Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 7 (21): 3167-3176, 2007
ISSN 1812-5654

Estimation of Glass-Forming Ability and Glass Stability of Sb_2S_3-As_2S_3-Sb_2Te_3 Glasses by Thermal Properties

[1]K. N'Dri, [1]J. Sei, [1]D. Houphouët-Boigny, [1]G. Kra and [2]J.C. Jumas
[1]Laboratoire de Chimie des Matériaux Inorganiques, UFR-SSMT,
Université de Cocody, 22 B.P 582 Abidjan 22, Côte d'Ivoire
[2]Laboratoire des Agrégats Moléculaires et des Matériaux Inorganiques, CNRS ESA 5072,
Université Montpellier II, Place Eugène Bataillon, F-34095 Montpellier Cedex 5, France

Abstract: Glass forming ability parameters defined by $T_{rg} = T_g/T_m$ and $K_h = (T_x^h - T_g)/(T_m - T_x^h)$, glass stability parameters such as $K_w = (T_x^h - T_g)/T_m$, $\Delta T = T_x^h - T_g$ and $K_{ll} = T_x^h/(T_g+T_m)$ and the degree of undercooling $\Delta T_r = (T_m - T)/T_m$ are analysed for glasses of the ternary system Sb_2S_3-As_2S_3-Sb_2Te_3 as function of the As_2S_3 concentration. These parameters are formulated by different combinations of the following characteristic Differential Scanning Calorimetry (DSC) temperatures: the glass transition temperature (T_g), the onset crystallization temperature (T_x^h), the peak crystallization temperature (T_c^h) and the melting temperature (T_m). Variations of the above parameters indicate that the studied glasses can vitrify easily and become increasingly stable when the concentration of As_2S_3 increases. Good correlations between ΔT_r and K_h and between ΔT_r and parameters (K_w, ΔT and K_{ll}), are found implying a low frequency of homogeneous nucleation in the thermally stable glasses. The degree of undercooling ΔT_r is an important parameter for the glass forming ability and the glass stability of Sb_2S_3-Sb_2Te_3-As_2S_3 glasses.

Key words: Glass transition temperature, crystallization temperature, melting temperature, glass forming ability, glass stability, degree of undercooling

INTRODUCTION

The ability of substances to vitrify on cooling from the melt is known as glass-forming ability (GFA). Glass formation of materials containing one or more elements sulphur (S), selenium (Se) or tellurium (Te) in combination with elements from IVth and Vth group of the periodic table is relatively easy. Many kinds of these materials have been prepared by means of melt quenching method (Saffarini and Saiter, 2006; Repkova *et al*., 2006; Singh *et al*., 2006; Soliman and El-Den, 2007; El-Mokhtar, 2007). Several parameters or criteria have been proposed to reflect the relative GFA among bulk glasses on the basis of different calculation methods (Lu and Liu, 2002, 2003). One is the reduced glass transition temperature $T_{rg} = T_g/T_m$ which is the ratio between the glass transition temperature T_g and the melting temperature T_m of the corresponding glass-forming system (Kumar *et al*., 2006; Chol-Lyong *et al*., 2006). Another parameter $K_h = (T_x^h - T_g)/(T_m - T_x^h)$, where T_x^h is the onset crystallization temperature, is also used as a measure of the glass-forming tendency of materials by Farid (2002), Aljihmani *et al*. (2003) and Nikhil Sur *et al*. (2006).

Once a glass is made for instance by fast quenching a melt, its stability can be easily investigated. Thus the supercooled liquid range $\Delta T = T_x^h - T_g$ (Kumar *et al*., 2006), the parameter $K_w = (T_x^h - T_g)/T_m$ (Avramov *et al*., 2003; Nasciemento *et al*., 2005) and a new criterion $K_{ll} = T_x^h/(T_g+T_m)$ of Lu and Liu (2002, 2003) are used to evaluate the glass stability against crystallization on heating.

The thermal stability of the metastable supercooled liquid obtained at temperatures between T_g and T_m or liquids temperature T_l can be discussed from the kinetics aspect because it would be informative. In supercooled liquids, the frequency of homogeneous nucleation depends on the degree of undercooling $\Delta T_r = (T_m - T)/T_m$ as predicted by the classical theory of homogeneous nucleation.

The aim of this study is to calculate the values and interpret the variations of the glass-forming parameters (T_{rg} and K_h), the glass stability parameters (ΔT, K_h and K_{ll}) and the degree of undercooling (ΔT_r) for vitreous samples of the ternary system Sb_2S_3-As_2S_3-Sb_2Te_3 as function of As_2S_3 concentration. Correlations between these parameters will be made in order to show the importance

Corresponding Author: K. N'Dri, Laboratoire de Chimie des Matériaux Inorganiques, UFR-SSMT, Université de Cocody, 22 B.P 582 Abidjan 22, Côte d'Ivoire

of the degree of undercooling for glass forming ability and glass stability and a possible relationship between glass-forming ability and glass stability for glasses of the above system will be verified.

MATERIALS AND METHODS

Glasses of Sb_2S_3-As_2S_3-Sb_2Te_3 system were prepared by our vitreous semiconductors group in «Laboratoire de Chimie des Matériaux Inorganiques», by direct synthesis from pure starting elements such as As, Sb, Te and S. Quartz ampoules were filled with ~ 0.3 g of the mixed elements and then evacuated to $\sim 10^{-3}$ torr, sealed and heated to 900°C at the rate of 1°C min^{-1}. The tubes were held at this temperature for 24 h and quenched in ice-water. The glassy state in the quenched samples was confirmed by X-ray diffraction (as no sharp peak was observed) at room temperature using the Cu-Kα radiation (λ =1.5405 Å). The shaded area representing the domain of glass formation in the Sb_2S_3-As_2S_3-Sb_2Te_3 system is shown in Fig. 1.

The thermal characteristic temperatures such as the glass transition temperature (T_g), the onset crystallization temperature (T_x^h), the peak crystallization temperature (T_c^h) and the melting temperature (T_m) were measured in «Laboratoire des Agrégats Moléculaires et des Matériaux Inorganiques», by using DSC 121 Setaram apparatus at a heating rate of 5°C mn^{-1} in the studied temperature range (from 25 to 650°C). For studied glasses of the ternary system Sb_2S_3-Sb_2Te-As_2S_3, glass-forming ability was estimated using the following numerical parameters: The reduced glass transition temperature, $T_{rg}= T_g/T_m$ and $K_h(T_x^h) = (T_x^h - T_g^h)/(T_m^h - T_x^h)$ or $K_h(T_c^h) = (T_c^h - T_g)/(T_m - T_c^h)$ parameters. The glass stability parameters were also estimated by $K_w(T_x^h) = (T_x^h - T_g)/T_m$ or $K_w(T_c^h) = (T_c^h - T_g)/T_m$, $K_{ll}(T_x^h) = T_x^h/(T_g+T_m)$ or $K_{ll}(T_c^h) = T_c^h/(T_g+T_m)$ and $\Delta T(T_x^h) = T_x^h - T_g$. The degree of undercooling was evaluated by $\Delta T_r(T_x^h) = (T_m - T_x^h)/T_m$ (Komatsu *et al*., 1997). In this study we alternatively substitute T_x^h and T_c^h (except for $\Delta T_r(T_x^h)$ and $\Delta T(T_x^h)$) and calculate the values of glass-forming ability and glass stability parameters given by above expressions and analysis will be made for them.

