Room temperature ferromagnetic behavior in the nanocrystals of Fe doped ZnO synthesized by soft chemical route

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In the present study, nanocrystalline undoped and Fe (5 wt.%) doped ZnO powder has been synthesized by soft chemical route. The structural, nano/microstructural, vibrational and magnetic properties of these samples have been studied as a function of calcination temperature (400 °C to 1100 °C). X-ray diffraction analysis of Fe doped ZnO powder has shown the major nanocrystalline wurtzite (ZnO) phase and the minor cubic spinel-like secondary nanocrystalline phase at 700 °C. At calcination temperature of 700 °C, the magnetization and coercivity have been enhanced in Fe doped ZnO. As the calcination temperature increased to 1100 °C, the major phase of ZnO and minor cubic spinel-like secondary phase turned into bulk in doped ZnO. Interestingly, the reduced magnetization and zero coercivity have been observed in this case. These changes are attributed to the conversion of secondary nanocrystalline ferromagnetic spinel phase to its bulk paramagnetic phase. The degree of inversion i.e. the occupancy of both sites with different symmetry by ferric ions is proposed to be solely responsible for the unusual behavior.

Keywords: ZnO nanocrystal; Fe doped ZnO nanocrystal; sol-gel route; X-ray diffraction; secondary phase; room temperature ferromagnetism

1. Introduction

In the recent past, ZnO based diluted magnetic semiconductors (DMS) have gained a considerable attention from the scientific community because of their amazing room temperature ferromagnetic (RTFM) properties which have a potential to be used in the next generation spintronics devices such as spin-light emitting diodes, spin-valve transistors [1, 2]. In the past few years, scientists have been investigating the effect of doping with transition metal (TM) ions (Mn, Fe, Ni, etc.) on ZnO nanoparticles by using various chemical routes, such as sol-gel [3, 4], citrate decomposition [5], hydrothermal [6], etc. However, even today much controversy remains concerning the mechanism that causes the RTFM behavior [3–21]. Recently, undoped nanocrystalline ZnO powders synthesized by various chemical routes [7–9] have been reported to exhibit RTFM but with very low

values of saturation magnetization and coercivity. More interestingly, several studies demonstrated the origin of RTFM which is correlated with several mechanisms [11–19] and carbon too [15, 16]. In TM doped ZnO system, the role of Fe ions has been widely studied both theoretically and experimentally. However, in the case of Fe doped ZnO, the controversy in the results indicates that the ferromagnetic ordering temperature is highly sensitive to the doping quantity, synthesis route, synthesis conditions and resulting product form (bulk, powder or thin film). Maximum solubility limit of iron in the ZnO lattice, actual oxidation state of iron (Fe^{2+} , Fe^{3+} or the combination of both), and appropriate magnetic model have been used to explain the origin of RTFM. Further, few reports evidenced the origin of ferromagnetism in sol-gel synthesized nanocrystalline Fe doped ZnO samples as a result of precipitates of the secondary phase of Fe_3O_4 [14] or clustering of Fe ions due to amorphous ferromagnetic Fe_3O_4 embedded in ZnO [18]. However, Mandal et al. [20] have shown

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that the secondary phase formation reduces the magnetization of single phase $\text{Zn}_{1-x}\text{TM}_x\text{O}$, and pointed out that the secondary phase is not responsible for magnetism in $\text{Zn}_{1-x}\text{TM}_x\text{O}$ [20]. Liu et al. [23] stated that RTFM is an intrinsic property of Fe doped ZnO and it is independent of the metallic clusters or secondary ZnFe_2O_4 phase. In addition, few reports claimed that RTFM in nanostructured Fe doped ZnO originates from the ferromagnetic interaction due to local electronic defects between Fe ions that replace Zn ions [21]. Also Zn vacancies may be responsible for the ferromagnetic order [22]. Thus, the origin of the observed RTFM in Fe doped ZnO is highly controversial. Different factors, such as sample preparation techniques, the nature of observed ferromagnetism and the nature of the secondary phase formed, etc., are the issues which still need more explanation. Moreover, even using similar preparation techniques and the same nominal doping concentrations, the magnetic properties are sometimes not reproducible. In view of these contradictions, Fe doped ZnO needs further attention for better understanding of its RTFM.

In this study, the issue of the major contribution to RTFM behavior due to the occurrence of secondary nanocrystalline magnetic cubic spinel ferrite phase in addition to the minor contribution due to nanocrystalline ZnO phase is addressed more carefully using various physical characterization techniques, X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy and superconducting quantum interference devices.

