Electronic structure studies of Fe-doped ZnO nanorods by x-ray absorption fine structure

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Abstract

We report the electronic structure studies of well-characterized polycrystalline Zn\textsubscript{1-x}Fe\textsubscript{x}O (x = 0.0, 0.01, 0.03 and 0.05) nanorods synthesized by a co-precipitation method using x-ray absorption fine structure (XAFS). X-ray diffraction (XRD) reveals that Fe-doped ZnO crystallizes in a single phase wurtzite structure without any secondary phase. From the XRD pattern, it is observed that peak positions shift towards lower \(2\theta\) value with Fe doping. The change in the peak positions with increase in Fe contents clearly indicates that Fe ions replace Zn ions in the ZnO matrix. Linear combination fittings at Fe \(K\)-edge demonstrate that Fe is in a mixed-valent state (Fe\textsuperscript{3+}/Fe\textsuperscript{2+}) with a ratio of \(\sim 7:3\) (Fe\textsuperscript{3+}:Fe\textsuperscript{2+}). XAFS data are successfully fitted to wurtzite structure using IFEFFIT and Artemis. The results indicate that Fe substitutes Zn site in the ZnO matrix in tetrahedral symmetry.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years spintronics materials continue to be of great interest to the scientific community due to their potential technological applications. The basic idea is to combine the characteristics of existing magnetic devices with semiconductor devices in order to realize the new generation of devices that are smaller, energy efficient and faster than presently available devices [1–9]. The key requirement in the development of such devices is efficient injection, transfer and detection of spin-polarized currents at/or above room temperature (RT). However, due to the well-known problem of resistance/lattice mismatch at metal/semiconductor interfaces, hindering an effective spin injection [10], much interest is now concentrated on the development of ferromagnetic (FM) semiconductors at RT.

The dilute magnetic semiconductors (DMSs) can be designed by replacing the fraction of the non-magnetic semiconductor cation by the 3d transition metal (TM) cations. DMSs are promising candidates for spintronics applications at ambient temperatures, provided their Curie temperature (\(T_C\)) is far above the RT. Therefore, a number of different semiconductor hosts have been investigated to test their magnetic properties. In the past, most attention was paid to (Ga, Mn)As [11–17] and (In, Mn)As [18–23] DMS systems. However, their reported highest \(T_C\) are only around 170 K for (Ga,Mn)As [24, 25] and 35 K for (In,Mn)As [25, 26]. Therefore, there is a strong incentive to develop new DMSs with much higher Curie temperatures. In particular, the calculations of Dietl et al [27] were the first to indicate that Mn-doped ZnO could exhibit FM above RT. Later Sato and Katayama-Yoshida also investigated ZnO-based DMS by \textit{ab initio} electronic structure calculations and reported FM ordering in 3d TM-doped ZnO [28, 29]. These theoretical
were subjected to subtraction of the atomic absorption using spectrum for analysis. Prior to analysis, the EXAFS spectra are taken and averaged to produce a high quality monochromator was about 1.5 eV in the energy range studied. The resolution of the edge region of a metallic Fe/Zn foil. The resolution of the beamline is monochromatized by a double-crystal Si (1 1 1) with a maximum storage current of 200 mA was utilized. This Pohang Accelerator Laboratory (PAL) operating at 2.5 GeV Fe of 36 kV and a current of 30 mA. For XAFS experiments at the Fe–ZnO matrix exists in a mixed-valent state (i.e. Fe2+ and Fe3+) in the case of films and nanoparticles. However, Shinagawa et al [38] reported that there is a possibility of the formation of the nanosized ZnFe2O4 spinel phase. Recently, our group has reported ferromagnetism in the Fe–ZnO system at RT prepared by ion implantation and followed by a swift heavy ion irradiation technique [39]. These results were explained in the light of the mixed-valent state of Fe ions (Fe2+/Fe3+) and hole mediated ferromagnetism as theoretically predicted by Dietl et al [27] and Sato et al [29].