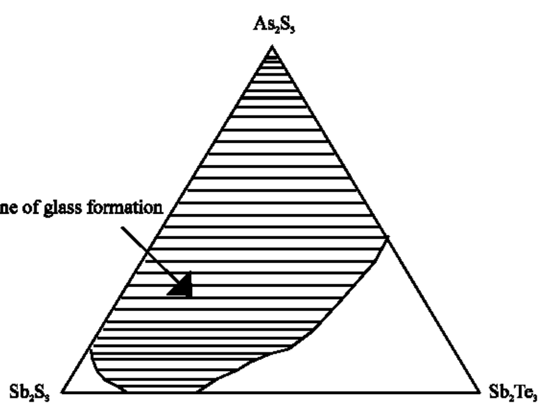

Fig. 1: Zone of glass formation in the Sb_2S_3-Sb_2Te_3-As_2S_3 system

RESULTS AND DISCUSSION

Positions of the glasses with their numbering used throughout this study are shown in (Fig. 2). Several glasses of Sb_2S_3-As_2S_3 (0 mol% Sb_2Te_3) binary system and a series of samples with the constant Sb_2Te_3 concentration of 20 mol% in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system were investigated by Differential Scanning Calorimetry (DSC) Table 1.

Glass-forming ability parameters: Using the data shown in Table 1, the reduced glass transition temperature (T_{rg}) values for glasses of Sb_2S_3-As_2S_3 system increase from 0.607 (10 mol% As_2S_3) to 0.714 (50 mol% As_2S_3). T_{rg} calculation is not possible for some glasses of this system having As_2S_3 concentration beyond 50 mol% because of the absence of the melting temperature T_m. On the ternary system Sb_2S_3-As_2S_3-Sb_2Te_3 with a constant concentration of 20 mol% Sb_2Te_3, the evolution of T_{rg} is not linear. T_{rg} has an optimal value equal to 0.765 (30 mol% As_2S_3) and decreased values are observed when increasing As_2S_3 concentration is up 30 mol% (Table 1).

The parameters $K_h(T_x^h)$ and $K_h(T_c^h)$, calculated with the onset and peak crystallization temperatures T_x^h and T_c^h, respectively (Table 1), increase from 0.039 to 0.710 on Sb_2S_3-As_2S_3 system (Fig. 3). But $K_h(T_x^h)$ and $K_h(T_c^h)$ can not be calculated when As_2S_3 concentration is beyond 50% because glasses exhibit no crystallization temperature. The crystallization and melting temperatures absence has been observed in the Sb_2S_3-As_2S_3 system by Durand *et al*. (1997) and in other systems such as Ge-Se-

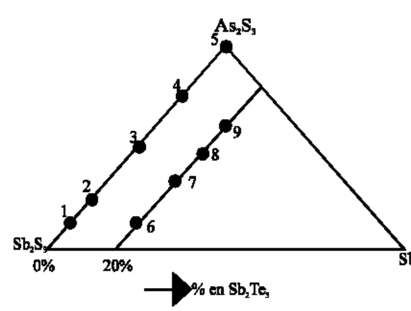

Fig. 2: Positions within the Sb_2S_3-Sb_2Te_3-As_2S_3 ternary system

Table 1: Composition of glasses, thermal properties (T_g, T_x^h, T_c^h and T_m) from DSC curves, values of glass forming ability parameters (T_{rg}, K_h (T_x^h) or K_h (T_c^h)), values of glass stability parameters (K_w (T_x^h) or K_w (T_c^h), (K_{ll} (T_x^h) or K_{ll} (T_c^h) and ΔT (T_c^h)) and degree of undercooling ΔT_r (T_x^h) for studied glasses and the ternary system Sb_2S_3-As_2S_3-Sb_2Te_3

Glasses	1	2	3	4	5	6	7	8	9
Sb_2Te_3 (%)	0.000	0.000	0.000	0	0	20.000	20.000	20.000	20.000
Sb_2S_3 (%)	90.000	75.000	50.000	25	0	70.000	50.000	35.000	20.000
As_2S_3 (%)	10.000	25.000	50.000	75	100	10.000	30.000	45.000	60.000
T_g (K)	493.000	491.000	487.000	485	487	471.000	470.000	466.000	461.000
T_x^h (K)	505.000	529.000	568.000	---	---	476.000	508.000	523.000	532.000
T_c^h (K)	516.000	532.000	584.000	---	---	491.000	519.000	527.000	542.000
T_m (K)	812.000	765.000	682.000	---	---	750.000	614.000	620.000	618.000
T_{rg}	0.607	0.642	0.714	---	---	0.628	0.765	0.752	0.746
K_h (T^h_x)	0.039	0.161	0.710	---	---	0.018	0.358	0.587	0.826
K_h (T^h_c)	0.077	0.176	0.990	---	---	0.077	0.516	0.656	1.066
K_w (T^h_x)	0.015	0.049	0.118	---	---	0.007	0.062	0.092	0.115
K_w (T^h_c)	0.028	0.054	0.142	---	---	0.027	0.080	0.098	0.131
K_{ll} (T^h_x)	0.387	0.421	0.486	---	---	0.390	0.468	0.482	0.493
K_{ll} (T^h_c)	0.395	0.423	0.500	---	---	0.402	0.478	0.485	0.502
ΔT (T^h_x) (K)	12.000	38.000	81.000	---	---	05.000	38.000	57.000	71.000
ΔT_r (T^h_x)	0.378	0.308	0.167	---	---	0.365	0.173	0.156	0.139

---: Absence of thermal properties (T_g, T_x^h, T_c^h and T_m) from DSC curves, values of glass- forming ability parameters (T_{rg}, K_h (T_x^h) or K_h (T_c^h)) and those of glass stability parameters (K_w (T_x^h) or K_w (T_c^h), (K_{ll} (T_x^h) or K_{ll} (T_c^h) and ΔT (T_x^h)) and value of degree of undercooling ΔT_{rg} (T_x^h) can't be calculated

