STRUCTURE AND SWITCHING PROPERTIES IN CHALCOGENIDE SYSTEMS AT THE BORDER OF GLASS FORMATION DOMAIN

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Abstract. *The switching properties in chalcogenide systems are related to the glass formation ability, while the peaking of the switching properties is related to the border of glass formation domain (GFD). Some of the intermediate phase windows in the literature have also been evidenced near the GFD. We have remarked a narrow domain of average electronegativity (centred on 2.38) for the chalcogenides compositions with intermediate phase situated close to the border of GFD. This feature led us to the possibility to predict new memory switching compositions.*

Keywords: Chalcogenide materials, Glass forming domain, Memory switching, Intermediate phase

1. Introduction

In the network glasses including chalcogenide systems the glass formation domain (GFD) has been widely investigated. A careful examination of the phase diagrams in the ternary chalcogenides has revealed one or two glass formation domains well separated from the rest of the diagrams. What is special with the demarcation line between GFD and the remained domain of hardly amorphizable compositions? We have observed that near- or across the border line between these domains one may often find compositions with memory switching properties (phase change materials) or compositions with special thermal properties (intermediate phases). A discussion about intermediate phases and memory switchingmaterials can be found in [1].

2. Glass formation ability

The glass formation ability was a top subject for many years in glass science. Many scientists tried to characterize the easiness to form glasses in different materials, based on various crystallo-chemical properties, especially the type of inter-atomic bonding.

It is well known that, in the same conditions of preparation (cooling rate, deposition rate, etc.), some materials can be frozen in the glassy state and others cannot. Why the melts of various alloys behave so differently during cooling?

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Myuller [2] firstly pointed out the main role played in the formation of glassy phase and amorphization in general, of the directional covalent bonds that create an intricate network, hard to transform into a crystalline lattice.

The suggestion of Winter-Klein [3] regarding the optimum number of p-electrons on an atom is a consequence of the second condition of the glass formation proposed by Myuller. These two conditions can be quantitatively considered, introducing the criterion of optimal number of bonds per atom, which forms in the vicinity ofthe melting temperature $T_m$in the structural unit of the material.

In the materials consisting of several structural units, the average number of bonds must be calculated considering the concentration of elements which form the structural unit.

Fritzsche [4] fundamented the role played by the average coordination number as an important characteristic that determines the ability of the atoms to form a disordered network.

Myuller et al. [5] and Goryunova et al. [6] have shown that the glass formation ability, essentially diminishes when the chemical bonds are metallized as a consequence of the delocalization of the valenceelectrons. The lowering of the glass formation ability of the melt at cooling determines the molecular building characteristic of materials consisting of light atoms [5]. These two effects can be quantitatively considered calculating the average principal quantum number $\bar{n}$.

The consideration of the optimum average of the number of bonds and optimum mean principal quantum number can be done taking the product of these two factors. The first estimation of the glass ability on this basis was tried by Blinov [7]. Later Baidakov and Blinov [8] introduced the mean number of bonds per atom in the structural unit, $\bar{k}$. Moreover, the authors normalized the product $\bar{n} \cdot \bar{k}$ to $\bar{Z}$, the average charge of the nuclei that form the structural unit. Thus $\bar{n} \cdot \bar{k}/\bar{Z}$ represents more correctly the *glass formation ability*. This parameter is higher for higher glass formation ability.

3. The glass formation ability and electronegativity

Various compositions either in glassy or crystalline form can be characterized using two parameters: $\bar{n} \cdot \bar{k}/\bar{Z}$(Glass Formation Ability, GFA) and Average Electronegativity (AE). In order to unify different electronegativity scales we have introduced an average scale. The average electronegativity of an element was calculated as: $e_{ave} = {\sum_i e_i}/{N}$, where e_i is the electronegativity of a given element from different scales (found in the literature) and N is the number of scales that contain the calculated electronegativity for that element.

Figure 1 shows the result in the case of the systems where intermediate phase (IP) was identified and accurately measured. The values of the intermediate phase boundaries are given in Table 2.

