

Structure analysis of coprecipitated ZnFe_2O_4 by extended x-ray-absorption fine structure

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Though the anomalous antiferromagnetism of zinc ferrite was a subject of intensive studies in the past, the unusually high magnetization of coprecipitated zinc ferrite at low temperatures has drawn renewed interest among researchers. The local structures of zinc ferrites around Fe and Zn atoms are measured using extended x-ray-absorption fine structure and the results are discussed in correlation with their magnetic properties. The structure around the Zn atom was found to differ between zinc ferrite produced by ceramic and coprecipitation techniques. The position of the second-nearest neighbor of the Zn atom for coprecipitated zinc ferrite was shorter than the one produced by the ceramic method. This suggests the possible occupation of the Zn atoms in the octahedral sites and the cause for the unusually high magnetization in coprecipitated zinc ferrite. Furthermore, the intensity of the peak is weak compared to the one produced by the ceramic method. This is thought to be due to the deformation induced by the occupation of zinc ions in the octahedral sites, causing a decrease in the structural periodicity.

I. INTRODUCTION

Zinc ferrite (ZnFe_2O_4) is usually assumed to be a completely normal spinel with zinc ions exclusively occupied in the tetrahedral sites. This is described as an anomalous antiferromagnetic substance with a Néel temperature around 10 K. The magnetic behavior of ZnFe_2O_4 has drawn much interest and has been a subject of intensive studies.^{1,2} To explain the anomalous behaviors, it has been suggested that small amount of Fe ions occupy tetrahedral (*A*) sites and the Fe(*A*) ions and their 12 nearest neighbors at octahedral (*B*) sites form a cluster. Each of the Fe (*B*) spins is coupled with the Fe (*A*) spins by *AB* interaction which is much stronger than the *BB* interaction.³ These experiments have been carried out on polycrystalline samples prepared by the ceramic method. However, very recent research on ultrafine ZnFe_2O_4 prepared by the coprecipitation technique,⁴ with a defect-free crystal structure,⁵ has showed unusually higher magnetization.⁶ Furthermore, the magnetization was found to vary with particle size and takes a maximum around 8 nm diameter.^{7,8} In this paper, we report the results of structure analysis of coprecipitated ZnFe_2O_4 using extended x-ray-absorption fine structure (EXAFS), in search of an answer to the high magnetization observed in coprecipitated ZnFe_2O_4 . This may solve the unresolved problem of scientific interest and provide clues to produce particles with high magnetization.

II. EXPERIMENT

A. Sample preparation and characterization

The ZnFe_2O_4 samples were prepared by the following procedure:

(a) Ceramic method—The powders of ZnO and Fe_2O_3 of chemical grade were mixed at a mole ratio of 1:1 in a mechanical mixer. The mixture was calcined at 1373 K for 3 h in oxidizing atmosphere and cooled slowly. Then the product was ground in a mechanical grinder for 1 h. After, it was calcined again at 1373 K for 3 h in the oxidizing atmosphere,

slowly cooled to room temperature, and ground to powder again.

(b) Coprecipitation technique—The coprecipitated ZnFe_2O_4 was prepared by the method described in Ref. 4.

(c) Coprecipitation followed by annealing—The coprecipitated ZnFe_2O_4 is calcined at 1373 K for 3 h, cooled slowly, and ground to powder in a grinder.

The ferrites prepared by the above methods were examined by x-ray diffraction. The local structure was analyzed using EXAFS by measuring the absorption spectra at Fe and Zn *K*-edges. The sample was mixed with polythelene and pellets were made. The magnetization of these products were also measured in a vibration sample magnetometer (VSM) in the 5 K to room temperature range.