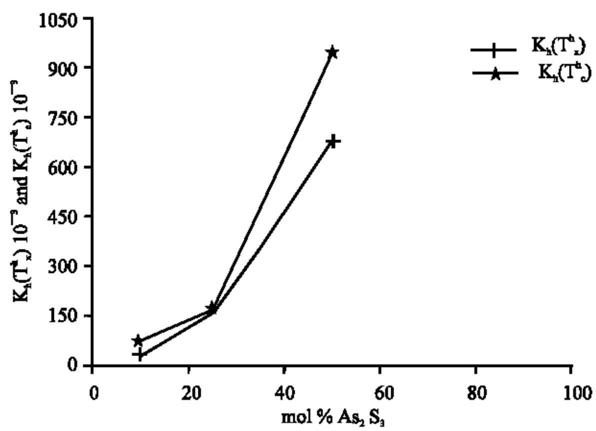

Fig. 3: Variation of K_h (T_x^h) and K_h (T_c^h) with the As_2S_3 concentration in the Sb_2S_3-As_2S_3 binary system

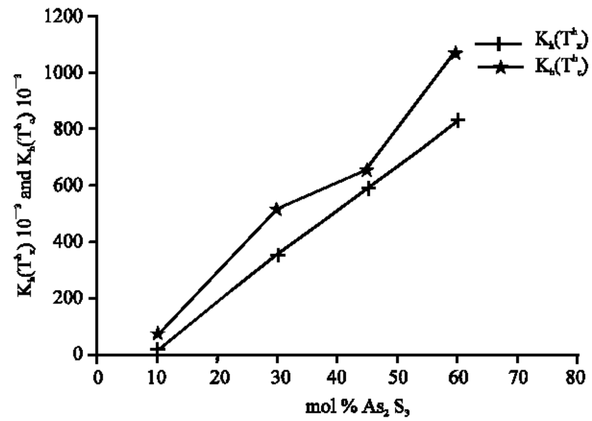

Fig. 4: Variation of K_h (T_x^h) and K_h (T_c^h) with the As_2S_3 concentration in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 20 mol%

Te-Sn, Sb-Se-Ge-Ga and $TeSe_3IAs_4$ by Feng *et al.* (1999) and Jean-Luc Adam (2001), respectively. The glass-forming ability of Sb_2S_3-As_2S_3 glasses having As_2S_3 concentration beyond 50 mol% is higher than GFA of their counterparts of the aforesaid system because they do not exhibit any crystallization and melting temperature (Table 1). The absence of these thermal characteristics can be associated with the glass-forming ability because glass without crystallization temperature can be a good glass former and can have a good glass-forming ability. For Sb_2S_3-As_2S_3-Sb_2Te_3 glasses containing a constant Sb_2Te_3 concentration of 20 mol%, K_h (T_x^h) and K_h (T_c^h) parameters increase from 0.018 to 0.826 and from 0.077 to 1.066, respectively as shown in Fig. 4. In spite of the differences between the values of K_h (T_x^h) and K_h (T_c^h), they show similar trends in all studied cases (Fig. 3, 4). even if values of K_h (T_c^h) are higher than those of K_h (T_x^h).

Variations in T_{rg} and K_h parameters are largely due to the variations in the thermal properties of glasses. These parameters seem to depend on compositions. Even if T_{rg} does not give the width of the temperature interval it also determines how close to the liquidus temperature the decreasing mobility in the liquid starts to reduce the nucleation rate. T_{rg} plays a crucial role in determining the glass-forming ability of an alloy because the higher is the ratio, the higher is the Glass-Forming Ability (GFA) according Uhlmann (1977) and Davies (1975). It has been confirmed that T_{rg} = 2/3, the two thirds rule, holds well generally for wide variety of inorganic glass forming substances (Sakka and Mackenzie, 1971). Thus for the liquids having T_{rg} equal to or more raised than 2/3, the formation of glasses would be easy because it leads to low nucleation rates. As pointed out by Turnbull (1969), these liquids are good glass formers. It is clearly shown that the two thirds rule holds well for the studied glasses of Sb_2S_3-As_2S_3-Sb_2Te_3 system.

The increase of $K_h(T_x^h)$, $K_h(T_c^h)$ and T_{rg} (except of T_{rg} of 20% Sb_2Te_3) with increasing As_2S_3 concentration can enable to suggest that As_2S_3 (covalent compound) incorporation supports the Glass-Forming Ability (GFA). In other words, GFA increases with increase in As_2S_3 concentration. For these glasses $K_h(T_x^h)$, $K_h(T_c^h)$ and T_{rg} reflect the GFA effectively. GFA in the Sb_2S_3-As_2S_3-Sb_2Te_3 system is conditioned by the presence of a glass forming compound As_2S_3. This indicates that As_2S_3 glass is the best glass forming system among the vitreous samples of the above system. There is in this case an obvious correlation between covalence and glass-forming ability. It is possible to suggest that the presence of covalent bondings gives flexibility (elasticity) to the structure that is a necessary factor for the topological disordering of the structure during glass formation. The enough large flexibility that permits to the elementary components (atoms, cations, coordination polyhedra) to occupy different positions one relative to another, which fact does not create long range order and does not lead to the simultaneous appearance of strains, that destroy the structure, gives the ability to oxide and chalcogenide systems to form glasses. T_{rg} evolution of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses containing 20 mol% Sb_2Te_3 is not linear like $K_h(T_x^h)$, $K_h(T_c^h)$ and T_{rg} seen above. For these glasses, T_{rg} cannot reflect the GFA. This behaviour was found in many bulk metallic glasses (Lu and Liu, 2002) and phosphate glass systems (Ouchetto *et al*., 1991).

Glass stability parameters: In this study, values of the supercooled liquid region $\Delta T(T_x^h)$, $K_w(T_c^h)$ or $K_w(T_x^h)$ parameter and Lu-Liu parameter $K_{ll}(T_x^h)$ or $K_{ll}(T_c^h)$, used for stability assessment of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses, Table 1. Generally, the difference $\Delta T(T_x^h) = T_x^h - T_g$, gives a measure of thermal stability of the glass (Kamboj and Thangaraj, 2003). For the present study, its values are found to be in the range 12-81 K on the binary system Sb_2S_3-As_2S_3 and 05-71 K on the ternary system Sb_2S_3-As_2S_3-Sb_2Te_3 (containing 20 mol% Sb_2Te_3). Values of $K_w(T_x^h)$ or $K_w(T_c^h)$ parameters and Lu-Liu parameters $K_{ll}(T_x^h)$ or $K_{ll}(T_c^h)$ increase when As_2S_3 concentration increases on the binary system Sb_2S_3-As_2S_3 (Fig. 5, 6) and on the ternary system Sb_2S_3-As_2S_3-Sb_2Te_3 with 20 mol% Sb_2Te_3 (Fig. 7, 8). When the concentration of As_2S_3 is beyond 50 mol%, ΔT, K_w or K_{ll} can not be calculated for certain glasses of Sb_2S_3-As_2S_3 system because these glasses exhibit T_g but no crystallization temperature (Table 1). There is consequently no melting temperature

