Evidence of two Bi sites from EPR of Mn^{2+} in Bi-doped amorphous germanium chalcogenides

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Electron paramagnetic resonance spectra of Bi-doped $Ge_{20}S_{80-x-y}Bi_xMn_y$ and $(GeSe_{3.5})_{100-x-y}Bi_xMn_y$ glassy semiconductors have been observed using Mn^{2+} as a microprobe for the first time. Experimental data on the g value and the line parameters in various samples studied indicate that Bi atoms in germanium chalcogenide glassy semiconductors occupy two different types of sites in the material at low and high Bi concentrations, respectively. This supports our earlier findings on Bi dopant in germanium chalcogenide glass using high-pressure, x-ray diffraction, and differential-thermal-analysis methods.

In contrast to the tetrahedrally bonded amorphous semiconductors, chalcogenide glasses usually do not exhibit ESR signals from defects under normal conditions.[1] Mott, Davis, and Street[2] and also Kastner, Adler, and Fritsche[3] suggested that paired localized states appear in glassy chalcogenide semiconductors because of the presence of charged defect centers C_3^+, C_1^-. This leads to the absence of ESR signals in chalcogenide glasses under normal conditions, because two electrons on the same defect site experience effective negative correlation energy. ESR signals from defects, however, have been observed exceptionally for the Ge_xS_{1-x} system among chalcogenide glasses.

In the systems having undetectable unpaired spin density, incorporation of transition-metal impurity atoms like Mn can be utilized to observe an ESR signal corresponding to the added impurity. Analysis of such a signal can provide information about the lattice site and the environment in which the added paramagnetic center is situated. In our continuing program of investigation of bismuth-doped n-type amorphous germanium chalcogenides,[4–13] we have observed ESR spectra of the added Mn paramagnetic centers in these doped chalcogenide semiconductors for the first time. An attempt has been made to gain information about the nature of the environment around the added paramagnetic center.

Several compositions of the doped semiconducting materials $(GeSe_{3.5})_{100-x-y}Bi_xMn_y$ and $Ge_{20}S_{80-x-y}Bi_xMn_y$ were prepared by the conventional melt-quenching technique starting with proper quantities of the high-purity material (99.999%), and characterized by differential thermal analysis and x-ray diffractometry as reported earlier.[13] The electron-spin-resonance spectrum of the materials was observed using a Jeol JeS-Fe 3X homodyne X-band spectrometer operating in the frequency range 8 to 9.6 GHz and using field modulation of 100 kHz. Low-temperature measurements were made using an insertion-type Dewar vessel.

The undoped Ge_xSe_{1-x} glass does not show any ESR signal.[14] With addition of manganese, it exhibits two absorption lines with g values centered at 4.3 and 2.0. In this study we have concentrated on samples with higher Mn concentration (0.1 to 0.5 at. %) and have tried to observe the behavior of the $g=2.0$ line with different amounts of Bi and Mn in the host material $GeSe_{3.5}$ glass. The behavior of the line around $g \approx 2.0$ in various amorphous compositions studied is presented in Fig. 1. Line parameters of the peak, ΔH_T (peak-to-peak width), ΔH_W (half width), and I_p (peak intensity), are summarized in Table I. The temperature dependence of the line was also observed in the $x=10$, $y=0.5$ sample up to a temperature of 100 K. The values of g have been calculated at approximately zero crossing point. Since the resonance lines are very broad and asymmetric, g values will have greater uncertainty in the magnitude, e.g., ± 0.03.

