Physical properties of chalcogenide glasses from the GeSe$_2$-Sb$_2$Te$_3$-PbSb$_2$Te$_4$ system

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ABSTRACT

Chalcogenide glasses from the GeSe$_2$-Sb$_2$Te$_3$-PbSb$_2$Te$_4$ system are synthesized by direct monotemperature synthesis from the initial compounds. The thermal properties (temperatures of glass-transition T_g, crystallization T_{cr} and melting T_m, as well as the Hruby's criterion of the glassy samples are determined using DTA. On their basis the Hruby's criterion K_G is calculated. The density and the Vickers microhardness of the glasses are measured and using the obtained values the compactness C, the elasticity modulus E and the thermomechanical properties (micro-voids volume V_h and energy for formation of a micro-void E_h) are calculated. A correlation between these properties and the glasses composition is established and discussed.   © 2014 Trade Science Inc. - INDIA

KEYWORDS

Thermal properties;
Density;
Microhardness;
Thermomechanical properties;
Elasticity modulus.

INTRODUCTION

The chalcogenide glasses can find application in the optics, electronics, sensorics and other areas of the contemporary technics[1-5]. They can be synthesized relatively easy in a bulk form and the thin films can be deposited by conventional methods. The glassy chalcogenide semiconductors are characterized by high corrosion steadiness and stability of the properties[6]. Besides, they are relatively cheap electronic material when they are developed in thin film form.

The GeSe$_2$ is hardly obtained in glassy state, but combined with an element or compound with modifying properties it is recognized as one of the best glass-formers[7]. Such modifier in the current case is the Sb$_2$Te$_3$. This compound possesses very good thermoelectrical properties. At T=300 K its thermal power is α≈90 μV/К; the specific electrical conductivity σ=2000÷4000 S/cm; the holes concentration is 7.10^{19} cm^{-3}; and the electrical band gap ΔE=0.19 eV[8].

The pseudo-ternary compound PbSb$_2$Te$_4$ decomposes in the glasses to PbTe and Sb$_2$Te$_3$[9], which helps the formation of more complicated glassy network and more stable glasses, respectively. The PbSb$_2$Te$_4$ is new thermoelectric material with p-type conductivity, band gap at 0 К ΔE_o = 0.27 eV, and it is characterized by significant anisotropy of its thermoelectrical and thermomagnetic properties[10]. The monocrystalline PbSb$_2$Te$_4$ has electrical conductivity σ=2350 Ω^{-1}cm^{-1} and thermal conductivity λ=29.1×10^{-2} W/(cm.K) at 300 К[11].

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For the polycrystalline stoichiometric $PbSb_2Te_4$ these values are respectively: $\sigma=2120\ \Omega^{-1}cm^{-1}$ and $\lambda=19.2\times10^{-2}\ W/(cm.K)$[12]. The total thermal conductivity λ_{tot} changes from 2.6×10^{-2} (at 320 K) to 2.0×10^{-2} W cm^{-1} K^{-1} (at 600 K)[13].

The region of glass formation in the $GeSe_2$-Sb_2Te_3-$PbSb_2Te_4$ system[14] spreads from the point, corresponding to 100 % $GeSe_2$ and lies partially on the $GeSe_2$-Sb_2Te_3 (from 0 to 32.5 mol % Sb_2Te_3) and $GeSe_2$-$PbSb_2Te_4$ (from 0 to 27 mol % $PbSb_2Te_4$) sides. No glassy phases were obtained on the Sb_2Te_3-$PbSb_2Te_4$ side.
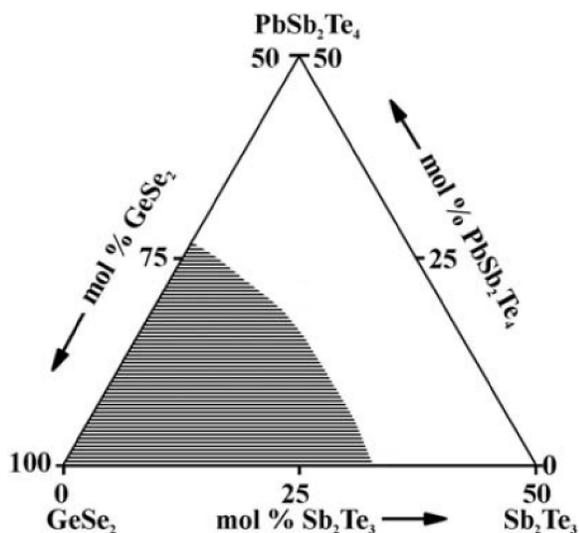
Figure 1 : Region of glass formation in the $GeSe_2$-Sb_2Te_3-$PbSb_2Te_4$ system.

