OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 3, March 2010, p. 295 - 298

EPR study of Se-Te-Zn glassy system with and without Mn doping

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Se-Te and Se-Te-Zn glasses were prepared by melt quench technique and doped with paramagnetic manganese probe. Electron paramagnetic resonance (EPR) spectrum showed the presence of hyperfine structure (hfs) in Se-Te-Zn glasses (without Mn- doped). It showed the presence of Mn in Zn as trace impurity. EPR results indicated that manganese (Mn) modify the crystal field environment and which is becoming distorted cubic type in nature.

(Received February 20, 2010; accepted March 12, 2010)

Keywords: EPR, Se-Te-Zn, Glass, Mn-doping, Glass

1. Introduction

Electron paramagnetic resonance (EPR) is promising method for investigating the structure of disordered solids [1]. Amorphous chalcogenide semiconductors do not generally exhibit electron para magnetic resonance (EPR) signal originating from defects under ambient conditions [2]. In such materials, having undetectable free spin density, incorporation of transition metal impurities Mn, can induce paramagnetic defect centres and modify the microenvironment of the glass [3]. The EPR of transition metal ions can easily be detected at room temperature and it can provide valuable information about the site symmetry and the environment around the paramagnetic defects and also allow one to obtain valuable information of short range order in atomic arrangement [1]. Paramagnetic Mn impurity has been used in the past as a microprobe to observe EPR signal in chalcogenide glasses [4-7]. It is interesting to note that the system $Se_{80-x}Te_{20}Zn_x$ (with composition x = 0, 2 and 4) exhibits EPR signal with hfs (six lines at around $g \approx 2.0$) corresponding to Mn whose intensity increases with increase in Zn concentration. The signal may be attributed to the Mn which is likely to be present in Zn as trace impurity. The presence of Mn as trace impurity in the added Zn metal in ZnSe system has also been reported in the literature [8]. When this Zn (Mn trace impurity) enters into the host network of Se-Te, the Mn-impurity enters into the lattice as Mn^{2+} and exhibits its characteristics six lines.

2. Experimental details

Bulk amorphous chalcogenide semiconducting materials in the compositions $Se_{70}Te_{30}$, $Se_{80}Te_{20}$ and $Se_{80-x}Te_{20}Zn_x$ (x = 0,2,4 and 6) without and with Mn doping (0.1 at % of Mn) were prepared from high purity elements by a conventional melt-quenching technique as reported elsewhere [10-11]. The amorphous/glassy nature of the synthesized materials was confirmed using XRD and differential scanning calorimetry.

The electron spin resonance (EPR) signals of the present samples were recorded at room temperature with JEOL JES Fe 3X homodyne model in X-band frequency (8.8 to 9.6 GHz) at the field modulation of 100 kHz. As a reference for magnetic field, DPPH with g= 2.0036 was used.

3. Results and discussion

The EPR spectra of undoped samples $Se_{80}Te_{20}$ and $Se_{70}Te_{30}$, did not show any absorption line. The observed EPR spectra of (0.1 at %) Mn-doped ($Se_{70}Te_{30}$) and ($Se_{80}Te_{20}$) samples are shown in Fig.1. In the absorption spectrum of both the doped composition, a broad line at g ~ 1.98 is observed. No hyperfine splitting (hfs) due to Mn impurity appeared. On annealing the Mn doped samples, the EPR signal disappeared is reported elsewhere [11]. It is interesting to note that the samples $Se_{80-x}Te_{20}Zn_x$ with x = 1, 2, 4 and 6 (without Mn doping) exhibit EPR signal.

