Irregular distribution of metal ions in ferrites prepared by co-precipitation technique structure analysis of Mn–Zn ferrite using extended X-ray absorption fine structure

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Abstract

The tetrahedral/octahedral site occupancy of non-magnetic zinc ion, added to maximize the net magnetic moment of mixed ferrites has been found to depend on the method of preparation. In this paper, we qualitatively analyze the metal ion distribution in Mn–Zn ferrite particles prepared by co-precipitation and ceramic methods using extended X-ray absorption fine structure (EXAFS) technique. The results suggest that the differences observed in the magnetic properties of the samples prepared by different methods are not only due to the difference in particle size but also due to the difference in cation distribution. The difference in cation distributions between ferrites of similar composition prepared differently has been found to depend on the crystal field stability energies of the metal ion of interest and associated cations. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ferrites; Coprecipitation; Fine particles; EXAFS

1. Introduction

In current technology, considerable efforts are being made to produce useful devices of small sizes, which require a reduction in the dimension of the bulk material. As a result, novel behavior in electronic, optical and magnetic properties in dimensionally reduced materials has been uncovered [1–3]. Among magnetic materials, ferrite has been used in many industrial applications and is prepared either by ceramic or co-precipitation techniques [4]. However, it has been found that ferrite particles of similar composition differ in their magnetic properties depending on the preparation technique. One of the reasons for such behavior is believed to be due to the differences in particle size. A decrease in particle size leads to an increase in non-magnetic fraction on the surface of the particle [5]. In ferrites, the non-magnetic zinc ions are known to occupy the tetrahedral sites and included to maximize the net magnetic moment in the unit cell.

In the recent past, there has been considerable research on co-precipitated zinc ferrite [6,7] which shows anomalous magnetic behavior compared with the ones produced by ceramic method. Since

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the magnetization decreased with the increase in particle size, this phenomenon could not be explained by the presence of non-magnetic fraction due to spin disorder on the surface of the particle [8–9]. Results of the local structure analysis by EXAFS suggested that the Zn ions which occupy both tetrahedral and octahedral sites in co-precipitated zinc ferrite caused the anomalous magnetic behavior [10]. Since the zinc ions are known to occupy tetrahedral sites only, we consider the above zinc ion distribution to be irregular. From the magnetic material research point of view, it is important to know whether this irregular distribution of zinc ions that leads to unusual magnetic properties is something confined to zinc ferrite only or common to any co-precipitated ferrite that has zinc ion as a constituent. And also, it will be interesting to investigate whether such irregular distribution of ions is confined to zinc only.

In this paper, we have made an attempt to obtain some insight into the metal ion distribution in Mn–Zn ferrite using the EXAFS. The metal ion distribution of Mn–Zn ferrite (MnO : ZnO : $Fe_2O_3 = 0.5 : 0.5 : 1.0$), prepared by using various methods such as, (a) co-precipitation, (b) ceramic method and (c) co-precipitated and calcined at 1373 K, has been determined qualitatively and the results are discussed together with their magnetic properties.

2. Experimental

Preparation of Mn–Zn ferrite samples:

The Mn–Zn ferrite samples prepared by three different methods were used in this study.

(i) To prepare co-precipitated Mn–Zn ferrite, mixed solutions of manganese, zinc and ferric chlorides were used to obtain the following final ratios – MnO : ZnO : $Fe_2O_3 = 0.5 : 0.5 : 1.0$. Then, sodium hydroxide solution was added until the pH of the mixed metal ion solution reached 13 and boiled for 1 h at 373 K. Then the precipitate was filtered, washed with deionized water and dried at 333 K.

(ii) The co-precipitated sample was calcined at 1373 K for 3 h under nitrogen purging and cooled slowly. The cooled product was ground to fine powder.

(iii) In ceramic method, the powders of ZnO/ $MnCO_3$ and Fe_2O_3 of chemical grade were mixed at a specified mole ratio in a mechanical mixer. The mix was calcined at 1373 K for 3 h under inert atmosphere and cooled slowly. The cooled product was ground to fine powder. This procedure was repeated twice before obtaining the final product.

