fe_8^{3+}\right)^{oct}\left[Fe_8^{3+}Sb_{16}^{3+}\right]^{tet}O_{48}S_4$. The interpretation of the complex magnetic hyperfine interactions observed at 4 K must await investigation of the magnetic properties of apuanite.

4 Conclusion

The minerals versiliaite and apuanite have been synthesised for the first time. The results from ^{57}Fe Mössbauer spectroscopy are indicative of a formulation for versiliaite as $\left(Fe_4^{2+}Fe_4^{3+}\right)^{oct}\left[Fe_4^{3+}Sb_{12}^{3+}\right]^{tet}O_{32}S_2$ and of apuanite as $\left(Fe_4^{2+}Fe_8^{3+}\right)^{oct}\left[Fe_8^{3+}Sb_{16}^{3+}\right]^{tet}$ $O_{48}S_4$. Further elucidation of the complex magnetic patterns recorded at low temperature await interpretation of investigations of the structural and magnetic properties of versiliaite and apuanite at low temperatures. The results indicate scope for the synthesis of new structurally-related low-dimensional materials with different compositions and new properties.

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