On the basis of the properties of the initial compounds, one can assume that the glasses from the chalcogenide $GeSe_2$-Sb_2Te_3-$PbSb_2Te_4$ system will possess properties, appropriate for their application as active material for development of electronic elements and sensors.

In connection with all presented above, the aim of the present work is to determine the thermal (temperatures of glass-transition T_g, crystallization T_{cr} and melting T_m, as well as the Hruby's criterion K_G), physicochemical (density d, compactness C and microhardness HV), mechanical (elasticity modulus E) and thermomechanical (micro-voids volume V_h and energy for formation of a micro-void E_h) properties of chalcogenide glasses from the $GeSe_2$-Sb_2Te_3-$PbSb_2Te_4$ system and to find an explanation of their compositional dependence, if such exists.

EXPERIMENTAL

The initial compounds $GeSe_2$, Sb_2Te_3 and $PbSb_2Te_4$, as well as the samples from the investigated system were synthesized by direct monotemperature synthesis in evacuated to a residual pressure of 1.10^{-3} Pa quartz ampoules. The initial elements used for the synthesis of $GeSe_2$, Sb_2Te_3 and $PbSb_2Te_4$ were with purity of 5N for the Ge, Se, Te and 4N for the Sb and Pb. The synthesis conditions (temperature, duration of the isothermal steps and heating rate) were conformed to the physicochemical properties of the initial components. The maximum synthesis temperature of the samples from the investigated system was $800\pm10\ °C$ (duration of 3 h at constant vibration stirring of the melt). After a decrease of the temperature to $770\pm10\ °C$ the melt was tempered for 10 minutes and quenched in a water+ice mixture (cooling rate of 10-15 °C s^{-1}).

The phase transformations temperatures of the glasses (glass transition T_g, crystallization T_{cr} and melting T_m) were determined by differential thermal analysis (DTA) using measuring set from the F.Paulik-J.Paulik-L.Erdey system, produced by MOM-Hungary. The DTA was carried out as the glassy samples in quantity of 0.3 g were heated at rate of 10 °C / min in evacuated and sealed Stepanov's vessels. Calcinated γ-Al_2O_3 was used as a reference substance.

The Hruby's criterion (K_G) was used for evaluation of the glass-forming ability of the samples:

$$K_G = \frac{T_{cr} - T_g}{T_m - T_{cr}} \qquad (1)$$

The density of the glassy samples was measured by hydrostatic method in toluene as immersion fluid. The Vickers microhardness (HV) was measured using MIM-7 microscope with built in microhardnessmeter PMT-3 at loading of 20 g (30 measurements per sample). The accuracy of both measurements is $\pm$ 5 %.

The compactness C was calculated using the equation[15]:

$$C = d\left\{\sum_i \frac{M_i x_i}{d_i} - \sum_i \frac{M_i x_i}{d}\right\}\left[\sum_i M_i x_i\right]^{-1} \qquad (2)$$

where M_i, x_i and d_i are the molar mass, the molar part and the theoretical density of the ith component, respectively.

The elasticity modulus was calculated using Eq.

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(3)[16]:

E = 0.147.HV[GPa],   (3)

For calculation of the thermomechanical properties (micro-voids volume V_h and energy for their formation E_h) the following equations were used[16]:

$$V_h = 5.04 \cdot 10^{-3}\, \frac{T_g}{HV}\ [nm^3]$$ (4)

$$E_h = 29.75 T_g\ [J\ mol^{-1}]$$ (5)

RESULTS AND DISCUSSION

The thermal characteristics of glasses from the investigated system are shown in TABLE 1. For convenience during the analysis of the results the m parameter is introduced, which expresses the ratio between the GeSe₂ (x) and Sb₂Te₃ (y) – m = Sb₂Te₃/(GeSe₂+Sb₂Te₃) = y/(x+y). Due to the same reason the third component from the system (PbSb₂Te₄) is marked with z in the dependencies.

