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Comparative analysis of some physico-chemical properties of the glassy systems $(GeSe_5)_{100-x}In_x$ and $(GeTe_5)_{100-x}In_x$

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Our study concerns the two glassy systems $(GeSe_5)_{100-x}In_x$ and $(GeTe_5)_{100-x}In_x$ which contain different chalcogen elements. Se and Te rich glasses are interesting in view of the possibility of their application in switching and memory devices. They show, however, high values of electrical resistance implying certain limitations as short lifetime and low sensitivity. To eliminate these limitations we added In as a third element into the Ge-Se (Te) matrix. As a result of the addition of In new properties are expected, which can be related with structural transformation. The investigation of the physico-chemical properties gives useful information about the real structure of the glasses.

In this paper some physico-chemical properties of the glasses were studied, such as density, compactness, molar volume, number of constraints per atom and overall mean bond energy. The correlations between the composition and the properties of the glasses were discussed in terms of the supposed structural changes that occur in the investigated chalcogenide materials.

Key words: chalcogenide glasses, physico-chemical properties, structure

INTRODUCTION

The physico-chemical properties of chalcogenide semiconducting glasses are strongly dependent on their composition. Normally, control of the properties and expansion of the scope of applications of two-component systems is achieved through introduction of a third component. The addition of a third component expands the glass-forming area and also creates compositional and configurational disorder. Thus, the addition of In in the binary systems Ge-Se and Ge-Te is expected to affect some of their physico-chemical properties [1]. The chosen concentration ratio of the investigated glasses provides good flexibility of the structure, which facilitates the photoinduced changes in these materials.

In this paper we report the results of the studies of some physico-chemical properties as density, compactness, molar volume, number of constraints per atom and overall mean bond energy of these glasses and the results are discussed in respect to the composition of the glasses. The relation between chemical bonding and basic physico-chemical properties of the glasses (transformation temperature, density) is an essential feature of any comprehensive theory relating their structure and properties [2, 3].

EXPERIMENTAL

Bulk samples with composition $(GeSe_5)_{100-x}In_x$ and $(GeTe_5)_{100-x}In_x$, x = 0, 5mol% were prepared by melt-quenched technique [4]. The initial elements Ge, Se (Te) and In were used with 4N purity elements. The respective amounts of the initial elements were evacuated in quartz ampoules with a residual pressure 1.33×10^{-3}Pa. The synthesis was carried out in furnace „Firemagic FM4 Plus" with a constant rate of 5×10^{-2}K/s up to final temperature 1300K. Glasses were obtained after quenching in a mixture of water and ice with quenching rate of 1×10^{2}K/s.

The density of the bulk samples was measured by the pycnometer method with an accuracy of ±0.5%.

The compactness was calculated using the formula [5]:

$$\delta = \frac{\sum_i \frac{c_i A_i}{\rho_i} - \sum_i \frac{c_i A_i}{\rho}}{\sum_i \frac{c_i A_i}{\rho}}, \qquad (1)$$

where c_i is the atomic fraction, A_i – the atomic weight, ρ_i – the density of the components and ρ is the measured density of the bulk sample.

The molar volume was determined from the density data by the equation:

$$V_m = \frac{1}{\rho}\sum_i c_i A_i \, . \qquad (2)$$

The average coordination number was estimated according to [3] as:

$$Z_{glass} = 4x + 2y + 3z, \qquad (3)$$

where x, y and z are the atomic fractions of Ge, Se (Te) and In, respectively.

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The number of constraints per atom can be calculated by theoretical arguments according to the Phillips model [6]:

$$N_{co} = N_d \quad (4)$$

i. e. the number of the topological constraint N_{co}, evaluated for an atom, is equal to the number of degrees of freedom N_d. N_{co} is defined by the formula:

$$N_{co}(Z_{glass}) = N_a + N_b = \frac{Z_{glass}}{2} + (2Z_{glass} - 3) \quad (5)$$

where N_a and N_b are the radial and axial bond strengths, respectively.

Using the correlation proposed by Tichy *et al.* [7] for chalcogenide-rich systems we could determine the values of the overall mean bond energy:

$$< E >= \overline{E}_c + \overline{E}_{rm}, \quad (6)$$

where $\overline{E}_c$ is the average heteropolar bond energy and $\overline{E}_{rm}$ is the average homopolar bond energy.

RESULTS AND DISCUSSION

The results obtained for the density of the bulk samples from the system Ge-Se-In (Table 1) show that the density increases after indium addition. It is known that the variation of the density is related to the atomic weight and to the atomic volume of the chemical elements contained in the chalcogenide glassy system. The atomic weight of Se and In is $A_{Se}=7.9\times10^{-2}$kg/mol and $A_{In}=11.5\times10^{-2}$kg/mol, respectively, i.e. the atomic weight of In is higher and by replacement of Se atoms with In atoms (increasing content of indium) the density increases. In the system Ge-Te-In, with increasing the In content the values of the density decrease. The Te atomic weight is $A_{Te}=12.6\times10^{-2}$kg/mol, i. e. the atomic weight of In is lower than that of Te and by replacing tellurium with indium atoms (increasing of In content) the value of the density decreases. The compositions containing Te are denser than the compositions containing Se due to the higher atomic weight of Te.

The strength of the chemical bond is associated with the compactness of the material, i. e. with the "free volume" or it can be related to the density of defect states in the samples [8]. The dependence of the compactness on the In content for both systems is the same as the compositional dependence of the density (Table 1). The Te containing compositions show lower values of compactness than the Se containing compositions, i. e. bigger structural changes would be expected for the Te containing compositions.

