

STRUCTURAL AND ESR ANALYSIS OF THE PREPARED $Zn_{1-x}Mn_xSe$ COMPOUNDS

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Abstract. $Zn_{1-x}Mn_xSe$ compound semiconductors with different Mn content have been successfully synthesized via solid solution method. The energy dispersive X-ray analysis (EDX) of as-prepared $Zn_{1-x}Mn_xSe$ compounds were carried out and showed that Mn contents are 0.0, 0.07, 0.14 and 0.23. The X-ray powder diffraction (XRD) patterns showed polycrystalline single phase cubic (Zinc blende) structures for all examined samples. The lattice parameter and cell volume were determined and reveal that both are increasing by raising Mn^{2+} content (x). XRD analysis showed that Mn incorporated as interstitial sites inside the lattice. The expected interstitial site to be occupied with Mn^{2+} cations are that of Wykoff's notation (b) with coordinates of equivalent positions 1/2, 1/2, 1/2. The $Zn_{1-x}Mn_xSe$ powder compounds were examined by electron spin resonance (ESR) technique and reveal a broadening signal increases by raising Mn contents $x = 0.07, 0.14$ and 0.23 . The Lande-factor was determined for the examined samples.

Keywords: $Zn_{1-x}Mn_xSe$, EDX, XRD, ESR.

INTRODUCTION

Zn-containing chalcogenide semiconductors are important materials with large band gaps and relatively high refractive indices. Doped ZnSe have considerable technological promise for various industrial applications as fabrication of light emitting diodes or blue-green laser diodes [1—3] mid-infrared lasers, laser windows and other optoelectronic devices [4—9]. ZnSe and its alloys are used for n-type window layer for window layer for thin film heterojunction solar cells and rear-window layer of thin film Si-based solar cells [10, 11]. ZnMnSe is one of the most widely studied diluted magnetic semiconductors. Recently, this material system has attracted large attention as a suitable candidate for the use in optoelectronic devices as a spin aligner [12]. The aim of present work is the preparation and structure characterization of $Zn_{1-x}Mn_xSe$ compounds. The effect of increasing Mn incorporated as magnetic element in ZnSe compound semiconductor on structure and spectral analysis of electron spin resonance technique were studied.

EXPERIMENTAL

$Zn_{1-x}Mn_xSe$ ($x = 0, 0.07, 0.14, 0.23$) semiconductor compounds have been prepared by solid solution technique using high purity 99.999 % for zinc and sele-

mium, and purity 99.99 % for manganese. Each compound was weighed from pure elements then mixed in an evacuated silica ampoule under vacuum up to 10^{-6} Torr. The ampoules containing compound were shaken several times to insure the homogeneity during the process of syntheses at $1000 \pm 20^\circ$ C. The quantitative chemical composition analysis of the prepared compound was examined using Energy Dispersive X-ray Analysis (EDX) type (Oxford INCA x-sight). The internal structure of all prepared powder samples were examined by X-ray diffraction technique using Philips X'Pert Graphics diffractometer equipment with $CuK\alpha$ radiation source. The scan mode in the 2θ range was from 5° to 85° with step size 0.03° and time 2 sec. per step. Electron spin resonance (ESR) measurements were performed for undoped and doped ZnSe powder compound, using X-band ESR spectrometer (Bruker, EMX) at room temperature. A stander rectangular cavity (4102 ST) operating at 9.7 GHz with a 100 kHz modulation frequency was used.

RESULT AND DISCUSSION

The quantitative chemical composition analysis of the prepared powder was determined using energy dispersive X-ray analysis (EDX) technique. The measurements were determined at different five positions

in every compound and its results reveal no stoichiometry deviation in all the representative bulk compositions samples. The resulted data of $Zn_{1-x}Mn_xSe$ show that $x = 0, 0.07, 0.14, 0.23$. The EDX spectra are shown in Fig. 1, Fig. 2, Fig. 3 and Fig. 4 respectively.