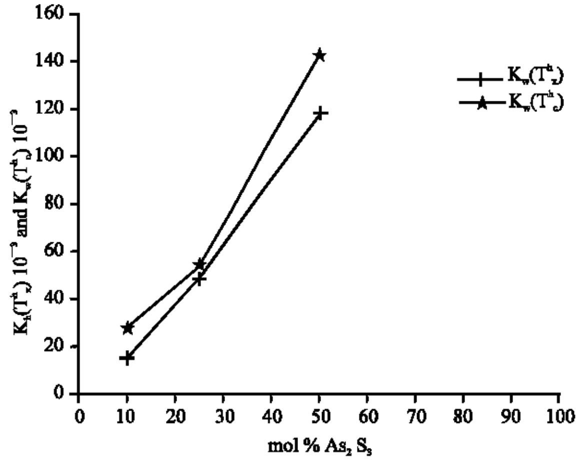

Fig. 5: Variation of $K_w(T_x^h)$ and $K_w(T_c^h)$ with the As_2S_3 concentration in the Sb_2S_3-As_2S_3 binary system

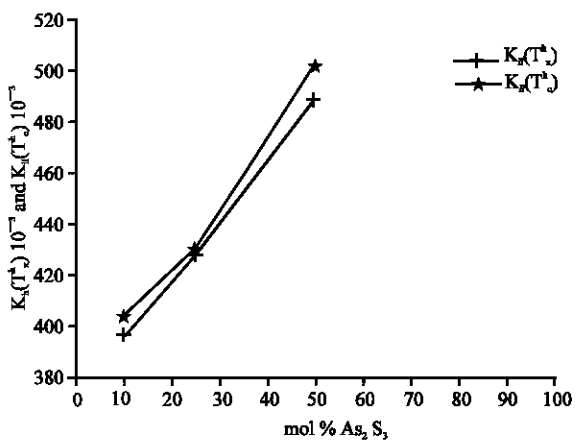

Fig. 6: Variation of $K_{ll}(T_x^h)$ and $K_{ll}(T_c^h)$ with the As_2S_3 concentration in the Sb_2S_3-As_2S_3 binary system

of the crystallized species. Very stable against devitrification, these glasses can be pulled into optical fibers (Jean Luc Adams, 2001). All values of $K_w(T_c^h)$ and $K_{ll}(T_c^h)$ obtained from (T_c^h) are superior to those of $K_w(T_x^h)$ and $K_{ll}(T_x^h)$ calculated with T_x^h. The alternative use of T_c^h instead of T_x^h in these expressions does not result in significant differences in these glass stability parameters. Even if K_w and K_{ll} obtained at T_c^h and T_x^h don't give the width of the temperature interval like $\Delta T(T_x^h)$, they can be suggested to represent the glass stability because they have similar trends when they are plotted versus As_2S_3 concentration (Fig. 5-8). It is obvious that the thermally stable glasses in the above systems are obtained when the As_2S_3 concentration increases. In other words, the thermal stability of these glasses against crystallization increases with increase in

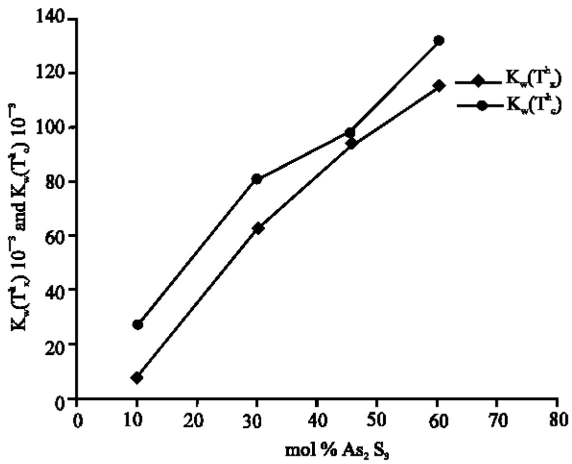

Fig. 7: Variation of K_w (T^h_x) and K_w (T^h_c) with the As_2S_3 concentration in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 20 mol%

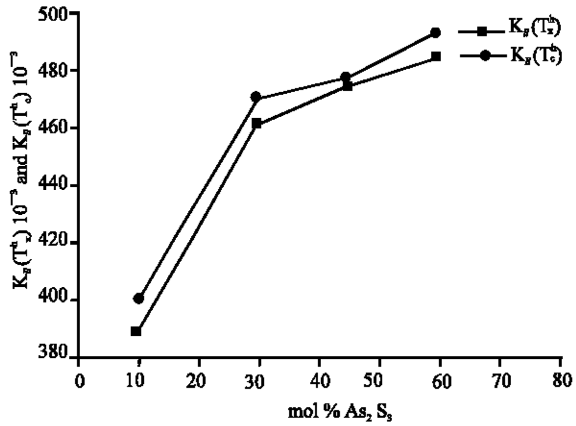

Fig. 8: Variation of $K_{//}$ (T^h_x) and $K_{//}$ (T^h_c) with the As_2S_3 concentration in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 20 mol%

As_2S_3 concentration. As can be shown in Table 1 the increases in ΔT (T^h_x) in the two systems mainly result from the increase of T^h_x . This implies that the added As_2S_3 acts effectively as an inhibitor of crystallization. The onset-crystallization T^h_x can serve as an important factor estimating the stability of glass (Hen *et al.*, 1991). On the other hand, it is reasonable to assign that As_2S_3, a covalent compound, acts as network breaking agents to decrease T_g and T_m because both of them decrease with increasing As_2S_3 concentration as shown in Table 1.

Increased values of $\Delta T(T_x^h)$ may indicate that the supercooled liquid can remain stable in a wide temperature range without crystallization. Thus, As_2S_3 incorporation has a stabilizing effect because ΔT (T_x^h) becomes wide when its concentration increases. It is desirable to have ΔT as large as possible in order to achieve a large working range during operations such as perform preparation for fibre drawing according Feng *et al.* (1999). The partial replacement of Sb_2S_3 (less covalent) by As_2S_3 (covalent), on Sb_2S_3-As_2S_3 and Sb_2S_3-As_2S_3-Sb_2Te_3 (with 20 mol% Sb_2Te_3) systems, can exhibit a predominantly character which increases the resistance of the glass to devitrification. Thus, As_2S_3 involves probably the formation of high stable network structure which may be due to the presence of covalent bondings. That means that As_2S_3 acts to increase the homogeneity of glass and strengthening the glass network. In the same time it acts to increase the covalence character by forming stable units which ensure effectively the stability of the glasses. According to a previous study (El-Idrissi Raghni *et al.*, 1995), the Raman and IR bands of Sb_2S_3-As_2S_3 glasses are attributed to AsS_3 and SbS_3, the trigonal pyramidal units in which As and Sb obey the 8-N rule (N is the number of electrons needed to complete its valence shell). Results of ^{121}Sb Mössbauer spectroscopy of 20 and 40 mol% Tl_2S sections of Sb_2S_3-As_2S_3-Tl_2S glasses (Durand *et al.*, 1997) and those of 10 mol% Sb_2Te_3 section of Sb_2Se_3-As_2Se_3-Sb_2Te_3 glasses (Leh Deli *et al.*, 2005), indicate that the isomer shifts are negative in all vitreous compounds studied by the above researchers. These isomer shifts are found to be between -5.06 and -4.56 mm sec^{-1} for Sb_2S_3-As_2S_3-Tl_2S glasses and between -5.16 and -4.79 mm sec^{-1} for those of Sb_2Se_3-As_2Se_3-Sb_2Te_3. Antimony (Sb) in these glasses exists only as Sb(III) species. So its coordination is pyramidal (SbS_3). As there is no available information on the structure of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses containing a constant concentration of 20 mol% Sb_2Te_3, we can suggest that these glasses also consist of mixed glass networks with the combination of SbS_3 and AsS_3, the trigonal pyramidal units as seen in the case of Sb_2S_3-As_2S_3 glasses. There is obvious correlation between covalence and glass stability.