2. Experimental details

Compounds with a nominal composition of Zn1−xFexO (x = 0.0, 0.01, 0.03 and 0.05) were synthesized by the co-precipitation method. Analytical grade metal nitrates [Zn(NO3)2 ⋅ 6H2O, Fe(NO3)3 ⋅ 9H2O] were used to prepare Fe–ZnO samples. The details of the synthesis of Fe–ZnO and other magnetic characterizations are reported elsewhere [40]. The samples are in the form of nanorods with a perfect crystalline structure and exhibit ferromagnetism at RT [40]. The x-ray diffraction (XRD) measurements were carried out at RT using a Philips X’pert (MPD 3040) x-ray diffractometer with a Cu Kα source (λ = 1.5406 Å) operated at a voltage of 36 kV and a current of 30 mA. For XAFS experiments at Fe K- and Zn K-edges, 10B XRS KIST-PAL beamline of the Pohang Accelerator Laboratory (PAL) operating at 2.5 GeV with a maximum storage current of 200 mA was utilized. This beamline is monochromatized by a double-crystal Si (1 1 1) monochromator detuned from 30% to 40% to suppress higher order harmonic content from the beam. All the scans were made in the transmission mode with nitrogen–argon gas-filled ionization chambers as detectors. The Fe K- and Zn K-edge energy was calibrated using the first inflection point of the edge region of a metallic Fe/Zn foil. The resolution of the monochromator was about 1.5 eV in the energy range studied. Several scans are taken and averaged to produce a high quality spectrum for analysis. Prior to analysis, the EXAFS spectra were subjected to subtraction of the atomic absorption using the AUTOBK program [41] and corrected for monochromator induced energy shifts using the spectra of Fe and Zn foil. The model for fitting was constructed using Athena 0.8.056 [42]. Self-absorption of the samples through various algorithms available with Athena was checked and found negligible for all applicable algorithms. All data were collected to 16.0 Å−1 at Fe K- and Zn K-edges, but used up to 13.0 Å−1 in our calculations to minimize the errors. Fourier transform (FT) formation and background removal procedures for isolating the oscillatory part of the absorption coefficient were done using the Athena.

3. Results and discussion

3.1. XRD data analysis

XRD pattern obtained from Zn1−xFexO (x = 0.0, 0.01, 0.03 and 0.05) is shown in figure 1. XRD data were analysed using Powder-X software [43] which reflects that all the samples exhibit single phase nature with wurtzite lattice and exclude the presence of a secondary phase. In order to obtain a better insight into the effect of Fe doping on the diffraction of doped ZnO, we have carried out a careful analysis of peaks position in the XRD pattern using the (0 0 2) plane. From the analysis of the peaks position it is observed that the peaks position shifted towards lower 2θ values with increase in the Fe contents. This shift in the peak position clearly reflects that Fe replaces Zn in the ZnO matrix.
provide the information on the valence state of the functioning ions in a system. The observed XAFS spectral features of Fe–ZnO are very similar to those of Fe2O3 (with a positive shift of the white line), indicating a mixed-valent state (Fe2+/Fe3+) of Fe ions. Previously, we have shown that O K-edge spectra (O1s–2p hybridization) of Fe-doped ZnO nanorods [40] do not show any resemblance to any reference compound spectra; therefore, the possibility of Fe2O3/ZnFe2O4 (or FeO/Fe2O3) precipitation in ZnO matrix below the detectable size limit of XRD is ruled out. It is also noted that the pre-edge spectral features of Fe–ZnO (the Fe-doped ZnO system) are different from the Fe metal foil (Fe0) which excludes the formation of metallic phase in the system. The pre-edge peak near 7114 eV (marked by an arrow) results from the 1s to 3d transition and has a significant intensity because of 3d–2p orbital mixing.