The EDX data for $Zn_{1-x}Mn_xSe$ ($x = 0$) powder sample gives the average atomic percentage of Zn : Se is 50.89 : 49.11. The additive of Mn as magnetic element to the other three compounds $Zn_{1-x}Mn_xSe$ ($x = 0.07, 0.14, 0.23$) illustrates that the ratio of zinc to selenium decreases than ZnSe sample because of the incorporation of Mn^{2+} ions. The increase in dopant Mn in the last three samples is depicted as the increase in area under Mn peaks as shown in Fig. 2, Fig. 3 and in Fig. 4.

X-ray diffractograms of the four powder semiconductor compounds are represented in Fig. 5. From

this figure it is clear, that all compounds crystallized in single phase (zinc blende) structure. It was reported that $Zn_{1-x}Mn_xSe$ compounds have zinc blende structure for manganese content range $0 \leq x \leq 0.3$ [13]. This result matched with the ICDD card No. (37-1463) and agrees with the results reported by Lv et al. (2004) [14], Robinson (2000) [15] and Shi et al. (2008) [16].

Fig. 5 illustrates that, the addition of Mn leads to peak shift towards the lower angle [17], this shift increases slightly as Mn concentration increases as indicated by d -values in Table 1. This means that, the addition of Mn leads to slightly change in unit cell volume. In order to elucidate the effect of Mn additives more clearly, Crysfire program has been used to determine the unit cell parameters. The calculated values

