Freudenbergite – a New Example of Electron Hopping

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Mössbauer spectra of freudenbergite samples with different composition have showed that although the Fe and Ti populate the octahedra randomly, Fe prefers the M(1) site over the M(2) site by approximately 1.3:1. Ti was able to accommodate mixed valence more easily than Fe, but some samples showed dynamic electron hopping in the Fe ions, which also affected the diffuse reflectance in the 400-800 nm region.

1. Introduction

The monoclinic freudenbergite structure of $Na_2Fe^{3+}{}_2Ti_6O_{16}$ is composed of double sheets of edge sharing $(Fe,Ti)O_6$ octahedra parallel to (001), with corner sharing along [100] to make a 3D structure [1]. The charge compensating Na^+ ions are in the channels between the octahedra. We have recently [2] examined several samples of ferric and ferrous freudenbergite and showed that some samples of freudenbergite with mixed valence can undergo electron hopping, as evidenced by temperature dependence of the quadrupole splitting in their Mössbauer spectra.

2. Sample preparation

Several samples of freudenbergite were prepared. Most were prepared from aqueous mixtures of $NaNO_3$, $Fe(NO_3)_3.9H_2O$, and Ti isopropoxide as previously described [2, 3]. The compositions were chosen to correspond to ferric freudenbergite, $Na_2Fe^{3+}{}_2Ti_6O_{16}$ **(1),** to ferrous freudenbergite, $Na_2Fe^{2+}Ti_7O_{16}$, **(2)**, with additional samples containing aluminium to try and achieve mixed valence. These had the composition $Na_2Al_{2-2x}Fe_xTi_{6+x}O_{16}$, with $x = 0.50$, **(3),** and 0.25, **(4)**, and were heated in argon. Both used 10% excess of Na and 10% excess of Ti to try to keep all the Fe in the freudenbergite. A further sample, **(5),** was prepared from the oxides of iron, titanium and aluminium in sodium hydroxide, with several sequences of sintering, pressing and grinding. This method produces a slightly reduced freudenbergite.

SEM studies of the samples showed that those from the aqueous mixture method were all homogeneous. However, the solid state reaction sample was two-phase with the second phase being an iron-free alumina-based composition.

All the samples were checked by XRD and SEM. The XRD showed that sample **1** had a few percent of the ferric brownmillerite Fe_2TiO_5, which has Mössbauer parameters very similar to those expected for freudenbergite [6]. Samples **2** and **3** had freudenbergite as the only iron-containing phase. These results were all confirmed by SEM.

We note that in the previous report of our experiments on some of these samples [2], the sample labels **2** and **3** were reversed between the description of the preparation, which is correct, and the description of the spectra. Samples **2** and **3** in the preparation description in [1] correspond to the same samples in this report.

3. Results

3.1 Colour, composition and diffuse reflectance spectra

We have made ten samples of freudenbergite with different compositions of Fe, Ti and Al in the octahedral sites to try and achieve ferric, ferrous and mixed ferric-ferrous systems. Heating was carried out in both air and argon. However, only two of the samples gave mixed valence and these two also exhibited electron hopping. The remainder were either pure ferric or pure ferrous. The cation charges in the octahedra should sum to 30, assuming a stoichiometric Na concentration, and even when compositions were chosen to try and force mixed valence, e.g. $Na_2Al_{2-2x}Fe_xTi_{6+x}O_{16}$, which was all ferrous, or $Na_2AlFeTi_{6+x}O_{16}$, which was all ferric, the mixed valence was accommodated by the Ti and not by the Fe.

It was noticeable that the two samples with electron hopping were black (**2**) or blue-black (**5**) and the remainder were coloured through the gold-green-grey hues, except for the two ferrous samples of $Na_2Al_{2-2x}Fe_xTi_{6+x}O_{16}$, with x = 0.50 and 0.25 (**3** and **4**), which were also black. As Coey [4] points out, materials which host spontaneous charge transfer are usually black, with a metallic lustre, but the converse, strong broadband absorption in the visible is not a guarantee of thermally-activated electron hopping. However, the colour of these last two samples raises the possibility that they are close to an electron hopping regime. We note that the Fe^{2+} - Ti^{4+} charge band absorbs in the red, so the crystals are usually blue.

