

Structural and Magnetic Properties of $x\text{Fe}_2\text{TiO}_4 \cdot (1-x)\text{Fe}_3\text{O}_4$ ($0.75 \leq x \leq 1$)

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Titanomagnetites (TMs) [pseudobinary $(1-x)\text{Fe}_3\text{O}_4 \cdot x\text{Fe}_2\text{TiO}_4$ oxides, where, e.g., TM75 corresponds to $x = 0.75$] are magnetic minerals with a spinel structure. Ulvöspinel (Fe_2TiO_4) and TMs were made using a solid-state synthesis technique, and transmission electron microscopy (TEM) characterization and measurement of the TM samples were performed to further confirm the homogeneity of the samples and cation site occupancies. The Mössbauer spectra in the TMs exhibited an anomalous composition dependence at $x = 0.95$, when fitted with two instead of three quadrupole split doublets. This result was reinforced by the obtained dependence of the recoilless fraction on the composition, which exhibited an extremum at $x = 0.95$.

Index Terms—Martian minerals, Mössbauer studies, remnant magnetization, titanomagnetite (TM).

I. INTRODUCTION

MARS presently has no active dipolar magnetic field and its global magnetic field is of crustal origin. To explain the remnant magnetic state on Mars and investigate the global magnetic mapping of this terrestrial planet, it is necessary to catalog abundant materials that may contribute to a large remnant magnetization [1]–[3].

Titanomagnetites (TMs) are solid solutions of magnetite and ulvöspinel (Fe_2TiO_4) having an inverse spinel structure and $Fd\bar{3}m$ space group, with cubic close packed oxygen anions. It is represented as a pseudobinary line in Fe–Ti–O ternary phase diagram. Due to its abundance on the Martian surface, the formation of TM solid solutions with different Ti concentrations and their magnetic properties may be important in understanding the geomagnetism of Mars. Synthesis of a series of TMs has required advanced solid state synthesis techniques and the precise control of oxygen fugacity. Previously, TMX solid solutions of compositions $x = 0.75 - 1.0$, i.e., TM75 to TM100, were successfully synthesized, and lattice constants of these solid solution samples were calculated using X-ray diffraction (XRD) data via Nelson and Riley (N&R) method. The lattice constants as a function of composition ($x > 0.75$) were fitted to a straight line, agreeing closely to the literature value. In this paper, TEM characterizations of the TM samples were performed, and lattice constants measured by TEM were compared with calculated N&R values [4]. TEM observations were also compared with high-resolution TEM (HRTEM) simulated picture to determine atomic site occupancies.

The stoichiometry of magnetite, ulvöspinel and TMs are all AB_2O_4 and A-sites are tetrahedrally coordinated while B-sites are octahedrally coordinated. Magnetically, A-site moments

are aligned antiparallel to B-site moments, so magnetization would depend on composition and cation distribution. To maintain charge balance, when a Fe^{3+} is substituted by a Ti^{4+} ion, an additional Fe^{3+} must convert to Fe^{2+} but it is uncertain that on which sites this conversion would happen. In a random substitution, this charge conversion occurs on both the A and B sites simultaneously. In the Neel model, thought to predict ground state configurations, Fe^{3+} is converted to Fe^{2+} on the B-sites until they are exhausted ($x = 0.5$) and after which conversion takes place on the A-sites. With different Ti^{4+} content and preparation conditions, TMs have different orderings of cation distributions on A and B sites that would affect their magnetic behavior, thus need further investigation. Cation ordering can play an important role in determining magnetic properties [5], [6] in spinels.

Also of issue is how the cations are distributed around oxygen anions in the spinel structure. Pauling's rules [7] define the bond strength of a cation–anion bond s as the ratio of cation charge to the cation coordination number. Structural stability is inferred when the sum of the strengths of cation bonds reaching any anion balances the anionic charge. It is instructive to investigate these rules for spinels from Fe_3O_4 to Fe_2TiO_4 . Given that each oxygen anion in the spinel structure is tetrahedrally coordinated by three B-sites and one A-site [7], [8], we can perform a bond valence analysis for Fe_3O_4 in a normal spinel structure. Here, the octahedrally coordinated Fe^{3+} cations all have bond strengths, $s = 3/6 = 1/2$, as does the tetrahedrally coordinated Fe^{2+} cation, $s = 2/4 = 1/2$. For Fe_3O_4 in an inverse spinel structure, the A-site Fe^{3+} cation has a bond strengths, $s = 3/4$. Fe^{3+} ($s = 1/2$) and Fe^{2+} ($s = 1/3$) on the B-sites have bond strengths that average to $5/12$ and the net charge at an oxygen anion node is balanced. The two chemically distinct charge states on a single crystallographic site is accommodated at finite temperatures by electron hopping that switches Fe^{3+} to Fe^{2+} and vice versa on the B-sites.