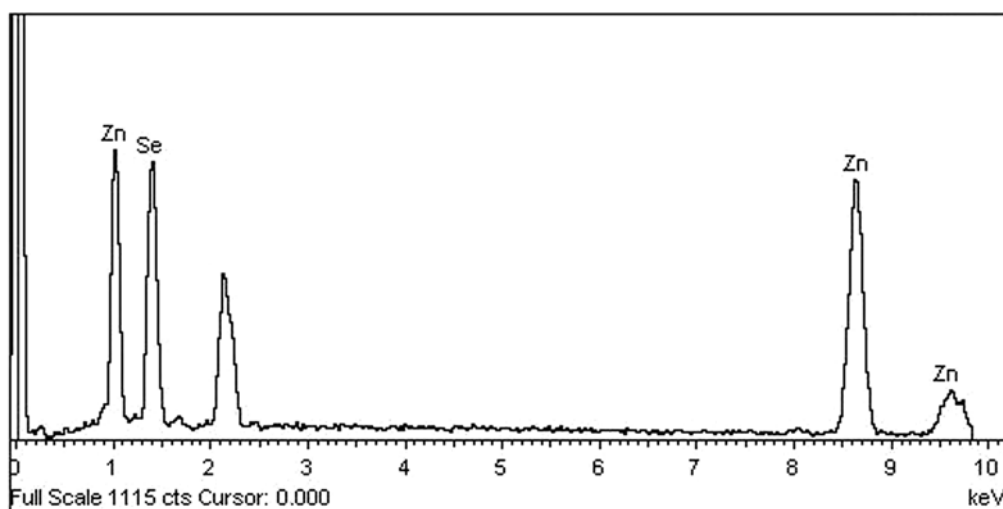


Fig. 1. EDAX spectrum for as-prepared $Zn_{1-x}Mn_xSe$ ($x = 0$) powder compound

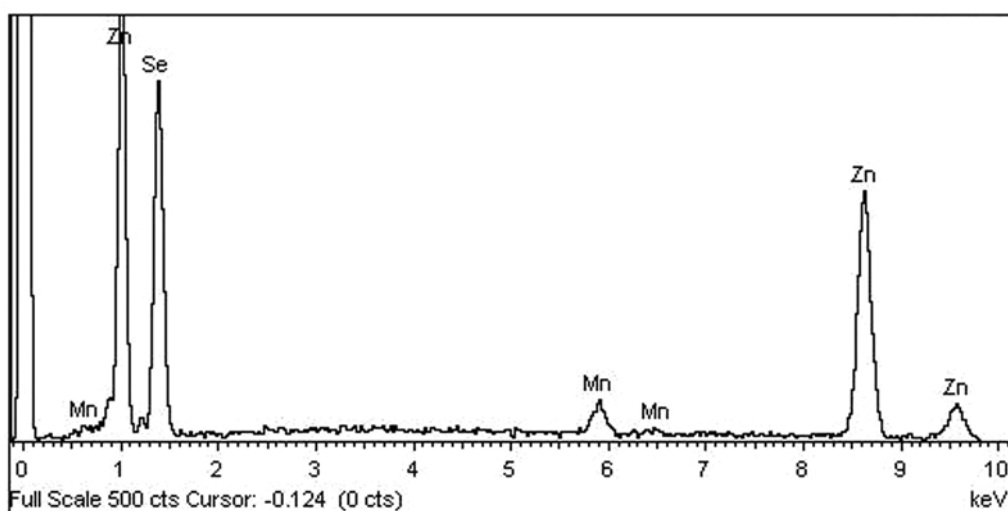


Fig. 2. EDAX spectrum for as-prepared $Zn_{1-x}Mn_xSe$ ($x = 0.07$) powder compound

obtained are tabulated in Table 2 and depicted in Fig. 6. Table 2 shows the obtained lattice parameter (a) as a function of Mn content and as shown from Fig. 6 the obtained values of the lattice parameter (a Å) exhibits linear content dependence.

Such remarkable change in the lattice parameter of the investigated samples and consequently the unit cell volume, may be attributed to the fact that the Goldsmith ionic radius of Mn^{2+} (0.66 Å) for coordination number 4 [18] is higher than that of Zn^{2+} (0.60 Å) for coordination number 4.

Now, it is worth mentioning, that the small difference between the ionic radii of Mn^{2+} and Zn^{2+} as not matching the increase in the unit cell volume of the investigated sampled as clearly shown in the Fig. 6. Hence, this may attract the attention to another reason,

in addition to the difference in ionic radii, responsible for this increment.

The second reason may be explained if we take into consideration the molecular structure of ZnSe. It has been reported in literature, that ZnSe (Zinc blende or sphalerite) [19] crystallizes in face centered cubic (FCC) structure with space group $F\bar{4}3m$ (No. 216) and four molecules per unit cell. This means that four Zn cations are distributed among the sites of Wyckoff notation (a) with coordinates of equivalent positions 0, 0, 0 [20], while four Se anions are distributed among the sites of Wyckoff notation (c) with coordinates of equivalent positions $1/4, 1/4, 1/4$. This configuration leads to interstitial sites of Wyckoff notation (b) and (d) with coordination of equivalent positions $1/2, 1/2, 1/2$, $3/4, 3/4, 3/4$ respectively. It is worth mentioning also,

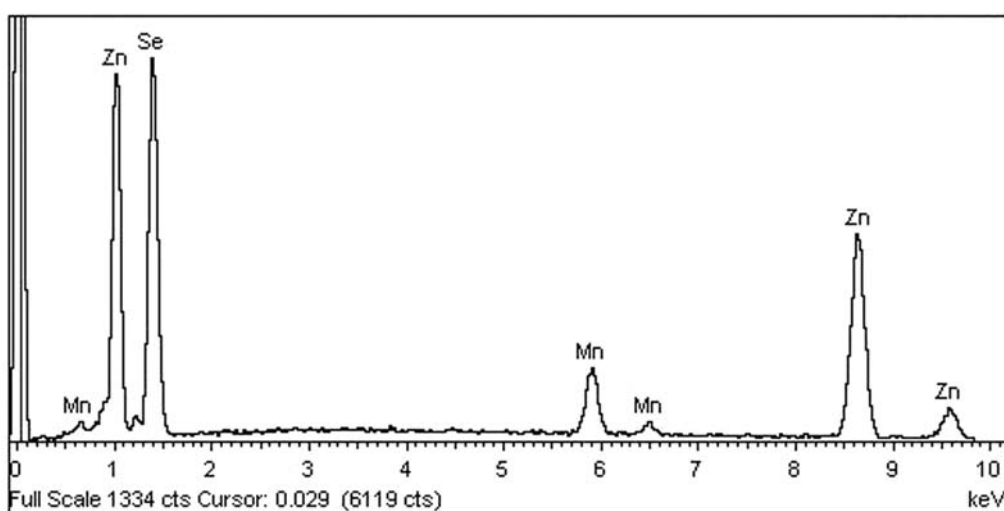


Fig. 3. EDAX spectrum for as-prepared $Zn_{1-x}Mn_xSe$ ($x = 0.14$) powder compound