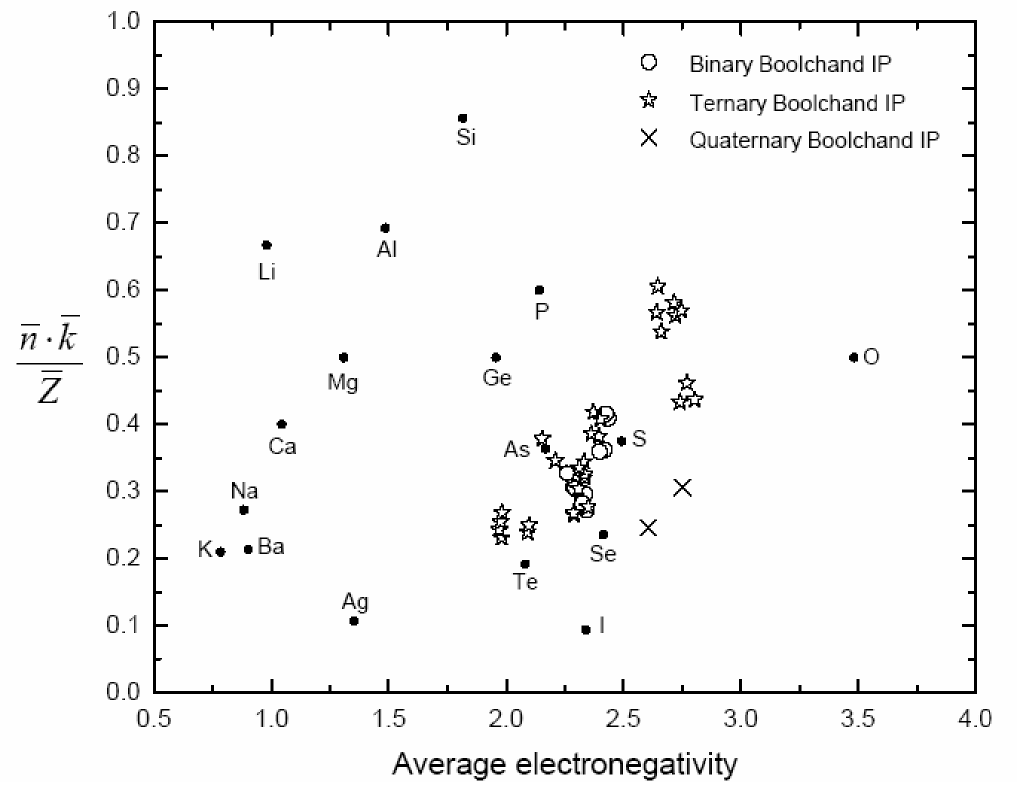

Fig. 1. The position of IP when glass formation ability is plotted versus average electronegativity and the elements representing the composition limits for the systems.

Table 2. Intermediate phases used in the plot: Glass Formation Ability-Electronegativity.

Intermediate phase	$x_c(1)$	$x_c(2)$	$\frac{\overline{n}\cdot\overline{k}}{\overline{Z}}$ (1)	$\frac{\overline{n}\cdot\overline{k}}{\overline{Z}}$ (2)	e_{ave} (1)	e_{ave} (2)
As_xS_{100-x}	22	29	0.362	0.360	2.421	2.398
P_xS_{100-x}	16	19	0.409	0.416	2.436	2.426
As_xSe_{100-x}	29	34	0.272	0.282	2.343	2.323
P_xSe_{100-x}	28	40	0.296	0.327	2.338	2.305
Si_xSe_{100-x}	20	26	0.304	0.327	2.294	2.258
Ge_xSe_{100-x}	20	26	0.286	0.306	2.323	2.286
$Ge_x\ As_xS_{100-2x}$	11	15	0.382	0.386	2.398	2.363
$Ge_xAs_xSe_{100-2x}$	29	37	0.347	0.378	2.210	2.154