The chemical compositions of the ferrites prepared by different methods were analyzed using the inductively coupled plasma (ICP) technique. The crystallinity of the ferrite was examined by an X-ray diffractometer. The magnetic properties of the ferrite, from room temperature to the liquid Helium, were studied with a SQUID. The EXAFS spectra at Mn, Zn and Fe K-edges were obtained in a laboratory EXAFS [11] system in the transmission mode. The incident and transmitted intensities I_0 and I were measured simultaneously using an ionization chamber and a scintillation counter. Si(2 2 0) crystal was used as a monochromator. The data were analyzed using the Rigaku EXAFS program REX.

3. Results and discussion

The Mn–Zn ferrite powders (MnO : ZnO : $Fe_2O_3 = 0.5 : 0.5 : 1.0$) produced by (a) co-precipitation (sample A), (b) ceramic (sample B) and (c) co-precipitation followed by calcinations (sample C) methods were examined using an X-ray diffractometer and the diffractograms are shown in Fig. 1. The results confirmed that all the samples crystallize in the spinel structure irrespective of the method of preparation. The lattice parameters of samples A, B and C are 8.42, 8.49 and 8.49 Å, respectively. The average particle size of sample A, was evaluated using BET method and was found to be 13 nm. The TEM photographs of the same are shown in Fig. 2(a). For the ferrite samples B and C, the particle size ranges from a few microns to a few tens of microns depending upon the grinding time. The SEM photographs of the same are shown in Figs. 2(b) and (c).
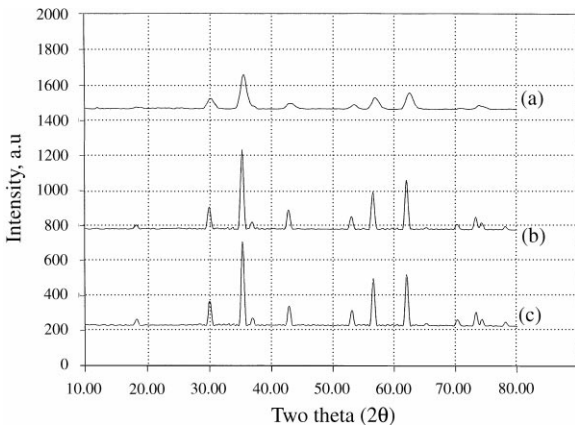
Fig. 1. X-ray diffraction patterns of Mn–Zn ferrite prepared by (a) co-precipitation, (b) ceramic and (c) co-precipitated and calcined methods.

Magnetizations of Mn–Zn ferrite samples were measured using the superconducting quantum interference device (SQUID) from liquid Helium temperature to 293 K and is shown in Fig. 3. Magnetization of sample A is smaller than sample B. However, the value of sample C is comparable to the one prepared by the ceramic method. The difference could be associated to their particle sizes. Considerable amount of study has been made in determining the cation distribution of ferrites prepared by using both the methods. It is believed that not all but some specific ions need high temperatures to occupy themselves in stable positions. One such ion is zinc in co-precipitated zinc ferrite. Zinc ions were irregularly distributed when they were prepared at temperatures around 373 K using
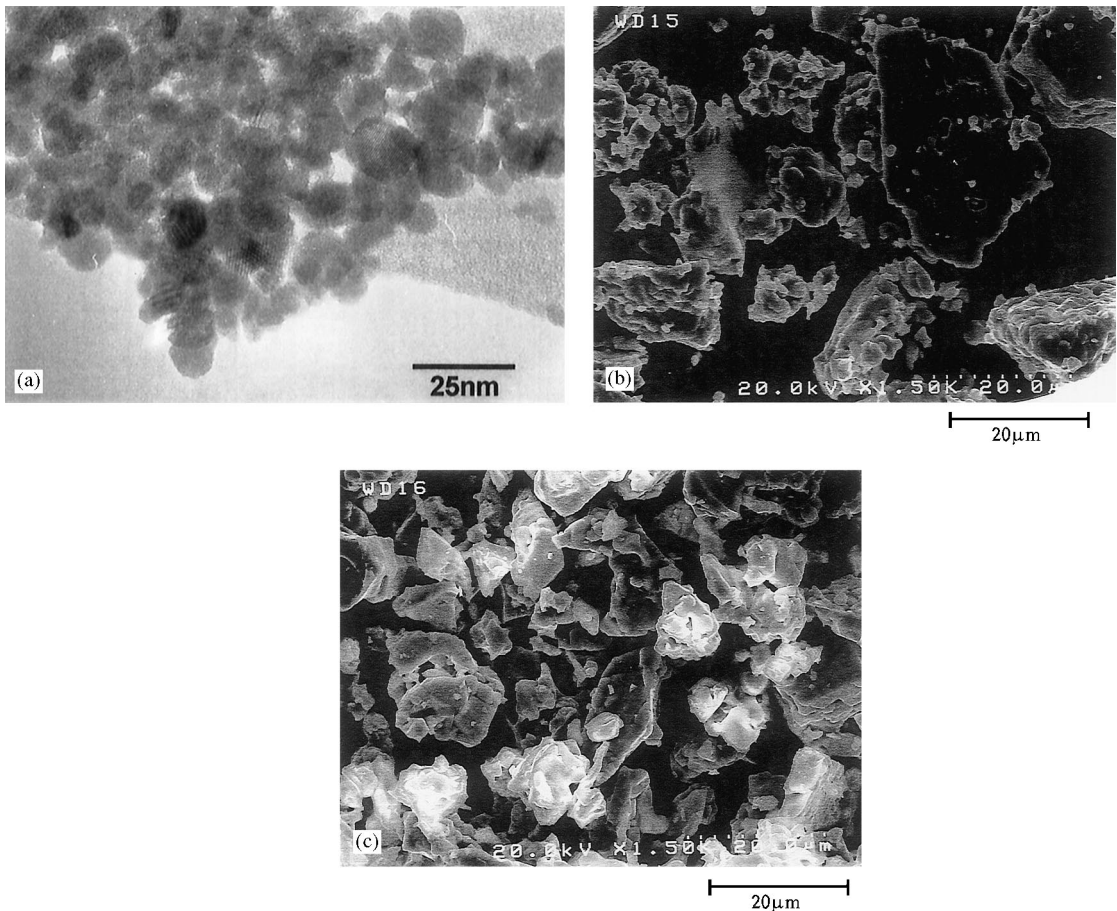

