Journal of Non-Crystalline Solids 77 & 78 (1985) 1229-1232
North-Holland, Amsterdam

STRUCTURAL BASED INTERPRETATION FOR THE ELECTRICAL CONDUCTION IN Ag-As_2S_3 GLASSES

M.F. KOTKATA, M.M. RADWAN*, F.M. METAWE and C.S. MOHAMED

Physics Department, Faculty of Science, Ain Shams University, Cairo, Egypt
* Physics Department, Military Technical College, Cairo, Egypt

The electrical conduction in three glasses of the system $Ag_x(As_{0.4}S_{0.6})_{100-x}$ with x=6, 15 and 25, has been studied. Below T_g, the dc conductivity increases with increasing absolute temperature in accordance with the thermal activation formula: $\sigma = C \exp(-E_\sigma/2kT)$. The addition of silver (6-25 at.%) to As_2S_3 leads to a big decrease in E_σ (1.29 to 0.38 eV), relative small increase in σr.t.(20°C) (1.4×10^{-12} to 5.6×10^{-9} ohm^{-1}cm^{-1}), and very pronouced decrease in the pre-exponent C. The small variation in the value of C of As_2S_3 and $Ag_6(As_{0.4}S_{0.6})_{94}$, (4 and 0.2 ohm^{-1}cm^{-1}), confirms the non-variation of the orpiment structure due to the addition of up to 6 at.% Ag. The decrease in E_σ for the 6 at.% Ag glass is discussed in terms of Mott's charged dangling bonds. The X-ray radial distribution function tetrahedral base structure for higher Ag percentage glasses is confirmed by the value of E_σ and the very low value of C (less than 10^{-4} ohm^{-1}cm^{-1}).

1. INTRODUCTION

The conductivities of amorphous semiconductors are generally much less sensitive to nonstoichiometry and the presence of impurities than are those of crystalline semiconductors. Mott's explanation of this fact, the so-called 8-N rule[1] is widely accepted. However, the large conductivity increase caused by the addition of Ag or Cu in As_2S_3 and As_2Se_3[2-5] are exceptions of this general rule. Edmond[2] has showed that an addition of up to 1 at.% Ag into As_2S_3 would increase its conductivity by a factor of 10^4. To explain this Mott and Davis[6] supposed that the increased conductivity arises not from the formation of impurity levels, but from structural changes caused by the presence of Ag, of such a kind as to reduce the disorder. The nature of these structural changes was discussed by Liang et al.[7] in their structural studies of glassy Cu-As_2Se_3 alloys. Latter, Mott[8] introduced another explanation for those exceptions in terms of the "charged dangling bonds".

In the present work the electrical conduction in three glasses of the $Ag_x(As_{0.4}S_{0.6})_{100-x}$, $0<x<25$, system has been studied. The obtained results are correlated with the structural changes reported before[9] in the investigated alloys.

0022-3093/85/$03.30
(North-Holland Physics Publishing Division)

2. EXPERIMENTAL

Bulk glasses of the system $Ag_x(As_{0.4}S_{0.6})_{100-x}$, with x=6, 15 and 25, were prepared by heating mixtures from As_2S_3 rods and Ag wires (both 99.999% pure) of a given composition in vacuum-sealed (10^{-5} Torr) fused silica ampoules at 700°C for 10 hours during which the molten solution was occasionally shaken vigorously, then followed by icy water quenching. X-ray diffraction (with CuK_α radiation on a vertical Philips diffractometer) and DTA (Shimazo model DT-30) were used to identify the RDF structural changes and transition temperatures of the investigated materials. The method of the RDF structural determination is given elsewhere[9].

Flat samples, roughly circular in shape, with diameter about 10 mm were ground and wet polished to different thickness between 1.5 and 2 mm for conductivity measurements. The samples were introduced between two co-axial brass electrodes. The contact of the samples was activated by graphite. The specific conductivity, σ, was measured under controlled equilibrium conditions in the temperature range below T_g to prevent any possible transformations. The current passing through the samples was measured using shielded wires with a Keithley 616 digital electrometer.

3. RESULTS AND DISCUSSION

Fig.1 shows DTA thermograms for the prepared $Ag_x(As_{0.4}S_{0.6})_{100-x}$ materials. The heating rate is 10°C/min.

The values of T_g, T_c and T_m are given in Table 1 as a function of composition.

TABLE 1. CHARACTERISTIC TRANSITION TEMPERATURES OF THE INVESTIGATED GLASSES OF THE SYSTEM $Ag_x(As_{0.4}S_{0.6})_{100-x}$

Composition		T_c, °C			T_m, °C
	T_g,°C	Begin	Peak	End	
$Ag_6(As_{0.4}S_{0.6})_{94}$	157	237	280	292	417
$Ag_{15}(As_{0.4}S_{0.6})_{85}$	147	195	238	250	311
		251	265	275	367
		276	287	293	423
$Ag_{25}(As_{0.4}S_{0.6})_{75}$	160	191	230	250	297
		257	271	288	369
					415

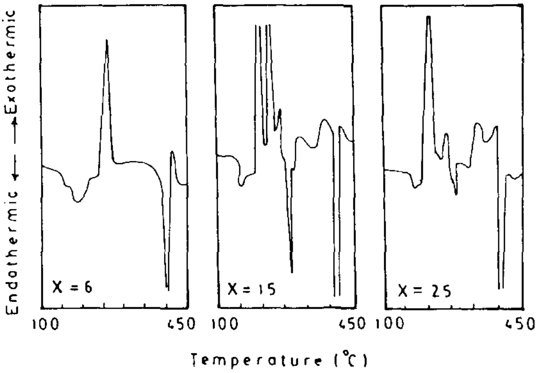

FIGURE 1
DTA thermograms of the glasses $Ag_x(As_{0.4}S_{0.6})_{100-x}$. Heating rate is 10°C/min.

