Journal of Optoelectronics and Advanced Materials Vol. 3, No. 4, December 2001, p. 855 - 860

COMPOSITIONAL TRENDS OF THE PROPERTIES IN CHALCOGENIDE Ge-Se-Ga GLASSES*

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Chalcogenide glasses of $(GeSe_4)_{1-x}Ga_x$ and $(GeSe_5)_{1-x}Ga_x$ systems, with 5, 10, 15, 20 at % Ga were investigated. Density, molar volume and compactness of the samples were calculated. The value of the density increases regularly with the addition of Ga to the Ge-Se matrix. The increasing in Ga content leads to a structural change due to a gradually replacement of Se atoms by Ga atoms. The strength of the chemical bond is connected to the "free volume" in material or density of the defects in the sample. The largest changes in the structure (higher sensitivity) are expected in the samples with small compactness of the structure. The number of constrains per atom (Nco) as a function of the average coordination number is calculated. It is seen that the number of degrees of freedom increases with gallium addition and the flexibility of the system increases as a consequence.These glasses are assumed to be composed of cross-linked structural units of tetrahedral $GeSe_2$ and pyramidal Ga_2Se_3 and excess, if any of Se. Bonds are formed in the sequence of decreasing bond energies until all available valences for the atoms are saturated.

(Received June 8, 2001; accepted November 29, 2001)

Keywords: Amorphous materials, Chalcogenide glasses, Properties, Structure

1. Introduction

Chalcogenide glasses have been attracted great attention as promising materials for different applications. Due to some unique optical and electrical phenomena, they are expected to be promising material in the IR optics, microelectronics [1, 2]. Composition complexity induces new properties in the glasses. Germanium chalcogenides with a third element - Sb [3], As [4], In [5] are widely investigated. Glass-forming region in the Ge-Ga-Se system is determined by Mitkova and Boncheva [6]. The properties of chalcogenides in dependence on chemical composition are of interest, especially in considering the effects of average coordination number, Z, number of covalent bonds per atom [7]. The structure of glasses is an important issue, knowledge of which is necessary for understanding the material's properties and also for the material engineering. Although methods to investigate crystalline structure are well established, they fail to work as well for amorphous materials. Considerable effort has been devoted to elucidate the bonding nature and a deeper understanding of the structure of chalcogenide glasses using new conceptual approaches related to the question of short range order on the basis of average valence [8] and coordination numbers [9], while the theoretical framework of rigidity percolation [10] has been applied to explain macroscopic properties of covalent networks.

In this paper we have reported results from measurements of glasses in $(GeSe_4)_{1-x}Ga_x$ and $(GeSe_5)_{1-x}Ga_x$ systems. The relation between chemical bonding and basic physicso-chemical parameters of the glasses is an essential demand for any comprehensive theory relating their structure and properties.

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* presented at the First International Workshop on Amorphous and Nanostructured Chalcogenides, Bucharest, June 25-29, 2001

2. Experimental

Bulk glasses of $(GeSe_4)_{1-x}Ga_x$ and $(GeSe_5)_{1-x}Ga_x$ systems, with 5, 10, 15, 20 at % Ga were prepared with the melt-quenched technique, using 4N purity elements of Se, Ge and Ga. Evacuated ampoules with the initial substances were heated in a rotated furnace. The synthesizes were carried out with a constant heating ratio of 3 K/min up to a final temperature 1000 K. Glasses were obtained after a quenching in a mixture of water and ice. The morphology of the bulk glasses was examined by the X-ray diffraction technique.

