JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 10, October 2007, p. 3093 - 3096

Physico-chemical properties of Ge-Te-Ga glasses

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Bulk glasses of Ge-Te-Ga system have been prepared by melt-quenched technique. Basic physico-chemical characteristics like density, microhardness, compactness have been investigated. The average bond energy {E} has been calculated. The physico-chemical behaviours of the studied glasses have been discussed on the basis of the experimental derived parameters and theoretical calculated one.

(Received July 3, 2007; accepted October 1, 2007)

Keywords: Chalcogenide glasses, Physico-chemical properties, Structure

1. Introduction

Chalcogenide glasses are broad family of glasses attractive since many years because of their exclusive optical properties and potential application in the optics. They own a wide spectral transmission window far in the infrared region and this makes them promising material in the IR optics and microelectronics [1, 2].

The glasses from the Ge-Te family are known as glasses with window of transparency shifted completely in the IR region. The use of chalcogenides as material for phase-change optical discs is associated with the Ovshinsky name [3] and with Ge-Sb-Te glasses [4]. The advantages of this family of glasses are due to the specific structure and optical behaviors they show. Variations in the glassy compositions are known to be followed by variations in the properties.

Glasses from the Ge-Te-Ga system are not well studied and only a few papers can be found in the literature about their behaviours and possible application [5]. The relatively insufficient scientific interest toward addition of Ga into Ge-Te matrix is probably due to the strong metallic behaviour and anticipated small glass forming region in this system as reported by Apykhtin [6].

The lack of information stimulated present study of the physico-chemical properties of Ge-Te-Ga chalcogenide glasses as a function of the composition and the average coordination number (Z).

2. Experimental

Two series of $(GeTe)_yGa_x$ glasses were prepared by melt quenching method. The Ge/Te ratio was maintained constant y= 4 or 5 and the Ga content, x, was increased from 0 to 20 mol.% by step of 5 mol.%. Starting elements of Ge, Te and Ga with 5N purity were sealed in evacuated quartz ampoules (1, 33.10^{-3} Pa residual pressure) and heated with a constant heating rate of 3 $K.min^{-1}$ up to temperature 1300 K. Continuous vibrational stirring were applied for sample homogenisation during the heating process. The glasses were obtained after quenching in a water-ice mixture. The bulk glasses were analyzed by X-ray diffraction technique.

The density (ρ) of the samples was measured by Archimedes method using glycerine as immersion fluid and was calculated with accuracy less than ±1 % by the formula described elsewhere [7]. The molar volume (Vm) of the samples was derived from the experimental density data. The compactness (δ) was obtained from the experimental and theoretical density values by the formula:

$$\delta = \left(\sum_i \frac{c_i A_i}{\rho_i} - \sum_i \frac{c_i A_i}{\rho} \right) \left(\sum_i \frac{c_i A_i}{\rho} \right)^{-1} \quad (1)$$

The microhardness experiments on the studied amorphous materials were performed by Knoop approach using MHP 160 microindentor combined with a Vertival microscope (Carl Zeiss). The formula used for calculation of the microhardness (H_μ) was the following:

$$H_\mu = P/Ad^2 \quad (2)$$

where P is applied load in kilopouds, d [mm] – the length of the longer diagonal imprint and A-technological parameter equal to 0.07028. The error of the microhardness values is below 2 %.

The coordination numbers of Ge, Te and Ga were estimated using the (8-N) rule (N is the number of electrons in the outer shell of the atom) ZGe=4, Z_{Te}=2 and Z_{Ga}=3 respectively and used for evaluation of the average coordination number of the sample (Z) [8]. The number of constrains (Nco) per atom was calculated by some theoretical arguments and the average bond energy <E> was received according to Tichy equations [9].

3. Results and discussion

Results obtained from the density experiments show increase in the values as the gallium content increases. The calculated density values as a function of the third component, gallium are presented in Fig. 1. The size of

Ge and Ga atoms is close (atomic radii of 1,22 and 1,26 A respectively) and the increase in the density is due most probably to the lowering in the tellurium content since the tellurium atom posses bigger covalent radii of 1,36 A. The introduction of smaller atoms leads to formation of more dense structure as confirm by the experimental data shown in Fig. 1. Peculiarity of both curves drawn is a small deflection in the slope that will be discussed below.