ing in of the structural units (s.u.) $SbTe_{3/2}$, while at the combined introduction of Sb₂Te₃ and PbSb₂Te₄, two new s.u. are built in. The first of them includes the trigonal pyramids $SbTe_{3/2}$, the source of which are both the initial component Sb₂Te₃ and the PbSb₂Te₄ compound, and the second - linear fragments –Pb–Te– (s.u. : $PbTe_{1/2}$), which are carried by the PbSb₂Te₄ (PbSb₂Te₄ → PbTe+Sb₂Te₃). The : $PbTe_{1/2}$ s.u. lead to looseness of the glasses structure (their compactness C decreases). Therefore, the T_g change in the concentration intervals $0.0 \leq m \leq 0.1$ and $0 \leq z \leq 10$ mol % is limited by the effect, provoked by the introduction of the s.u. $SbTe_{3/2}$, while outside these borders – by the s.u. $PbTe_{1/2}$.

The $T_{cr}(m)_{z=10}$ and $T_{cr}(z)_{m=0.1}$ dependencies (TABLE 1) are practically linear with negative angle coefficient, which is logical since at the complication of the glasses composition as a result of the participation of 3, 4, 5 or more chemical elements the probability for arise of crystalline nuclei with following crystallization of different by composition phases increases. The exit of the sys-

TABLE 1 : Composition and thermal characteristics of glasses with composition (GeSe₂)ₓ(Sb₂Te₃)ᵧ(PbSb₂Te₄)_z.

№	Composition			m	T_g, °C	T_{cr}, °C	T_m, °C	K_G
	GeSe₂	Sb₂Te₃	PbSb₂Te₄					
20	90	10	0	0.1	232	443	477	6.20
12	90	0	10	0	208	385	453	2.60
18	85.5	4.5	10	0.05	237	390	462	2.13
3	81	9	10	0.1	246	361	457	1.20
2	72	18	10	0.2	217	246, 328	477	0.75
5	72	8	20	0.1	193	246, 304	438, 477	0.64

The parallel analysis of the compositional dependencies of the glass-transition temperature $T_g – T_g(m)_{z=10}$ и $T_g(z)_{m=0.1}$, respectively, shows the presence of well expressed maximum for the composition, corresponding to p. 3 (GeSe₂)₈₁(Sb₂Te₃)₉(PbSb₂Te₄)₁₀. This means in practice, that the glasses around this composition are the most stable ones and the introduction of PbSb₂Te₄ up to 10 mol % increases the T_g and stabilizes the glasses structure. On the other hand, the glasses from the binary GeSe₂-Sb₂Te₃ system in the compositional interval $0.0 \leq m \leq 0.1$ possess higher T_g values compared to the glasses from the binary GeSe₂-PbSb₂Te₄ system around $0 \leq z \leq 10$ mol %. This T_g deviation has to be related to a change in the structure, which initially is built only by $GeSe_{4/2}$-tetrahedrons. With the addition of Sb₂Te₃ the structure becomes denser due to the build-

tem from one relatively stable condition as a result of ongoing crystallization inevitably leads to decrease of the glasses stability and from there to decrease of the crystallization temperature. It has to be marked, that at the compositions, corresponding to p. 2 and 5, 2 exothermal effects of crystallization are observed. This is not by chance, since these compositions are situated near the outline, tracing the glass forming region. The nearness of the crystallization temperatures of the "high temperature" effects (328 and 304 °C) of p. 2 and 5, as well as the coincidence of the T_{cr} of the "low temperature" effects (246 °C) of the same points, make us assume that the crystallizing phases in these two samples are near or equal by composition. The higher crystallization temperature could be related to the crystallization of the Sb₂SeTe₂ phase, proven in our previous

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works on this system[9,14]. Most probably, the second phase crystallizing at the lower temperature is elemental alloy from the Te-Se system, rich of Te.

The melting temperature (T_m) of the samples containing 10 mol % $PbSb_2Te_4$ (z=10) lightly increases with the increase of m – TABLE 1. The second endothermal effect at T_m=477 °C is most probably related to the existence of an eutectic in the $GeSe_2$-Sb_2Te_3 system, reported by Surinach et al.[17]. Since the thermal analysis was led up to 750 °C and taking into account the fact that the $GeSe_2$ compound melts at 740 °C and the compounds, which could be formed as a result of the high temperature processes passing in the melt, are with lower melting temperature, one can say that all endothermal effects connected to T_m do not refer to "pure" chemical compounds, but to solid solutions. This strongly bothers the addressing of a given melting temperature to defined crystallized phase. Analyzing the path of the obtained $T_m(m)_{z=10}$ dependence one can say that the addition of any of the possibly existing phases in this system - GeSeTe $(T_m \sim 650$ °C); GeSe $(T_m$=675 °C); Sb_2Te_3 $(T_m$=620°C), $PbSb_2Te_4$ $(T_m$=637 °C), will lead to decrease of the T_m of the glasses. We do not take into account the influence of the PbTe, which has higher melting temperature than this of $GeSe_2$, since the PbTe content is constant. This leads to the conclusion that the T_m increase with the increase of m is most probably related to the peculiarities of the liquidus line in the $GeSe_2$-Sb_2Te_3-$PbSb_2Te_4$ system, as well as to the formation of an intermediate phase with melting temperature a little bit higher than this of the $GeSe_2$.