In general, the pre-edge centroid position depends strongly on the Fe oxidation state; however, the pre-edge intensity is mostly influenced by the Fe coordination geometry. The low intensity of the pre-edge peak refers to geometries with a centre of symmetry (e.g. octahedral); whereas the high intensity refers to non-centrosymmetric geometries (e.g. tetrahedral). It can be seen in figure 2(a) that the intensity of the pre-edge peak has a considerable spectral weight in the Fe-doped ZnO system as compared with the reference compounds and shifted towards the higher photon energy side. These changes in the spectral feature of Fe-doped ZnO show that the local electronic structure of Fe ions is different from that of the reference compounds of Fe metal foil (Fe0), Fe2O3(Fe3+) and Fe3O4(Fe2+/Fe3+), but bears a close resemblance to the Fe3O4(Fe2+/Fe3+) spectra. In Fe2O3, Fe2+–Fe3+ are equally distributed in the octahedral and tetrahedral sites, whereas in the case of Fe–ZnO most of the Fe2+-Fe3+ ions are at the tetrahedral site of the ZnO matrix (explained below in the EXAFS analysis). A shift in photon energy (∼1.5 eV) towards the higher energy side indicates more Fe3+ components in the Fe-doped ZnO as compared with Fe2O3, i.e. the presence of more charge carriers (electron/hole), which are responsible for the structural evolution of the local environment of Fe atoms in Fe–ZnO. In order to obtain a better insight into the valence state of Fe ions, a linear combination fitting (LCF) of the reference spectra was carried out from −10 eV to 50 eV from the edge energy. Figure 2(b) shows the observed and simulated XAFS spectra of the Fe-doped ZnO system. It is observed that all the XAFS spectra can be best simulated only when the Fe2O3 (Fe2+/Fe3+) spectrum is included, and Fe metal foil (Fe0) is excluded. The exclusion of Fe foil in the LCF fitting also indicates the absence of a metallic phase and/or clusters in the Fe-doped ZnO system. In this analysis, both the relative weights and absorption edge energies are allowed to vary. The energy shifts are within ±0.5 eV. Table 1 shows the LCF analysis results, which proves the presence of a mixed-valent (Fe3+/Fe2+) state of Fe ions with a maximum ratio of ∼7:3 (Fe3+:Fe2+). The R-factor and chi-square values are related to the accuracy of the best fit and show a very small variation of the percentage error in the calculated XAFS spectra. Zn K-edge XAFS spectra do not show any spectral variation for all Fe concentrations in ZnO (not shown here), which indicates that the Zn related defects are negligible.

3.2. Near-edge x-ray absorption fine structure (NEXAFS) analysis

In order to study the local electronic structure around Fe and Zn atoms, we have carried out the XAFS/EXAFS experiments at Fe K- and Zn K-edges. The XAFS/EXAFS techniques have been established as a powerful method to understand the local structure of 3d TM-oxide systems. Photons at characteristic energies are absorbed to produce the transition of a core electron to an empty state above the Fermi level and are governed by the dipole selection rules. XAFS is a fingerprint of the electronic state (valence state) of TM cations and is highly sensitive to inspect the presence of TM clusters and other impurities in the host matrix, whereas the quantitative structural information about the metal environment (3d–3d coordination state) can be obtained from the EXAFS analysis. Figure 2(a) shows the Fe K-edge XAFS spectra of Zn1−xFexO (x = 0.01, 0.03 and 0.05). As a guide to the valence state of Fe ions, reference Fe K-edge XAFS spectra of Fe metal foil (Fe0), FeO (Fe2+), Fe2O3 (Fe3+) and Fe3O4 (Fe2+/Fe3+) are also shown. It is well known that the peak positions and the spectral line shape of the 3d metal K-edge XAFS spectrum depend on the local electronic structure of the metal ions and, therefore,

![Figure 2. Normalized Fe K-edge XAFS spectra of Zn1−xFexO (x = 0.01, 0.03 and 0.05) at RT: (a) observed XAFS spectra compared with those of reference compounds of FeO(Fe0), Fe2O3(Fe3+) and Fe3O4(Fe2+/Fe3+); (b) calculated XAFS spectra of Zn1−xFexO simulated (solid line) by using LCF of reference compounds plotted with the experimental data (dots). (Colour online.)](image)
3.3. EXAFS analysis

