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X-ray absorption, neutron diffraction, and Mössbauer effect studies of MnZn–ferrite processed through high-energy ball milling

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MnZn–ferrite has been prepared via high-energy ball milling of elemental oxides MnO, ZnO, and α-Fe_2O_3. Neutron diffraction measurements suggest a high density of vacancies in a spinel structure. The spinel phase appears to comprise 99.8 wt % of the material in the sample milled for 40 h, with the remainder attributable to unreacted α-Fe_2O_3. The x-ray absorption near-edge structure was analyzed to provide an understanding of the charge state of the constituent Fe ions. This analysis reveals about 2/3 of Fe cations to be trivalent, increasing to about 3/4 after a 5 h anneal at 450 °C. The heat treatment is also observed to induce a cation redistribution in the ball-milled ferrite toward that of a standard processed via ceramics methods. Results from Mössbauer spectroscopy determine the average hyperfine fields in the sample milled 40 h to be 289 and 487 kOe at 295 and 78 K, respectively. The average isomer shift is 0.32 mm/s at 295 K and 0.46 mm/s at 78 K, values which are typical of iron (III) in a spinel oxide lattice. As expected for a cubic-like environment, the quadrupole shifts are very small, ranging from 0.07 mm/s at 295 K to 0.00 mm/s at 78 K. © *1999 American Institute of Physics.* [S0021-8979(99)76708-3]

I. INTRODUCTION

The technique of high-energy ball milling (HEBM) has been the subject of great interest in recent years due to its promise for producing improved and/or novel materials through mechanical attrition or alloying.[1] Spinel ferrites are particularly attractive candidates for such processing studies due to their importance both in solid-state microwave devices and in soft magnet applications where loss minimization is critical.[2] Despite these motivations, there have been few investigations of ferrite production via ball milling.[3–9]

The two most critical parameters in ferrite characterization are the valence and distribution of the cations. From this, the net magnetic moment per ion and sublattice interactions can be determined, leading to a complete understanding of a ferrite's magnetic properties. Previously, we reported the formation of MnZn–ferrite ($Mn_{0.5}Zn_{0.5}Fe_2O_4$) from HEBM of MnO, ZnO, and α-Fe_2O_3, as indicated by x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS) studies.[6] We found the milled ferrites to have a higher inversion parameter than a standard ferrite of similar stoichiometry, with an unusually high population of Zn ions on the octahedral sublattice.

In this article, we provide the first use of neutron diffraction (ND) measurements to structurally characterize ball-milled ferrites and find evidence for a high density of vacancies in a spinel structure. The spinel phase appears to comprise 99.8 wt % of the material in the sample milled for 40 h, with the remainder attributable to unreacted α-Fe_2O_3. In addition, we report valence information for the Fe cations in milled MnZn–ferrites through x-ray absorption near-edge studies (XANES). This analysis reveals about 2/3 of Fe cations to be trivalent, increasing to about 3/4 after a 5 h anneal at 450 °C. Concurrent in the heat treatment is a redistribution of cations toward equilibrium conditions, as evidenced by multiple scattering EXAFS analysis. Finally, magnetic properties have been measured via Mössbauer spectroscopy performed at 295 and 78 K, providing evidence consistent with the structural analysis obtained from ND.

II. EXPERIMENT

Processing of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ was accomplished by combining MnO, ZnO, and α-Fe_2O_3, totaling 5 g, with the molar ratio 1:1:2 in a steel vial of the SPEX 8000 high-energy shaker mill. The vial was loaded with two stainless steel 8 g balls and two 1 g balls in air and shaken at about 1200 Hz. In order to maintain an equal ball:powder mass ratio for all samples, the vial was cleaned and reloaded with 5 g of new material for each milling trial.

ND studies were performed at room temperature at the University of Missouri Research Reactor (MURR) Facility. A monochromatic beam of neutrons of wavelength 1.7675 Å

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was selected for the experiment. The powder diffractometer uses position sensitive detectors. The sample was contained in a thin walled vanadium container 3 mm in diameter and 7 cm long which was placed in front of the beam. The sample was rotated slowly around its axis to average the powder orientations. Data were acquired in five 20° spans from 5° to 105° in roughly 12 h total measurement time. The data were analyzed using the GSAS code of programs for Rietveld analysis.

Mössbauer spectra were obtained on a constant-acceleration spectrometer which utilized a room temperature rhodium matrix Co^{57} source and was calibrated at room temperature with α-Fe foil. The Mössbauer absorbers contained 40 mg/cm^2 of the powdered material.