The density was measured hydrostatically in a medium of diiodine-methane at a constant temperature. A single Ge crystal was used as a reference material. The density was calculated from the formula:

$$\rho = (\frac{m_0}{m_0 - m_1})\rho_1 \quad (1)$$

Where m_o, m_l and r_l are respectively the weigth of the sample in air, the weight of the sample in the liquid and the density of the reference crystal.
The compactness was calculated using formula

$$\delta = \frac{\sum_i \frac{c_i A_i}{\rho_i} - \sum_i \frac{c_i A_i}{\rho}}{\sum_i \frac{c_i A_i}{\rho}} \quad (2)$$

where Ai, xi and ρ are the atomic weigth, atomic fraction and density The investigation involves 10 measurements of each sample and statistical processing of the data.

The average coordination number Z was evaluated using the (8-N) rule where N is the number of the electrons in the outer shell in the atom. Z of the compositions was calculated using the formula 8-(4x+2y+3z), where x, y, z are the atomic fractions of the Ge,Se and Ga, respectively. The molar volume (Vm) was determined from the density data by the equation

$$V_m = \frac{1}{d}\sum_i x_i M_i \quad (3)$$

where Mi is the molecular weight of the i^{-th} component, and xi is the atomic percentage of the same element in the sample.

3. Results and discussion

Tables 1 and 2 present the values of the density (d), molecular weight (M), and molar volume (Vm) of the various compositions from the $(GeSe_4)_{1-x}Ga_x$ and $(GeSe_5)_{1-x}Ga_x$ glasses. The results show the variation of the density and specific volume with the composition. The values of the density increase regularly with the addition of Ga to the Ge-Se matrix. It is known that the variation in density is related to the change in the atomic weight and the atomic volume of the elements in the system. The atomic weights of Se and Ga are very similar, but the replacement of selenium by gallium causes an increase in density.

Table 1. Properties of $(GeSe_5)_xGa_{1-x}$ glasses.

Composition	Density, g/cm^3	M, g.mol-1	Vm, cm^3.mol^{-1}
$Ge_{17}Se_{83}$	4.34	77.88	17.94
$Ge_{16}Se_{79}Ga_5$	4.36	77.48	17.77
$Ge_{15}Se_{75}Ga_{10}$	4.42	77.08	17.44
$Ge_{14}Se_{71}Ga_{15}$	4.5	76.68	17.04
$Ge_{13}Se_{67}Ga_{20}$	4.6	76.28	16.58

Table 2. Properties of $(GeSe_4)_xGa_{1-x}$ glasses.

composition	density, g/cm^3	M, g.mol-1	Vm, cm^3.mol^{-1}
$Ge_{20}Se_{80}$	4.23	77.69	18.37
$Ge_{19}Se_{76}Ga_5$	4.34	77.29	17.81
$Ge_{18}Se_{72}Ga_{10}$	4.38	76.89	17.55
$Ge_{17}Se_{68}Ga_{15}$	4.44	76.49	17.23
$Ge_{16}Se_{64}Ga_{20}$	4.45	76.09	17.1

For these materials the average coordination number indicates the average number of bonds per atom which must be broken to obtain fluidity. In ternary systems investigated by us according to the 8-N rule the numbers of the nearest-neighbor atoms for Ge, Se and Ga are respectively 4, 2 and 3. For a given bond strength we expect the specific volume to decrease with coordination number. Fig. 1 present graphical relations of the calculated values of molar volume versus coordination number. The V-Z dependencies for both systems of glasses are qualitatively similar with a weak deviation from linearity around Z = 2.4.

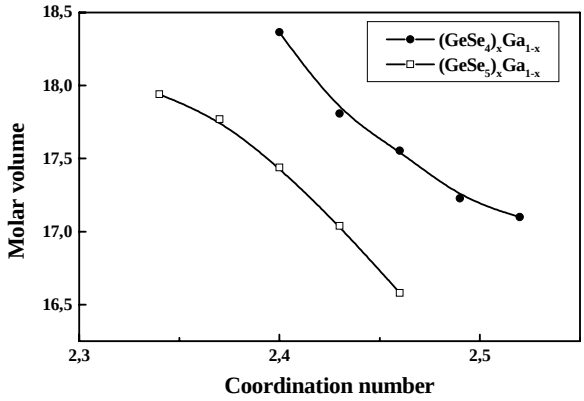

Fig. 1. The variation of molar volume with the coordination number.