It is well known that the local structure around a probe atom can be described by studying the fine structure above the absorption edge [44]. In order to know the local structure around the Fe and Zn atoms, we have done EXAFS analysis. The EXAFS spectrum can be understood in terms of the EXAFS equation. The EXAFS equation can be written in terms of the contribution from all scattering paths of the photoelectron [45, 46]:

\[ \chi(k) = \sum_i \chi_i(k), \]

(1)

where

\[ \chi_i(k) = \frac{(N_i S_i^2)}{R_i^2} \frac{F_{\text{eff}}(k)}{k^2} \sin \left[ 2k R_i + \phi_i(k) \right] e^{-2\sigma_i^2 k^2} e^{-2R_i/k_i}. \]

(2)

with

\[ R = R_0 + \Delta R \quad \text{and} \quad k^2 = \frac{2m_e (E - E_0 + \Delta E_0)}{\hbar}. \]

(3)

Equation (2) is multiple-scattering (MS) expansion as a sum over MS paths \( R \), where \( k \) is the wave number measured from the threshold \( E_0 \), \( N_i \) is number (coordination number) of atoms of type \( i \) at a distance \( R_i \) from the absorbing atom, \( S_i \) is amplitude factor, \( F_{\text{eff}}(k) \) is the effective scattering amplitude, \( \phi_i \) is phase of the back-scattering factor, \( k_i \) is elastic mean free path of the photoelectron and finally \( \sigma_i \) which characterizes the thermal and structural disorder, is the rms (root mean square) fluctuations in the effective path length \( R = R_{\text{path}}/2 \), which corresponds to a peak in the EXAFS FT, known as the Debye–Waller (DW) factor (exp(−2\( \sigma^2 k^2 \))). \( \sigma_i \) is mean square variation in inter-atomic distances. The absorption coefficient (\( \mu \)) was analysed and processed by the Athena V0.8.058. EXAFS data were then subjected to theoretical calculations using Artemis V0.8.012 [42] with the IFEFFIT package version 1.2.11c [47].

Figures 3(a) and (b) show the Fe and Zn \( k^3 \)-weighted EXAFS oscillation spectra of \( \text{Zn}_{1-x} \text{Fe}_x \text{O} \) (\( x = 0.0, 0.01, 0.03, 0.05 \)) along with FeO, \( \text{Fe}_x \text{O}_2 \), Fe metal foil and Zn metal foil for comparison. \( k^3 \chi(k) \) for the pure and Fe-doped ZnO as a function of the photoelectron wave vector \( k \) provides detailed information about the average immediate atomic environment of the given lattice site [48, 49]. To minimize the errors, we have considered the data with \( k \) in the range 2–13 Å\(^{-1}\) for further analysis. It is also confirmed that for the Fe concentrations from \( x = 0.01 \) to 0.05, the samples have similar \( k^3 \chi(k) \) curves matching the \( \text{Fe}_3\text{O}_4 \) curve, which is in agreement with the results of the near-edge XAFS.

In figure 3(a) qualitative similarities to \( \text{Fe}_3\text{O}_4 \) spectra and the effect of Fe doping on the ZnO matrix are clearly visible and are highlighted by vertical dashed lines. In figure 3(b) no visible effect of the addition of Fe into the ZnO matrix is seen, implying that Fe is doped at the Zn site without the formation of any impurity phase. Figures 3(a) and (b) also prove the good quality of the single phase sample and the XAFS data collected.