Diffuse reflectance spectra of powders is made up of light which has been reflected from the surface, and hence resembles the inverted specular reflectance spectrum, and light which has penetrated the sample before being scattered and hence contains the transmission spectrum. For a strong absorber, the former effect dominates. Diffuse reflectance spectra were taken of samples **1**, **2** and **3** over the range 200-800 nm, using a Carey 1e spectrophotometer. Sample **1** showed a very rapid drop-off in reflected intensity between 500-600 nm (Fig. 1a), very similar to the spectra of the ferric α-, β- and γ-FeOOH polymorphs [5]. In contrast, the spectra of the other two samples (Fig. 1b, 1c) showed a continuous increase from 400 nm up to 800 nm, very similar to wüstite [5]. Wüstite is non-stoichiometric $Fe_{1-x}O$, where the charge balance is maintained by a small percentage of the iron ions being ferric, so that it is mixed valence.

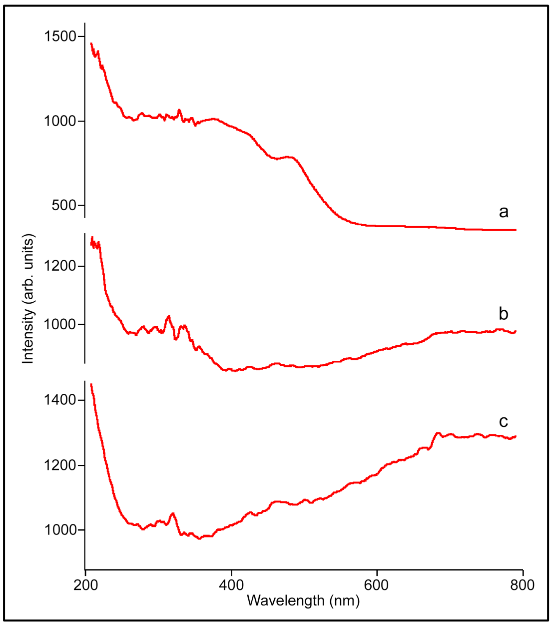

Fig 1. Diffuse reflectance spectra of (a) **1**, (b) **2** and (c) **3**

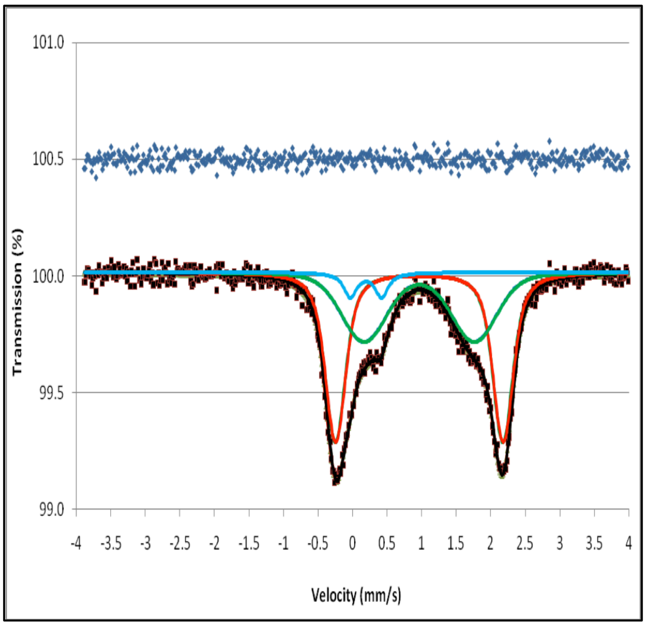

Fig. 2. Room temperature Mössbauer spectrum of **4**.