The strength of the chemical bond is connected to the compactness in material or density of the defects in the sample [11]. The compositional variation of the compactness characterized by coordination number of the investigated glasses is given in Fig. 2. The biggest changes in the structure (higher sensitivity) are expected in the samples with small compactness of the structure. The prominent features observed in these figures repeat the relation of the density.

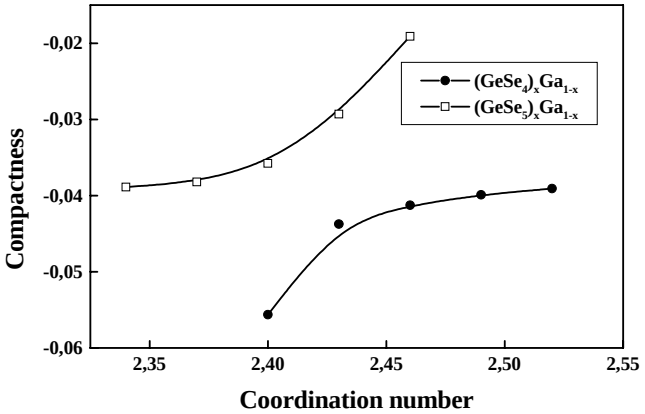

Fig. 2. Dependence of the compactness on Z for $(GeSe_4)_xGa_{1-x}$ and$(GeSe_5)_xGa_{1-x}$ glasses.

Based on the chemical bonds expected to be presented in the glasses from ternary system Ge-Se-Ga we can investigate the compositional trends in the properties. First approximation is to neglect the dangling bonds and the weak Van der Vaals interactions. Taking short-range structure into account, Phillips [12] has asserted:

$$Nco=Nd \tag{4}$$

i.e. number of topological constraint Nco, evaluated for an atom is equal to the number of degrees of freedom. For a material with coordination number Z, Nco(Z) is a sum of Na(radial) and Nb (angular) valence-force constraints

$$Nco(Z)= Z/2 + (2Z-3). \tag{5}$$

Values of Na, Nb and Nco calculated for the $(GeSe_4)_{1-x}Ga_x$ and $(GeSe_5)_{1-x}Ga_x$ systems are given in Tables 3 and 4. It can be seen that the parameters show the same trend with increasing gallium content as the experimental parameters given in Tables 1 and 2.

Table 3. Values of Z, Na, Nb and Nco for $(GeSe_5)_xGa_{1-x}$ glasses.

composition	Z	Na	Nb	Nco
$Ge_{17}Se_{83}$	2.34	1,17	1,68	2,85
$Ge_{16}Se_{79}Ga_5$	2.37	1,185	1,74	2,925
$Ge_{15}Se_{75}Ga_{10}$	2.4	1,2	1,8	3
$Ge_{14}Se_{71}Ga_{15}$	2.43	1,215	1,86	3,075
$Ge_{13}Se_{67}Ga_{20}$	2.46	1,23	1,92	3,15

Table 4. Values of Z, Na, Nb and Nco for $(GeSe_4)_xGa_{1-x}$ glasses.

composition	Z	Na	Nb	Nco
$Ge_{20}Se_{80}$	2.4	1,2	1,8	3
$Ge_{19}Se_{76}Ga_5$	2.43	1,215	1,86	3,075
$Ge_{18}Se_{72}Ga_{10}$	2.46	1,23	1,92	3,15
$Ge_{17}Se_{68}Ga_{15}$	2.49	1,245	1,98	3,225
$Ge_{16}Se_{64}Ga_{20}$	2.52	1,26	2,04	3,3