The compositional dependence of the molar volume also repeats the compositional dependence of the density (Table 1).

The dependence of the physico-chemical properties on the composition could be investigated based on the expected chemical bonds in the glasses. The first approximation consists of ignorance of the unstable chemical bonds and the weak van der Waals forces. It is assumed that atoms predominantly combine with atoms of different types than of the same kind in chalcogenide glasses [9], i. e. chemical bond between atoms from the same kind will only occur, if there is an excess of these atoms. Furthermore, the bonds are formed in sequence of increasing bond energies until all available valences of the atoms are saturated. In the investigated chalcogenide glassy systems Ge-Se-In and Ge-Te-In, which are enriched in Se, or Te, respectively, the homopolar Se bonds or Te bonds are formed in the presence of unsaturated valences of Se or Te atoms after all heteropolar bonds are created. By In addition the number of the homopolar selenium, respectively tellurium bonds decreases and the number of degrees of freedom per atom increases (Table 1), which leads to an increase in the stability of the glassy systems (the number of degrees of freedom for an atom moving in a 3-dimensional space is $N_d=3$, and for the ideal glass $N_{co}=3$ [10], with an optimum mechanical stability of the network).

The physico-chemical properties of the chalcogenide glasses are related to their mean bond energy, which is a function of the average coordination number and of the bond type and bond energy between the atoms of the glass components. According to [6], the structure of the glassy system Ge-Se-In is realized by a network composed of tetrahedral $GeSe_2$ structural units and pyramidal In_2Se_3 structural units. Based on the model of the chemically ordered covalent random network [11] they are combined with the additional Se atoms. The remaining Se atoms are combined in chains. The structure of the glassy system Ge-Te-In is also realized by a network composed of tetrahedral $GeTe_2$ structural units and pyramidal In_2Te_3 structural units. They are also combined with the additional Te atoms, and the remaining Te atoms are combined in chains. No formation of Ge-Ge bonds at a Ge content up to 33mol% is expected [12].

Table 1. Composition and physico-chemical properties of the investigated samples.

Composition, mol%	Z_{glass}	Density, 10^3kg/m^3	Compactness, 10^{-2}	Molar volume, 10^{-5}m^3/mol	N_{co}	<E>,10^{-19}J
$Ge_{17}Se_{83}$	2.34	4.34	-3.95	1.80	2.85	3.58
$Ge_{16}Se_{79}In_5$	2.37	4.54	-0.09	1.75	2.93	3.61
$Ge_{17}Te_{83}$	2.34	5.86	-4.86	2.02	2.85	3.62
$Ge_{16}Te_{79}In_5$	2.37	5.55	-12.61	2.12	2.93	4.18

The value of the In-Se bond energy (4.27×10^{-19}J) [13] is higher than that of the Ge-Se bond energy (3.39×10^{-19}J) [14], and the value of the In-Te bond energy (3.60×10^{-19}J) [15] is higher than that of the Ge-Te bond energy (3.32×10^{-19}J) [15], i. e. the overall mean bond energy increases by indium addition (Table 1) and the bonds between atoms of the glass components become more stable. The formation of stronger bonds could be responsible for the variations in their physico-chemical properties. Te containing compositions possess higher overall mean bond energy than Se containing compositions because of the higher value of the Te-Te bond energy (3.24×10^{-19}J) [15] in comparison to that of the Se-Se bond energy (2.82×10^{-19}J) [14].

CONCLUSIONS

The values of the density of the compositions containing Te are higher than the values of the density of the compositions containing Se. The increase in the In content leads to variation of the density in both investigated systems Ge-Se-In and Ge-Te-In in a different way.

Because of their lower compactness, more structural changes would be expected in the compositions containing Te.

The compositional dependence of the molar volume repeats the compositional dependence of the density.

The increase in the number of degrees of freedom with addition of In leads to an increase in the sustainability of the glassy system.

The overall mean bond energy of the glassy alloys containing Te is higher than the overall mean bond energy of the glassy alloys containing Se. By In addition the bonds between the atoms of the glass components become more stable.

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СРАВНИТЕЛЕН АНАЛИЗ НА НЯКОИ ФИЗИКО-ХИМИЧНИ СВОЙСТВА НА СТЪКЛОВИДНИТЕ СИСТЕМИ $(GeSe_5)_{100-x}In_x$ И $(GeTe_5)_{100-x}In_x$

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(Резюме)

Изследвани са системите $(GeSe_5)_{100-x}In_x$ и $(GeTe_5)_{100-x}In_x$, съдържащи различни халкогенни елементи. Стъклата, обогатени на Se и Te, са интересни от гледна точка на възможността за приложението им в превключващи устройства и памети. Но те притежават високи стойности на електрическо съпротивление, което предполага някои ограничения като кратко време на живот и ниска чувствителност. За подобряване на качествата на тези материали е добавен трети елемент In в Ge-Se (Te) матрицата. Добавянето на In може да бъде свързано със структурни промени в стъклата и се очаква те да проявят нови свойства. Изследването на физико-химичните свойства дава полезна информация за реалната структура на стъклата.

Настоящата работа е свързана с определянето някои физико-химични свойства на стъклата като плътност, компактност, моларен обем, брой връзки на атом и пълна средна енергия на връзките. Зависимостите на свойствата на изследваните халкогенидни материали от техния състав са дискутирани от гледна точка на възникването на структурни промени в тях.