2. Experimental

Nanocrystals of Fe (5 wt.%) doped and undoped ZnO were prepared by sol-gel route using precursors as Zn nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and Fe nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$. Sol-gel route allows mixing of the chemicals at atomic level and thus reducing the possibility of undetectable impurity phase. The precursors were weighed and mixed thoroughly according to stoichiometric ratio of 0.95:0.05. Further, the prepared stoichiometric mixture of nitrates and anhydrous citric acid was

kept in the mole ratio of 1:1.5 and weighed. The stoichiometric mixture of nitrates was dissolved in adequate quantity of distilled water and its solution was formed. Citric acid $[\text{C}_6\text{H}_8\text{O}_7]$ was dissolved well with the solution of precursors by continuous stirring with magnetic stirrer at 60 °C for 15 min to 20 min to obtain a transparent gel. This transparent gel was then kept in water bath for several hours to get dried gel. The obtained dried gel was then grinded to powder using an agate mortar. The obtained powder was calcined at 400 °C, 700 °C, and 1100 °C temperatures for 3 h under air atmosphere. Nanocrystalline undoped ZnO, which was used then as a reference material, was obtained at calcination temperature of 400 °C by following the same experimental procedure but without Fe nitrate.

Nanocrystals of undoped and Fe (5 wt.%) doped ZnO were synthesized successfully by sol-gel method. X-ray diffraction patterns of all the powder samples of undoped ZnO calcined at 400 °C and Fe (5 wt.%) doped ZnO calcined at different temperatures were recorded at room temperature by using a rotating angle X-ray diffractometer (BRUKER AXS D8 ADVANCE) with a monochromator employing $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) to identify the crystalline nature and phase evolution. The average crystallite size of the crystalline powder samples was calculated using Scherrer formula. Transmission electron microscope (TEM, model Technai 20 G²) was used at an accelerating voltage of 200 kV to confirm the crystallite size by recording the micrographs of the selected samples. Selected area electron diffraction (SAED) patterns were also recorded to identify the crystal structure of major and minor phases in the calcined samples of Fe (5 wt.%) doped ZnO. The information about the secondary cubic spinel ferrite phase and active chemisorbed species (if any) in the calcined samples of Fe (5 wt.%) doped ZnO was obtained from their vibrational modes in the wave number range of 400 cm^{-1} to 4000 cm^{-1} by recording spectra using Fourier transform infrared spectrometer (JASCO FT/IR 6100) at room temperature in KBr medium. The magnetic measurements (M-H) of Fe (5 wt.%) doped ZnO calcined at different temperatures were carried out using

a standard superconducting quantum interference device (SQUID) MPMS (Quantum Design) magnetometer with the maximum applied field of ± 10 kOe.

3. Results and discussion

Fig. 1 displays the X-ray diffraction (XRD) patterns of undoped ZnO calcined at 400 °C and Fe (5 wt.%) doped ZnO calcined at various temperatures, recorded at room temperature for understanding their crystallographic nature. The sample of undoped ZnO calcined at 400 °C is labeled as Z(4) and samples of Fe (5 wt.%) doped ZnO calcined at 400 °C, 700 °C and 1100 °C are labeled as ZF(4), ZF(7) and ZF(11), respectively. All diffraction peaks of Z(4) and ZF(4) match well with the standard data for a hexagonal ZnO wurtzite structure (JCPDS Card No. 36-1451) and no characteristic peaks of any other impurities are detected in the XRD patterns [5, 14, 20, 23, 24]. XRD pattern of ZF(7) reveals the dominant diffraction peaks, indexed to the major wurtzite structure of ZnO with some additional minor peaks marked with * as shown in Fig. 1c [25]. The minor peaks appear at $2\theta = 29.85^\circ$, 35.25° and the respective Miller indexed diffraction planes are (2 2 0) and (3 1 1) which corresponds to the standard Bragg positions of cubic spinel type AB_2O_4 (cubic $a = b = c = 8.35$ Å) structure (Fig. 1c). The broadening of the diffraction peaks in Fig. 1 is observed in Z(4), ZF(4) and ZF(7), respectively, indicating nanocrystalline nature of the crystallites.