Degree of undercooling parameter: The calculated values of $\Delta T_r(T_x^h)$ at the onset crystallization temperature (T_x^h) for examined glasses, are shown in Table 1. It is indicated that ΔT_r (T_x^h) values depend on the thermal characteristics such as T^h_x and T_m. T^h_x increases but T_m decreases when As_2S_3 concentration increases on Sb_2S_3-As_2S_3 binary system and on 20 mol% Sb_2Te_3 section of Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system. As indicated in Fig. 9 and 10, T_x^h decreasing and T_m increasing imply the increasing of ΔT_r (T_x^h). So at the higher value of T^h_x (lower value of T_m) in each system, corresponds to the smaller value of ΔT_r (T_x^h) and a small undercooled region $(T_m$-$T_x^h)$ is observed. At the smaller value of T^h_x (higher value of T_m) corresponds to the higher value of ΔT_r (T_x^h) and a

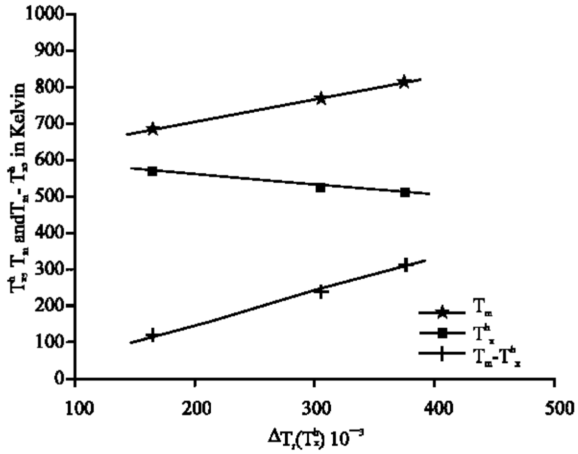

Fig. 9: Evolution of the onset crystallization temperature T^h_x, the melting temperature T_m and the undercooled liquid region T_m- T^h_x versus the degree of undercooling Δt_r (T^h_x) on the Sb_2S_3-As_2S_3 binary system

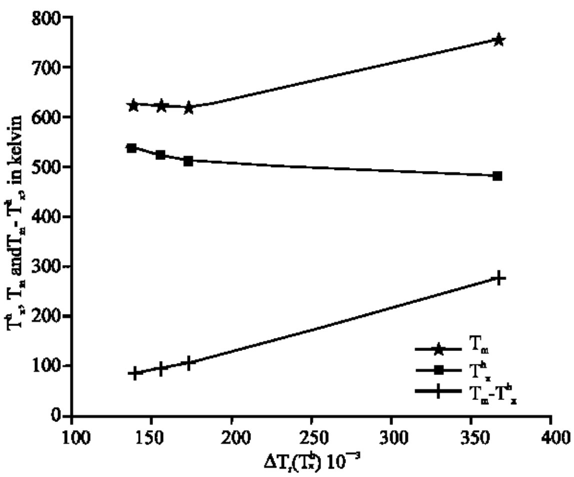

Fig. 10: Evolution of the onset crystallization temperature T_x^h, the melting temperature T_m and the undercooled liquid region T_m-T_x^h versus the degree of undercooling ΔT_r (T^h_x) on the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 20 mol%

wide undercooled region is also observed. The degree of undercooling depends on the extended undercooled region which depends on T_x^h and T_m. The variation of the degree of undercooling, ΔT_r (T_x^h), as a function of As_2S_3 concentration is shown in Fig. 11. ΔT_r (T_x^h) decreases linearly on Sb_2S_3-As_2S_3 system but it decreases exponentially on the Sb_2S_3-As_2S_3-Sb_2Te_3 (containing 20 mol% Sb_2Te_3) with increasing of As_2S_3 concentration. In the two cases, it is seen that small values of ΔT_r (T^h_x)

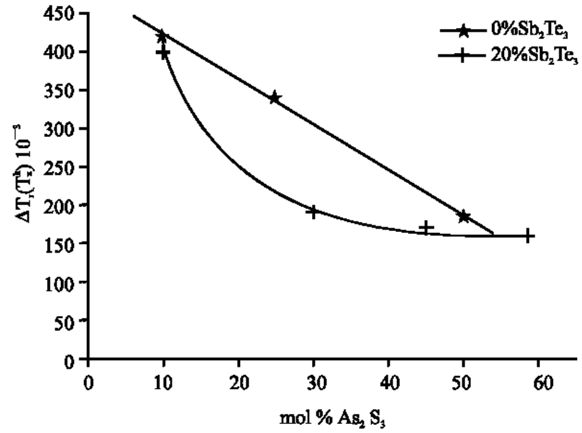

Fig. 11: Variation of ΔT_r (T^h_x) with the As_2S_3 concentration in the Sb_2S_3-$A_{s2}S_3$-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentrations of 0 and 20 mol%

are obtained when the concentration of As_2S_3 increases. The decreased values of ΔT_r (T^h_x) can be explained by progressive substitution of Sb_2S_3 by As_2S_3 as it is seen above in the cases of glass-forming ability and glass stability. Thus, added As_2S_3 can diminish the degree of undercooling and the undercooled region. These results imply that the glasses with high concentration of As_2S_3 have a possibility of a low frequency of homogeneous nucleation because ΔT_r (T^h_x) decreases in respect to the classical theory of homogenous nucleation. A similar trend was reported in (30-x)K_2O-xNb_2O_5-70TeO_2 glasses (Komatsu *et al*., 1997) when Nb_2O_5 concentration increases.

Correlations between the degree of undercooling, glass-forming ability and glass stability: Similar trends were observed when glass-forming parameters (K_h (T^h_c), K_h (T^h_x)) and glass-stability parameters (K_w (T^h_x or T^h_c) and K_{ll} (T^h_x or T^h_c) are plotted versus As_2S_3 concentration. So, we will use only values of K_w (T^h_c) and K_{ll} (T^h_c) obtained with T^h_c temperature during correlations in which these parameters are used.