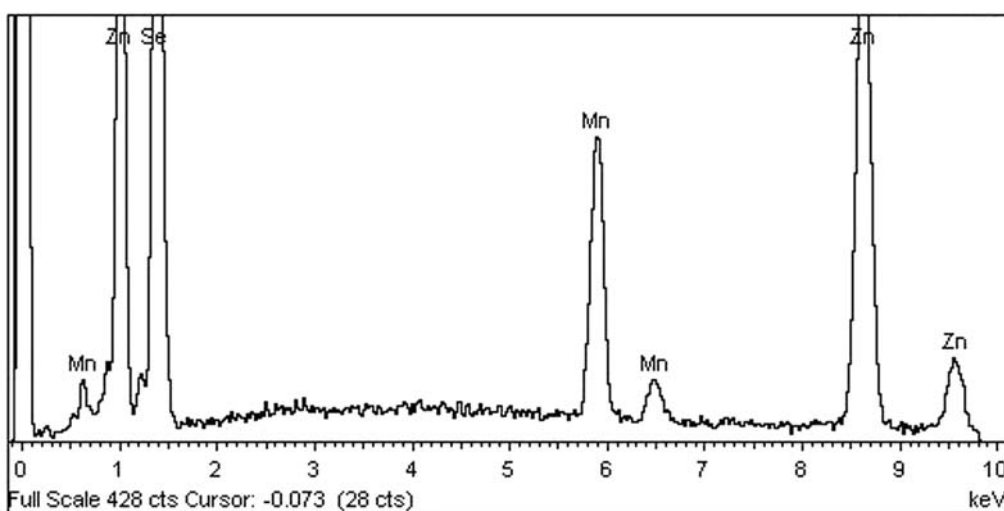


Fig. 4. EDAX spectrum for as-prepared $Zn_{1-x}Mn_xSe$ ($x = 0.23$) powder compound

that the X-ray diffraction patterns Fig. 5 showed that the nominal composition structure with different Mn concentration are single phase with no additional lines corresponding to any other phases of elements or binary compound along the whole measured 2θ ranges, which provide clear evidence of formation of a series of solid solutions of the investigated series. This may

be clear evidence that Mn^{2+} dissolves completely in ZnSe structure without any change in the molecular structure. In this case Mn^{2+} is introduced into the ZnSe structure to replace Zn^{2+} or to be introduced interstitially. Since Mn^{2+} cations were applied to the ZnSe as additives, so one can expect that Mn^{2+} cation incorporates into the ZnSe lattice interstitially. In this case, the