The experimental results on $Ge_{20}S_{80-x-y}Bi_xMn_y$ glasses are presented in Fig. 2 and these are distinctly different from Ge-Se host glass. The observed resonance line in the $x=4$ sample is quite different from that in the

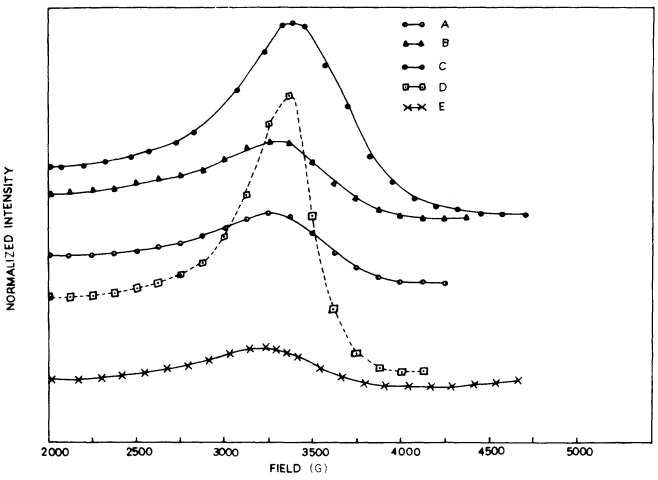

FIG. 1. ESR spectra of $(GeSe_{3.5})_{100-x-y}Bi_xMn_y$ glass. (A) represents $(GeSe_{3.5})_{97.5}Bi_2Mn_{0.5}$, (B) represents $(GeSe_{3.5})_{97.75}Bi_2Mn_{0.25}$, (C) represents $(GeSe_{3.5})_{89.5}Bi_{10}Mn_{0.5}$, (D) represents $(GeSe_{3.5})_{99.5}Mn_{0.5}$, (E) represents $(GeSe_{3.5})_{97.9}Bi_2Mn_{0.1}$. The spectra are normalized to facilitate the comparison of the relative intensity of the signal.

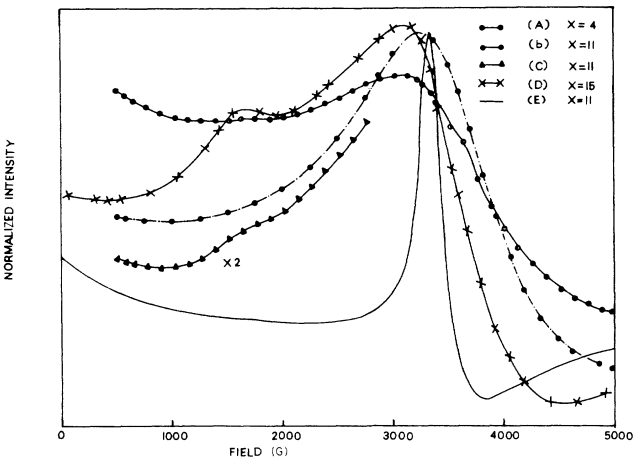

FIG. 2. ESR spectra of $Ge_{20}S_{80-x-y}Bi_xMn_y$ glass. (A) $Ge_{20}S_{75.5}Bi_4Mn_{0.5}$, (B) $Ge_{20}S_{68.5}Bi_{11}Mn_{0.5}$, (C) spectra of $Ge_{20}S_{68.5}Bi_{11}Mn_{0.5}$ multiplied by two, (D) $Ge_{20}S_{64.5}Bi_{15}Mn_{0.5}$, (E) $Ge_{20}S_{68.5}Bi_{11}Mn_{0.5}$ (annealed at 512 °C). Spectra are normalized to facilitate the comparison of the intensity of the signal.

$x=11$ and 15 samples. Interestingly, there is only a single line at $g=1.76$ in the $x=4$ sample whereas a second line at $g=3.85$ starts appearing in $x=11$ and 15 compositions. The line parameters are also compared in Table I. A continuous increase in g value with the addition of Bi impurity is observed. There is a remakable effect of annealing the sample at 512 °C as shown in Fig. 2. A completely different line appears in the annealed composition. The line parameters are included in Table I. The g values, as before, have been calculated at approximately zero crossing value due to broadness and asymmetry of the lines.