The influence of $PbSb_2Te_4$ in the $T_m(z)_{m=0.1}$ dependence is even more complicated, since with the approaching of the compositions towards the border, limiting the glass forming region conditions for crystallization of more than one phase are created. In this case the phases are two and their temperatures have "logical" values – lower than T_m of the composition, corresponding to p.3.

On the thermogram of the sample with composition, corresponding to p. 5, one more effect is observed, which coincides to an effect of p. 2. If we exclude this endothermal effect, which was related above to the closeness of this composition to the eutectic in the $GeSe_2$-Sb_2Te_3 system, the path of the $T_m(z)_{m=0.1}$ dependence is logical as far as it is typical for the melting effects of "solid solutions" (in this case we make analogy to a solid solution with the same composition as the glass). For this time it is hard to relate these melting temperatures to the composition of a current phase. In any case, this phase will obligatory contain the components of these eventual compounds, whose melting temperature is lower than the melting temperature of $GeSe_2$ (GeSeTe, GeSe, Sb_2Te_3, as well as eventually this of Se and/or Te).

The Hruby's criterion K_G characterizes the ability of a given composition to pass into glassy state. For calculation of K_G the higher values of T_{cr} and T_m have been used. With the increase of the Sb_2Te_3 at constant $PbSb_2Te_4$ content (z=10), the Hruby's criterion lightly decreases, as at m>0.1 a tendency towards saturation is observed – TABLE 1. The behavior of the $K_G(z)_{m=0.1}$ dependence is analogical - K_G decreases with a tendency towards saturation at z>10. The path of these two dependencies is logical, since with the increase of m, respectively of z, the composition of the chalcogenide glasses approaches the glass forming border.

The obtained values of the density d of the samples from the $GeSe_2$-Sb_2Te_3-$PbSb_2Te_4$ system (TABLE 2) fall between the values of the initial components densities ($d_{GeSe_2} = 4.34$ g.cm^{-3}[6], $d_{Sb_2Te_3} = 6.57$ g.cm^{-3}[18] and $d_{PbSb_2Te_4} = 7.5$ g.cm^{-3}[19]).

TABLE 2 : Density d, compactness C, microhardness HV, elasticity modulus E and thermomechanical characteristics (V_h and E_h) of glassy samples from the $GeSe_2$-Sb_2Te_3-$PbSb_2Te_4$ system

№	z	m	d, g/cm³	C	HV, kgf/mm²	E, GPa	$V_h.10^{-3}$, nm³	E_h, kJ/mol
20	0	0.1	4.498	-0.0451	95	13.97	0.0268	15.02
12	10	0	4.530	-0.0954	109	16.02	0.0222	14.31
18	10	0.05	4.648	-0.0958	94	13.82	0.0273	15.17
3	10	0.1	4.745	-0.0988	83	12.20	0.0315	15.44
2	10	0.2	5.046	-0.0816	80	11.76	0.0309	14.58
5	20	0.1	4.925	-0.1375	67	9.85	0.0351	13.86

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In the $d(m)_{z=10}$ and $d(z)_{m=0,1}$ dependences the density increases (TABLE 2) This is related to the different density values of the initial components Sb_2Te_3 and $PbSb_2Te_4$.

The compactness C does not depend in practice on the composition up to $m \le 0.10$ and weakly increases with the change of m from 0.10 to 0.20. The search of correlation between the $d(m)$ and $C(m)$ dependencies at z=const is impeded to a large degree due to the physicochemical properties of the initial component $PbSb_2Te_4$, which melts incongruently and it is absolutely possible that during the synthesis of the glasses it "masks" the influence of the composition on the density.