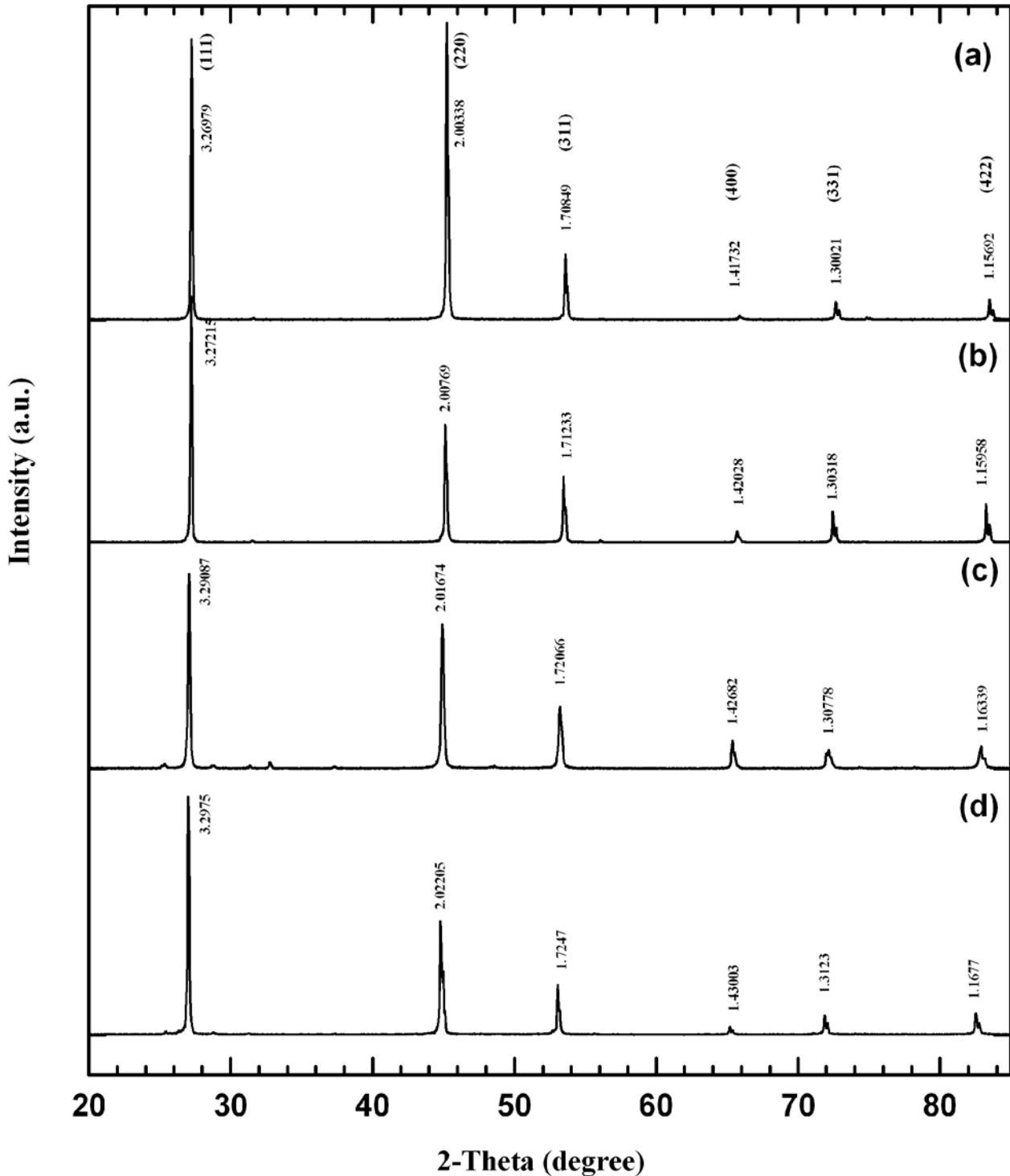


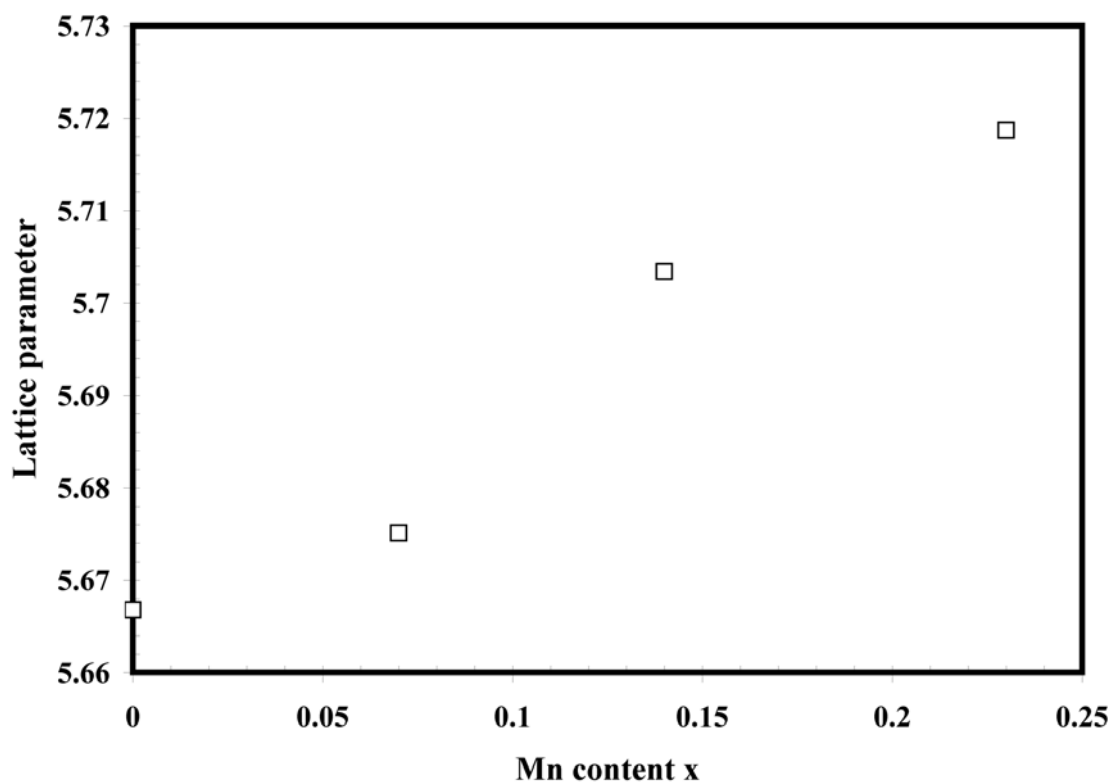
Fig. 5. X-ray diffraction patterns for $Zn_{1-x}Mn_xSe$ (a) $x = 0$, (b) $x = 0.07$, (c) $x = 0.14$ and (d) $x = 0.23$ powder compounds

Table 1. The d -values corresponding to (hkl) for all prepared sample due to increasing Mn content

hkl	$Zn_{1-x}Mn_xSe$			
	$x = 0$	$x = 0.07$	$x = 0.14$	$x = 0.23$
	d (Å)	d (Å)	d (Å)	d (Å)
111	3.26979	3.27215	3.29087	3.2975
220	2.00338	2.00769	2.01674	2.02205
311	1.70849	1.71233	1.72066	1.72470
400	1.41732	1.42028	1.42682	1.43003
331	1.30021	1.30318	1.30778	1.31230
422	1.15692	1.15958	1.16339	1.16770

Table 2. Calculated lattice parameter (a) and unit cell volume for all samples corresponding to increase of Mn content

Sample	Mn concentration	Lattice parameter (a) Å	Cell volume (Å) ³
$Zn_{1-x}Mn_xSe$	$x = 0$	5.6668	181.975
	$x = 0.07$	5.6751	182.776
	$x = 0.14$	5.7034	185.527
	$x = 0.23$	5.7187	187.022