The ESR spectra of Mn^{2+} ions in amorphous semiconductors usually exhibit absorption lines centered at $g=4.3$ and 2.0.[14] They may or may not exhibit resolved hyperfine structure.[15] Particularly at higher Mn^{2+} concentration (>0.01 at.%) strong dipole-dipole interaction broadens the hfs and it is smeared out.

The ESR spectra of Mn^{2+} can be described by the spin Hamiltonian

$$H=g_0\beta SH+D[S_z^2-\tfrac{1}{3}S(s+1)+E(s_x^2-s_y^2)]\ ,$$

where $g_0=2.0023$, $S=\frac{5}{2}$, and other symbols have their usual meaning.[14] When either D or E is large compared

TABLE I. Line parameters of the resonance line in $(GeSe_{3.5})_{100-x-y}Bi_xMn_y$ and $Ge_{20}S_{80-x-y}Bi_xMn_y$. ΔH_T (peak-to-peak width), ΔH_W (half width), and I_p (peak intensity). g_1 and g_2 are g values of two resonance lines in Ge-S-Bi-Mn glass, respectively. The estimated uncertainty in g values of broad lines is ± 0.03.

Sample	g	H_W (G)	H_T (G)	I_p arbitrary units
$(GeSe_{3.5})_{99.5}Mn_{0.5}$ (glass)	1.85	250.0	1075.0	7.0
$(GeSe_{3.5})_{97.5}Bi_2Mn_{0.5}$ (glass0	1.92	237.5	750.0	2.1
$(GeSe_{3.5})_{97.75}Bi_2Mn_{0.25}$ (glass)	1.92	275.0	686.5	1.7
$(GeSe_{3.5})_{97.9}Bi_2Mn_{0.1}$ (glass)	1.92	275.0	686.5	1.7
$(GeSe_{3.5})_{97.9}Bi_2Mn_{0.1}$ (annealed at 400 °C)	1.89	250.0	880.0	3.8
$(GeSe_{3.5})_{89.5}Bi_{10}Mn_{0.5}$ (glass)	1.90	180.0	660.0	9.9
$(GeSe_{3.5})_{89.5}Bi_{10}Mn_{0.5}$ (annealed at 400 °C)	1.89	170.0	660.0	10.2
$Ge_{20}S_{75.5}Bi_4Mn_{0.5}$ (glass)	$g_1=1.76$	1290	1850	9.1
$Ge_{20}S_{68.5}Bi_{11}Mn_{0.5}$ (glass)	$g_1=1.80$ $g_2=3.97$	460	1840	2.2
$Ge_{20}S_{68.5}Bi_{11}Mn_{0.5}$ (annealed at 512 °C)	$g_1=1.89$	60	460	27.6
$Ge_{20}S_{64.5}Bi_{15}Mn_{0.5}$	$g_1=1.85$ $g_2=3.85$	700	1420	8.5

with $g_0\beta H$, the strong-field approach should be applied. The relation $X=D/E=1/\lambda$ represents the relationship between axial symmetry and rhombic symmetry of the crystal field surrounding Mn^{2+}. The value of $\lambda=\frac{1}{3}$ is identical with the maximum possible orthorhombic symmetry and the corresponding g value is 4.3. When $g_0\beta H$ is large compared with D and E, the weak-crystal-field approach should be used and the g value equals 2.0. In this case the crystal field is of cubic symmetry. It has been usually accepted that the line with $g=4.3$ is characteristic of the Mn^{2+} ions incorporated into the glass network and the line with $g=2.0$ is caused by the Mn^{2+} ions forming clusters, pairs, or microcrystalline inclusions.[16] The Mn^{2+} sites which do not satisfy the special condition of $E/D=\frac{1}{3}$ produce signals with largely scattered g values and hence of very broad linewidth beyond detection.[15]