X-ray absorption data were collected using beamlines X23B and X23A2 of the National Synchrotron Light Source at Brookhaven National Laboratory. The beamlines use double-crystal, fixed-exit monochromators, with Si (111) crystals in X23B and Si (311) crystals in X23A2. All spectra reported here were collected using the transmission technique.[10] The storage ring current and energy at the time of data collection were 200–350 mA and 2.5 GeV, respectively. Samples consisted of powders spread uniformly onto adhesive tape with several layers of powdered tape constituting a single sample. The number of layers was chosen empirically to provide nearly one absorption length at the absorption edge being measured.

EXAFS analysis followed established procedures[11] leading to the Fourier transformation of EXAFS data to radial coordinate space (Å). Quantitative analysis of the cation distribution followed the approach previously employed by Harris *et al.*[12] which included the least-squares fitting of multiple-scattering simulated XAFS data generated using the FEFF codes of Rehr *et al.*[13]

III. RESULTS AND DISCUSSION

ND measurements yield a fit in which 99.8 wt % of the sample ball milled 40 h is attributable to the *spinel* structure. The remaining 0.2 wt % is attributed to unreacted α-Fe$_2$O$_3$. It is interesting to note that in the fit, 85.2 wt % appears as $Mn_{0.5}Zn_{0.5}Fe_2O_4$ and 14.6 wt % as γ-Fe$_2$O$_3$. However, even though Mössbauer spectroscopy should be sensitive to the latter, no evidence for the existence of γ-Fe$_2$O$_3$ is observed. These results can be reconciled by recognizing that γ-Fe$_2$O$_3$ ([Fe$_8$]{Fe$_{13.33}\square_{2.67}$}O$_{32}$) is a spinel with a 2.67 octahedral-site vacancies per unit cell (there are 8 formula units per unit cell). Therefore, it is likely that the ferrite generated via HEBM exists in the spinel structure typical of $Mn_{0.5}Zn_{0.5}Fe_2O_4$, but contains a high number of vacancies, creating ambiguity in fitting a γ-Fe$_2$O$_3$ component.

ND measurements on a sample generated through 21 h HEBM suggest a higher degree of unreacted α-Fe$_2$O$_3$ (5.3 wt %). The remaining 94.7 wt % appears in the spinel structure, with 80.2 wt % fit as $Mn_{0.5}Zn_{0.5}Fe_2O_4$, and 14.5 wt % fit as γ-Fe$_2$O$_3$.

XANES studies have been used to determine the valence of the Fe cations in the ball-milled ferrites. By comparing a given electronic process' absorption energy in Fe ions in the
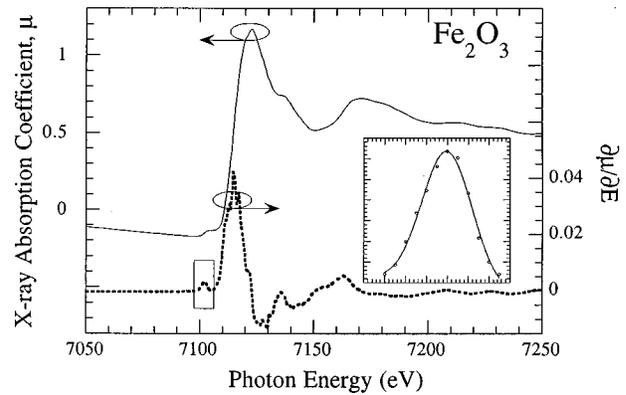

FIG. 1. Absorption coefficient μ as a function of energy E, the derivative $\delta\mu/\delta E$, and a Gaussian fit (inset) to the peak near 7100 eV in $\delta\mu/\delta E$, for the α-Fe$_2$O$_3$ standard.

ferrite to that of a standard, the effective atomic charge on the absorbing atoms has been inferred. Figure 1 shows the absorption coefficient μ as a function of energy E for one standard (α-Fe$_2$O$_3$), the derivative $\delta\mu/\delta E$, and a Gaussian fit (inset) to a peak in $\delta\mu/\delta E$.

The energetic difference between this peak's location in a series of standards and in an FeO foil is plotted as solid points in Fig. 2. The standards used were Fe$_3$O$_4$, γ-Fe$_2$O$_3$, and α-Fe$_2$O$_3$. Two points near 1.1 eV overlap and are barely distinguishable from each other. In addition, since the valence of Fe in FeO is known to be +2, the FeO foil was used as a fourth data point. As expected, the data nearly comprise a straight line, and the linear fit has been included in the figure.