It is seen that the values of Nco increase with gallium addition. The glassy network is influenced by mechanical constraints Nco. For the ideal glass Nco=Nd, (Nd=3), where the mechanical stability of the network is optimized [13]. In chalcogenide glasses atoms are supposed to combine more favourably with atoms of different kinds than with the same kind [14]. This condition is equivalent to assuming the maximum amount of possible chemical ordering. In using this assumption, bonds between like atoms will only occur if there is an excess of a certain type of atom. Bonds are formed in the sequence of decreasing bond energies until all available valences for the atoms are saturated. After all these bonds are formed, if there are still unsatisfied Se valences, 'excess bonds', which must be satisfied by the formation of Se-Se bonds. The addition of gallium atoms decreases the number of homopolar Se bonds, i.e. the stability of the system increases. The flexibility of the system increases in a similar way due to the Ga addition.

The properties of the chalcogenide glasses are related to the overall mean bond energy <E>, which is a function of the average coordination number Z, the type of the bonds and the bond energy, forming the system. Using the correlation proposed by Tichy [15] for chalcogenide-rich systems we could determine the values of <E>. Finally the overall mean bond energy is given by:

$$<E>= \bar{E}_c + \bar{E}_{rm} \tag{6}$$

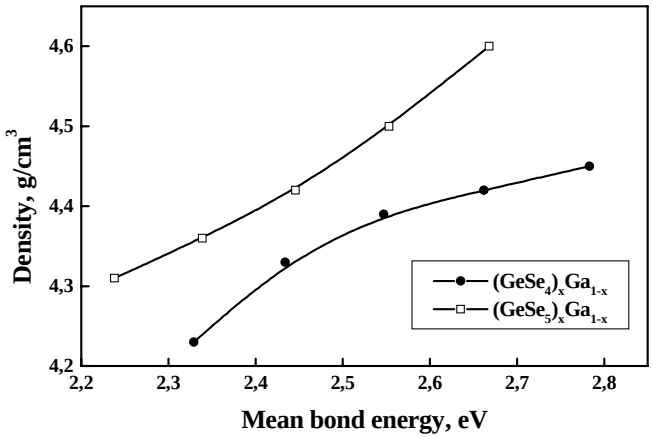

Fig. 3. The relation of the density with the mean bond energy.

where $\bar{E}_c$ is the mean bond energy of the average cross-linking/atom (heteropolar bond energy) and $\bar{E}_{rm}$ is the average bond energy per atom of the "remaining" matrix (homopolar bond energy).

The graphical presentation of the density versus <E> in Fig. 3 shows a similar dependence as the experimental data presented below. We believe that our results can be taken as a demonstration that the bonding arrangement mainly determines the values of the physical-chemical properties in chalcogenide glasses. It is known that the structure of the Ge-Se-Ga glasses is made up from tetrahedral $GeSe_2$ and pyramidal Ga_2Se_3 units [13]. The $GeSe_2$ and the Ga_2Se_3 units are connected with extra Se atoms. The excess Se atoms are connected in chains. Ge-Ge bonds are not expected to form up to 33 at. % Ge. According to ref. 10, the bond energy of Ga-Se bonds (65 kcal/mol) is bigger than Ge-Se bond energy (55.4 kcal/mol), which indicates that when the Ga content increases, the average bond energy of the system increases. The formation of stronger bonds could be the cause of the changes which occur in their properties.

The stability of the glass network is associated with the atomic arrangement that becomes more tightly bound and with shorter bond lengths resulting in smallest mean atomic volume and hence with highest compactness.

4. Conclusions

The properties of chalcogenide glasses with a constant ratio Ge:Se =4 or 5 were investigated and the influence of the gallium content was analyzed. Gallium atoms change the compact structure of $GeSe_2$ units creating new structural units of Ga_2Se_3 and reducing Se homopolar bond. The density, the compactness and the strength of the bonds vary due to variation of the gallium content. It is shown that the investigated parameters exhibit similar trends of their relations with the average coordination number connected with the three-dimensional bonding in the glasses.

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