III. RESULTS AND DISCUSSION

A. Magnetization of ZnFe_2O_4

The magnetization temperature curves of ZnFe_2O_4 prepared by the methods described in the previous section was measured using VSM in the temperature range 5–293 K at 6 kOe are given in Fig. 1. As can be seen, the magnetization shows an increase with decreasing temperature and attains maximum around 20 K, in the case of ZnFe_2O_4 produced by the ceramic method and coprecipitation followed by annealing. But, in the case of coprecipitated ZnFe_2O_4 , the magnetization continues to increase with decreasing temperature and the increase at 6 K is about $16\times$ that of the value at room temperature. The x-ray-diffraction analysis confirmed that ZnFe_2O_4 produced by all three methods crystallized in the spinel structure and the cation distribution in the structure is believed to be the main cause for the differences in magnetic behavior among zinc ferrites prepared by different methods. The reason for higher magnetization has been suggested to be due to high concentration of magnetic clusters in coprecipitated zinc ferrite. Neutron-diffraction studies have revealed a high concentration of Fe ions in the *A* sites that form clusters with the Fe atoms in the *B* sites. It also has been reported that the ZnO: Fe_2O_3 ratio of coprecipitated

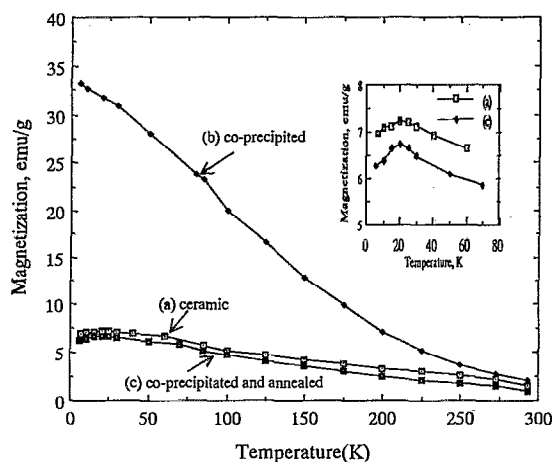


FIG. 1. Magnetization temperature curves of ZnFe_2O_4 produced by different methods.

ZnFe_2O_4 is the same as that of the one produced by the ceramic method, meaning that there is no density difference among the ferrite produced by different methods. Therefore the concentration increase of Fe ions in A sites would lead to the occupation of zinc ions in the B sites. To find an explanation for the above differences, structure information of zinc ferrites is necessary.

B. EXAFS of ZnFe_2O_4

EXAFS is an ideal tool to investigate the local structure of matter. The local structure information, such as interatomic distances (in the case of spinel structure, this would lead to the determination of the sites occupied by the atoms), coordination number, and the kind of surrounding atoms around a selected x-ray absorbing atom could be studied.

The EXAFS spectra of ZnFe_2O_4 prepared by the methods described in Sec. II at the Fe K-edge are measured and the Fourier transform of the above spectra are given in Fig. 2. The two intensive peaks in the Fourier transform are centered around distances of 1.45 and 2.6 Å. In the case of ZnFe_2O_4 , if we assume the Fe atoms to occupy exclusively

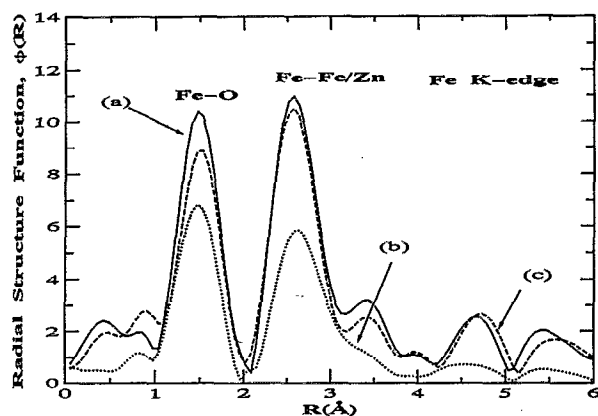


FIG. 2. Fourier transforms of ZnFe_2O_4 prepared by (a) the ceramic method, (b) coprecipitation, and (c) coprecipitated and annealed, at the Fe K-edge.