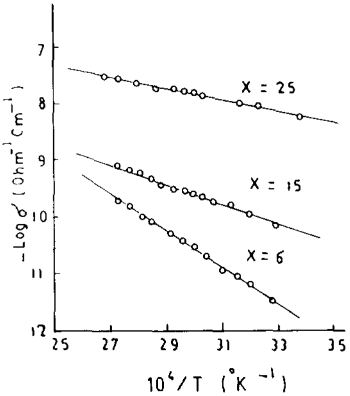

FIGURE 2
Temperature dependence of dc conductivity of the glasses $Ag_x(As_{0.4}S_{0.6})_{100-x}$.

Below the glass transition temperature, T_g, the dc conductivity versus inverse absolute temperature behaviour is given in Fig. 2 for the glasses investigated.

The conductivity σ increases exponentially with increasing absolute temperature T. This behaviour is similar to the experimental results reported for other chalcogenide glasses[6]. The lines drawn in Fig.2 for the function log $\sigma = f(1/T)$ are least squares fit. The activation energy has been calculated from the slopes of these lines in accordance with the thermal activation formula $\sigma = C\ \exp(-E_\sigma/2kT)$.

The characteristic electrical quantities E_σ (activation energy of conduction) $\sigma_{r.t.}$ (conductivity at room temperature) and C (pre-exponential factor) are given in Table 2 as a function of composition alongside the values of density, d, of the glasses investigated.

The relatively big decrease in the value of E_σ from 1.29 to 0.38 eV, together with the relatively small increase in $\sigma_{r.t.}$ from 1.4×10^{-12} to 5.6×10^{-9} $\mathrm{ohm^{-1}cm^{-1}}$ as the addition of Ag to As_2S_3 is increased from 6 to 25 at.%, can be interpreted in terms of the structure variations in these glasses. It was shown[9] that addition of up to 6 at.% Ag atoms into glassy As_2S_3 does not destroy its orpiment based structure. The layered structure is conserved but parallelism is slightly destroyed. The Ag atoms do not fit regularly in the structures, but ra-

TABLE 2 : PROPERTIES OF Ag-As_2S_3 SEMICONDUCTING GLASSES

Glass Composition	d, gm/C.C.	E_σ, eV	$-\log\sigma_{r.t.}$	-log C
$Ag_6(As_{0.4}S_{0.6})_{94}$	3.552	1.29	11.85	0.8
$Ag_{15}(As_{0.4}S_{0.6})_{85}$	4.164	0.69	10.32	4.4
$Ag_{25}(As_{0.4}S_{0.6})_{75}$	4.828	0.38	8.25	4.9

ther intercalate between the layers. As the silver content increases, the structure changes markedly and the average coordination number increases from 2.6 for pure As_2S_3 to about 4.2 for 25 at.% Ag glassy alloy. Large portions of this latter alloy have a short range order similar to that in crystalling $AgAsS_2$ but on a network similar that associated with amorphous Ge or Si, a result similar to that obtained by Liang et al.[7] for glassy Cu-As_2Se_3 alloys. These structure changes are clearly manifested in the large decrease, repeatedly found in the value of C about 10^{-5} $ohm^{-1}cm^{-1}$ for 25 at.% Ag alloy (Table 2). The small difference in the values of C between 4 $ohm^{-1}cm^{-1}$ for As_2S_3 (Ref.2) and 0.2 ohm^{-1} cm^{-1} for 6 at.% Ag alloy (Table 2) is in agreement with the reported non-variation in the structure.

The decrease in the value of the activation energy from 2.04 eV for As_2S_3 (Ref.2) to 1.29 eV for $Ag_6(As_{0.4}S_{0.6})_{94}$, that is about 1/3, is in excellent agreement with the 1/3 decrease predicted in the model of "charged dangling bonds".

The compositions containing higher Ag-content were found to have a tetrahedral structure due to an average of four electrons per atom. This type of bonding leads typically to energy gaps of less than leV. The values observed for E_σ are 0.69 eV and 0.38 eV for compositions containing 15 and 25 at.% Ag (Table 2) which again, agrees with the structure of these glassy compositions.

REFERENCES

1) N.F. Mott, Phil. Mag. 19 (1969) 835.
2) J.T. Edmond, J. Non-Cryst. Solids 1 (1968) 39.
3) A.E. Owen, Glass Ind. 48, 637 (1967) 695.
4) M.I. Frasev and A.E. Owen, Proc. 10th Int. Conf. on Amorphous and Liquid Semiconductors, Tokyo (1983).
5) A.V. Danilov and M.K. El-Mously, Fiz. Tverd Tela 5 (1963) 2015.
6) N.F. Mott and E.A. Davis, Electronic Processes in Non-Crystalline Materials, (Clarendon, Oxford) 1979.
7) K.S. Liang, A. Bienenstock and C.W. Bates, Phys. Rev. B10 (1974) 1528.
8) N.F. Mott, Phys. Mag. 34 (1976) 1101.
9) M.M. Radwan, Ph.D. Thesis, University of Dundee, U.K. (1982).