$Ge_{7.5}As_xTe_{92.5-x}$	21	28	0.239	0.250	2.091	2.097
$Ge_xP_xS_{100-2x}$	10	13.5	0.407	0.418	2.404	2.373
$Ge_xP_xSe_{1-2x}$	9	14.5	0.276	0.303	2.348	2.308
$Ge_xP_xTe_{100-2x}$	9	14.5	0.276	0.303	2.348	2.308
$Ge_{25}I_xS_{75-x}$	16.5	15.3	0.320	0.325	2.333	2.335
$Ge_{25}I_xSe_{75-x}$	16.5	15.4	0.265	0.268	2.287	2.288
$Al_{15}Si_xTe_{85-x}$	4	8	0.231	0.243	1.982	1.971
$Al_{20}As_xTe_{80-x}$	16	24	0.255	0.268	1.977	1.984
$(Na_2O)_x(SiO_2)_{100-x}$	24	17.9	0.567	0.581	2.643	2.716
$(K_2O)_x(SiO_2)_{100-x}$	16.4	14.5	0.562	0.569	2.723	2.746
$(Na_2O)_x(GeO_2)_{100-x}$	14	19	0.436	0.433	2.803	2.740
$(Ag_2S)_x(As_2S_3)_{100-x}$	8	13	0.344	0.336	2.332	2.311
$(AgI)_x(AgPO_3)_{100-x}$	9.5	37.8	0.306	0.247	2.750	2.604

The parameters $\bar{n}$, $\bar{k}$ and $\bar{Z}$ for A_xB_y, where $x+y=1$, are calculated in the following way: $\bar{n} = xn_A + yn_B$, $\bar{k} = xk_A + yk_B$, $\bar{Z} = xZ_A + yZ_B$.

As seen in Fig. 1 the intermediate phases from various systems are all concentrated in a narrow region of the graph corresponding to $\bar{n} \cdot \bar{k}/\bar{Z}$ in the range 0.2 – 0.6 while the average electronegativity of the intermediate phase (BIP) extends from 1.9 to 2.8.

4. The glass formation domain and memory switching materials

Ge-As-Te System. The glasses from Ge-As-Ch system are very used as optical materials. These glasses are easily obtained and they are transparent in visible region. The area of GFD is significantly dependent on the cooling rate of the studied system (Fig. 2, black line [9, 10-13] vs. green dotted line [14-16]). Glasses with low quantity of Ge (less than 25%) are the most suitable for memory applications [17-20]. Some memory switching compositions are very close to the margin of GFDs, others are outside or inside of GFDs. A surprising feature revealed by us is the intersection of the IP window with the borderline that separates the two domains (GFD and domain with easy crystallization) (Fig. 2).

Al-As-Te System. In this system (Fig. 3) some memory switching composition seems to be situated on the border of GFD. The IP window is situated on the border of the GFD. Glasses in this system exhibits electrical and pressure induced-switching [21-25].

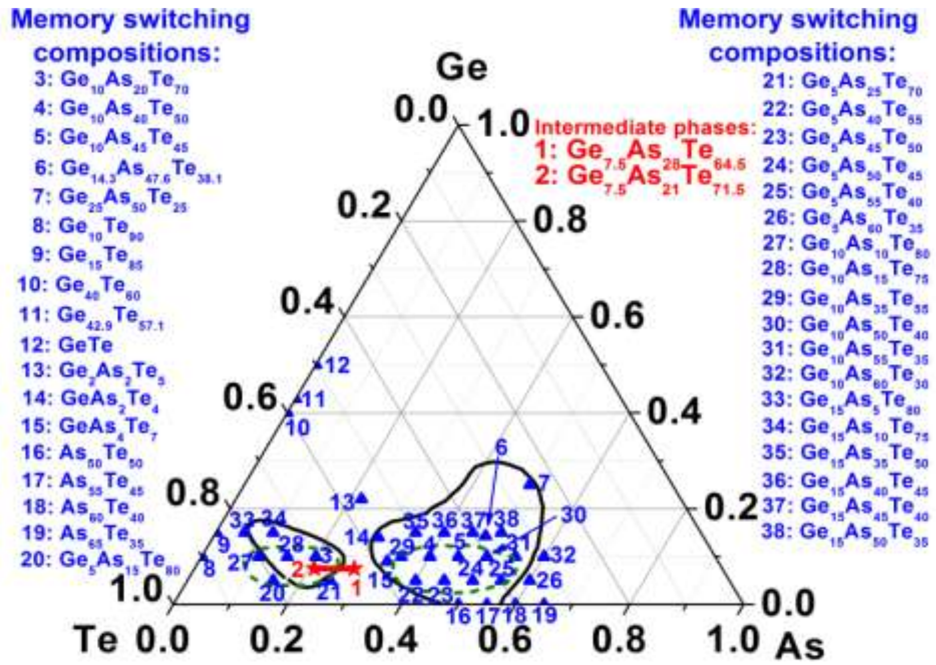

Fig. 2. Glass formation domain (defined by black curved line [9, 10-13] and green dotted line [14-16]), ternary IPs (red lines between stars denoted with 1 and 2)[18, 26, 27]for a) Ge-As-S, b) Ge-As-Se and c) Ge-As-Te systems. Blue triangles represent phase change compositions [17-20, 11].