XRD pattern of ZF(11) exhibits also an increase in the intensity of the peaks of major and secondary phases with an increase in the calcination temperatures, indicating an increase in the crystal growth by decomposition of citrate gel network at high temperature. Thus, the full width at half maximum (FWHM) of the major and minor peaks of ZF(11) is observed to decrease, illustrating an increase in the crystallite size (Fig. 1d). The as-synthesized compound contains $ZnO + Fe_2O_3$, therefore additional Miller indexed diffraction planes of secondary phase are assigned to $ZnFe_2O_4$ [5, 24]. Few reports described the occurrence of the secondary $ZnFe_2O_4$ phase in highly doped Fe (10 %)

Fig. 1. X-ray diffraction patterns of (a) undoped ZnO calcined at 400 °C and Fe (5 wt.%) doped ZnO calcined at (b) 400 °C, (c) 700 °C, (d) 1100 °C.

ZnO synthesized by conventional solid state reaction method [24] and sol-gel method [5].

The average crystallite size of Z(4), ZF(4), ZF(7) and ZF(11) with major wurtzite ZnO and secondary cubic spinel ferrite AB_2O_4 phases in ZF(7) and ZF(11) was calculated using Scherrer equation, wherein FWHM was corrected for instrumental broadening and summarized in Table 1.

The lattice parameters of the major wurtzite phase and secondary cubic spinel phase were calculated using equation 1 and equation 2, respectively

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

and

$$\frac{1}{d_{hkl}^2} = \left(\frac{h^2 + hk + k^2}{a^2} \right) \quad (2)$$

where d_{hkl} is the interplanar spacing obtained from Bragg law, and h , k and l are Miller indices denoting the plane. From the XRD of ZF(7), a small measurable shift is established in the respective diffraction peak positions of the nanocrystalline secondary inverted spinel ferrite $ZnFe_2O_4$ phase relative to that of bulk spinel ferrite phase. These measurable shift in the peak position is likely to originate from the local chemical inhomogeneity

Table 1. Average crystallite size and lattice parameters of (i) major wurtzite ZnO (ii) secondary cubic spinel ferrite ZnFe_2O_4 phases in crystalline Z(4); ZF(4); ZF(7) and ZF(11) calculated from XRD spectra.

Sample	Average crystallite size of major ZnO phase [nm]	Average crystallite size of secondary ZnFe_2O_4 phase [nm]	Wurtzite lattice parameters a and c of major ZnO phase		Spinel lattice parameters 'a' of secondary ZnFe_2O_4 phase [Å]
			a [Å]	c [Å]	
Z(4)	38	Absent	3.23 ± 0.02	5.20 ± 0.02	Absent
ZF(4)	40	Absent	3.25 ± 0.02	5.2 ± 0.02	Absent
ZF(7)	42	25	3.27 ± 0.02	5.25 ± 0.02	8.42 ± 0.02
ZF(11)	95	90	3.29 ± 0.02	5.27 ± 0.02	8.46 ± 0.02

and distortions due to structural defects which, in turn, can be ascribed to the increase in cation inversion on A-sites and B-sites of ZnFe_2O_4 cubic spinel phase. For the study of structural and magnetic behavior of Fe (5 wt.%) doped ZnO at room temperature, two typical representative samples have been selected, viz. (i) ZF(7) where the secondary nanocrystalline ZnFe_2O_4 phase has evolved and (ii) ZF(11), where the secondary bulk ZnFe_2O_4 phase has evolved.

Further, a detailed TEM study was carried out on ZF(7) and ZF(11) samples to confirm the crystal structure of major and minor phases. Fig. 2a shows the micrograph of ZF(7) sample in the low resolution TEM which exhibits more or less spherical particles having a particle size-distribution ranging from 20 nm to 100 nm. The particle diameters were estimated from the low-resolution TEM data using a standard software (Image-J). The particle diameter histogram fitted with lognormal distribution function is shown in Fig. 2b. The average particle size ZF(7) has been obtained as 38 nm which is consistent with the size estimated from the XRD analysis. The crystallographic analysis of ZF(7) and ZF(11) has been further carried out by recording the selected area electron diffraction (SAED) pattern to confirm the occurrence of the secondary cubic spinel ferrite ZnFe_2O_4 phase (Fig. 3). SAED patterns clearly show the concentric diffraction ring pattern with spots over the rings for each representative sample, indicating that the particles are crystalline in nature and free from any major lattice distortion. Indexing of both SAED patterns have demonstrated the crystal symmetry corresponding to the major hexagonal wurtzite ZnO and minor

Fig. 2. (a) low resolution TEM micrograph of ZF(7) nanoparticles; (b) nanometric particle size distribution of ZF(7) sample fitted with a lognormal distribution function, from which the average particle size was estimated as ~ 38 nm.