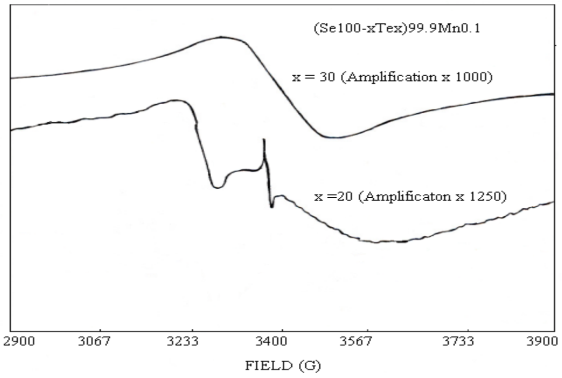

Fig. 1. Electron paramagnetic resonance spectra of 0.1 at % Mn doped in amorphous semiconducting system $Se_{70}Te_{30}$ and $Se_{80}Te_{20}$.

Electron paramagnetic resonance spectra of the amorphous alloys in the system $Se_{80-x}Te_{20}Zn_x$ (x=1, 2, 4 and 6) are presented in Fig 2. Absorption line at around g~2 with hfs (six lines) appears in compositions (x = 1, 2, 4 and 6) whose intensity increases with increase in Zn impurity. In x=6 composition the hfs signal becomes very prominent. No detectable signal was found at any other g value. The experimental parameter such as the amplifier gain etc. are kept the same for all compositions except x= 6.

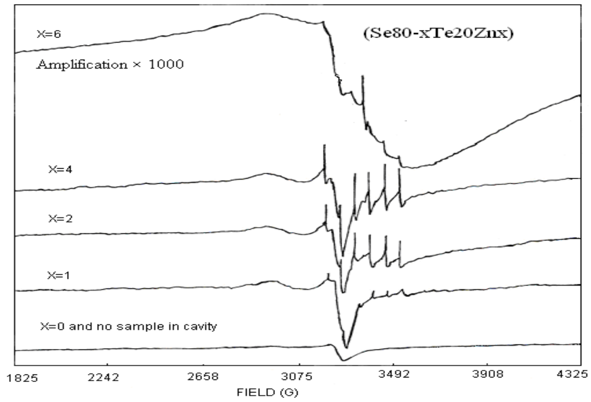

Fig. 2. EPR spectra of amorphous semiconducting system $Se_{80-x}Te_{20}Zn_x$,

The presence of typical six lines in hfs at g~2 is characteristic of Mn^{2+} in the lattice. The hfs appearing in compositions with x =1, 2, 4 and 6, therefore, corresponds to Mn – impurity which is present as a trace impurity element in metal Zn used in the synthesis of the compositions. In the literature, study of ZnSe also showed similar results, i.e. the Mn trace impurity was found in the added Zn metal [8].

In order to ascertain the presence of Mn in Zn, the EPR spectrum of Zn metal was taken but no absorption line in the spectrum was observed. This shows that the Mn-impurity present in Zn metal is not magnetically active. However, when this Zn (Mn trace impurity) is added in the host network of Se-Te, the Mn-impurity enters into the lattice as Mn^{2+} [11] and exhibits its characteristic six hfs lines. To further confirm the presence of Mn-related signal, we added 0.1 at % Mn into various Zn containing alloys in the system ($Se_{80-x}Te_{20}Zn_x$) (with x= 0, 1, 2, 4, 6). The spectra of amorphous alloys $(Se_{80-x}Te_{20}Zn_x)_{99.9}Mn_{0.1}$ (x = 0, 1, 2, 4 and 6) is shown in Fig.3. The EPR signal of Mn doped $Se_{80-x}Te_{20}Zn_x$ for compositions corresponding to x = 2 and 4 shows hyperfine line at about g~2, whereas, for x = 6 composition there is a unique broad line.

When Mn (having electro negativity 1.5) is added to Se-Te-Zn system, it can replace Zn substitutionally in the lattice. The probability of formation of Mn-Se bond becomes greater than the formation of Mn-Te bond [13].