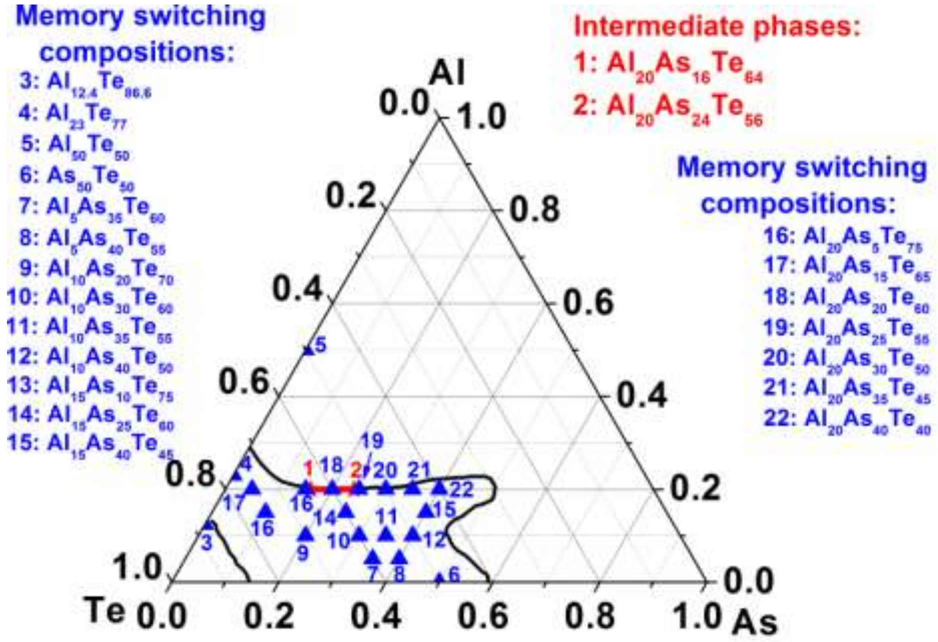

Fig. 3. Glass formation domain (defined by black curved line) [9, 10], ternary IPs [18] and phase change compositions [21-25, 11] for Al-As-Te system.

5. Discussion

We make the hypothesis that the compositions situated on phase diagrams near the GFD borderline (not limited to a particular section on GFD demarcation line) have a particular structure (mixture of nanocrystalline and nanoamorphous nuclei) and present special thermal and memory switching properties. This feature could be related to the excellent memory switching properties of the compositions in the vicinity of the border of GFD. During memory switching in “on” state (conductive state) a certain part of nanoamorphous nuclei is transformed in nanocrystalline nuclei and during memory switching in “off” state (nonconductive state) a certain part of nanocrystalline nuclei is transformed in nanoamorphous nuclei [28]. In the cases when memory switching compositions are situated outside of GFD we make the following hypothesis: in that region a secondary GFD does exist. In the cases when memory switching compositions are situated inside of GFD in that region it is probably also a restraint secondary domain with an enhanced crystallization capability.

It is, also, remarkable that the IP window is situated just across the border of GFD.

The narrow average electronegativity (centred on 2.38) is characteristic to the IP phases and switching compositions.

6. Conclusions

Intermediate phases are special phases in close relation with the electronegativity of the alloys and to their glass formation ability. The average electronegativity of the intermediate phases is situated around 2.38.

The glass formation ability (GFA) for BIP is situated in the range 0.20 – 0.60 corresponding to a not too large glass formation ability.

From the point of view of the crystallo-chemical parameters, the intermediate phases are concentrated in a strictly limited region situated in the middle part of the GFA and AE parameters.

We have shown that memory switching compositions in ternary chalcogenide systems are situated mainly at – or close to – the borders of the GFD.

The narrow interval, which defines the intermediate phase (IP), is situated in several cases close to - or intersects - the border of the glass formation domain.

Finally, we suggest that the compositions along the borders of the GFD might consist of a homogeneous mixture of nanocrystallites and nanoamorphous nuclei, and are useful for making device quality memory switches.