Correlation between ΔT_r (T^h_x) and K_h(T^h_x), for studied glasses containing 0 and 20 mol% Sb_2Te_3, is shown in Fig. 12 which indicates that ΔT_r (T^h_x) decreases when K_h (T^h_c) increases. The same behaviour is observed between ΔT_r (T^h_x) and the other glass-forming ability parameter T_{rg} (Fig. 13) of Sb_2S_3-As_2S_3 (0 mol% Sb_2Te_3) binary system. In other words, the frequency of homogeneous nucleation becomes lower when GFA becomes higher. According to Nasciemento *et al.* (2005), a high glass forming ability is associated with slow crystallization rate. From this assertion, it can be

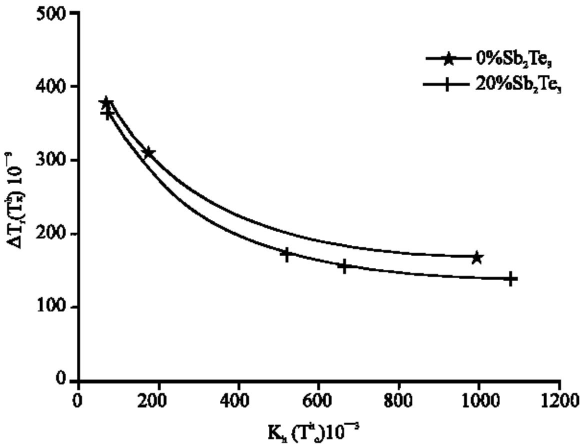

Fig. 12: Correlation between $\Delta T_r(T_x^h)$ and $K_h(T_c^h)$ in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentrations of 0 and 20 mol%

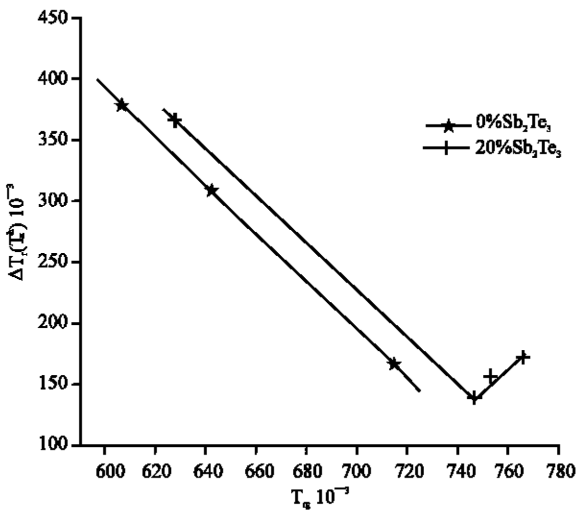

Fig. 13: Correlation between $\Delta T_r(T_x^h)$ and T_{rg} in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentrations of 0 and 20 mol%

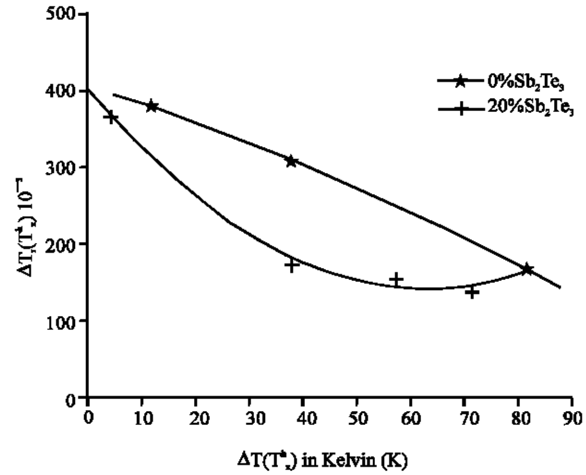

Fig. 14: Correlation between $\Delta T_r(T_x^h)$ and $\Delta T(T_x^h)$ in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentrations of 0 and 20 mol%

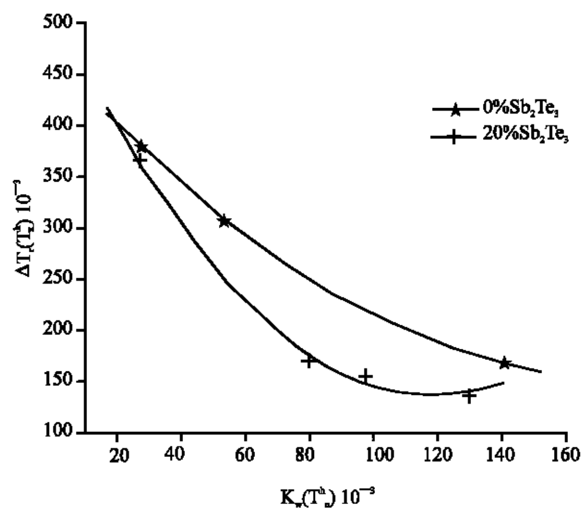

Fig. 15: Correlation between $\Delta T_r(T_x^h)$ and $K_w(T_c^h)$ in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentrations of 0 and 20 mol%

suggested that an undercooled liquid having high glass-forming ability (high value of $K_h(T_c^h)$ or T_{rg}) can be a good glass forming material. Because it can be easily quenched into a glass by using small cooling rate. But an undercooled liquid having small glass-forming ability (low value of $K_h(T_c^h)$ or T_{rg}) cannot be a good glass-forming material. Because it requires high cooling rate to be quenched into a glass. For the studied glasses, $\Delta T_r(T_x^h)$ can be an important parameter for the glass-forming ability because a good correlation is obtained.

Correlation between $\Delta T_r(T_x^h)$ and $\Delta T(T_x^h)$ of glasses with 0 and 20 mol% Sb_2Te_3 shows that $\Delta T_r(T_x^h)$ decreases when $\Delta T(T_x^h)$ increases (Fig. 14). Supercooled liquid having wide supercooled liquid region ($\Delta T(T_x^h)$ is wide) is characterized by a low degree of undercooling (($\Delta T_r(T_x^h)$ is low). That means that the supercooled liquid is stable in wide temperature range without crystallization and with high resistance to the nucleation and growth of crystalline phases (Kapaklis *et al.*, 2003). The same behaviour is observed when $\Delta T_r(T_x^h)$ is correlated with the other glass stability parameters such as $K_w(T_c^h)$ and $K_{//}(T_c^h)$ (Fig. 15 and 16). At the higher values of $\Delta T(T_x^h)$, $K_w(T_c^h)$ and $K_{//}(T_c^h)$ corresponds with lower value of $\Delta T_r(T_x^h)$. Thus, when the glass stability parameters become higher, the frequency of homogeneous nucleation becomes lower ($\Delta T_r(T_x^h)$ decreases) and vice versa. The relationship between $\Delta T_r(T_x^h)$ and parameters ($\Delta T(T_x^h)$,