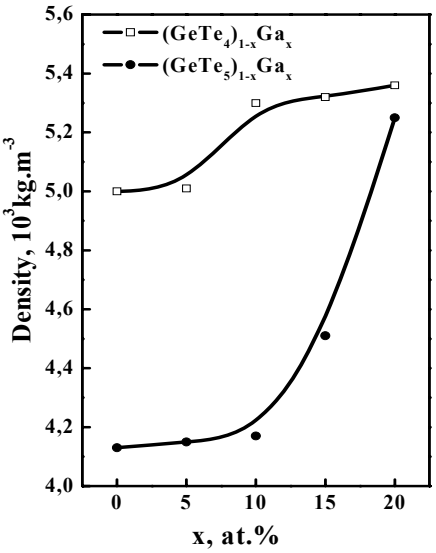

Fig. 1. Density dependence on the composition of the Ge-Te-Ga glasses

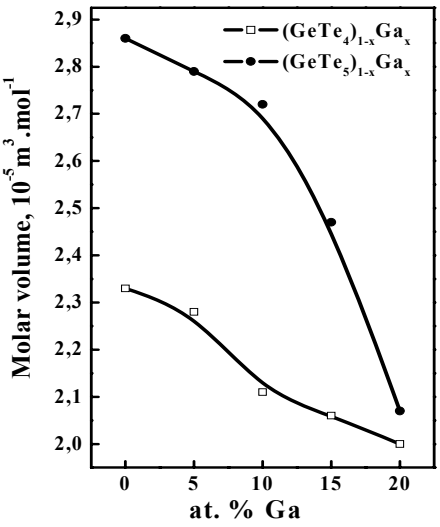

Fig. 2. Graphical relation between the molar volume and the composition of the glasses.

Fig. 2 presents the molar volume of the glasses as a function of the composition. The values of molar volume of the samples are dependent on the atomic weight and the atomic volume of the elements in the system but also on the experimental obtained density of the samples. The volume of the samples from both systems decreases with the addition of Ga to the Ge-Te matrix. The substitution of Ge and Te with atomic weights 72.6 $g.mol^{-1}$ and 127.7 $g.mol^{-1}$ respectively by Ga with 69.7 $g.mol^{-1}$ atomic weight is most probably responsible for the lowering in the molecular weight of the glass. The observed reduction in the molar volume values can be viewed as defined by both facts: decrease in the molecular weight and increase in the density of the glasses under study.

From the experimental density values the compactness of the glasses has been obtained and the results are presented in the Table 1. The values are in direct proportion to the density of the glasses i.e. an increasing with gallium is observed. More compact and dense packing is formed due to the increase of atoms smaller in atomic radius and less heavy in weight.

The calculated values of Nco for the $(GeTe_4)_{1-x}Ga_x$ and $(GeTe_5)_{1-x}Ga_x$ systems are also included in the Table 1. It is obvious that Nco increases with the addition of Ga. For the ideal glass Nco is equal to Nd, (Nd = 3), where the mechanical stability of the network is optimized [10]. The calculated constrains for atom Nco exhibit values close to 3 and thus reveal the stability of the glasses under study.

In the chalcogenide glasses the atoms are supposed to combine more favourably with atoms of different kinds than with the same kind [11] i.e. the bonds between like atoms are possible if there is an excess of these atoms. The bonds are formed in the sequence of increasing of bond energies until all available valences of the atoms are saturated. After all these bonds are formed, if there are still unsaturated valences of Te, they must be saturated by the formation of Te-Te bonds. The addition of Ga decreases the number of homopolar Te bonds and that leads to increasing of the stability of the system. The number of degrees of freedom increases which lead to the increasing of the flexibility of the system due to the addition of gallium. This fact could explain the variations in the behaviours of the glasses and experimental results with the addition of gallium. The average bond energy <E> that is measure of the glass stability is also found to increase with gallium. The values are theoretical calculated on the basis of Tichy equation [9] and the values depend on the bond energies of every possible bond in the glass. The bond energy of Ga-Te bonds (252kJ/mol) is bigger then Ge-Te bond energy (200kJ/mol), which indicates that when the Ga content increases, the average bond energy of the system increases. The formation of stronger bonds could be responsible for the variations in their properties.