The decomposition (partial or full) of $PbSb_2Te_4$ by the scheme $PbSb_2Te_4 \rightarrow PbTe+Sb_2Te_3$ leads to increase of the total quantity of Sb_2Te_3, which cannot be left non-reflected in the $d(m)$ and $C(m)$ dependencies at z=const. Furthermore, instead of talking about analysis of the $PbSb_2Te_4$ influence, one should talk about influence of PbTe on the glasses characteristics. Besides, both $PbSb_2Te_4$ and PbTe possess high molecular mass and they can participate, and most probably participate, with structural units $SbTe_{3/2}$ and linear fragments -Pb-Te-. This means that three factors will influence the path of the above-stated dependencies simultaneously in opposite directions: building of the linear fragments into the structure, as well as building of the trigonal pyramids $SbTe_{3/2}$, which by their side can lead to both increase or decrease of the micro-voids. Depending on which effect is limiting, the compactness C will increase (weakly or strongly) or will decrease. Evidence for this are the $C(m)_{z=10}$ and $C(z)_{m=0.1}$ dependencies (TABLE 2). In the first case the limiting influence on the C path has the densification of the structure under the impact of the building of the $SbTe_{3/2}$ pyramids into the $GeSe_{4/2}$ tetrahedrons. In the second case, limiting is the influence of the breakage of the Se-, Te- and (Se-Te)-bridges and the building of the linear -Pb-Te- fragments between the atoms of Se-, Te- or Se-Te.

The analysis of the $HV(m)_{z=10}$ and $HV(z)_{m=0.1}$ dependencies (TABLE 2) shows well expressed tendency towards decrease of the microhardness values with the increase of m (z=10) and z (m=0.1). This path of the concentration dependencies of HV is most probably related to the partial HV values of the initial components $GeSe_2$, $PbSb_2Te_4$ and Sb_2Te_3, which decrease in the same row: 100-200[6], 45[19] and 18 kgf/mm²[20], respectively.

The $E(m)_{z=10}$ and $E(z)_{m=0.1}$ dependencies have analogical path (TABLE 2), as in the first dependence a tendency towards saturation at m>0.1 is observed. This similar path of the concentration dependencies of HV and E is caused by their mutual relation in Eq. (3).

Two factors (T_g and HV) with opposite action influence the path of the concentration dependencies $V_h(m)_{z=10}$ and $V_h(z)_{m=0.1}$. They are directly connected to the glasses structure and influence simultaneously, according Eq. (4), the values of V_h – TABLE 2. Hence, the reasons, which lead to change of the concentration dependencies of HV and T_g, also reflect on the concentration path of V_h. The more important in this case is to mention, that in the $0.0 \le m \le 0.1$ interval, the T_g and HV act in one direction (T_g increases, while HV decreases) and according to Eq. (4) the micro-voids volume V_h increases. At m>0.1 T_g and HV act in opposite direction: the decrease of T_g leads to decrease of V_h and the decrease of HV leads to increase of V_h. The influence of the first factor (T_g) is limiting, which explains both the weak decrease of V_h and its saturation tendency. This means in practice that the system tends towards structural relaxation.

The $E_h(m)_{z=const}$ and $E_h(z)_{m=const}$ dependencies go over the path of the $T_g(m)_{z=10}$ and $T_g(z)_{m=0.1}$ dependencies, according to Eq. (5), going through maximum at m=0.1 and z=10, respectively – TABLE 2.

CONCLUSIONS

Chalcogenide glasses from the $GeSe_2$-Sb_2Te_3-$PbSb_2Te_4$ system were synthesized.

The temperatures of glass-transition (T_g), crystallization (T_{cr}) and melting (T_m), as well as the density d and the microhardness (HV) of the samples were measured by classical analysis methods. The characteristic temperatures T_g, T_{cr} and T_m vary between 193-246, 246-443 and 438-477 °C, respectively, and the path of their concentration dependencies is limited by a row of factors: the ratio between the structural units $GeSe_{4/2}$, $SbTe_{3/2}$ and $PbTe_{1/2}$; the closeness of the samples composition to the glass forming borders; the number and the kind of the crystallizing phases; the peculiarities of the liquidus line in the investigated system; the melting

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temperatures of the intermediate phases. The density values of the samples fall between these of the initial components, which together with the physicochemical specifics of the $PbSb_2Te_4$ dictate the path of the $d(m)_{z=10}$ and $d(z)_{m=0.1}$ dependencies. The path of the concentration dependencies of HV is related to the partial HV values of the initial components, the physicochemical properties of $PbSb_2Te_4$ and to above-counted factors, influencing the characteristic temperatures.