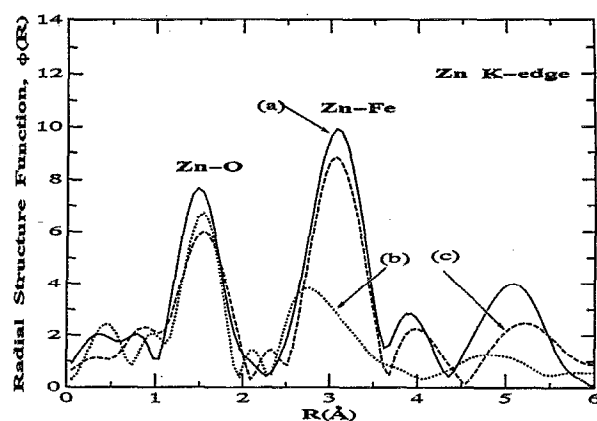


FIG. 3. Fourier transforms of ZnFe_2O_4 prepared by (a) the ceramic method, (b) coprecipitation, and (c) coprecipitated and annealed, at the Zn K-edge.

in the octahedral sites, the second-nearest peak is a result of the scattering from Fe-Fe atoms and Fe-Zn atoms, where Zn atoms are occupied exclusively in the A sites.

Considering the peak intensities between ZnFe_2O_4 samples, it could be seen that the peak intensity of coprecipitated ZnFe_2O_4 is weak compared to the samples produced by other methods. As far as the peak positions are concerned, the distance between the central atom and the second-nearest peak is marginally greater in the case of coprecipitated ZnFe_2O_4 .

EXAFS spectra of ZnFe_2O_4 at the Zn K-edge were measured. Fourier transforms of the same are given in Fig. 3. The two intensive peaks in the Fourier transform are centered around 1.5 and 3.1 Å in the case of ZnFe_2O_4 produced by the ceramic method and coprecipitation followed by annealing, whereas, in the case of coprecipitated ZnFe_2O_4 , the peaks centered around 1.6 and 2.8 Å and the intensity of the peak at 2.8 Å was very weak compared to the ones produced by other methods.

The Fourier transform of the spectra at Fe and Zn K-edges for ZnFe_2O_4 produced by ceramic and coprecipitation methods showed considerable difference in amplitude of radial structure function. A similar observation was made by Maeyama *et al.*⁹ for ZnFe_2O_4 of 56 and 5 nm diameters. The reduction in radial structure function, which is directly related to the coordination number, was considered due to the increase in the surface atomic layer for finer particles. The broadening of the metal-metal peak in the Zn K-edge has been considered due to the amorphous state of the sample.

In our study, if we consider the second-nearest peak in the Fourier transform of the spectrum at the Zn K-edge in all three samples, it is clear that the peak of coprecipitated ZnFe_2O_4 has become broader and the peak maximum lies at a distance shorter than in the other two cases. The peak broadening can be caused as a result of (a) the disordered state of the sample and (b) scattering from atoms two different distances; i.e., the peak is a result from the contribution of two different peaks. If it is true that the zinc atoms occupy only the A sites, it is not possible to get a response at shorter atomic distance than that of ZnFe_2O_4 produced by the ceramic method.

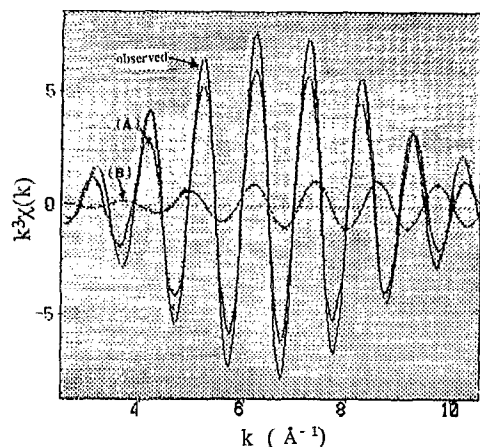


FIG. 4. The inverse Fourier transform of the second peak (Zn-Fe) in Fig. 3(a) and the contributions from shells (a) Zn(A)-Fe(B) and (b) Zn(B)-Fe(B).