Coming to the experimental data on Bi-doped $Ge_{20}S_{80-x-y}Bi_xMn_y$, it is important to notice that in the $x=4$, $y=0.5$ composition the expected $g=4.3$ resonance line is not observable. This may imply that Bi doping of the glass violates the condition $E/D=\frac{1}{3}$ and produces signals with largely scattered values of g which makes the $g=4.3$ line very broad beyond detection. Further, absence of hfs in all the samples indicates strong dipole-dipole interaction. Asymmetry in the resonance line is also indicative of extensive scattering of g values even in the $g=1.8$ line. The intrinsic ESR signal in Ge-S glass has its origin in Ge and S dangling bonds. The resonance line close to $g=2.0$ is caused by phase-separated Mn-chalcogen particles in the host material with Mn occupying similar sites to Ge.[15] It has been pointed out in the literature[1,15] that in Ge-S glass a whole variety of internal crystal fields may exist whose origin and nature is not yet understood.

It is possible that addition of Bi atoms to this system (up to 4 at. %) produces magnetically inactive BiS_3 units and does not produce any new resonance line. The main resonance line close to $g=1.9$ in the $x=11$ and 15 samples has an increase in its g value as shown in Fig. 2 which indicates some modification in the crystal field of cubic symmetry for the line close to $g=1.9$. Increase in the Bi content to 11 and 15 at. % in the material produces new magnetically active defect centers which give a new resonance absorption line with $g=3.85$. We associate the new defect centers with unpaired spins at the clusters comprising all the three elements, Ge, Bi, and S. These unpaired spins are sitting in a symmetry environment close to rhombic symmetry ($g=4.3$ corresponds to a rhombic symmetry environment). This feature is an interesting part of our results. Drastic changes in the line parameters of the line close to $g=1.9$ in the $x=11$ sample on crystallization shows the sensitivity of the features of the resonance line in the glassy samples.

It is important to mention here that there may also be a possibility for Mn to enter into the systems in charged states other than Mn^{2+}, since a $g=4.3$ line, which is the signature of Mn^{2+}, is not observable. Manganese atoms can exist in sites surrounded by a variety of internal crystals fields present in the host glass. The shape of the lines seems to be more Dysonian rather than Lorentzian or Gaussian. The values of g are less than the free-electron values. These features may indicate two possibilities: (i) The lines possibly originate from Mn sites sitting in highly conducting regions in the sample, or (ii) the internal crystal fields are weak with strong spin-orbit coupling. Further experiments are in progress to make the picture clear. The above arguments are also applicable to the data on Ge-S-Bi glass discussed later.

Before we discuss the feature of the line close to $g=1.9$ in Ge-Se-Bi, a close look at the ESR in Mn-doped $GeSe_{3.5}$ is essential.[14] The line close to $g=2$ in Ge_xSe_{1-x} has no hyperfine structure. The intensity of the line approximately follows the Curie law down to 114 K where the resonance line disappears. It has been suggested that this line is caused due to Mn^{2+} ions forming clusters embedded in the glassy matrix of Ge-Se. The other weak line at $g=4.3$ observed in the glass has been associated with the incorporation of Mn^{2+} in the amorphous network and is indicative of a distorted crystalline electric field in the vicinity of probe ions. These Mn^{2+} ions are strongly covalently bonded and possibly occupy the same sites in the Ge-Se network as Ge atoms.

In the present investigation of Bi-doped $GeSe_{3.5}$ glasses, a $g=4.3$ line has not been observed within the resolution of the spectrometer. It is believed that the g values for Mn^{2+} sites in the doped glasses are widely distributed which makes the line very broad and unobservable by the spectrometer. Glasses in the system As-S-I doped with Mn also do not exhibit a $g=4.3$ line for low concentration.[17] A remarkable feature of our results is that the compositions $x=2$ and 10 exhibit lines close to $g=1.9$, having distinctly different shape, intensity, and width. In $x=2$ composition the variation in Mn concentration ($y=0.1$, 0.25, 0.5) simply changes values of the line parameters ΔH_W, I_p, and ΔH_T and does not influence the shape of the line which indicates its strong relation with the Mn concentration. There is significant change in ΔH_T, I_p, and ΔH_W parameters when Mn is added to a bismuth-doped ($x=2$) sample as compared to their values for the line in $(GeSe_{3.5})_{99.5}Mn_{0.5}$. It seems that the reso-