Table 1. Theoretical calculated and experimentally obtained physico-chemical parameters.

composition	Zglass	N_{CO}	<E>, eV	δ, 10^{-2}
$Ge_{20}Te_{80}$	2.40	3.00	2.33	-18.27
$Ge_{19}Te_{76}Ga_5$	2.43	3.08	2.48	-18.02
$Ge_{18}Te_{72}Ga_{10}$	2.46	3.15	2.62	-13.16
$Ge_{17}Te_{68}Ga_{15}$	2.49	3.23	2.77	-12.72
$Ge_{16}Te_{64}Ga_{20}$	2.52	3.30	2.92	-11.96
$Ge_{17}Te_{83}$	2.34	2.85	2.26	-32.71
$Ge_{16}Te_{79}Ga_5$	2.37	2.93	2.39	-32.32
$Ge_{15}Te_{75}Ga_{10}$	2.40	3.00	2.53	-31.92
$Ge_{14}Te_{71}Ga_{15}$	2.43	3.08	2.67	-26.28
$Ge_{13}Te_{67}Ga_{20}$	2.46	3.15	2.84	-14.09

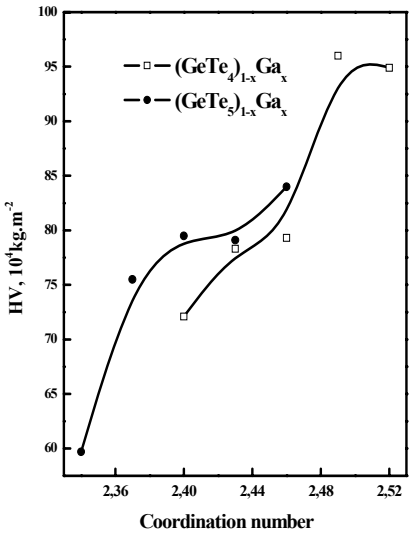

Fig. 3. Dependence of the microhardness on coordination number.

Fig. 3 presents the microhardness of the glasses as a function of the average coordination number. It can be seen that for both systems the value of Hμ increases with the addition of Ga into the Ge-Te matrix. The slight deflection in the microhardness increase is shown at Z = 2.43, which corresponds to 15 mol % Ga content in the $(GeTe_5)_{1-x}Ga_x$ system and 5 mol.% Ga in the $(GeTe_4)_{1-x}Ga_x$. We should notice that the variations in the studied physico-chemical behaviours show similarity as a function of the composition. The similarity is in the trend of the curves, namely they increase (or decrease) with the composition but not linearly. The deflection in the microhardness experimental curves coincides with the deflections observed in the other physico-chemical properties reported above. The change in the slope is always around average coordination number 2,43 and 15 mol % Ga content in the $(GeTe_5)_{1-x}Ga_x$ system and 5 mol.% Ga in the $(GeTe_4)_{1-x}Ga_x$, respectively as seen from the Fig. 1-3. Our explanation of this peculiarity in the physico-chemical behaviours is based on the assumption that most probably structural transformation occurs close to these compositions. Most probably a transformation from floppy to rigid structure takes place close to these compositions according to the Phillips-Thorpe model [12]. The transition is associated with tight bonding, shorter bond length and followed by sharp decrease of the volume. This hypothesis needs a more profound structural study to approve the indirect structural observation and this study is in progress.

4. Conclusions

The density, the microhardness and the compactness of the glasses from $(GeTe_4)_{1-x}Ga_x$ and $(GeTe_5)_{1-x}Ga_x$ systems increase with the Ga content. The variations in all the studied physico-chemical behaviours show similar trend of the curves, namely they increase (or decrease) by different rate with the composition. These changes are around average coordination number 2,43 and this is probably due to structural transformation in the studied glasses.

Acknowledgements

The authors gratefully acknowledge the financial support of the University of Chemical Technology and Metallurgy under project No. 10427.

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