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The magnetic and electric properties of ferrites are influenced by the cation distribution within the crystalline spinel lattice. Methods such as extended x-ray-absorption fine structure (EXAFS) have been used to determine cation occupancies within the crystalline structure of materials such as manganese zinc ferrite (MZFO); however, it is not practical to be used for daily analysis. Fourier transform infrared (FTIR) spectroscopy is another technique which has the potential to determine cation occupancy while offering speed and convenience. In the literature it has been demonstrated that in ferrite systems FTIR data can be correlated to cation percentages when comparing tetrahedral (T_d) and octahedral (O_h) sites. FTIR spectra were collected on a series of MZFO nanoparticles in the range from 200 to 600 cm^{-1} and two absorbance peaks were observed. The first absorption region shifted with changing sample composition as calculated from transmission EXAFS experiments and elemental analysis. The data was normalized to the maximum of the peak of interest and the shifts were correlated to cation occupancy. © *2006 American Institute of Physics.*
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This study investigates the use of Fourier transform infrared (FTIR) spectroscopy for determining cation occupancy in manganese zinc ferrite (MZFO). One technique that has been successful in determining cation occupancies within bulk and nanoparticle mixed metal ferrites is extended x-ray-absorption fine structure (EXAFS).[1] However, this method is not practical for daily laboratory analysis to develop synthetic routes due to the necessity of traveling to a synchrotron-radiation source. It has been demonstrated in ferrite systems that FTIR data can be correlated to cation occupancy in tetrahedral and octahedral sites.[2] In our work, elemental analysis by inductively coupled plasma-optical emission spectroscopy (ICP) is used to determine the cation concentrations and ratios between the components in the system. Cation distributions within the ferrite lattice, as determined by EXAFS, were then used to establish a correlation with measured FTIR absorption bands. These bands were assigned to different cation-oxygen vibrational frequencies based on the quality of the data fit and trends observed.

To establish the versatility of this method the MZFO data was collected using both nanoparticulate MZFO as well ceramic bulk samples. The ceramic standards were prepared by mixing α-Fe_2O_3, Mn_2O_3, and ZnO powders in a ball mill and subsequent annealing at 1200 °C.[3] Reverse micelle techniques were used to synthesize the nanoparticles, as detailed by Calvin *et al.*[1] EXAFS spectroscopy was performed at beam line X11A of the National Synchrotron Light Source at Brookhaven National Laboratory. Elemental analyses for the

samples detailed by Calvin *et al.* are discussed therein; the remaining samples were prepared for ICP in the same manner and analyzed using a Varian Vista-MPX ICP-OES. Samples were prepared for FTIR by grinding them with mortar and pestle into a mixture with silver bromide at approximately a 1:10 mass ratio. The mixture was then pressed in a 13 mm pellet die at an applied load of 9 tons, to yield approximately 1-mm-thick pellets. The spectra were collected on a Nicolet Nexus 670 FTIR with a polyethylene beam splitter, deuterated triglycine sulfate (DTGS) detector, and a purge cell apparatus to minimize moisture in the measuring environment. A single beam background spectrum was taken to minimize CO_2 and H_2O signals in the measurements. A AgBr spectrum was collected and used for the background subtraction of each sample. The spectra of the samples were collected in the far-IR region from 600 to 200 cm^{-1} and normalized to the maximum absorbance value between 450 and 300 cm^{-1}, to account for differences in the thickness and concentration of each pellet.

The FTIR spectra we collected contained two absorption regions between 600 and 200 cm^{-1}. This region was chosen based on a potential-energy study by Waldron in 1955 in which he derived that 480 cm^{-1} was an approximate mean between the cut-off frequencies of the oxygen and metal cation vibrations.[4] In our data the first region (ν_1) did not resolve into separate peaks, while the second region revealed the presence of three bands (ν_2, ν_3, and ν_4), as seen in Fig. 1. The maximum value of ν_1 shifted within the range of 553 and 571 cm^{-1} for the various samples of MZFO. The percentage of interstitial sites occupied by a specific metal within the spinel structure can be calculated from ICP and
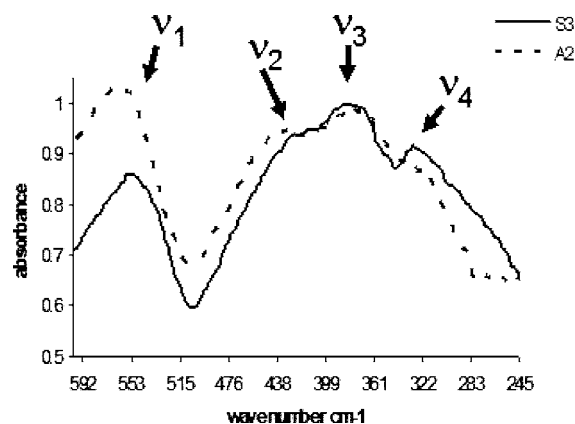
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FIG. 1. Plot of absorbance vs wave number for two of the MZFO samples showing all four absorbance bands and the two absorbance regions.

EXAFS data. This allows a direct comparison of the shifts in the absorbance peaks with the percentage of either interstitial site occupied by a given cation.

Two common assumptions are made when investigating MZFO; one is that the zinc occupies only tetrahedral sites,[5] and the second is that the amount of Mn^{3+} present is insignificant. Based on these assumptions the percentage of the available octahedral sites occupied by Mn^{2+} was compared to the changes in the ν_1 absorbance band. From this comparison a strong correlation to the EXAFS-determined occupancies was found, as shown in Fig. 2. This plot can also be done with $Fe^{2+/3+}$ octahedral occupancy since the first absorption region is actually a combination of the six coordinated Mn^{2+}–O stretch and $Fe^{2+/3+}$–O stretch. Since Mn^{2+}, Fe^{2+}, and Fe^{3+} have similar masses and similar bond lengths when octahedrally coordinated,[5] the two stretches appear as one unresolved peak that shifts due to the ratio of concentrations of Mn^{2+} to $Fe^{2+/3}$.