R E F E R E N C E S

[1] M. Popescu, A. Velea, F. Sava, A. Lőrinczi, accepted for publication in Phys. Status Solidi B (**2013**).

[2] R. L. Myuller, Izv. Akad. Nauk SSSR, Ser. Fiz. (Russ.) V. 4(4) (**1940**).

[3] A. Winter-Klein, *Structure and Physical Properties of the Glass*, in: Glassystate (Russ.) Moscow-Leningrad, p.45 (**1965**).

[4] M. Fritzsche, Non-Crystalline Semiconductors, Acta Polytech., Second Electr. Eng. Ser., No. 50, p. 3-46 (**1983**).

[5] R. L. Myuller, *Himia tviordovo tela* (russ.) (Chemistry of the solid state), Leningrad p. 9-63 (**1965**).

[6] N. A. Goryunova, B. T. Kolomiets, *On the problem of glass formation in the chalcogenide glass*, in Stekloobraznie sostoianie (Glassy state) (Russ.), Leningrad p. 71-78 (**1960**)

[7] L. N. Blinov, Fiz. Him. Stekla (Russ.), 12(1), 121 (**1986**).

[8] L. A. Baidakov, L. N. Blinov, Fiz. Him. Stekla (Russ.) T13(3), 340 (**1987**).

[9] M. Popescu, *Non-Crystalline Chalcogenides* (Kluwer Academic Publisher, Dordrecht, **2000**).

[10] Z.U. Borisova, *Glassy Semiconductors*, (**1981**).

[11] D. Lencer, M. Saligna, B. Grabowski, T. Hickel, J. Neugebauer, M. Wuttig, Nat. Mat 7, 972 (**2008**).

[12] G. Z. Vinogradova, S. A. Dembovskii, J. Neorgan. Him. (J. of Anorg.Chem.)16, 2036 (**1971**).

[13] R. L. Myuller, G. M. Orlova, V. N. Timofeeva, G. I. Ternova, in: Solid State Chemistry, edited by Z. U. Borisova (Consultants Bureau, New York, 1966).

[14] G. Z. Vinogradova, *Glass formation and phase equilibrium in chalcogenide systems* (Nauka, Moscow, 1984), p. 96.

[15] B. T. Kolomiets, N. A. Goriunova, V. P. Silo, *Glass formation relation in chalcogenides*, in "The glassy state" (Publishing House of the Soviet Academy of Sciences, **1960**).

[16] N. A. Goriunova, B.T. Kolomiets, Solid state physics 2(2), 280 (**1960**).

[17] R. Pinto and K. V. Ramanathan, App. Phys. Lett. 19(71), 221 (**1971**).

[18] M. Fedel, Vacuum 44(8), 851 (**1993**).

[19] Sigeru lizima, Michio Sugi, Makoto Kikuchi, K. Tanaka, Solid State Communications 8, 153 (**1970**).

[20] J. A. Savage, J. Non Cryst. Solids11, 121 (**1972**).

[21] S. Murugavel, S. Asokan, Phys. Rev. B 58 (61), 3022 (**1998**).

[22] R. A. Narayanan, S. Asokan, A. Kumar Phys. Rev. B 63 (61), 092203 (**2001**).

[23] A. Algeria, A. Arruabarrena, F. Sanz, J. Non Cryst. Solids 58, 17 (**1983**).

[24] J. Colmenero J.M. Barandiaran, phys. stat. sol. (a) 62, 323(**1980**).

[25] S. Murugavel, K.V. Achary, S. Asokan, J. Non Cryst. Solids 191, 1327 (**1995**).

[26] E. Cernoskova, T. Qu, S. Mamedov, Z. Cernosek, J. Holubova, P. Boolchand, J. of Phys. and Chem. of Solids 66, 185 (**2005**).

[27] T. Qu, D.G. Georgiev, P. Boolchand, M. Micoulaut, *The intermediate phase in ternary GexAsxSe1-2x glasses*, in "Supercooled Liquids, Glass Transition and Bulk Metallic Glasses", edited by T. Egami, A. L. Greer, A. Inoue, S. Ranganathan, Mater. Res. Soc. Symp. Proc. 754, CC8.1.1 (**2003**).

[28] M. Popescu, A. Velea, *Physica Status Solidi* (b) 249(10), 1966-1971 (**2012**).