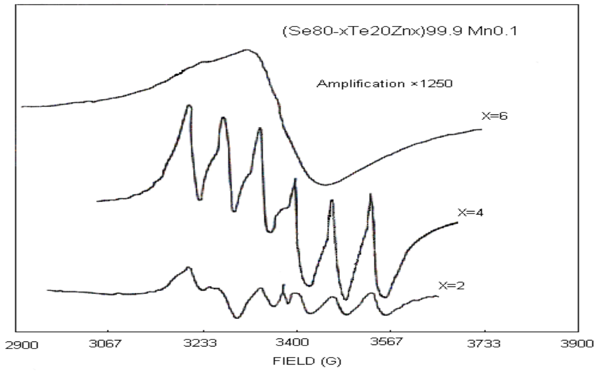

Fig. 3. Electron paramagnetic resonance spectra of 0.1 at % Mn doped amorphous semiconducting system $Se_{80-x}Te_{20}Zn_x$.

Table 1. EPR parameters for ΔH_{pp} peak to peak width, Hfs the hyperfine splitting parameter , Ipp the peak intensity , A the hyperfine splitting constant and g the Lande g factor.

Sample	g	ΔH_{pp}(Gauss)	H_{fs}(Gauss)	Ipp (AU)	$A\times10^{-4}(cm^{-1})$
$Se_{80-x}Te_{20}Zn_x$					
x = 1	1.95	347.2	53.2	4.0	50.2
x = 2	2.00	333.3	55.6	4.6	51.9
x = 4	2.05	340.3	44.0	6.0	41.9
x = 6	1.92	625.0	55.6	8.3	49.8
$(Se_{100-x}Te_x)_{99.9}Mn_{0.1}$					
x = 30	1.99	216.7	---	4.2	---
x = 20	1.98	400.0	---	6.3	---
$(Se_{80-x}Te_{20}Zn_x)_{99.9}Mn_{0.1}$					
x = 2	2.00	344.4	57.8	2.6	53.8
x = 4	1.98	394.4	64.4	9.9	59.5
x = 6	1.98	133.3	---	6.8	---

When Mn (having electro negativity 1.5) is added to Se-Te-Zn system, it can replace Zn substitutionally in the lattice. The probability of formation of Mn-Se bond becomes greater than the formation of Mn-Te bond [13].

Manganese enters as Mn^{2+} and should be replacing sites occupied by Zn^{2+} centres. This is obvious from the appearance of hfs (six lines) characteristic of Mn^{2+} sites in the network. This supports the fact that a part of the added Zn impurity is definitely entering in the Se-Te chain and ring network as Zn^{2+} states. The concentration (0.1 at %) of Mn corresponds to about 10^{20} atoms/cm^3.

The concentration of Zn atoms in x=1 alloy is also about 10^{20} atoms/cm^3. Hence at lower Zn concentration almost all the Zn atoms are entering as Zn^{2+}. In another study thermal diffusion of Zn into As_2S_3 has also shown that Zn impurity diffuses as Zn^{2+} [14]. Study of Mn doped ZnSe and ZnTe by EPR has concluded that manganese atoms are incorporated as Mn^{2+} in the lattice and sit at Zn^{2+} sites. Field around Mn^{2+} impurity is cubic or close to cubic nature [15]. Ionic radii of Zn^{2+} and Mn^{2+} are 0.74Å and 0.8Å respectively. Accordingly replacement of Zn^{2+} by Mn^{2+} will induce some lattice distortion which would produce crystal field of distorted cubic in nature.

We consider the spin Hamiltonian (χ) with S=5/2 and I=5/2,

$$\chi = g\beta_e \vec{B}.\vec{S} + A\vec{I}.\vec{S} + higher\ \ order\ \ terms \qquad (1)$$

and the values of g and A for various compositions studied in this work are summarized in Table-1. The various line parameters H_{PP}, peak to peak width; $H_{1/2}$, half width; I_{pp}, peak intensity, for various compositions are also summarized in the Table 1. The hyperfine splitting (hfs) is also included in this Table. To obtain the values of A, following relation between A and hfs is used [10].