Figures 4(a) and (b) show the results of FT of EXAFS oscillation \( k^3 \chi(k) \), representing the radial distribution function (RDF) at the Zn K-edge and Fe K-edge, respectively. The graphs show the positions of atoms (Zn and Fe) which contribute to the scattering wave construction. Several peaks can be clearly observed at a longer radial distance, indicating that the local structure around the Fe atoms are well ordered with respect to short range ordering. In figure 4(a), the peak positions located at 1.56 Å and 2.90 Å correspond to the Zn–O and Zn–Zn bonding distances whereas the main peaks in figure 4(b) correspond to Fe–O (1.93 Å) and Fe–Fe (2.94 Å), respectively. These comparable inter-atomic distances of

| Sample     | Fe\(^{2+}\) | Fe\(^{3+}\) | R-factor | Chi-square |
|------------|------------|------------|----------|------------|
| Fe\(_{0.01}\)Zn\(_{0.99}\)O | 0.3333     | 0.6667     | 6.49 × 10^{-4} | 6.12 × 10^{-2} |
| Fe\(_{0.03}\)Zn\(_{0.97}\)O | 0.3333     | 0.6667     | 5.27 × 10^{-4} | 4.64 × 10^{-2} |
| Fe\(_{0.05}\)Zn\(_{0.95}\)O | 0.2777     | 0.7223     | 4.03 × 10^{-4} | 3.62 × 10^{-2} |
Fe–Fe and Zn–Zn bonding clearly indicate that Fe atom replaces Zn atom with a small variation of \( \sim 0.04 \, \text{Å} \). This small variation of \( \sim 0.04 \, \text{Å} \) is also visible at the first peak of Fe–O bonding (marked by an arrow in figure 4(b)), indicating that the local structure of Fe atoms changes with increasing Fe concentration \((x = 0.01–0.05)\). The observed change in the local environment of Fe and Zn atoms is consistent with the EXAFS analysis done by Lin et al.\[50\]. Moreover, the FT curve for Fe\(_3\)O\(_4\) shows a cubic inverse spinel structure, which is missing in Fe–ZnO. The FT curves, as shown by arrows, point to T\(_d\) (tetrahedral) and O\(_d\) (octahedral) symmetries \[51\] in figure 4(b). Hence the FT plots show that Fe-doped ZnO holds a tetrahedral symmetry and the absence of a Fe\(_2\)O\(_3\) related spinel phase such as ZnFe\(_2\)O\(_4\). Further, Fe doping seems to affect the two shoulder peaks (as shown in the inset of figure 4(a) for \( x = 0.03, \) and 0.05 with undoped ZnO) at 0.83 and 1.17 Å only, which have become less broad after Fe doping. Shoulder peaks were significant for undoped ZnO (figure 5(b)) than for Fe–ZnO. These shoulder peaks are also discussed by Mu et al.\[52\] and explained on the basis of the size of the dopant and steric effects.

To get a better insight into the doping effects, the EXAFS data are fitted to the wurtzite structure of ZnO using the IFEFFIT code \[47\]. Background subtraction and data merging were done with Athena \[42\]. Theoretical models were constructed using the IFEFFIT \[47, 55\] codes and the crystallographic atomic positions of ZnO. After background removal the spectra were Fourier-transformed over a photoelectron wavenumber \((k)\) in the range 2.0–13.0 Å\(^{-1}\). The amplitude reduction factor \((S^2_{0})\) and energy shift parameter \((\Delta E_0)\) are calculated from Zn foil as 0.68 ± 0.10 and 5.47 ± 0.60 eV, respectively, and kept constant for further calculations. The mean inter-atomic distance \((R)\) and variance \((\sigma^2)\) are determined by individual fits. The \(S^2_{0}\) (amplitude factor) value is low, as expected, and this may be due to the dead time correction and fluorescence data mode. But as the \(S^2_{0}\) value remains almost constant with addition of paths and \(R\) range, it can be used further for the Fe-doped ZnO. Single-scattering (SS) and MS paths were taken into account in the data analysis. It is also noted that below \(R_{\text{eff}} < 4.56 \, \text{Å}\) only SS paths are used for the doped samples, while MS is missing in the case of undoped ZnO.