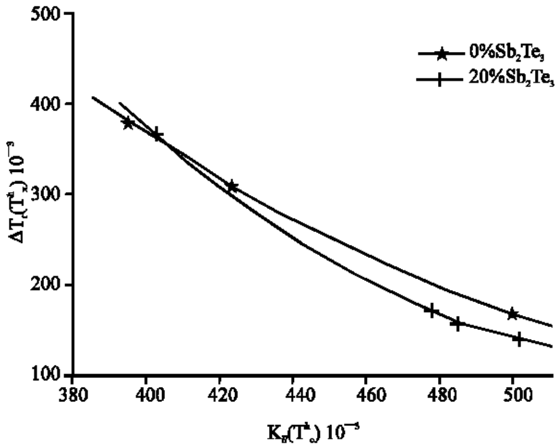

Fig. 16: Correlation between $\Delta T\ (T^h_x)$ and $K_{gl}\ (T^h_c)$ in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentrations of 0 and 20 mol%

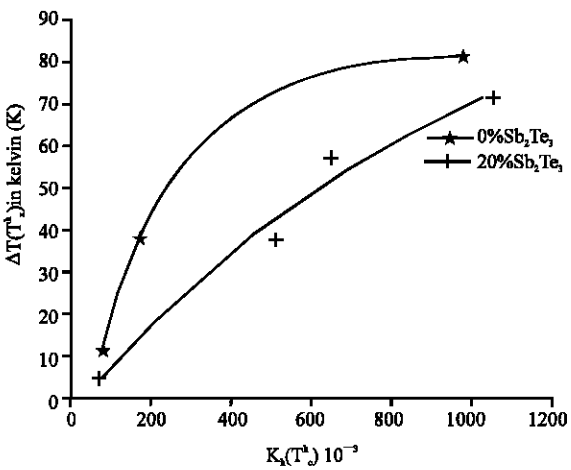

Fig. 17: Correlation between $\Delta T\ (T^h_x)$ and $K_h\ (T^h_c)$ in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentrations of 0 and 20 mol%

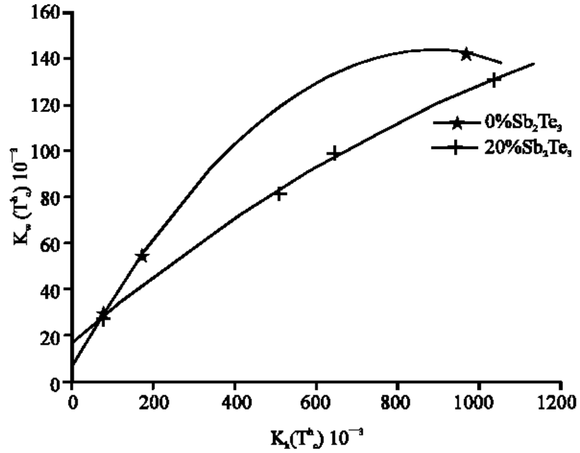

Fig. 18: Correlation between $K_w\ (T^h_c)$ and $K_h\ (T^h_c)$ in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentrations of 0 and 20 mol%

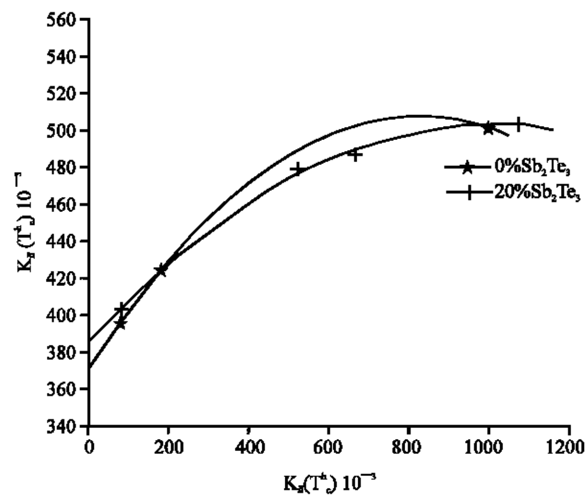

Fig. 19: Correlation between $K_{gl}\ (T^h_c)$ and $K_h\ (T^h_c)$ in the Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentrations of 0 and 20 mol%

$K_w\ (T^h_c)$ and $K_{gl}\ (T^h_c)$) shown in Fig. 14-16 indicates a good correlation. $\Delta T_r\ (T^h_x)$ is one of the key parameter for the glass stability of As_2S_3 based glasses.

Both $\Delta T\ (T^h_x)$ and $K_h\ (T^h_c)$ of glasses with 0 mol% and 20 mol% Sb_2Te_3 increase with the increasing in As_2S_3 content (Fig. 17). In another words, a wide supercoooled liquid region shows a high glass-forming ability. A large $\Delta T\ (T^h_x)$ value may indicate that the supercooled liquid is stable in a wide temperature without crystallization, this leads to a larger GFA of the alloy (Inoue *et al*., 1993). There is a correlation between glass-forming ability and glass stability. As discussed above, the overall liquid phase stability is positively related to the quantity of $\Delta T\ (T^h_x) = T^h_x - T_g$ while the crystallization resistance is proportional to T^h_x. The increase of $\Delta T\ (T^h_x)$ can lead to an increase of liquid phase stability at metastable state and hence an increase in the GFA. Therefore, the GFA is positively associated with the $\Delta T\ (T^h_x)$ for glasses of Sb_2S_3-As_2S_3-Sb_2Te_3 system. So $K_h\ (T^h_c)$ can be used to represent $\Delta T\ (T^h_x)$ or T_{rg} and vice versa for these glasses based on As_2S_3. That means $\Delta T\ (T^h_x)$ is a good criterion for characterization of GFA for these glasses used in the experiment. This speculation has been well confirmed in several glass-forming alloy systems in which the supercooled liquid region correlates reasonably well with the GFA of alloys (Shen and Schawrz, 1999). The same trend is observed between $K_h\ (T^h{}_c)$ and the other parameters of glass stability ($K_w\ (T^h{}_c)$ and $K_{gl}\ (T^h{}_c)$ of 0 and 20 mol% Sb_2Te_3 (Fig. 18, 19). According to Hruby (1972), the higher is the value of K_h for certain glass, the higher its stability against crystallization on heating and presumably, the higher the glass ability to vitrify on cooling. Glass which vitrifies easily (high K_h (T_c^h)) is a thermally stable glass (high ΔT (T_c^h)). Glass forming ability K_h (T_c^h) governs the thermal stability of studied glasses. This behaviour is observed when each glass stability parameter is plotted as a function of T_{rg} in Sb_2S_3-As_2S_3 binary system but not in the case of T_{rg} of 20% Sb_2Te_3 in Sb_2S_3-As_2S_3-Sb_2Te_3 system. Thus T_{rg} is not a good indicator of glass-forming ability for these glasses containing 20 mol% Sb_2Te_3.