Fig. 2. Scanning electron microscope photographs of Mn–Zn ferrite prepared by (a) co-precipitation (b) ceramic and (c) co-precipitated and calcined methods.
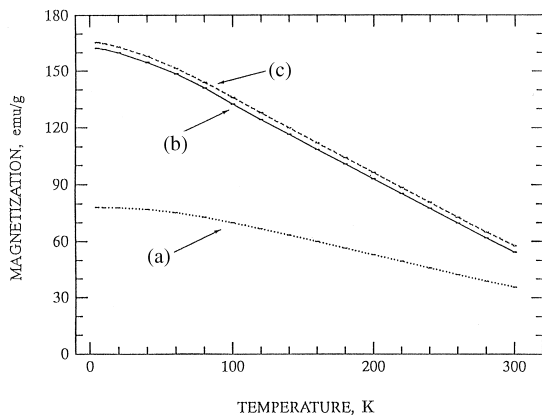
Fig. 3. Magnetization–temperature curves of Mn–Zn ferrite prepared by (a) co-precipitation, (b) ceramic and (c) co-precipitated and calcined methods.

co-precipitation technique [10]. If such irregular distribution of zinc ions is obtained in any ferrite prepared by co-precipitation, this phenomenon will be of great significance to researchers in magnetic materials. Before looking into the positive implications of this phenomenon on magnetic materials research, it is rather necessary to find out whether the irregular distribution of zinc ions is something specific to zinc ferrite or to any mixed ferrite containing zinc ions. The EXAFS has been considered a useful and supportive tool for analyzing problems of this nature. Elemental selectivity is one of the main characteristics of EXAFS and could be utilized in the case of mixed ferrites. By analyzing the EXAFS data taken at the absorption edge of the atom of interest, the type of atom, co-ordination number and inter atomic distances around each type of atom can be determined separately.

3.1. Analysis of Mn–Zn ferrite at Mn K-edge

The absorption spectrum at Mn K-edge measured for $Mn_{0.5}Zn_{0.5}Fe_2O_4$ (Table 1) samples A, B and C are shown in Fig. 4. If we compare the EXAFS spectra at Mn K-edge, the profiles show a clear difference between samples A and B.