Figure 5 shows the EXAFS data (dotted lines) of pure and Fe-doped ZnO and simulated data (solid lines). The primary purpose of this fit is to demonstrate the efficacy of the fitting model, and therefore the final results are compared with the nominal crystal structure to quantify any systematic error. To this end, all measured distances are close to...
Table 2. EXAFS fitting results for Zn K-edge spectra for the pure ZnO with Fe-doped ZnO samples (x = 0.0, 0.01, 0.03 and 0.05). While k range = 2.0–13.0 Å, R range = 1.0–6.0 Å, R-space fitting, dk = 2, k-window = hanning, N in parentheses is defined as coordination number (CN) or degeneracy. Scattering path is shown by # in parentheses of the first column.

| Path               | R$_{eff}$ (N/Å) | $\sigma^2$ for x = 0.0 | $\sigma^2$ for x = 0.01 | $\sigma^2$ for x = 0.03 | $\sigma^2$ for x = 0.05 | R$_{eff}$ (N/Å) |
|--------------------|-----------------|-------------------------|--------------------------|--------------------------|--------------------------|----------------|
| X–O$_1$ (#1)       | 1.95(3)         | 4.98                    | 2.74                     | 3.05                     | 3.05                     | 1.95 (3) for Zn–O$_1$
| X–O$_2$ (#2)       | 2.03(1)         | 4.98                    | 2.74                     | 3.05                     | 3.05                     | 1.99 (2) for Zn–O$_2$
| X–Zn$_6$ (#4)      | 3.20(6)         | 9.97                    | 5.47                     | 6.10                     | 6.10                     | 3.20 (6) for Zn–Zn$_1$
| X–Zn$_8$ (#5)      | 3.25(3)         | 9.97                    | —                        | 6.10                     | 6.10                     | 3.23 (5) for X–Zn$_1$
| X–O$_{14}$ (#11)   | 3.79(3)         | —                       | 5.47                     | 6.10                     | 6.10                     | 3.83 (5) for Zn–O$_2$
| X–O$_{12}$ (#12)   | 3.83(6)         | 9.97                    | 5.47                     | 6.10                     | 6.10                     | 4.16 (5) for Zn–O$_2$
| X–O$_{25}$ (#25)   | 4.53(6)         | —                       | 5.47                     | 6.10                     | 6.10                     | 4.56 (6) for Zn–Zn$_2$
| X–Zn$_8$ (#28)     | 4.56(6)         | 9.97                    | 5.47                     | 6.10                     | 6.10                     | 4.75 (15) for X–Zn$_2$
| X–O$_{37}$ (#37)   | 4.58(12)        | —                       | 5.47                     | 6.10                     | 6.10                     | 4.75 (15) for X–Zn$_2$
| X–Zn$_{12}$–Zn (#38)| 4.83(24)        | —                       | 5.47                     | 6.10                     | 6.10                     | 4.83 (5) for Zn–Zn$_2$
| X–O$_{12}$–O (#40) | 4.84(12)        | —                       | 5.47                     | 6.10                     | 6.10                     | 4.83 (5) for Zn–Zn$_2$
| X–O$_{14}$–Zn (#41)| 4.84(12)        | —                       | 5.47                     | 6.10                     | 6.10                     | 4.83 (5) for Zn–O$_2$
| X–O$_{42}$ (#42)   | 4.99(6)         | 9.97                    | 5.47                     | 6.10                     | 6.10                     | 4.99 (6) for Zn–O$_2$
| X–O$_{43}$ (#43)   | 5.00(3)         | 9.97                    | 5.47                     | 6.10                     | 6.10                     | 4.99 (4.5) for X–O$_3$

Table 3. The values of EXAFS fitting parameters $E_0$, $\Delta R$ and uncertainties in k and R for Fe-doped ZnO systems ($x = 0.0, 0.01, 0.03$ and 0.05).