**Fig. 6.** The relation between Lattice parameter (a) Å against Mn content

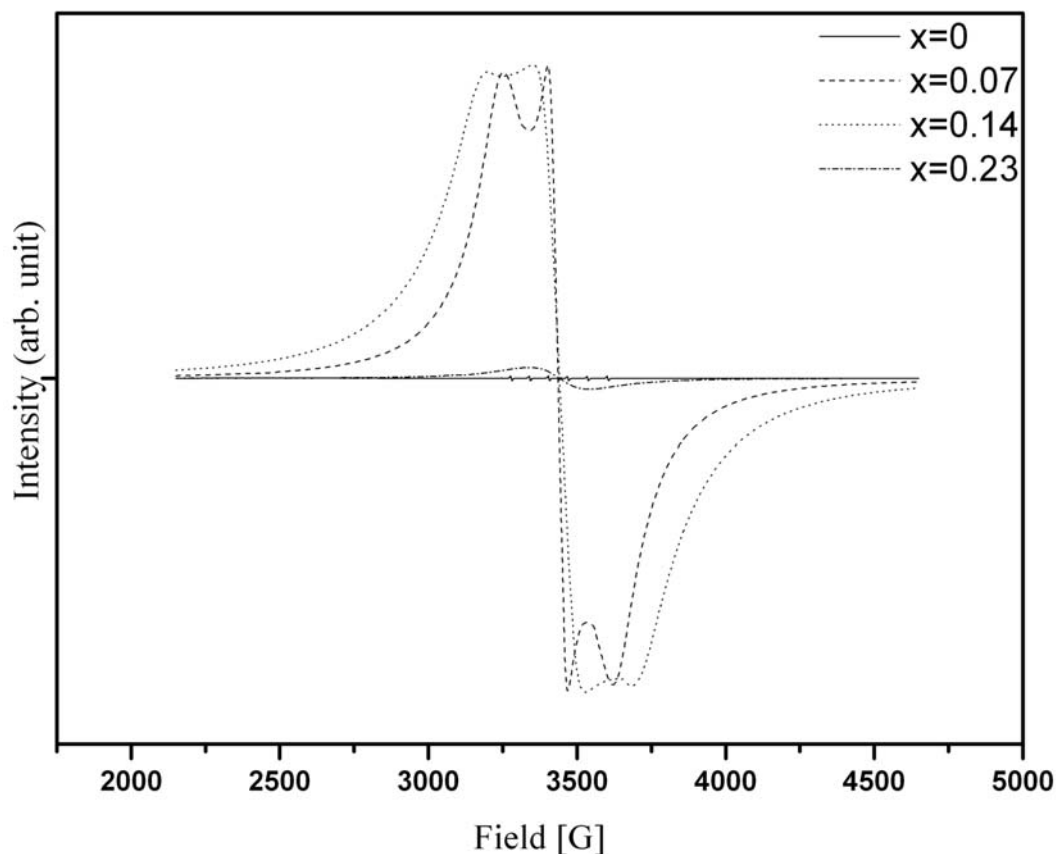


Fig. 7. Room-temperature ESR spectra of $Zn_{1-x}Mn_xSe$ ($x = 0, 0.07, 0.14$ and 0.23) powder compounds

expected interstitial site to be occupied with Mn^{2+} cations is that of Wykoff notation (*b*) with coordinates of equivalent positions $1/2, 1/2, 1/2$. This situation has been proposed because Se^{2-} anion occupies the sites midway along the cube diagonal between Zn and Mn which can be shared to form the cation coordination polyhedron. Also, it may be thought, that this configuration leads to stable atoms with strong covalent bonding.

Electron spin resonance (ESR) is a physical method of observing resonance absorption of microwave power by unpaired electron spins in a magnetic field. The fact that there is slight change in the XRD pattern of $Zn_{1-x}Mn_xSe$ compounds of different x suggests that ESR could give sensitive information and revealing technique to probe the changes in a crystal lattice structure [21]. When spinning electrons are placed in an external static magnetic field, the direction of spin electrons is in the same or opposite to that of the external magnetic field. The spectroscopic splitting Lande-g factor of an ESR signal is an important parameter, since unpaired electrons in different environments have slightly different g factors, resulting in the appearance of signals for different centers at different

magnetic field strengths. The g-factors for free electron are $g_e = 2.0023$ [22], the shift from this value is caused by the spin-orbit interaction of the electron in the atomic orbital.

Fig. 7 represents the electron spin resonance (ESR) spectra for $Zn_{1-x}Mn_xSe$ ($x = 0, 0.07, 0.14, 0.23$) powder compound semiconductor. It is clear from Fig. 7 that, there are some noise may be the six known lines hyperfine interaction appears in ZnSe powder, this could be attributed to the presence of very small impurities $\leq 0.001\%$ in the Zn or Se elements which was not detected by EDX or X-ray diffraction techniques. It was reported [23] that, ZnSe without Mn^{2+} dopant have no ESR signal. It was observed that, the $Zn_{1-x}Mn_xSe$ ($x = 0.07$) spectra reveals that the appearance of the two overlapped signals at different magnetic fields. This two signals have the same spectroscopic splitting Lande-g factor ($g = 2.0086$) measured at the center of the signal, which due to free spin. The presence of two ESR signals may be created by the absorption of the microwave power by two electrons in two different valance states of Mn.