The Fourier transforms of the absorption spectra at Mn K-edge for all three ferrites are shown in Fig. 5. Inter atomic distances within a radius of 4 Å are given in Table 2. Depending on the site occupied by

Table 1
Results of chemical analysis of $Mn_{0.5}Zn_{0.5}Fe_2O_4$

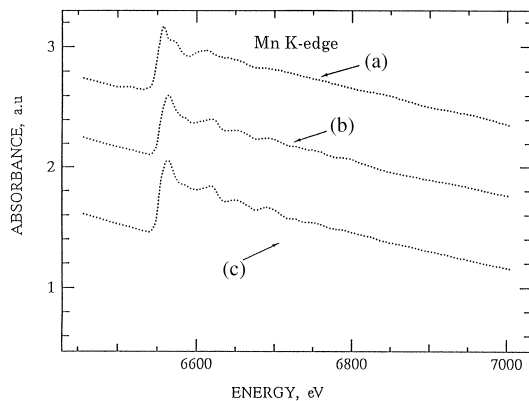| Sample	Mn (wt%)	Zn (wt%)	Fe (wt%)	Atomic wt% (Mn + Zn)/Fe
$Mn_{0.5}Zn_{0.5}Fe_2O_4$ (ceramic)	11.6	13.77	47.4	50.1
$Mn_{0.5}Zn_{0.5}Fe_2O_4$ (co-precipitated)	11.9	14.2	48.42	50.04

Fig. 4. EXAFS spectra of Mn–Zn ferrite prepared by (a) co-precipitation, (b) ceramic and (c) co-precipitated and calcined methods, at Mn K-edge.
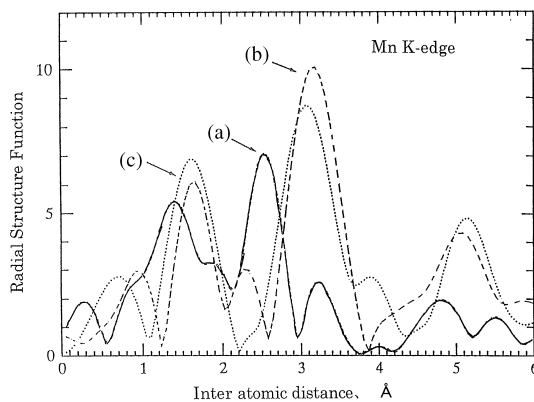

Fig. 5. Fourier transforms of Mn–Zn ferrite prepared by (a) co-precipitation, (b) ceramic and (c) co-precipitated and calcined methods, at Mn K-edge.

the cation, cation–oxygen and cation–cation distances differ very much. If we assume that Mn ions occupy the tetrahedral sites only, then the distance

Table 2
Lattice parameter and distances (Å) between atoms in tetrahedral (A) and octahedral sites (B) within a distance of 4 Å

Atomic pairs	Sample	$Mn_{0.5}Zn_{0.5}Fe_2O_4$		
		Co-precipitated	Ceramic method	Co-precipitated and fired
Lattice parameter		8.42	8.49	8.49
Mn(A)/Zn(A)–Mn(A)/Zn(A)	4	3.64	3.67	3.67
Mn(A)/Zn(A)–Fe(B)	12	3.49	3.52	3.52
Fe(B)–Fe(B)	6	2.97	3.0	3.0
Fe(B)–Mn(A)/Zn(A)	6	3.49	3.52	3.52
Mn(A)/Zn(A)–O	4	1.87	1.89	1.89
Fe(B)–O	6	2.06	2.08	2.08

between Mn ion and the first nearest neighbor oxygen should be 1.89 Å. Furthermore, the distance between the Mn ion and its second nearest neighbor, which is a cation in the octahedral site, will be at a distance of 3.52 Å. Therefore, if an atom in the spinel structure shows a peak at a distance less than 3.52 Å, then, there is a possibility for the atom under consideration to occupy the octahedral site. In the latter case the second nearest neighbor is a metal atom in the octahedral site at a distance of 3 Å. It should be noted that the peak positions in the Fourier transformed profile have to be corrected for phase shifts to arrive at the exact distances between atoms.

The Fourier transform profile at the Mn K-edge suggested that the Mn ions occupied the octahedral sites in the case of sample A and tetrahedral sites in the case of sample B. Furthermore, in the case of sample C, as in the case of zinc ferrite, the Mn ions show a profile similar to that for the one prepared by ceramic method. These differences in the EXAFS spectra as well as in the Fourier transformed profiles of ferrite prepared by different methods clearly confirm that the manganese ion too behave similar to the zinc ions in zinc ferrite. Therefore, the peak position of the second nearest neighbor suggests that the manganese ions occupy the octahedral sites in sample A and tetrahedral sites in samples B and C.