Absorption features in Fe-Ti materials are typically in the 400-2000 nm region, but assigning their origin is notoriously difficult [6]. This is particularly true when there are multiple possibilities, such as the homonuclear inter-valence transitions, $Fe^{2+} \leftrightarrow Fe^{3+}$, $Ti^{3+} \leftrightarrow Ti^{4+}$, or the heteronuclear $Fe^{2+} + Ti^{4+} \leftrightarrow Fe^{3+} + Ti^{3+}$, and will not be attempted here.

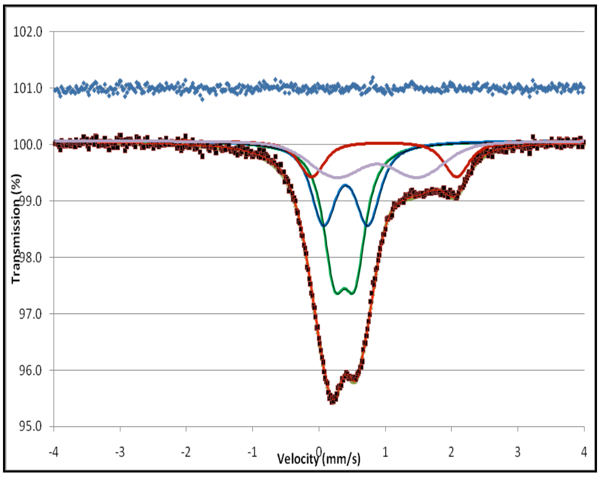

Fig. 3a. Mössbauer spectrum of **5** showing broadening due to electron hopping.

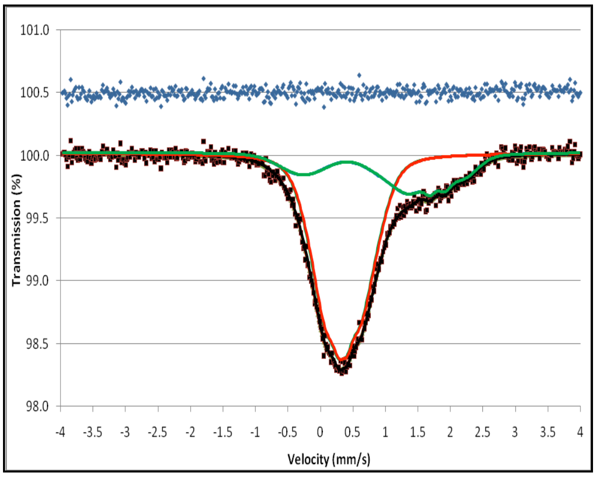

Fig. 3b. Mössbauer spectrum of **5** in an applied field of 1.6 T showing modification of the electron hopping.

3.2 Mössbauer spectra

The Mössbauer spectrum of **4** at room temperature is shown in Fig. 2. It has been fitted, similarly to that of **3** [1], to two ferrous doublets and a weak ferric doublet, all with Voigtian lineshapes, and the parameters for both samples are given in Table 1. The top blue line is the difference between the data and the fit in all the spectra. It is notable that the width of the inner doublet is approximately 2.5 times larger than that of the outer one.

The Mössbauer spectrum of **5** at room temperature is shown in Fig. 3a, with the effect of the electron hopping in the ferrous component evident in the broadened right hand region. Each of the ferrous and ferric components have been fitted to two doublets with the inner ferrous doublet being noticeably broadened. The fit to the ferric doublets was very unstable, depending critically on the allowed width of the lines as characterised by the standard deviation, σ(Δ), of the Gaussian spread in the quadrupole splitting, Δ. However, the total ferric area remained quite constant at 66%. Fig. 3b shows **5** in a transverse applied field of 1.6 T. This modified the electron hopping so that each valence state was now able to be fitted to one unresolved sextet with a Gaussian spread of hyperfine fields. The mean hyperfine fields of 2.6 T for the ferric sites and 4.2 T for the ferrous sites are both significantly larger than the applied field, due to enhancement by the magnetization of the paramagnetic iron ions.