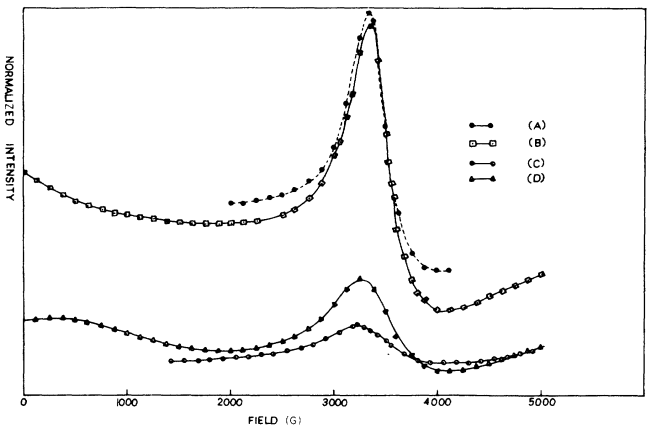

FIG. 3. Effect of annealing on the ESR spectra of (A) $(GeSe_{3.5})_{89.5}Bi_{10}Mn_{0.5}$ (virgin), (B) $(GeSe_{3.5})_{89.5}Bi_{10}Mn_{0.5}$ (annealed at 400 °C), (C) $(GeSe_{3.5})_{97.5}Bi_2Mn_{0.1}$ (virgin), (D) $(GeSe_{3.5})_{97.5}Bi_2Mn_{0.1}$ (annealed at 400 °C).

nance line in Bi-doped samples has either quite different origin than in the undoped sample or the local environments are dissimilar in the two cases.

In order to ascertain whether there is any effect of oxygen on the $g=1.9$ line, the $x=10$, $y=0.5$ sample was annealed in air at 200 °C for about 2 h and a resonance line was again observed in this annealed sample. No qualitative change was observed in the ESR signal at room temperature. The effect of temperature on the features of this resonance line indicates that peak height I_p continuously increases with decrease in temperature and becomes about 25% more intense at 113 K. There is no substantial change in ΔH_T and ΔH_W with temperature.

It is proposed that at low Bi concentration (2 at. %) the addition of Bi to the host network of $(GeSe_{3.5})_{99.5}Mn_{0.5}$ does not originate new ESR absorption lines and it only lowers the intensity of the ESR line of the host Ge-Se-Mn glass with possibly some change in its g values. It is suggested that magnetically inactive $BiSe_3$ units are formed in Ge-Bi-Se-Mn glasses which make the $GeSe_n$ chains more flexible and also dilute the host Ge-Se matrix. The line in the $x=2$, $y=0.1$ sample is quite weak and broad. The effect of annealing on the resonance lines in the $x=2$ and 10 samples is shown in Fig. 3. Looking at the intensity and shape of the resonance line in the $x=10$ sample suggests that its origin is different from that of the $x=2$ or 0 samples. The comparison of line parameters tabulated in Table I supports this view. It is quite likely that the three element clusters Ge-Bi-Se proposed by us in earlier communications[11,13,10] are the hosts of new paramagnetic centers responsible for the resonance line in the $x=10$ sample. We are continuing experiments to gain more information on these materials.

In conclusion we have observed ESR spectra in Bi-doped germanium chalcogenide glassy semiconductors using Mn as a microprobe for the first time with a view to gaining information about the mechanism of doping in this class of noncrystalline semiconductors. Our results indicate that Bi atoms possibly occupy two different types of sites in the material at low and high Bi concentrations, respectively.

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