Bull. Mater. Sci., Vol. 11, No. 4, December 1988, pp. 297–301. © Printed in India.

Energy gap studies on As–Sb–Se glasses

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MS received 19 August 1988; revised 2 November 1988

Abstract. Variation of optical energy gap E_0 with composition in several glasses belonging to the As–Sb–Se system have been studied. The photoacoustic technique, well-suited for highly absorbing samples, has been used for the measurements. Results reported on the $As_xSb_5Se_{95-x}$, $As_xSb_{10}Se_{90-x}$, $As_xSb_{15}Se_{85-x}$ and $As_xSb_{20}Se_{80-x}$ glasses of the As–Sb–Se family are explained on the basis of the chemically ordered network model.

Keywords. Band gap energy; chalcogenide glasses; photoacoustics.

1. Introduction

Amorphous chalcogenide semiconductors have attracted much attention in recent years because of their established use as photoconductors and their potential use as the active components in threshold and memory switching devices (Adler 1977; Mott and Davis 1979; Savage 1972; Zallen 1983). Among the glass forming alloys of the group $A_x^VB^{IV}{}_{100-x}$, the As_xSe_{100-x} family has been studied extensively (Lucovsky and Hayes 1979; Nemanich *et al* 1978; Street *et al* 1978). But there are not many studies on the effect of the replacement of As in the As–Se system by other elements. The results of the study of the low temperature elastic behaviour of As–Sb–Se glasses have been reported earlier (Gopal *et al* 1987). The composition dependence on glass transition temperature T_g, crystallisation temperature T_c, peak temperature of crystallisation T_p, crystallisation enthalpy ΔH_c etc. have been studied using differential scanning calorimetry (Mahadevan *et al* 1986; Giridhar and Mahadevan 1982).

Here we report the results of the measurement of the variation of the band gap energy E_0 with composition in glasses of the As–Sb–Se system using the photoacoustic (PA) technique. Such investigations will greatly help in selecting materials of the desired energy gap and optical absorption properties for special applications.

The compositions of the $As_xSb_ySe_{100-x-y}$ glasses studied (table 1) can be classified into four groups depending on the Sb content. In each group, the compositions $(As, Sb)_{40}Se_{60}$ fall along the pseudobinary section As_2Se_3–Sb_2Se_3 and represents the so-called 'stoichiometric' composition.

2. Experimental

Bulk glasses of the As–Sb–Se system have been prepared by the usual melt-quenching technique. High purity (5N) elements in appropriate atomic percent proportions are sealed in quartz ampoules under a vacuum of $\approx 10^{-3}$ torr. The sealed ampoules are heated in a furnace for nearly 24 h. During heating the ampoules are rotated continuously to ensure homogenization of the melt which is then quenched in ice

Table 1. Measured values of the optical energy gap E_0 of $As_xSb_ySe_{100-x-y}$ glasses.

System	x	Sample	E_0(eV)
$Ax_xSb_{20}Se_{80-x}$	10	$As_{10}Sb_{20}Se_{70}$	1·557
	15	$As_{15}Sb_{20}Se_{65}$	1·460
	20	$As_{20}Sb_{20}Se_{60}$	1·422
	25	$As_{25}Sb_{20}Se_{55}$	1·410
	30	$As_{30}Sb_{20}Se_{50}$	1·386
$As_xSb_{15}Se_{85-x}$	15	$As_{15}Sb_{15}Se_{70}$	1·640
	20	$As_{20}Sb_{15}Se_{65}$	1·540
	25	$As_{25}Sb_{15}Se_{60}$	1·495
	30	$As_{30}Sb_{15}Se_{55}$	1·477
	35	$As_{35}Sb_{15}Se_{50}$	1·447
$As_xSb_{10}Se_{90-x}$	20	$As_{20}Sb_{10}Se_{70}$	1·643
	25	$As_{25}Sb_{10}Se_{65}$	1·606
	30	$As_{30}Sb_{10}Se_{60}$	1·570
	35	$As_{35}Sb_{10}Se_{55}$	1·556
	40	$As_{40}Sb_{10}Se_{50}$	1·540
$As_xSb_5Se_{95-x}$	25	$As_{25}Sb_5Se_{70}$	1·762
	30	$As_{30}Sb_5Se_{65}$	1·694
	35	$As_{35}Sb_5Se_{60}$	1·638
	40	$As_{40}Sb_5Se_{55}$	1·627
	45	$As_{45}Sb_5Se_{50}$	1·610

water to obtain the glass samples. The quenching rate is about 200 K/s. The amorphous nature of the samples has been checked by X-ray diffractometry.