$$A\,(cm^{-1}) = \frac{g_N\beta_N}{S} B_{hf} = 1.4\times10^{-8}\ B_{hf} \qquad (2)$$

where g_N and β_N are nuclear g factor and nuclear magneton respectively. The value of hyperfine splitting constant A for Mn^{2+} in crystalline ZnSe and ZnTe is 60×10^{-4} and 56×10^{-4} cm^{-1} respectively [9]. This corresponds to cubic/near cubic sites for Mn^{2+} with surrounding anions. In the present study, the values of A in Se-Te-Zn alloys lies in the range (41-51) × 10^{-4} cm^{-1} with a low value (41×10^{-4} cm^{-1}) in composition with x=4. In Mn-doped Se-Te-Zn the value of A is increased to 59×10^{-4} indicating a modification in the crystal-field environment on the addition of Mn-impurity.

The crystal-field is becoming more of cubic type [15]. A relation between the splitting parameter A and ionicity of the bond i.e., greater value of A corresponds to greater ionicity, is reported by [9]. Addition of Mn to Se-Te-Zn composition increases the value of A making the Mn^{2+}-anion bonding more ionic. This means that in x= 4 composition the added Mn impurity preferably occupies Zn sites making Zn-Se bonding. In undoped composition the already present Mn trace impurity preferably occupies Zn sites making Zn-Te bond in x=4 composition. In composition with x=6 the disappearance of hfs on addition of Mn may be due to the broadening of lines with strong spin-spin interaction.

It is to be noted that Zn-Se bond is more ionic than Zn-Te bond. In the Mn-doped compositions, the increased ionicity of Mn^{2+} bond suggests the presence of Se neighbors as anion around Mn^{2+}. Hence, Mn^{2+} favours those Zn^{2+} sites which makes Zn-Se bond.

The position of the absorption line (with hfs) in various undoped and doped compositions appears at g ~ 2. This line has been associated with Mn^{2+} sitting at sites in a cubic field having axial perturbation. The cubic field is provided by Se or Te ions around Mn^{2+} sites. The g value has been determined at the approximate zero-crossing value.

In case of $Se_{70}Te_{30}$ and $Se_{80}Te_{20}$ compositions doped with Mn, the broad line at g ~ 2 also appears, which does not exhibit hyperfine splitting. The hfs lines may have been broadened due to strong spin-spin interaction.

The peak intensity I_{pp} increases with Zn concentration in $Se_{80-x}Te_{20}Zn_x$ compositions from 4.0 units in composition with x=1 to 8.3 units in composition with x=6 suggesting thereby the rise in the paramagnetic defect concentration. In Mn-doped samples, I_{pp} increases with x and reaches maximum value of 9.9 in composition with x=4 and thereafter, it falls to 6.8 in x=6 composition. The peak to peak width ΔH_{pp} in undoped compositions increases with Zn concentration from 340 gauss (G) in composition with x=1 to 625 G in x=6. The line broadening can be associated with a large number of types of structural units with different distances between atoms at which paramagnetic defects can be formed [1]. On doping the alloys with Mn impurity ΔH_{pp} is reduced from 344 G in composition with x=2 to 133 G in x=6. In the compositions without Zn ($Se_{80}Te_{20}$ and $Se_{70}Te_{30}$), ΔH_{pp} increases from 216 G in $Se_{70}Te_{30}$ to 400 G in $Se_{80}Te_{20}$ whereas I_{pp} decreases from 6.3 in $Se_{80}Te_{20}$ to 4.3 in $Se_{70}Te_{30}$. This suggests the presence of greater number of Se-related paramagnetic centres associated with Mn-Se bonds.

4. Conclusions

In the Se-Te compositions, Mn induced defects give an ESR signal at g≈2 which is associated with Mn-chalcogen clusters situated in the crystal field with axial symmetry. Doping of Mn to $Se_{80-x}Te_{20}Zn_x$ alloys seems to modify the crystal-field environment. The crystal-field is becoming more of cubic type. The disappearance of hfs may be due to the strong spin-spin interaction. In the Mn-doped compositions, Mn^{2+} favours those Zn^{2+} sites which makes Zn-Se bond.

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