DC ELECTRICAL CONDUCTIIVITY OF THE SYSTEM $(Ge\ Se_{2.5})_{1-x}\ (Ge\ Te_{2.5})_x$ IN THE GLASSY STATE

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ABSTRACT

Measurements of electrical conductivity and density were made on six samples of different compositions of Ge-Se-Te system in the glass formation region, along the Ge $Se_{2.5}$ - Ge $Te_{2.5}$ tie-line. The conductiivity and density were found to increase monotonically with increasing Te content. The results were correlated with structural changes, occurred by Te addition.

INTRODUCTION

In Ge-Se-Te system, the glass forming region exist in a finger shape extending from region with excess Se towards the Te-rich corner of the phase diagram[1,2]. The composition for which glasses form are well-defined, and easily reproducible[2]. The connectedness varies from two (in Se and Te) to four (in Ge), and therefore the bonding in these glasses is essentially covalent.

The composition dependence of several properties and their correlation with structure is an interesting aspect of study in chalcogenide glasses. To show the nature of this dependence, the dc electrical conductivity of Ge-Se-Te system, in the amorphous state, was measured for six different "Stiochiometric" compositions. These glasses lie along the Ge $Se_{2.5}$ - Ge $Te_{2.5}$ tie-line which lies completely inside the extended finger - shaped glass forming region.

EXPERIMENTAL

10gm. of the two binary systems Ge $Se_{2.5}$ and Ge $Te_{2.5}$ were first prepared by direct fusion of the calculated required weights of the pure elements: Ge, Se and Te (all of purity 99.999%), in quartz tubes under vacuum of less than 10^{-4} Torr. The tubes were heated at 950°C for 20 hrs, during which the tubes were shaken several times to

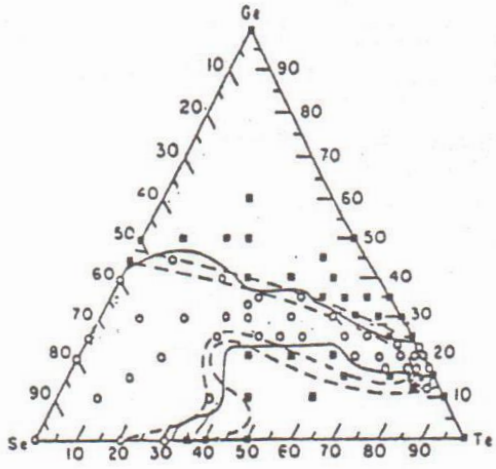

Fig. 1 : Glass formation in the system Ge-Se-Te for samples quenched from a 960oC melt in an ice bath. o amorphous; crystalline; --- inner brocken curve, water-quenched; outer brocken curve, spray cooled [(Ref. (4)].

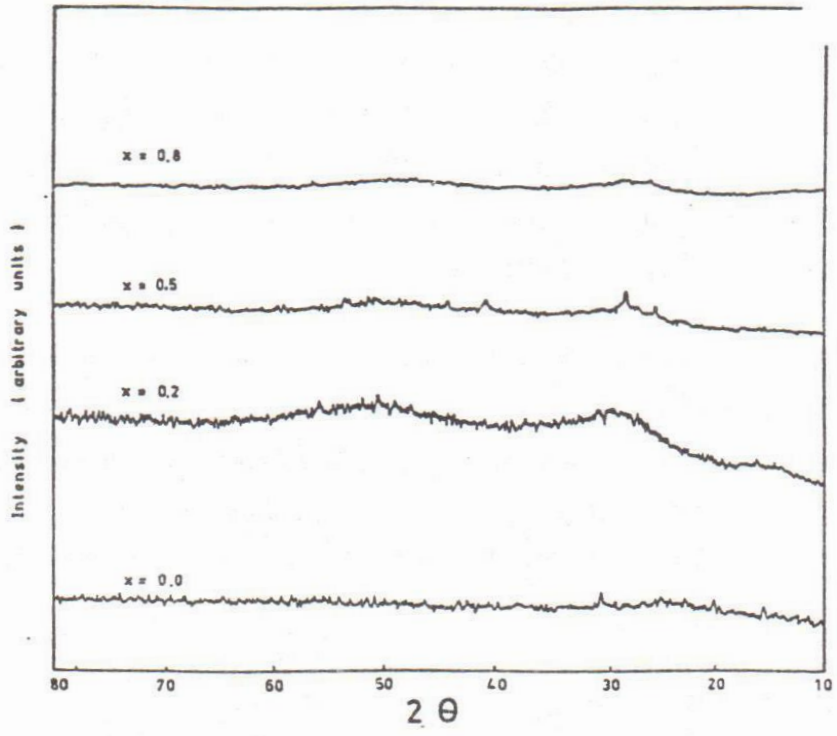

Fig. 2 :

insure reagency and homogeniety of the molten. The tubes were then removed from the furnace and quenched in cooled air current using a high electric fan.

These samples were used as parent materials to prepare the system $(Ge\ Se_{2.5})_{1-x}$ $(Ge\ Te_{2.5})_x$ (with x = 0.0, 0.2, 0.3, 0.5, 0.6, 0.8 and 1.0], by the the same method; when x exceeds a value of 0.5, quenching in icy water was essentially required.