| Fit/parameters | ZnO   | Fe$_{0.01}$Zn$_{0.99}$O | Fe$_{0.03}$Zn$_{0.97}$O | Fe$_{0.05}$Zn$_{0.95}$O |
|----------------|-------|------------------------|------------------------|------------------------|
| $E_0$ (eV)     | 5.68  | 6.63                   | 5.80                   | 5.83                   |
| $R$-factor     | 0.03032 | 0.05421               | 0.05220                | 0.05211                |
| $\Delta R$     | 0.01332 | 0.04118               | 0.03244                | 0.0355                 |
| k-uncertainty (%) | 5.28 | 4.23                   | 2.80                   | 2.89                   |
| R-uncertainty (%) | 9.35 | 9.11                   | 8.80                   | 8.85                   |

those measured by diffraction, although outside the systematic errors. Considering that only four fit parameters describe all the bond lengths up to 5 Å, the systematic errors in the pair distances are expected to be within about 0.02 Å, [56] as observed. All the $\sigma^2$ parameters are small, as expected for a well-ordered crystal lattice. The fits to the Zn K-edge data from all the samples give similar results, so systematic errors are expected to be better than 0.1. However, this error may be smaller when a higher fraction of a particular substituent species resides on the Zn (1) site, as determined.

Table 2 shows the fit results for Zn K-edge data on pure ZnO and Fe-doped ZnO, which presents the bond length ($R$), relative DW factor ($\sigma^2$) and $S_0^2$ value for X–O and X–X coordinations, if X = Fe and Zn. In the EXAFS simulation model, one of the Zn atoms is replaced by the Fe-substituted ZnO system and taking Fe as the central absorber in the feff.inp file. All scattering paths are included within the fitting range, but only those SS paths with independent pair distances are reported here. All other path distances are constrained to those paths. The data are fitted in the range between 1.0 and 6.0 Å in real space and the $k^3$-weighted data are transformed between 2.0 and 13.0 Å$^{-1}$ after a Gaussian narrowing of 0.2 Å. Other parameters and error percentages are shown in table 3. These fits have about 20 degrees of freedom [57]. Moreover, the data also show a reduction in the amplitude of the peak near $r \sim 2.9$ Å of 70% compared with the experimental peak, indicating the percentage of Fe atoms residing on the Zn site. Parameters such as $\sigma^2$ and quality factor ($R$) are taken care of and are good for this fitting.

The bond length and other parameters derived from EXAFS calculations as shown in table 3 are consistent with our experimental finding and other published results [52–54]. The bonding length of ZnO obtained from the EXAFS experiments fits well to the values calculated by Artemis (see table 2). In the case of pure ZnO, the Zn–Zn bonding length is 3.20 Å, which is consistent with the XRD (3.251 Å) results [40, 52]. However, the bond lengths of Zn–O and Zn–Zn were found to increase (see table 2) with Fe doping, which is in good agreement with our previous report [40]. The increase in the Zn–Zn bonding length might be due to the steric effect. In a wurtzite structured ZnO unit cell, one oxygen atom is neighbouring four Zn atoms forming the geometry of a triangular pyramid with oxygen located at the pyramid centre. The substitution of a Fe atom in the place of a Zn atom takes less space than a Zn atom and hence Zn–O and Zn–Zn distances should be a bit larger.

4. Conclusions

In summary, the electronic structure of Zn$_{1-x}$Fe$_x$O ($x = 0.0, 0.01, 0.03$, and 0.05) polycrystalline nanorods synthesized by a co-precipitation method has been studied using XAFS. XRD measurements reflect single phase polycrystalline nature with wurtzite lattice and exclude the presence of any secondary phase. LCF fitting on XAFS spectra indicates that Fe exists in Fe$^{3+}$/Fe$^{2+}$ mixed-valent state and in tetrahedral symmetry. We have also performed IFFEFT fitting using the wurtzite structure of ZnO and calculated Zn–O and Zn–Zn inter-atomic distances and other parameters, which are consistent with the values presented in this study.
available in the literature. The EXAFS analysis of Fe $K$ - and Zn $K$-edges reveals that all the Fe ions occupy Zn positions in the ZnO matrix. It is expected that this study can provide new structural information useful for material design and property optimization of TM-doped ZnO DMS materials.

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