In the second absorption region, the separate bands do not appear to shift but the relative intensity of each peak changes. This change in intensity of individual bands can be attributed to concentration differences between samples as well as different concentrations of a given metal in tetrahedral sites. The lowest-frequency band, ν_4, corresponds to Zn^{2+}, which is the heaviest metal in the system. The change
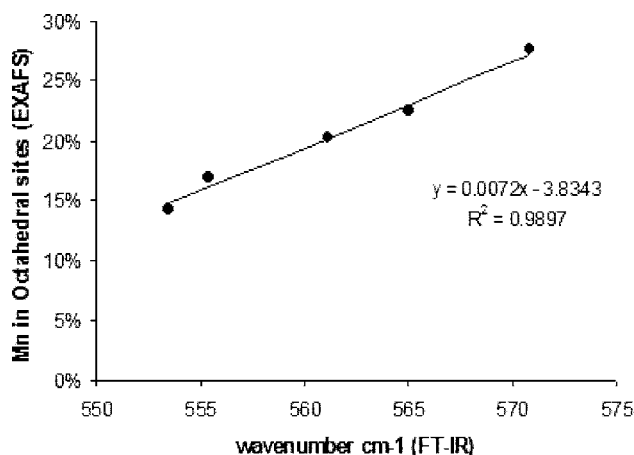

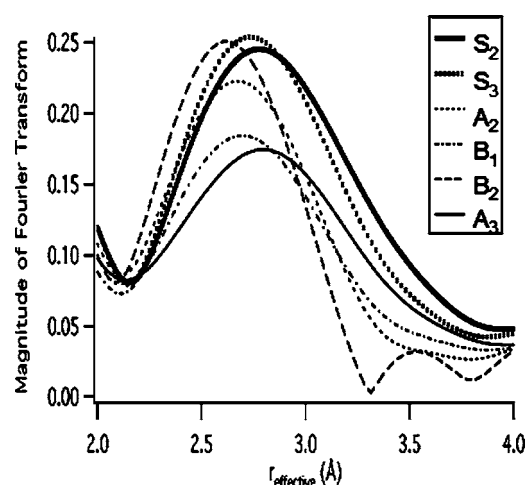FIG. 2. Plot of the percentage of the available octahedral sites occupied by Mn^{2+} vs wave number.

FIG. 3. Plot of the magnitude of Fourier transform vs effective radius (k weight of 1) for the Mn edge.

in intensity in this band, as seen in Fig. 1, is due to the amount of Zn^{2+} in the sample. The remaining two absorbance bands therefore correspond to Mn^{2+}/Fe^{2+}–O and Fe^{3+}–O when tetrahedrally coordinated. The Fe^{3+}–O stretch should have a higher natural frequency than the Mn^{2+}/Fe^{2+}–O stretch due to the significantly shorter bond length of the former. Thus ν_2 should correspond to the Fe^{3+}–O stretch, while ν_3 corresponds to the Mn^{2+}/Fe^{2+}–O stretch. This relationship is verified in our results because the intensity of ν_2 increases as the percentage of the tetrahedral sites occupied by Fe^{3+} increases, allowing the vibrational difference to become more apparent.

These results can be explained in terms of a classical mechanics model in which the cation-oxygen bonds are defined as springs. In comparing the two types of interstitial sites one can envision two harmonic-oscillator systems, each composed of a single mass in the center with one containing four springs and the other containing six springs. In either traverse motion or vibration along an axis, the four-spring system will have a lower natural frequency than that of a six-spring system based on the corresponding equations. For motion along an axis,

$$\omega \equiv \sqrt{\frac{k}{m}},$$

and for traverse motion,

$$\omega \equiv \sqrt{\frac{f}{l_b}},$$

where ω is frequency, k is the total spring constant of the system, m is mass, f is related to the driving force, and l_b is length of the spring which is related to bond length. Therefore, a four-bond system should have a lower natural frequency than the six-bond system given the same central metal.

Qualitative trends in site occupancy can also be seen by looking at the magnitude plots of the Fourier transform in EXAFS analysis. For a k weight of 1, predominately octahedral occupancy yields a peak at 2.6 Å and a node at 3.3 Å, as seen in Fig. 3. High tetrahedral occupancy removes the node

and shifts the peak toward 3.1 Å. MZFO sample A_3 was used as a double-blind validation step in which FTIR and the correlation curve in Fig. 2 were used to predict the site occupancy, which was then compared to independently determined EXAFS results. The two techniques showed impressive agreement, with FTIR indicating that 15% of the octahedral sites were occupied by manganese, while EXAFS yielded $13+/-2\%$ for the same value. This is particularly noteworthy because it represents an extrapolation rather than an interpolation; all of the samples used to calibrate Fig. 2 had a greater fraction of octahedral sites occupied by manganese than was found in this sample.

These results show a correlation of FTIR measurements to the data derived from EXAFS analysis. The resulting curve, shown in Fig. 2, can be used to determine the percent-age of the available octahedral sites occupied by Mn^{2+} and $Fe^{2+/3+}$. Using elemental analysis to determine the total concentration of zinc, manganese, and iron, the percentage of the tetrahedral sites occupied by each can be determined. This demonstrates that FTIR can be used to determine the cation occupancy in mixed metal ferrite systems.

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