The vitreous state was nonfirmed using x-ray diffraction technqique on powdered samples, which have not indicated the presence of any sharp peak [Fig. (2)]. The dc conductivity (s) was measured by the usual I-V method [3] on bulk samples of typical thickness of about 1.0mm using cu electrodes (Sandwich-configuration). The current was measured using 610C-Kiethly electrometer. The samples densities were determined by the method of hydrostatic weighting in toluene at room temperature[4].

RESULTS AND DISCUSSION

Variation of the dc conductivity (σ) with temperature up to 150°C, below the expected glass transition temperature, are shown inFig. (3) as ln σ vs 1/T. The dependence shows a thermally activated behaviour of Arhenious form; $\sigma = \sigma_o$ exp (-Eg/2kT), with Eg : activation energy. Table (1) summarizes the values of Eg, ln σ_o and ln σ_{20} (at 20°C), calculated from data of Fig. (3), for six compositions together with their corresponding densities. The density values quoted are the average of 3 - values.

Fig. (4) shows the variations of these data with Te-content. Assuming that porosity does not play a decisive role, the density increases monotonically with Te-content, and is practically independent of the ratio of Ge and Se. Similar observations were previously made [1,2], and were correlated to the mean atomic volume. Various empirical relations (either linear or quadratic) were proposed to experess the density-composition behaviour. Using least square fitting method, the data presented here can be fitted to a relation of the type $d = 4.223 + 1.67 \times 10^{-2}$ (Te), where (Te) is the tellurium content at 1%, with accuracy of ± 0.4%.

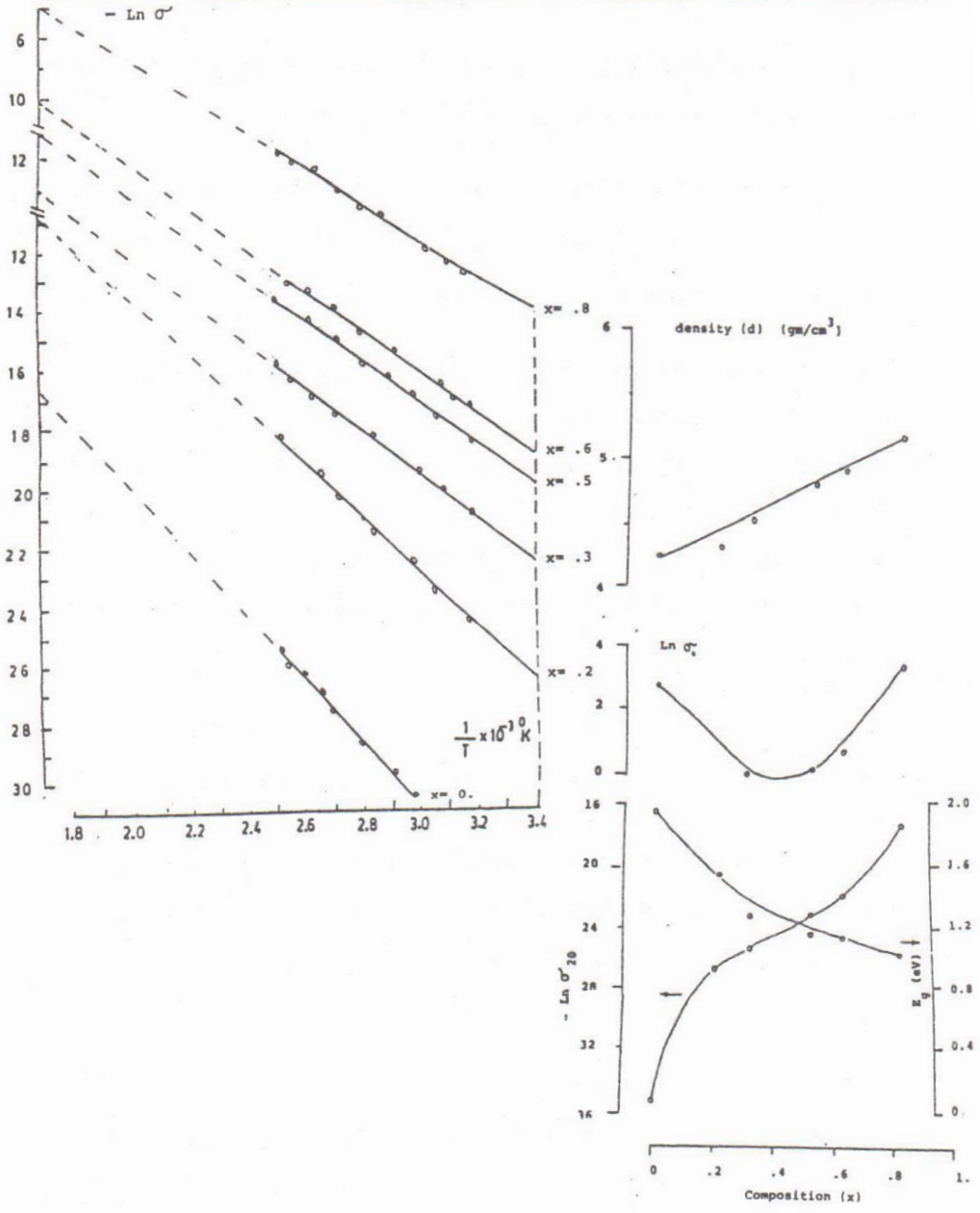

Fig. 3 : Dependence of dc conductivity on temperature for different compositions in the glassy state.