Fig. 3. SAED patterns for (a) ZF(7) and (b) ZF(11).

cubic spinel ZnFe_2O_4 systems. SAED recorded for ZF(7) and ZF(11) display few of the diffraction rings of major wurtzite ZnO phase which are indexed as (1 0 0), (1 0 1) and (0 0 2) planes with corresponding d-values of 2.8 Å, 2.6 Å and 2.48 Å respectively. Similarly, very distinct diffraction rings of minor cubic spinel ZnFe_2O_4 system are evidenced and indexed to (2 2 0), (3 1 1) and (4 4 0) planes with corresponding d-values of 2.984 Å, 2.543 Å, 1.491 Å, respectively. These

findings are also supported by an analysis of respective X-ray diffractograms in Fig. 1. The experimental results are in agreement with the report by Srivastava et al. [26] wherein the SAED pattern of nanocrystalline sample of highly Fe doped ZnO synthesized by sol-gel route evidenced the diffraction rings of (2 2 0), (3 1 1) and (4 4 0) planes corresponding to secondary cubic spinel ZnFe_2O_4 phase.

Fourier transform infrared spectroscopy (FT-IR) provides information about functional groups present in a compound. We have employed the FT-IR spectroscopy to study the metal cation-oxygen bonding due to the major ZnO and the secondary cubic spinel ZnFe_2O_4 phase and to identify the active chemisorbed species (if any) in ZF(4), ZF(7) and ZF(11) samples at room temperature.

Fig. 4. FT-IR spectra for samples (a) ZF(4), (b) ZF(7) and (c) ZF(11).

Thus, Fig. 4 shows FT-IR spectroscopic measurements recorded in the wave number range of 400 cm^{-1} to 4000 cm^{-1} at room temperature in KBr medium for all the samples and the observed vibrational bands are tabulated in Table 2. The broad absorption vibration band in the range of 1250 cm^{-1} to 1750 cm^{-1} is attributed to the carboxylate group (COO^- , CO^- , etc.) [27–30] and that at 3402 cm^{-1} is caused by stretching vibration of (OH) group due to the water of hydration [31, 32], thus, evidencing the formation

of active chemisorbed species like COO^- , CO^- , OH^- , on the surface of nanoparticles of ZF(4) as well as in ZF(7) (Table 2). However, these bands in ZF(11) do not occur, indicating the absence of active chemisorbed species with the increase in the calcination temperature, (Fig. 4c). In addition, the existence of lower and higher vibrational bands ($\nu_1\text{ [cm}^{-1}\text{]}$ and $\nu_2\text{ [cm}^{-1}\text{]}$) in the FT-IR spectra of ZF(7) and ZF(11) is in agreement with the previous landmark work of Waldron [33]. For bulk spinel ferrites, Waldron has assigned the lower vibration frequency band (ν_1) in the range of 450 cm^{-1} to 400 cm^{-1} and the higher vibration frequency band (ν_2) in the range of 630 cm^{-1} to 555 cm^{-1} to metal cation (Zn^{2+} or Fe^{3+}) – oxygen stretching at tetrahedral sites and octahedral sites, respectively. Such broader, weak in intensity and only lower vibrational band $\nu_1\text{ [cm}^{-1}\text{]}$ centered at around 460 cm^{-1} , is evidenced in FT-IR of ZF(4) which is assigned to the metal cation-oxygen bond stretching at tetrahedral sites of wurtzite structure.

FT-IR spectrum of nanocrystalline ZF(7) (Fig. 4b) exhibits the broad lower vibrational band ($\nu_1\text{ [cm}^{-1}\text{]}$) centered at around 520 cm^{-1} which is weak in intensity and the broad higher ($\nu_2\text{ [cm}^{-1}\text{]}$) vibrational band centered at around 652 cm^{-1} strong in intensity. These bands are assigned to metal (Zn^{2+} or Fe^{3+}) cation-oxygen stretching vibrations at tetrahedral sites and octahedral sites indicating the formation of cubic spinel ZnFe_2O_4 [20, 34, 35]. By deliberate inspection of both of these broad spectral bands of ZF(7) sample, a small measurable deviation is noticed in their respective peak position, indicating the introduction of higher content of magnetic Fe^{3+} ions at the tetrahedral sites of nanocrystalline ZnFe_2O_4 phase. These remarkable deviations in lower ($\nu_1\text{ [cm}^{-1}\text{]}$) and higher ($\nu_2\text{ [cm}^{-1}\text{]}$) vibrational bands are commonly observed in nanocrystalline ZnFe_2O_4 where the degree of inversion (occupancy of Fe^{3+} ions at A and B-sites) is reported to be different for different grain sizes and dependent on the synthesis method and sintering temperature [20, 36]. In Fig. 4c, it is noticed that the broadening of lower (511 cm^{-1}) and higher (636 cm^{-1}) vibrational bands of ZF(11) is significantly

Table 2. Vibration bands due to active chemisorbed species and cation-oxygen stretching at tetrahedral and octahedral sites corresponding to tetrahedral ν_1 [cm^{-1}] and octahedral ν_2 [cm^{-1}] sites respectively in ZF(4), ZF(7) and ZF(11).