Similarly in $Zn_{1-x}Mn_xSe$ ($x = 0.14$) compound, the appearance of the two overlapped signals at different

magnetic fields still present, and also the value of Lande-g factor equal to 2.00571 due to free electron interaction. But in $Zn_{1-x}Mn_xSe$ ($x = 0.23$) compound, there is one ESR signal of the Lande-g factor equal to 2.00547 which attributed to free electron interaction. As Mn content increases to 0.23 we deduce that, the signal tends to broad line without any overlapped signals at different magnetic field and the intensity of the signal decreased as shown in Fig. 7. When a high concentration of Mn^{2+} was doped in ZnSe, small clusters of Mn^{2+} formed during the nucleation-doping process, which results in strong dipolar interactions between Mn^{2+} ions, thus influence the hyperfine splitting of the ESR signal of Mn^{2+} ions to show the broadening of the peaks. This results are a good agreement with that detected at higher doping concentration of Mn by Beermann et al. (2004) [21] Yeom et al. (1996) [24] and Lakshmi et al. (2009) [25]. The broadening line also observed in magnetic semiconductors (Zn, Cd) (S, Se, Te): Mn [25]. The deviation of all g-factor values for $Zn_{1-x}Mn_xSe$ ($x = 0.07, 0.14$ and 0.23) from free electron g-factor value $g_e = 2.0023$ is attributed to spin-orbit interaction [22].

Mn^{2+} magnetic element have spin $S = 5/2$ and causes hyperfine splitting six lines interaction (hfs) [21, 22, 24, 26, 27]. These hyperfine splitting (hfs) interactions have been observed at low concentration of 0.003 and 0.008 % Mn^{2+} [21] because the Mn^{2+} hydration shell was not completely destroyed. At higher Mn^{2+} concentration these hyperfine splitting interaction disappear and cause a broad line spectrum due to Mn^{2+} - Mn^{2+} interactions [21, 25, 28]. This broadening attributed to the exchange interaction between Mn^{2+} ions becomes strong than the hyperfine interaction as observed by Yeom et al. (1996) [24].

The ESR signal on the Mn^{2+} -doped ZnSe, as other compounds of Mn^{2+} -doped II-VI group elements, indicates the presence of two different Mn^{2+} sites in the lattice. One is the Mn^{2+} substituting into the tetrahedral Zn^{2+} lattice site. The other is the anomalous surface/interior defect site [29]. In our semiconductor compounds the Mn^{2+} introduced interstitially inside the ZnSe host lattice as confirmed by X-ray diffraction.

CONCLUSION

The prepared $Zn_{1-x}Mn_xSe$ compound by solid solution technique have good stoichiometric material with $x = 0, 0.07, 0.14$ and 0.23 as examined by EDX technique. The X-ray diffraction patterns of the prepared powder samples show single phase zinc blende cubic structure. X-ray diffraction patterns reveal that, the additive of Mn leads to corresponding peak shift to-

wards the lower angle, this shift slight increase with increasing Mn content from $x = 0$ to $x = 0.23$. The cell parameters (lattice parameter) and consequently unit cell volume have an increase with increasing Mn content in the sample. The additives of Mn to ZnSe lattice affect the electron spin resonance (ESR) spectra, where the broad line becomes dominant by increasing Mn concentration from $x = 0.07$ to 0.23 and hyperfine splitting interaction was not observed. The $Zn_{1-x}Mn_xSe$ ($x = 0.07, 0.14$) and 0.23 compound have the Lande-g factors 2.0086, 2.00571 and 2.00547 respectively due to free electron interaction.

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