Fig. 4 : Density, Ln σ_0, Ln σ_{20} and E_g for different compositions.

With increasing Te-content, (χ from 0. to 0.8), the conduction activation energy Eg decreases successively from 1.9 to 1.03 eV. This monotonic decrease reflects the pronounced increase in σ_{20} by more than 8 orders of magnitude, although the change in the pre-exponential factor (σ_o) is irregular and not as much. In Fig. (5) the dependence of log σ_{20} on Eg, which is almost linear, is shown. This regular variation of σ when Se is replaced by Te is mainly due to the increased metallization of the chemical bonds and to the increase of the delocatization of electrons in the paired-electron covalent bonds.

The bond energies for Ge-Se, Ge-Te, Ge-Ge, Se-Se, Te-Se were found to be 49.1, 37.6, 44., 33., and 40.6 KCal/mole respectively [1.2]; the strongest being Ge-Se and the weakest being Te-Te bonds. The bonds where Se is sharing as one part are more stronger than those for Te.

In Ge-Se system, it is possible to realize a tetrahedral surrounding of the Ge atoms, so that the Ge-$Se_{4/2}$ structural units play the decisive role in the formation of the structure of glasses of the Ge-Se system. A ribbon-like microstructure of the type can be assumed, where the number of Se atoms in the bridges will depend on the Se content in the glass. A Se-$Se_{2/2}$ structural unit can also be assumed which is repeated every two Ge $Se_{4/2}$ unit so as to form Ge $Se_{5/2}$. A structure of this type can be assumed for the system $(Ge\ Se_{2.5})_{1-x}\ (Ge\ Te_{2.5})_x$.

where the Te atoms replace the Se atoms during quenching from the heat giving rise to an increase in metallization of the chemical bonds.

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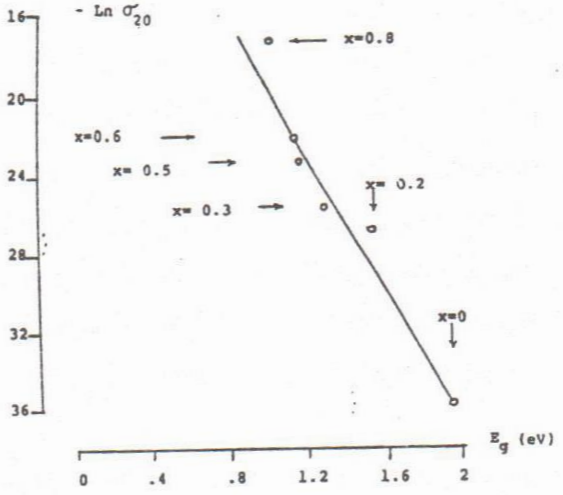
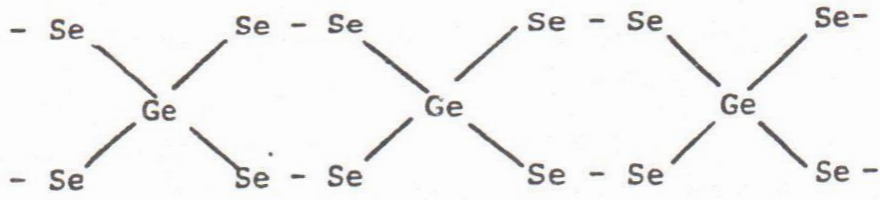


Fig. 5 : Dependence of $\ln\sigma_{20}$ on Eg for different compositions.



Ta.ble (1) : Values of density d, activation energy Eg ln σ_o and ln σ_{20} for different glasses

X	Sample	d (gm/cm^3)	E_g (eV)	ln σ_o	ln σ_{20}
0	$(Ge\ Se_{2.5})$	4.246	1.94	+ 2.75	- 35.6
0.2	$(GeSe_{2.5})\ 0.8\ (GeTe_{2.5})_{0.2}$	4.2933	1.54	+ 4.01	- 26.6
0.3	$(Ge\ Se_{2.5})\ 0.7\ (GeTe_{2.5})_{0.3}$	4.5447	1.29	- 0.075	- 25.5
0.5	$(GeSe_{2.5})0.5\ (GeTe_{2.5})_{0.5}$	4.8354	1.17	0.1	-23.088
0.6	$(GeSe_{2.5})_{0.4}\ (GeTe_{2.5})_{0.6}$	4.9243	1.15	0.73	- 22
0.8	$(GeSe_{2.5})_{0.4}\ (GeTe_{2.5})_{0.6}$	5.1999	1.03	3.3	- 17.16
1	$(GeSe_{2.5})$	6.0787	-	-	-