Furthermore, if we compare the peak position corresponding to Mn–O, inter atomic distances in sample B and C were larger than that of sample A. Normally, the Mn–O distance for the Mn ions in the tetrahedral site is shorter than that for the Mn
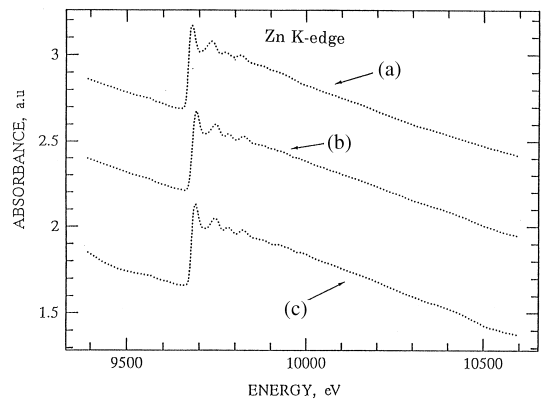

Fig. 6. EXAFS spectra of Mn–Zn ferrite prepared by (a) co-precipitation, (b) ceramic and (c) co-precipitated and calcined methods, at Zn K-edge.

ions in the octahedral site. But, from the calculations made by Verwey et al. [12] and Bo [13], for the complete lattice, it follows that for the spinel consisting of divalent and trivalent metal ions the inverse structure has the lowest lattice energy only when the oxygen parameter $u < 0.379$, whereas the normal structure has the lowest energy when $u > 0.379$. This could be the reason for the differences in the Mn–O distances among ferrites.

3.2. Analysis of Mn–Zn ferrite at Zn K-edge

The absorption spectra and Fourier transform profile of the ferrite samples A, B and C at Zn K-edge are given in Figs. 6 and 7, respectively. When the Zn atoms occupy the tetrahedral sites only, inter atomic distance between the zinc atom and its
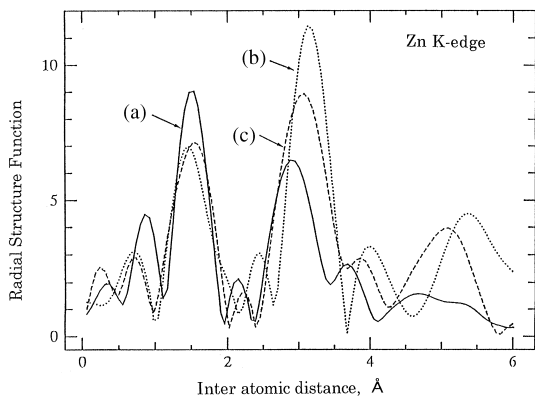
Fig. 7. Fourier transforms of Mn–Zn ferrite prepared by (a) co-precipitation, (b) ceramic and (c) co-precipitated and calcined methods, at Zn K-edge.

Fig. 8. EXAFS spectra of Mn–Zn ferrite prepared by (a) co-precipitation, (b) ceramic and (c) co-precipitated and calcined methods, at Fe K-edge.

Fig. 9. Fourier transforms of Mn–Zn ferrite prepared by (a) co-precipitation, (b) ceramic and (c) co-precipitated and calcined methods, at Fe K-edge.

second nearest neighbors will be 3.52 Å. On the other hand, if the zinc atoms occupy the octahedral sites, then the distance between the zinc atom and its second nearest neighbor will only be 3 Å.

If we compare the Fourier transform results of sample A with B, a decrease in the intensity of the second nearest peak along with a shift towards shorter inter atomic distance is observed. However, in the case of sample C, the position of the peak coincided with sample B. Similar observation was made when zinc ferrite samples prepared by different methods were analyzed at the Zn K-edge.