The open circles represent energetic differences between the peak's location in a series of ball-milled samples and that of FeO. The effective atomic charge has been assumed to lie on the linear fit from the standards data, yielding charge states of +2.66 and +2.68 for the sample ball milled 21 and 40 h, respectively. A heat treatment of 450 °C for 5 h in-
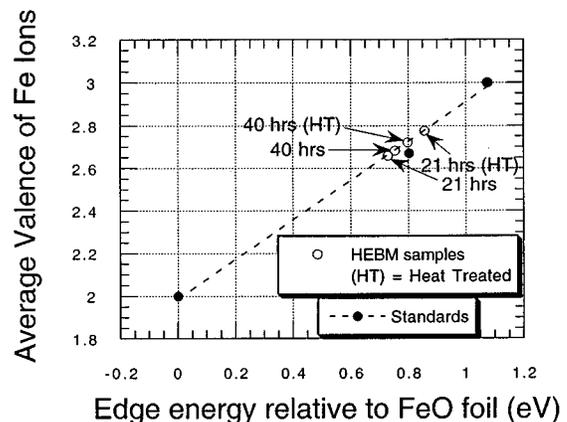

FIG. 2. Solid points (and linear fit): average valence of Fe ions in standards vs shift, relative to FeO foil, of the peak singled out in Fig. 1. Open circles: Average valence of Fe ions in MnZn–ferrites made via 21 h and 40 h HEBM, before and after 5 h heat treatment (HT) at 450 °C. The valence was determined by placing the data from shift measurements onto the linear fit from the standards data.
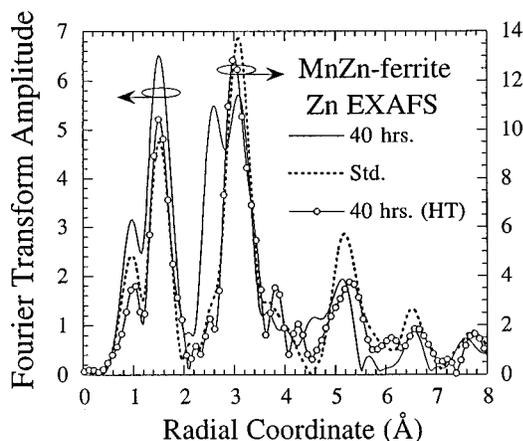
FIG. 3. Fourier-transformed Zn EXAFS data from the sample made via 40 h HEBM, both before and after 5 h heat treatment at 450 °C, and similar data from the standard. ''HT'' is used to denote the heat-treated sample. Note that the heat-treated sample and the standard share a common *y* axis, whereas the as-milled sample is on a different vertical scale.

creases the effective charge to $+2.78$ and $+2.72$, respectively. These data indicate that nearly 2/3 of the Fe cations are trivalent in the as-milled samples, increasing to nearly 3/4 after heat treatment, with the remaining Fe atoms existing as $+2$ cations.

The heat treatment at 450 °C also facilitates a redistribution of cations toward equilibrium conditions. In Fig. 3, the Fourier-transformed Zn EXAFS data collected from the MnZn–ferrite made from 40 h HEBM, both before and after the heat treatment, is compared to similar data from a standard prepared through ceramics means. Note that the heat-treated sample and the standard share a common *y* axis, whereas the as-milled sample requires a different vertical scale. In contrast to the sharp differences between the as-milled sample and the standard, the data for the heat-treated sample and the standard exhibit nearly the same peak amplitudes and radial distributions. Most notably, the heat treatment has resulted in the near removal of the peak near 2.6 Å while augmenting the peak near 3.0 Å, as in the standard. These peaks represent octahedral- and tetrahedral-site occupancy of the absorbing cations, respectively, indicating that the Zn cations now only reside on the tetrahedral sublattice.

Magnetic properties have been investigated via Mössbauer spectroscopy at 295 and 78 K. The spectrum collected at room temperature consists of broadened sextets, indicative of a distribution of hyperfine fields (HFFs). As might be expected, the distribution of HFFs sharpens at 78 K. The distribution was obtained using the fitting method of Wivel and Morup,[14] which represents the distribution of HFFs with

22 sextets. In these fits, the components of each sextet were held in the area ratio of 3:2:1:1:2:3 and the only variables were the isomer shift, the quadrupole shift, and the linewidth. The fitting procedure assumes no texture in the absorber and no relaxation on the Mössbauer time scale.

For the sample milled 40 h, the average values for the HFFs are 289 ± 5 and 487 ± 5 kOe at 295 and 78 K, respectively. The average isomer shift is 0.32 ± 0.01 mm/s at 295 K and 0.46 ± 0.01 mm/s at 78 K, values which are typical of trivalent Fe in a spinel oxide lattice.[15] Further, as expected for a cubic-like environment, the quadrupole shifts are very small, ranging from 0.07 ± 0.01 mm/s at 295 K to 0.00 ± 0.01 mm/s at 78 K. Because HEBM provides a broad particle size distribution often including very small particles (i.e., <10 nm), it is surprising that we observe no clear evidence for a superparamagnetic component. Further, we detect no significant fraction of unreacted Fe–oxide phases (i.e., γ-Fe$_2$O$_3$, α-Fe$_2$O$_3$) which would have been clearly present due to their unique HFFs.

ACKNOWLEDGMENTS

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