Assuming that Zn atoms are occupied in both tetrahedral and octahedral sites and the main contribution of the scattering to be only from shells Zn(B)-Fe(B) at 2.98 Å and Zn(A)-Fe(B) at 3.48 Å [even though the scattering from Zn(B)-Fe(B), Zn(B)-Zn(B) at 2.98 Å and Zn(A)-Fe(B), Zn(B)-Fe(A) at 3.48 Å shells are possible], curve fitting as well as individual contributions of these scatterings were evaluated. The values of the Debye-Waller factor and mean free path were determined from the analysis of zinc ferrite prepared by the ceramic method and were used in the analysis of coprecipitated and coprecipitated and annealed zinc ferrite. The best fit obtained for the second-nearest peak in Fig. 3(a) gave a value of $R=2.7\%$. The individual contribution of the scattering from shells Zn(A)-Fe(B) and Zn(B)-Fe(B), are given in Fig. 4 and it can be seen that the scattering is contributed to almost only by shell Zn(A)-Fe(B). But, in the case of coprecipitated zinc ferrite (fit $R=2\%$), in addition to the contribution of Zn(A)-Fe(B) scattering, a considerable contribution from Zn(B)-Fe(B) is also observed and is shown in Fig. 5. Also, when the coprecipitation followed by annealing sample was analyzed, it resembled very much that produced by the ceramic method.

This suggests that the shift as well as the broadening of the peak at a shorter distance is a result of the zinc atoms occupying the octahedral sites, too. In coprecipitated zinc ferrite, this may be possible, as the cation distributions are in a metastable state as they are produced at low temperature within a short period of time. If they are brought to higher temperature, stability is achieved and the Zn ions take the most stable position in A sites. This is demonstrated in the results on coprecipitated and annealed samples. The occupation of the zinc atoms in the octahedral sites may have caused some deformation which has reduced the periodicity

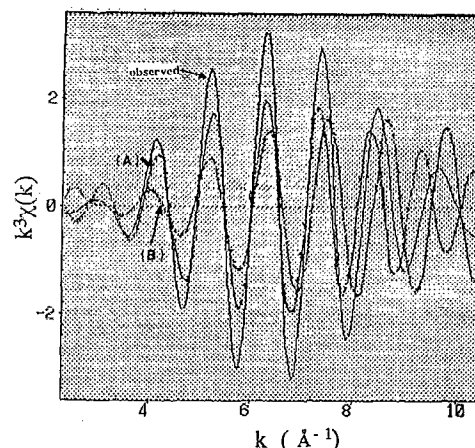


FIG. 5. The inverse Fourier transform of the second peak (Zn-Fe) in Fig. 3(b) and the contributions from shells (a) Zn(A)-Fe(B) and (b) Zn(B)-Fe(B).

of the structure and may have caused the reduction in the amplitude radial structure function.

Furthermore, the occupation of zinc ions in both tetrahedral and octahedral sites may have led to a magnetization mechanism which is different to the one observed in antiferromagnetic substances, or on the other hand, the concentration increase in Fe ions in tetrahedral sites due to the occupation of zinc ions in octahedral sites may have caused an increase in the concentration of magnetic clusters formed through AB interaction and leading to magnetization increase. However, it could be said that the cation distribution in coprecipitated zinc ferrite is the cause for the higher magnetization.

IV. CONCLUSION

The results of EXAFS analysis on coprecipitated zinc ferrite have suggested that the zinc ions are occupied both in A and B sites. The resulted cation distribution is believed to have caused the increase in magnetization, and the occupation of Zn ions in the B sites is believed to have led to the deformation in the structure that reduces the periodicity of the structure, causing a decrease in radial structure function amplitude.

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