3.3. Analysis of Mn–Zn ferrite at Fe K-edge

The absorption spectra and Fourier transform profile of the ferrite at Fe K-edge are given in Figs. 8 and 9, respectively. If some percentages of manganese and zinc atoms occupy the octahedral sites, then equal number of Fe atoms will occupy the tetrahedral sites. Consequently, the Fe atoms will occupy both tetrahedral as well as octahedral sites. Therefore, the peak corresponding to the second nearest neighbor consists of contributions from shorter and longer inter atomic distances. In the Fourier transform results at Fe K-edge, the intensity of the second nearest peak for sample A is reduced and the peak broadens and spreads over a wider range suggesting the presence of both the second and third nearest neighbor peaks in it. This suggests that the Fe ions occupy both tetrahedral
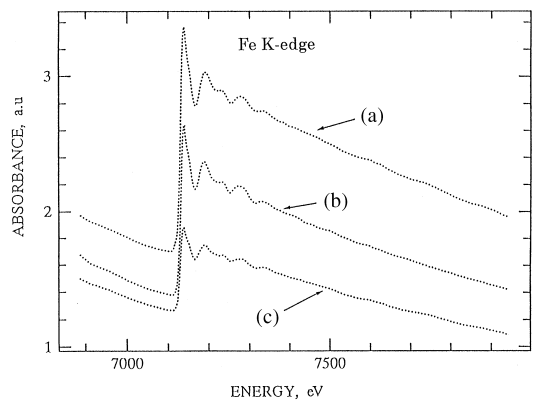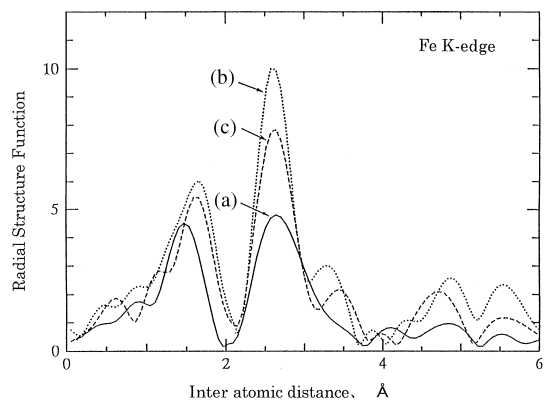
and octahedral sites in the case of sample A. However, in the case of sample C, the peak becomes sharper suggesting that most of the Fe ions occupy the octahedral sites.

From the above qualitative analysis using EXAFS, it could be said that the distribution of some specific metal ions in the spinel structure depends on the preparation method. When a ferrite is prepared the divalent and trivalent metal ions occupy the site for which they have higher crystal field stability energy (CFSE) [14,15]. For example, the Fe^{2+} ion has higher octahedral CFSE energy and occupies the octahedral sites. However, the metal ions in consideration in this study, such as,

Fe^{3+}, Mn^{2+}, Zn^{2+} have zero crystal field stability energy. Therefore, these ions can occupy either tetrahedral or octahedral sites depending on their preference energy of the second cation in the structure in co-precipitated ferrite. A study on co-precipitated magnetite as well as cobalt ferrite [16] carried out by the author did not reveal any drastic differences in cationic distribution between the ferrites prepared by co-precipitation and ceramic method. The reason being that the Fe^{2+} ions in the case of magnetite and Co^{2+} ions in the case of cobalt ferrite have octahedral site preference energy and occupy the octahedral sites. Therefore, the Fe^{3+} ions with zero preferential energy can occupy only the sites left vacant.

However, in the case of zinc ferrite or manganese zinc ferrite, all the ions used in the preparation of ferrite i.e. Fe^{3+}, Mn^{2+}, Zn^{2+} have zero octahedral preference energy. Therefore, all of them occupy the octahedral and tetrahedral sites randomly. Even though the ions have zero octahedral preference energy, we believe that there are significant differences in site preference energy at some specific temperature. Therefore, at temperatures as high as 1473 K the ions move to the stable positions, like Zn^{2+} from octahedral to the tetrahedral sites. In conclusion, the site distribution of ions that have zero CFSE (e.g. Fe^{3+}, Mn^{2+}, Zn^{2+}, etc.) depends very much on the preparation temperature (method) and the octahedral or tetrahedral CFSE (e.g. Co^{2+}, Fe^{2+}) of the associated metal ions [15].

4. Conclusion

The EXAFS analysis of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ suggests that the differences observed in magnetic properties of the samples prepared by different methods were not only due to the difference in particle size but also due to the differences in cation distribution. Even though Fe^{3+} and Mn^{2+} ions have equal magnetic moments, they do not contribute to the difference in magnetization due to the difference in cation distribution in tetrahedral and octahedral sites, the distribution of the non-magnetic zinc ions will influence the magnetization. In co-precipitation, ferrites are prepared relatively at very low temperatures and the metal atoms that have zero CFSE (Fe^{3+}, Mn^{2+}, Zn^{2+}) occupy the tetrahedral and octahedral sites randomly. The ions that have zero CFSE can be made to take selective sites by associating the above with an ion that has a high octahedral or tetrahedral CFSE. The above findings will allow us to design some magnetic material with interesting magnetic properties using the co-precipitation technique.

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