The photoacoustic (PA) spectrometer used for the optical absorpion studies is described elsewhere (Madhusoodanan *et al* 1988). The optical absorption coefficient is directly proportional to the PA signal amplitude (Rosencwaig 1980). The PA signal amplitude as a function of the wavelength of the incident radiation is recorded. The optical energy gap E_0 is determined from the normalized PA signal amplitude vs. incident wavelength plot (Weast 1977). The normalized PA spectra of two typical samples are shown in figure 1. Similar plots have been recorded for all the samples investigated.

3. Results and discussion

The measured energy gap values for 20 glasses belonging to the As–Sb–Se family are tabulated in table 1. The variation of E_0 with compositon for the four groups of glasses viz. $As_xSb_5Se_{95-x}$, $As_xSb_{10}Se_{90-x}$, $As_xSb_{15}Se_{85-x}$ and $As_xSb_{20}Se_{80-x}$ are shown in figure 2. The variation of E_0 with x in As_xSe_{100-x} glasses is also shown in the same figure (Madhusoodanan and Philip 1988) for comparison. From this figure it is clear that for a particular Sb concentration, as the As content increases (i.e. Se content decreases) E_0 decreases and shows a marked change in its rate of decrease at a particular concentration at which the As content and Sb content together is 40 atomic percent. This is the stoichiometric composition for the As–Sb–Se system of glasses. The rate of decrease in E_0 is higher for compositions with $(x+y) < 40$ than for those with $(x+y) > 40$. For the As_xSe_{100-x} family of glasses, E_0 shows a

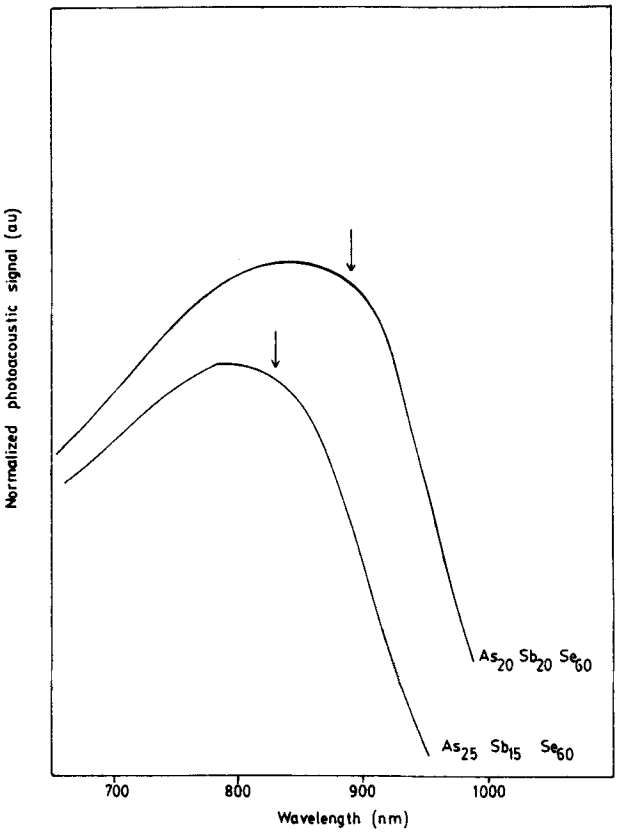

Figure 1. Normalized photoacoustic (PA) signal vs. wavelength for two typical glasses.

threshold minimum value at $x=40$, which is the stoichiometric composition As_2Se_3 (Madhusoodanan and Philip 1988). The behaviour observed in the As–Sb–Se family of glasses for compositions with $(x+y) < 40$ is very much similar to that observed for $x<40$ in As_xSe_{100-x} glasses but for compositions with $(x+y) > 40$, it is very much different from As_xSe_{100-x} glasses with $x>40$.

The dotted line in figure 2 shows the variation of E_0 along the stoichiometric compositions. It can be seen that with increase in Sb content E_0 decreases gradually.