Table 1. Fitted parameters to the room temperature Mössbauer spectra.

Sample	B	Ferric sites					Ferrrous sites				
	T	δ mm/s	Δ, ε mm/s	σ(Δ) mm/s	B T	Area %	δ mm/s	Δ, ε mm/s	σ(Δ) mm/s	B T	Area %
3	0	0.23(3)	0.48(5)	0	0	3.2	0.99(1)	2.43(1)	0.21	0	55.3
							1.00(1)	1.55(7)	0.50	0	41.5
4	0	0.19(2)	0.45(4)	0.02	0	5.5	0.96(1)	2.43(1)	0.18	0	53.1
							0.96(1)	1.60(9)	0.55	0	41.4
5	0	0.39(1)	0.30(1)	0.10	0	37.7	0.97(1)	2.18(3)	0.17	0	12.8
		0.40(1)	0.67(3)	0.16	0	27.6	0.87(3)	1.23(9)	0.63	0	21.9
5	1.6	0.35(1)	0.01(1)		2.4	73.1	1.10(4)	-0.69(3)		4.2	26.9

4. Discussion and Conclusions

In the fitting of **3** [1] and **4** (Fig 2), the isomer shifts of the weak ferric doublet in the two mainly ferrous samples were consistently lower than would be expected for an Fe^{3+} ion in an octahedral environment. Attempts to force them to a value in the region 0.35-0.38 mm/s produced a noticeably poorer fit. It was tentatively suggested in [1] that although the subspectrum could be due to an impurity, it was also possible that the parameters appropriate for a pure ferric freudenbergite had been altered by a change in lattice parameter. We now believe that the most likely explanation for the observed values is that the Fe^{3+} is in a tetrahedral environment, which does not exist in the freudenbergite structure. The samples were made with an excess of Na and a small amount of $NaAl_{11}O_{17}$ impurity was found in sample **3.** All the compounds $NaAlO_2$, $Na_7Al_3O_8$, $Na_{17}Al_5O_{16}$ and Na_5AlO_4 have Al in a tetrahedral coordination, with Fe^{3+} being able to substitute for Al^{3+} in all of them. Hence, we attribute the location of the Fe^{3+} to such a tetrahedral site and with only a few percent of the total iron being incorporated, it would be undetectable by XRD.

It would thus seem that the ferric doublet in the spectra of **3** and **4** is not associated with the freudenbergite so we can accept the areas of the two ferrous doublets without needing any modification. Following Stähle *et al.* [7], we will assign the outer doublet to the more distorted M(1) site. We then get the ratio of the populations of the two sites, M(1)/M(2), to be 1.28 for **3** and 1.33 for **4**, showing that although the filling of the octahedral sites by Fe^{2+} and Ti^{4+} appears to be random, in the sense that there is no clustering, there is a preference by the Fe^{2+} as the larger ion, for the larger M(1) site. Stähle *et al.* obtained a ratio of 1.22 for the M(1)/M(2) ratio for Fe^{3+} even though the ionic radius of Fe^{3+} of 0.064 nm is slightly smaller than that of Ti^{4+} at 0.068 nm.

We noted before that **3** and **4** were the only two of the non-electron hopping Mössbauer samples which were black. However, their spectra showed that the inner doublet was very much broader than the outer one, as was the case in **5** and the diffuse reflectance of **3** showed an increase in the 400-800 nm region, similar that of the electron hopping **5**. The raises the suggestion that electron hopping is close to occurring in **3** and **4** and furthermore that it is easier to achieve on the M(2) site, which is the less favoured site for Fe occupation. We must remember that the Fe concentration in the octahedra has dropped from 25% in ferric freudenbergite, to 6% in **3** and 3% in **4**, with the Al substitution inhibiting electron movement. Our results also show that mixed valence is easier to achieve for the Ti ions than for the Fe ions, but it is not clear whether the Ti mixed valence states are static or dynamic.

Acknowledgments

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