Cation distributions in ulvöspinel and by inference, all of the TMs in between, are more problematic. Consider now

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Fe_2TiO_4 , where Ti^{4+} occupy exclusively B-sites. Here, the A-site Fe^{2+} cation has a bond strength, $s = 1/2$ ($s = 2/3$) and Fe^{2+} ($s = 1/3$) on the B-sites have bond strengths which average to $1/2$ and again the net charge at an oxygen anion node is balanced. Here, however, two chemically distinct charge states on a single crystallographic site is more problematic as ulvöspinel has an eight order of magnitude larger resistivity, indicating electron hopping to be unlikely. If charge is localized, the averaging could be accommodated by having B-site cation configurations about oxygen anions ($\text{Ti}^{4+}\text{Ti}^{4+}\text{Fe}^{2+}$) and ($\text{Ti}^{4+}\text{Fe}^{2+}\text{Fe}^{2+}$) which average to insure charge balance; but neither configuration is locally stable. ($\text{Ti}^{4+}\text{Ti}^{4+}\text{Ti}^{4+}$) and ($\text{Fe}^{2+}\text{Fe}^{2+}\text{Fe}^{2+}$) configurations are unlikely as local stability is worse. If charge is localized in B-site cation configurations about oxygen anions ($\text{Ti}^{4+}\text{Ti}^{4+}\text{Fe}^{2+}$) and ($\text{Ti}^{4+}\text{Fe}^{2+}\text{Fe}^{2+}$), one would expect diffraction peak broadening [9] from distributed bond strains reflecting relative stability of the two configurations. These strains would also be detectable in Mössbauer spectra, especially at low temperatures.

Mössbauer spectroscopy is a powerful tool to investigate the magnetic properties of TMs [10] and the determination of the cation distribution as a function of molar fraction of the ulvöspinel component [10], [11]. However, no prior attempts have been made to measure the recoilless fraction and probe the phase evolution in the TM system. In this paper, we report on the structural, magnetic, and recoil-free properties of the $x\text{Fe}_2\text{TiO}_4 \cdot (1-x)\text{Fe}_3\text{O}_4$ system, with $x = 0.75 - 1.00$ using ^{57}Fe transmission Mössbauer spectroscopy. We derive the hyperfine parameters from the spectra and study them as a function of molar composition x .

II. EXPERIMENTAL PROCEDURE

1) *Single Phase Solid Solutions Synthesis:* The pseudobinary $(1-x)\text{Fe}_3\text{O}_4 \cdot x\text{Fe}_2\text{TiO}_4$ series ($0.75 \leq x \leq 1$) were produced by solid state synthesis [12]. First, Fe_2TiO_4 was prepared from Fe_2O_3 and TiO_2 mixed in stoichiometric proportions with 0.072 wt% of excess Fe powder. Components were ground in a high-energy SPEX mill using three different sizes of stainless steel balls to achieve increased homogeneity of the sample mix in a short time. The mix was then wet ground and pressed into 0.5 in diameter pellets and stacked into tube furnace for sintering 100 h at 1100°C , in flowing Ar environment to prevent oxidation. This synthesized Fe_2TiO_4 was characterized by XRD to prove its high purity [4], and then crushed into powders again, to be mixed with different molar fractions of commercially bought Fe_3O_4 powder to synthesize TM series. Similar steps as how ulvöspinel was synthesized, different compositions of TMs were SPEX milled and sintered in furnace at 1150°C , then quenched at 750°C in cold water to prevent hypothesized spinodal decomposition. As-quenched samples were characterized by XRD.