On the base of the experimental results from the measurements led, the Hruby's criterion K_G, the compactness C, the elasticity modulus E and the main thermomechanical characteristics (V_h and E_h) were calculated. The concentration dependencies of these characteristics were analyzed and discussed.

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REFERENCES

[1] N.Mehta; J.Sci.Ind.Res., **65**, 777 **(2006)**.
[2] Zakery; J.Non-Cryst.Solids, **330(1-3)**, 1 **(2003)**.
[3] X.Zhang, H.Ma, J.Lucas; J.Optoelectron.Adv.Mater., **5(5)**, 1327 **(2003)**.
[4] Quémard, F.Smektala, V.Couderc, A.Barthélémy, J.Lucas; J.Phys.Chem.Solids, **62**, 1435 **(2001)**.
[5] M.Frumar, B.Frumarova, P.Nemec, T.Wagner, J.Jedelsky, M.Hrdlicka; J.Non-Cryst.Solids, **352**, 544 **(2006)**.
[6] Z.U.Borisova; Halkogenidnie poluprovodnikovie stekla, Leningr.un-ta, Leningrad, in Russian, **(1983)**.
[7] G.Z.Vinogradova; Stekloobrazovanie I fazovie ravovesia v halkogenidnih sistemah, Nauka, Moskva, in Russian, **(1984)**.
[8] N.H.Abrikosov, et al.; Poluprovodnikovie halkogenidia i splavia na ih osnove, Nauka, Moskva, in Russian, **(1975)**.
[9] L.Aljihmani, V.Vassilev, T.Hristova-Vasileva; Rev.Metall., **109**, 21 **(2012)**.
[10] L.E.Shelimova, T.E.Svechnikova, P.P.Konstantinov, O.G.Karpinskii, E.S.Avilov, M.A.Kretova, V.S.Zemskov; Thermoelectric Properties of Layered Anisotropic p-type $PbSb_2Te_4$ Compound and Peculiarities of its Energy Spectrum, Presented at 5th European Conference on Thermoelectrics, Odessa (Ukraine), September 10-12, **(2007)**.
[11] L.E.Shelimova, O.G.Karpinskii, T.E.Svechnikova, I.Yu.Nihezina, E.S.Avilov, M.A.Kretova, V.S.Zemskov; Inorg.Mater., in Russian, **44(4)**, 436 **(2008)**.
[12] D.M.Freik, N.I.Dikun, V.M.Boichuk, R.I.Zapuhliak; J.Phys.Chem.Solid State, in Ukrainian, **10(4)**, 872 **(2009)**.
[13] L.E.Shelimova, T.E.Svechnikova, P.P.Konstantinov, O.G.Karpinskii, E.S.Avilov, M.A.Kråtova, V.S.Zemskov; The n- and p-type Mixed Layered Thetradimite-like Compounds with Low Lattice Thermal Conductivity: Growth, Structure and Thermoelectric Properties, Proceedings 2nd European Conference on Thermoelectrics, Krakow, 202-207 **(2004)**.
[14] L.Aljihmani, T.Hristova-Vasileva, V.Vassilev; J.Tech.Univ.Plovdiv, Fundamental Sciences And Applications, **16(2)**, 159 **(2011)**.
[15] L.Aljihmani, V.Vassilev, P.Petkov; J.Optoelectron.Adv.Mater., **5(5)**, 1187 **(2003)**.
[16] V.Vassilev, G.Vassilev, E.Fidancevska; Chalcogen. Lett., **5(2)**, 415 **(2008)**.
[17] S.Surinach, M.D.Baro, M.T.Clavaguera-Mora, N.Clavaguera; Thermochim.Acta, **133**, 287 **(1988)**.
[18] CRC Handbook of Chemistry and Physics; Internet version 2005, David R.Lide, (Ed); http://www.hbcpnetbase.com, CRC Press, Boca Raton, FL, **(2005)**.
[19] V.Vasilev, D.Atanasova, I.Mihailova, V.Parvanova, L.Aljihmani; Thermochim.Acta, **520**, 80 **(2011)**.
[20] V.Vassilev, M.Radonova, E.Fidancevska, S.Boycheva; Basic physicochemical properties of glasses in the $GeSe_2$-Sb_2Te_3-CdSe system, Proceedings 7th International Scientific Conference Unitech '07, Gabrovo, 23-24 November, **2**, II-365 **(2007)**.