Sample	Vibrational band			
	3402 cm^{-1} due to stretching of OH^- group	1250 – 1750 cm^{-1} due to stretching of CO^- , COO^- group	520 cm^{-1} due to metal (Zn^{2+} or Fe^{3+}) cation-oxygen stretching vibration at tetrahedral sites	652 cm^{-1} due to metal (Zn^{2+} or Fe^{3+}) cation-oxygen stretching vibration at octahedral sites
ZF(4)	Present	Present	Present	Absent
ZF(7)	Present	Present	Present	Present
ZF(11)	Absent	Absent	Present	Present

reduced and strong in intensity. This result confirms the reduction of the occupancy of Fe^{3+} ions at the tetrahedral sites of ZnFe_2O_4 , confirming the formation of the bulk of ZnFe_2O_4 phase in ZF(11) matrix.

The magnetic properties of the two representative samples ZF(7) and ZF(11) have been characterized by SQUID magnetometer at room temperature. Fig. 5 displays the magnetization (M) versus applied magnetic field (H) plots at room temperature for the samples ZF(7) and ZF(11) in the external applied magnetic field (H) ranging from ± 10 kOe. From the study of magnetization, corresponding magnetization measurements to the field of ± 5 kOe have been extracted.

The M-H plot of ZF(7) demonstrates the non-linear S-type behavior (magnetic hysteresis) with equal and distinct splitting of magnetization curves about the origin of the M-H plot. It is shown in the inset of Fig. 5. In contrast, ZF(11) exhibits linear magnetic behavior without splitting of magnetization curves in the applied field region. ZF(7) has revealed significant field dependent magnetization $M = 0.0838$ emu/g, while ZF(11) has revealed reduction in $M = 0.057$ emu/g in ± 5 kOe range. The occurrence of coercive field $H_c = 30$ Oe for ZF(7), caused the RTFM behavior due to the strong ferromagnetic exchange interaction whereas ZF(11) exhibited zero coercivity, indicating linear behavior. In the present work, the observed room temperature magnetic

Fig. 5. Field dependent magnetization for ZF(7) and ZF(11); the inset shows the results for ZF(7) magnified in the low field region.

parameters of ZF(7) are significantly stronger than the magnetic parameters reported for nanocrystalline undoped ZnO [7–9]. Thus, it is assumed that the enhanced RTFM behavior of ZF(7) is due to the dominant magnetic contribution from nanocrystalline ZnFe_2O_4 (25 nm) in addition to the minor magnetic contribution of nanocrystalline ZnO (42 nm). The nanocrystalline major phase of ZnO may have significantly minor contribution to RTFM behavior of ZF(7) due to adsorbed surface species such as COO^- , CO^- , OH^- evidenced by FT-IR spectroscopic results of ZF(7) [30]. Secondly, in the literature, nanocrystalline inverse