2) *TEM Characterization and Measurement:* The samples for TEM were originally in powder form acquired after grinding TMs pellets manually with ethanol in agate mortar. The powder samples were dispersed in ultrasonic bath for 10 min, and then a drop of the suspension was deposited onto

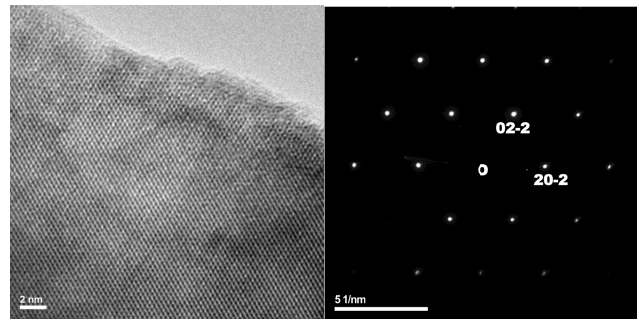


Fig. 1. HRTEM image of TM90. Zone axis: $[111]$, planes: $\{220\}$, $d\{220\} = 2.983 \text{ \AA}$, and lattice parameter $a(\text{TM90}) = 8.437 \text{ \AA}$. Two planes and the central beam are labeled.

carbon-coated copper grid, ready for TEM characterization. The HRTEM images were collected using a JEOL-2010 microscope with a double tilt holder ($C_s = 0.5 \text{ mm}$, accelerating voltage = 200 kV). Several zone axis diffraction patterns with the high-resolution images were acquired from different grains by tilting the specimen. These acquired images were further filtered and processed via Fourier filtering methods by CRISP software. Simultaneously, to examine the lattice structure of a single grain of the sample, multislice simulation was conducted using commercially available program JEMS developed by Pierre Stadelmann. After setting XRD refinement results as original structure model in multislice calculation, and microscope and specimen parameters as well, the software output a series of simulated pictures with varying thickness and defocus. Atom occupancies information was therefore obtained by comparing processed and simulated pictures.

3) *Mössbauer Studies:* Room temperature transmission Mössbauer spectra were recorded using an MS-1200 constant acceleration spectrometer with a $10 \text{ mCi } ^{57}\text{Co}$ source diffused in Rh matrix. Least-squares fitting of the Mössbauer spectra was performed with the NORMOS program.

III. RESULTS AND DISCUSSION

A. Transmission Electron Microscopy

As reported before [12], the TM75-100 samples were nominally single phase samples as characterized by XRD. Then, we calculated the lattice constants data using N&R method and it perfectly extended previous literature data. To confirm our lattice constant results, further measurement was performed by TEM (Fig. 1 is an example of TM90). Lattice constant results derived from TEM measurements followed the same compositional trend as observed in the previous N&R method values, with some systematic error. The ulvöspinel lattice constant is 8.499 \AA according to TEM data, taken using silicon standard. Our previously reported [13] ulvöspinel lattice constant is 8.531 \AA and literature data is 8.534 \AA .

TEM images were taken for samples TM75-100. HRTEM images of TM90 can be seen in Fig. 1, with zone axis $[111]$ and (220) planes. This further confirms the homogeneity of the sample. Fig. 2 compares TEM observations with HRTEM simulated picture to determine atomic site occupancies. The TEM observations were made on single-phase

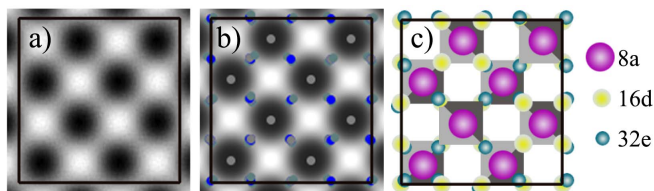


Fig. 2. Black frame marked the unit cell (2×2). (a) Actual TEM image taken from ulvöspinel single solid solution and the center black dots stand for Fe atoms at tetrahedral sites. (b) Simulated image. (c) Spinel structure.