CONCLUSION

Glass forming ability parameters (except of T_{rg} of 20 mol% Sb_2Te_3) and glass stability parameters increase but the degree of undercooling of glasses decreases when the content of As_2S_3 increases in Sb_2S_3-As_2S_3-Sb_2Te_3 system. This implies that glasses can be obtained easily and they can become most stable against crystallization. A low frequency of homogeneous nucleation can be suggested. The correlations between the degree of undercooling, glass forming ability and glass stability have shown that the degree of undercooling is an important parameter for the studied glasses.

REFERENCES

Aljihmani, L., V. Vassilev and P. Petkov, 2003. Composition trends of the physico-chemical properties in pseudoternary chalcogenide glasses. J. Optoelectronics Adv. Mater., 5 (5): 1187-1192.

Avramov, I., E.D. Zanotto and M.O. Prado, 2003. Glass-forming ability versus stability of silicate glasses. II. Theoretical demonstration. J. Non-Cryst. Solids, 320: 9-20.

Chol-Lyong, J., Xia Lei, D. Ding and D. Yuan-Da, 2006. Glass formation ability and kinetics of the $Gd_{55}Al_{20}Ni_{25}$ bulk metallic glass. Chin. Phys. Lett., 23 (3): 672-674.

Davies, H.A., 1975. The kinetics of formation of a Au-Ge-Si metallic glass. J. Non-Cryst. Solids, 17 (2): 266-272.

Durand, J.M., M.A. El Idrissi-Raghni, J. Olivier-Fourcade, J.C. Jumas and G. Langouche, 1997. 121Sb Mössbauer of Sb_2S_3-As_2S_3-Tl_2S glasses. J. Solid State Chem., 133: 458-465.

El Idrissi-Raghni, M.A., P.E. lippens, J. Olivier-Fourcade and J.C. Jumas, 1995. Local structure of glasses in the As_2S_3-Sb_2S_3 system. J. Non-Cryst. Solids, 192 and 193: 191-194.

El-Mokhtar, Kh. M., 2007. Thermal conductivity of $Ge_{25}Bi_{40}Te_{35}$ and $Ge_{25}Bi_{40}Sb_{35}$ semiconducting in solid and liquid states. Int. J. Mater. Sci., 2 (1): 9-16.

Farid, A.M., 2002. Effect of Ag content on the optical properties of a-$Ge_{15}Se_{85}$-xAgx alloys. Egypt J. Sol., 25 (1): 23-32.

Feng, X., H. Hu, F. Lin, Q. Chen and Z. Wang, 1999. Glass-forming tendency and thermal properties of chalcogenide glass Ge-Se-Te-Sn. Phys. Chem. Glasses, 40 (4): 225-228.

Hen, Z., Z. Bangwei, T. Zhaosheng, Y. Jueqi and H. Yiang, 1991. Preparation and thermal stability of metallic glasses $Cu_{83.3-x}NixP_{16.7}$. Phys. Review B, 43: 6430-6433.

Hruby, A., 1972. Evaluation of glass-forming tendency by means of DTA. Czech. J. Phys. B, 22: 1187-1193.

Inoue, A., T. Zhang and T. Masumoto, 1993. Glass-forming ability of alloys. J. Non-Cryst. Solids, 156-158: 473-480.

Jean-Luc Adams, 2001. Non-oxide glasses and their applications in optics. J. Non-Cryst. Solids, 287: 401-404.

Kamboj, M.S. and R. Thangaraj, 2003. Calorimetric studies of bulk Se-Te-Pb glassy system. Eur. Phys. J. Applied Phys., 24: 33-36.

Kapaklis, V., S. Baskoutas and C. Politis, 2003. Glass forming ability of bulk and mechanically alloyed $Zr_{55}Cu_{19}Ni_8Al_8Si_5Ti_5$ amorphous alloys. J. Optoelectronics Adv. Mater., 5 (5): 1255-1258.

Komatsu, T., K. Shioya and H.G. Kim, 1997. Thermal stability and optical properties of K_2O-Nb_2O_5-TeO_2 glasses. Phys. Chem. Glasses, 38 (4): 182-192.

Kumar, P., K.S. Bindra, N. Suri and R. Thangaraj, 2006. Transport properties of a-$Sn_xSb_{20}Se_{80}$-x (8 = x = 18) chalcogenide glass. J. Phys. D: Applied Phys., 39: 642-646.

Leh Deli, M., J.C. Jumas, E. Dichi and D. Houphouët-Boigny, 2005. 121Sb Mössbauer spectroscopy of 10 mol% Sb_2Te_3 section of pseudo-ternary Sb_2Se_3-As_2Se_3-Sb_2Te_3 glasses. J. Non-Cryst. Solids, 351: 2329-2332.

Lu, Z.P. and C.T. Liu, 2002. A New glass-forming ability criterion for bulk metallic glasses. Acta Mater., 50 (13): 3501-3512.

Lu, Z.P. and C.T. Liu, 2003. Glass formation criterion for various glass-forming systems. Phys. Rev., 91: 115505(1-4).

Nasciemento, M.L.F., L.A. Souza, E.B. Ferreira and E.D. Zanotto, 2005. Can glass stability parameters infer glass forming ability? J. Non-Cryst-Solids, 351: 3296-3308.

Nikhil Sur, K.S., P. Bindra, M.S. Kumar and R. Kamboj, Thangaraj, 2006. Thermal investigations in bulk $Se_{80-x}Te_{20}$Bix chalcogenide glass. J. Ovonic Res., 2 (8): 111-118.

Ouchetto, M., B. Elouadi and S. Parke, 1991. Study of lanthanide zinc phosphate glasses by differential thermal analysis. Phys. Glasses, 32: 22-28.

Repkova, M., P. Nemec and M. Frumar, 2006. Structure and thermal properties of Ge-In-S chalcogenide glasses. J. Optoelectronics Adv. Mater., 8 (5): 1796-1800.

Saffarini, G. and J.M. Saiter, 2006. Compactness in relation to the mean coordination number in glassy $GexBi_6Se_{94-x}$. Chalcogenide Lett., 3 (6): 49-53.

Sakka, S. and J.D. Mackenzie, 1971. Relation between apparent glass transition temperature and liquids temperature for inorganic glasses. J. Non-Cryst. Solids, 6 (2): 145-162.

Shen, T.D. and R.B. Schawrz, 1999. Direct measurement of strain in a Ge island on Si(001). Applied Phys. Lett., 75 (1): 46-48.

Singh, A.K., P. Kumar, K. Singh and N.S. Saxena, 2006. Thermal transport in $Se_{81}Te1_{5}Sb_4$ chalcogenide glass. Chalcogenide Lett., 3 (12): 139-144.

Soliman, A.A. and M.B. El-Den, 2007. Crystallization kinetics of the $Cu_{0.3}(SSe_{20})_{0.7}$ chalcogenide glass. Chalcogenide Lett., 4 (2): 35-47.

Turnbull, D., 1969. Under what conditions can a glass be formed? Contempt. Phys., 10: 473-488.

Uhlmann, D.R., 1977. Glass formation. J. Non-Cryst. Solids 25 (1-3): 42-85.