spinel ZnFe_2O_4 is reported to be ferromagnetic in its nanocrystalline form at room temperature [38–40]. Consequently, the inverse cubic spinel structured nanocrystalline ZnFe_2O_4 is represented by $[\text{Zn}_{1-\delta}^{2+}\text{Fe}_\delta^{3+}]_{\text{tetra}}[\text{Zn}_\delta^{2+}\text{Fe}_{2-\delta}^{3+}]_{\text{octa}}\text{O}_4$, where δ is a measure of the fraction of Fe^{3+} occupying (A) sites and is called the inversion parameter. The resulted enhanced RTFM behavior can be understood in terms of the distribution of significant amount of Fe^{3+} ions over tetrahedral (A) and octahedral (B) sites, resulting in the strong inter-sublattice (A-O-B) super-exchange interaction. A small shift in the respective positions of minor peaks corresponds to the nanocrystalline ZnFe_2O_4 phase according to X-ray diffractogram of ZF(7) while the occurrence of the broad lower and higher vibrational bands corresponding to tetrahedral and octahedral sites in the FT-IR spectra of ZF(7) has been established. These two results confirm the distribution of Fe^{3+} ions over A and B sites in nanocrystalline ZnFe_2O_4 , supporting the long range ferromagnetic inter-sublattice (A-O-B) superexchange interaction in nanocrystalline ZF(7) sample [37, 38]. Additionally, it has been reported that occupancy of A-sites by some Fe^{3+} ions increases with reduction of crystallite size of ZnFe_2O_4 to the order of nanometers, irrespective of the method of synthesis. Thus, the increase in A-O-B superexchange interactions results in T_c as high as 460 K [40, 41]. High value of T_c indicates increased magnetization due to the stronger inter-sublattice (A-O-B) superexchange interaction as compared to intra-sublattice (A-O-A and B-O-B) interactions. The experimental results obtained in this study are supported by few remarkable reports. Wang et al. [24] reported RTFM behavior in nanocomposites of Fe (10 at.%) doped ZnO synthesized by conventional solid state reaction route due to secondary phase of ZnFe_2O_4 in a 700 °C annealed sample, however, magnetic contribution of the major ZnO has not been reported. Beltrán et al. [40] reported an enhancement of RTFM behavior in Fe doped ZnO nanoparticles which was caused by formation of several additional defects along

with minor magnetic contribution of nanocrystalline ZnO [41]. On the other hand, the second representative ZF(11) sample has clearly demonstrated the linear behavior ($H_c = 0$ Oe) in the applied external field of ± 5 kOe with significant reduction in the value of field dependent magnetization $M = 0.057$ emu/g compared to ZF(7) (Fig. 5). Furthermore, due to crystallization process, with an increase in the calcination temperature, bulk ZnO (95 nm) and ZnFe_2O_4 (90 nm) phases have been detected in ZF(11) from XRD study along with the disappearance of adsorbed surface defects COO^- , CO^- , OH^- from FT-IR study. As it is well known that bulk ZnO exhibits diamagnetic behavior [42], it can be stated that the secondary magnetic bulk phase of ZnFe_2O_4 is a sole reason for linear magnetic behavior of ZF(11). It is well known that bulk ZnFe_2O_4 behaves as paramagnetic at 300 K and antiferromagnetic with a Néel temperature $T_N = 10.5$ K as a consequence of normal cubic spinel structure of ZnFe_2O_4 represented as $[\text{Zn}^{2+}]_{\text{tetra}}[\text{Fe}^{3+}\text{Fe}^{3+}]_{\text{octa}}\text{O}_4$, Zn^{2+} occupies A-sites and magnetic Fe^{3+} ions occupy B-sites with antiparallel moments [43]. In the ZF(11) sample, the evidenced paramagnetic behavior at room temperature is in agreement with the known facts. With the increased calcination temperature, the occupancy of A sites by Fe^{3+} ions in bulk ZnFe_2O_4 is decreased which resulted in a significant reduction in inter-sublattice (A-O-B) interactions and led to the intra-sublattice (B-O-B) interactions of Fe^{3+} ions at octahedral sites only. It resulted in the reduction of field dependent magnetization (M) in ZF(11) sample compared to ZF(7) sample. The analysis illustrates a close dependence of magnetic behavior of Fe (5 wt.%) doped ZnO on the crystalline nature of the major phase of wurtzite ZnO and secondary cubic spinel ferrite phase of ZnFe_2O_4 .

4. Conclusions

The observed enhanced RTFM behavior of nanocrystalline ZF(7) has been explained in terms of two contributing factors (i) minor RTFM contribution due to chemisorbed species

in the interface regions between nanocrystalline ZnO and nanocrystalline ZnFe_2O_4 (ii) enhanced major RTFM contribution due to nanocrystalline secondary inverted spinel phase of ZnFe_2O_4 . Bulk ZF(11) demonstrated well-defined paramagnetic behavior due to the conversion of both major wurtzite ZnO and minor cubic spinel ZnFe_2O_4 to bulk and the field dependent magnetization was found to decrease in comparison with the ZF(7). It is possible to explain these subtle changes on the basis of three contributing factors (i) as the chemisorbed species at the interface have disappeared, RTFM has also disappeared in ZF(11) (ii) increase in the size of nanocrystalline ZnO has led to its conversion to diamagnetic host lattice (iii) similarly, nanocrystalline inverted spinel phase of ZnFe_2O_4 has been converted into normal paramagnetic ZnFe_2O_4 phase.

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