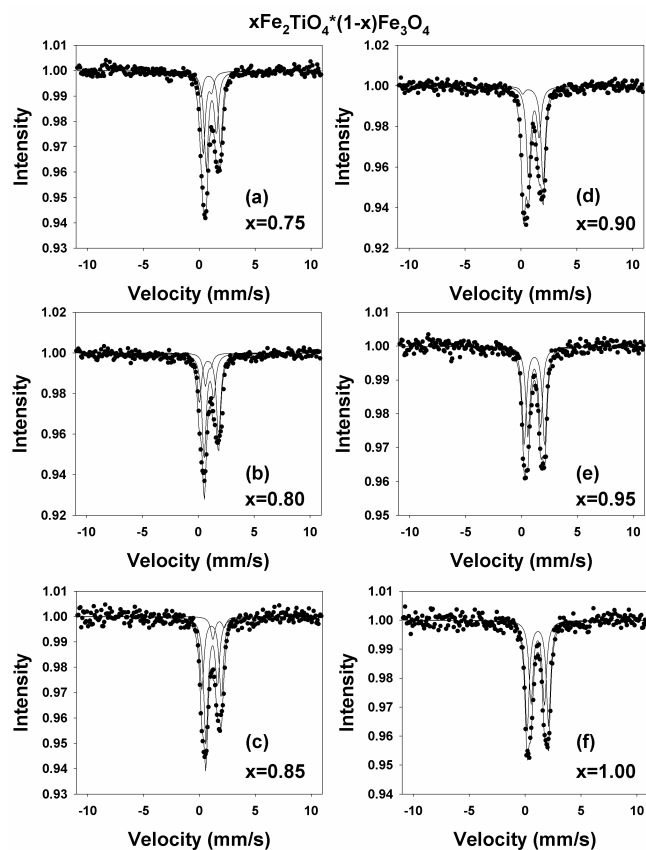


Fig. 3. Room temperature transmission Mössbauer spectra of the TM system at various molar concentrations.

ulvöspinel samples viewing crystals along the $[001]$ zone axis. The simulated picture is drawn based on an XRD refinement result. By comparing the simulated and real atom sites, it is concluded that 8a sites are occupied only by Fe atoms, and 16d sites occupied by both Fe and Ti atoms at equal concentration predicted probability. Oxygen atoms occupy the 32e sites. This confirms the assumption that Ti occupies the octahedral B-sites only as a random solid solution on this sublattice. HRTEM pictures of TM85 to 100 compositions were also taken and further confirm that the samples were homogenous single solid solutions in spinel structure with Ti^{4+} cations occupying exclusively octahedral B-sites.

B. Mössbauer Studies

Fig. 3 shows the room-temperature transmission Mössbauer spectra of the $(1-x)Fe_3O_4 \cdot xFe_2TiO_4$ system, with $x =$

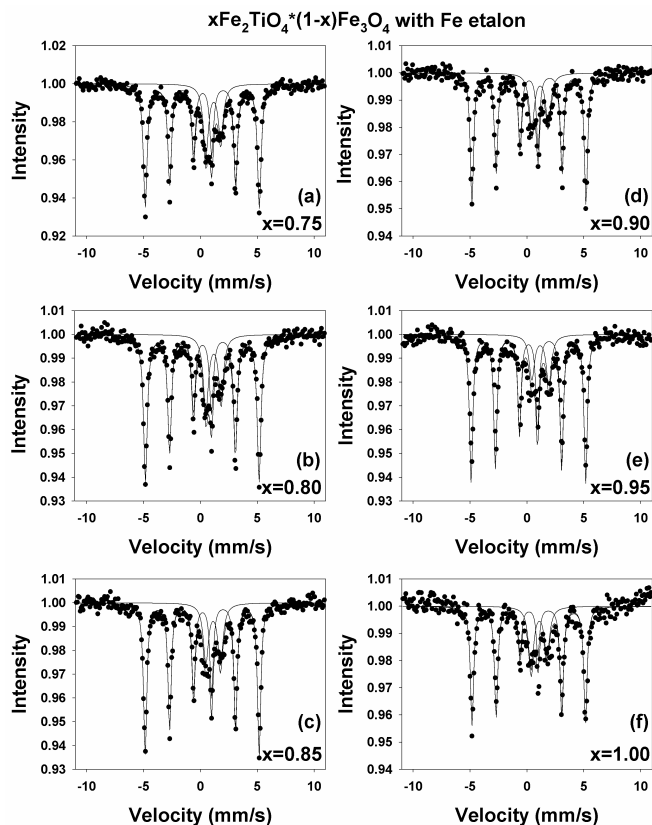


Fig. 4. Room temperature transmission Mössbauer spectra of the TM samples recorded simultaneously with the Fe foil.