The observed behaviour of the As–Sb–Se family of glasses can be explained on the basis of chemical bonding between atoms and changes in the short-range order that occurs in the glass network with increase in Sb concentration. For As_xSe_{100-x} with $0<x<40$ the short-range order is well defined and is similar to that of the parent glass: Se is two-coordinated and As is three-coordinated. The chemical order is maintained for As atoms, each of which (as in As_2Se_3) is bonded to three Se atoms. The composition dependence is brought about by the occupation of Se atoms in favourable positions in the network (Zallen 1983). In the As–Se system there are As–As, As–Se and Se–Se bonds or the Se atomic chains are interconnected with As atoms. In the Se rich glasses the network is dominated by Se atomic chains and addition of As atoms results in the formation of branching

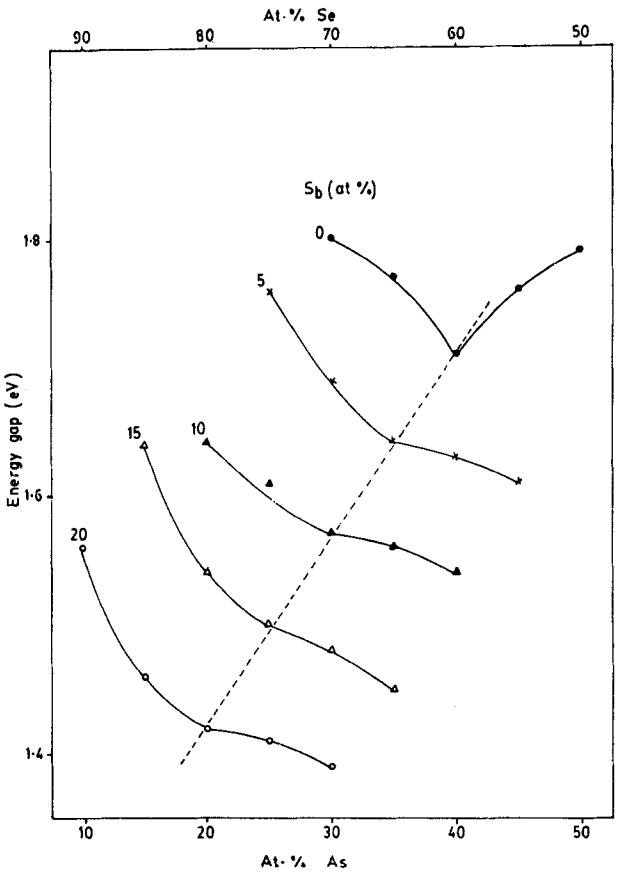

Figure 2. E_0 vs. composition for $As_xSb_ySe_{100-x-y}$ glasses. ●-As_xSe_{100-x}, ○-$As_xSb_{20}Se_{80-x}$, △-$As_xSb_{15}Se_{85-x}$, ▲-$As_xSb_{10}Se_{90-x}$, ×$As_xSb_5Se_{95-x}$.

chains on 3-fold coordinated As atoms in the basic structural units. The two coordinated Se atoms form $(Se)_n$ chains or $(Se)_8$ rings and the addition of 3-coordinated As atoms breaks these chains or rings to satisfy its coordination number and form a very complex network structure.

With the introduction of Sb atoms, the Se atom chains get interconnected with both As and Sb atoms. Based on the chemically ordered network (CON) model (Lucovsky and Hayes 1979), the As–Sb–Se glass can be thought of as being made up of completely cross-linked three-dimensional structural units of As_2Se_3 and Sb_2Se_3 with either As or Se in excess. Apart from As–Se, Sb–Se and Se–Se bonds in the network, As–As and Sb–Sb bonds also will be involved in forming the glass.

The bond energies of As–Se, Sb–Se, Se–Se, As–As and Sb–Sb bonds are 52, 51, 49, 46 and 42 kcal/mol respectively (Das *et al* 1974). The As–As bond energy is lower than the As–Se bond energy. With decreasing Se content in As rich glasses the Sb_2Se_3/As_2Se_3 ratio progressively increases resulting in a decrease in average bond energy and a corresponding decrease in E_0. For the Se rich glasses the As_2Se_3 content is larger than the Sb_2Se_3 content and results in the observed increase in optical energy gap. When the atomic percentages of As and Sb become equal to 20 (critical composition), the number of As–Se and Sb–Se bonds are equal. Since As

and Sb are isovalent one cannot expect any drastic change in the basic structure of the glass by replacing As by Sb. However as the Sb concentration increases the probability for the formation of Sb–Sb and Sb–Se bonds increases. Hence the average bond energy of the compound is reduced which effectively reduces E_0. These arguments agree well qualitatively with the observations.

Acknowledgement

The authors thank the Department of Atomic Energy (BRNS) for financial support.

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