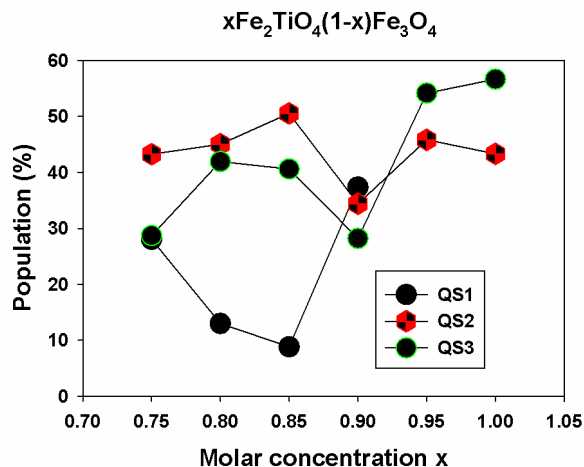


Fig. 5. Populations of the quadrupole split doublets as function of the molar concentration. QS1 and QS2 correspond to the two inequivalent tetragonal lattice sites for $x < 0.95$ and QS3 corresponds to the octahedral lattice sites.

0.75–1.00. The spectra corresponding to $x = 0.75$ – 0.90 could be analyzed by considering three quadrupole-split doublets, with the isomer shift and quadrupole splitting corresponding to tetrahedral (2) and octahedral (1) sites. The samples with $x = 0.95$ and 1.00 were best fitted with only two doublets, corresponding to one tetrahedral and another octahedral lattice sites. The populations of the doublets are represented as functions of the molar concentration x in Fig. 5. The local strains appear in a Mössbauer spectrum as a line broadening

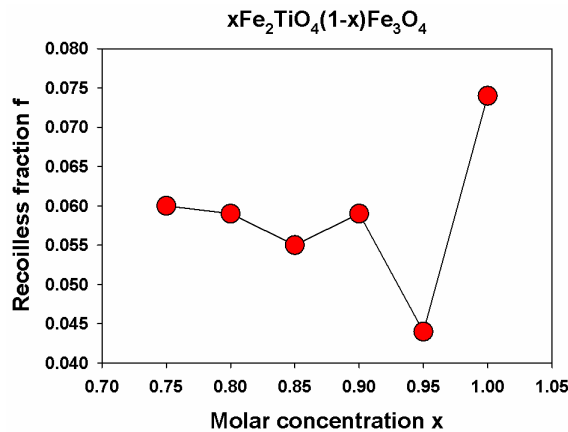


Fig. 6. Recoilless fraction of the TM system as function of the molar concentration x .

or asymmetry of the quadrupole doublets. Both can be seen in the Mössbauer spectra below. This confirms the hypothesis of our bond valence analysis in the introduction part above.

Fig. 4 shows the Mössbauer spectra of the system recorded simultaneously with the Fe foil etalon for the recoilless fraction (f) determination. This new method for determining f was introduced in [14] and applied consistently ever since. The recoilless fraction was determined from the spectral areal ratios and plotted in Fig. 6 as function of the composition. The occurrence of an extremum (minimum/maximum) in this plot at the molar concentration $x = 0.95$ reinforces the appearance of an anomalous composition dependence in the system under investigation.

IV. CONCLUSION

Single phase alloys of TM with compositions ($x = 0.75-1.0$) were successfully produced by solid-state synthesis techniques. TEM measurement further proved the homogeneity of the sample, and lattice constant results are in agreement with our previously reported XRD data, which perfectly extended literature data. Comparison of the simulated and real atom sites show that 8a sites are occupied only by Fe atoms, and 16d sites occupied by both Fe and Ti atoms at equal concentration predicted probability. Oxygen atoms occupy the 32e sites. This convinced our previous assumption that Ti occupies the octahedral B-sites only as a random solid solution on this sublattice. Future work on TEM will emphasize on the trend of cation distributions of different molar fraction of Ti^{4+} .

The solid solution with Fe_2TiO_4 molar fraction $x > 0.75$ shows paramagnetic behavior, with the appearance of only quadrupole doublets in the Mössbauer spectra. By observing both line broadening and asymmetry of the quadrupole doublets, it confirms the hypothesis in our bond valence analysis on TM's inverse spinel structure that there are local strains,

because of the charge localization by the averaging of two configurations on B-sites. Furthermore, from experiments on the recoilless fraction, the occurrence of an anomalous composition dependence has been shown in ulvöspinel and a TM with a concentration of $x = 0.95$.

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