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ESTIMATION OF GLASS-FORMING ABILITY AND GLASS STABILITY OF Sb_2Se_3-As_2Se_3-Sb_2Te_3 GLASSES BY USING THE THERMAL PROPERTIES

M. LEH DELI*, D. HOUPHOUET BOIGNY, G. KRA
Laboratoire de Chimie des Matériaux Inorganiques, UFR-SSMT, Université de Cocody, 22 Bp 582 Abidjan 22. Côte d'Ivoire

Glass forming ability parameters defined by $T_{rg} = Tg/Tf_1$ and $K_h = (Tc_1\text{-}Tg)/(Tf_1\text{-}Tc_1)$, glass stability parameters such as $K_w = (Tc_1\text{-}Tg)/Tf_1$, $\Delta T = Tc_1\text{-}Tg$ and $K_l = Tc_1/(Tg+Tf_1)$ and the degree of undercooling $\Delta T_r = (Tf_1\text{-}Tc_1)/Tf_1$ are analised for glasses of the ternary system Sb_2Se_3-As_2Se_3-Sb_2Te_3 as function of the As_2Se_3 concentration. These parameters are formulated by different combinations of the following characteristic Differential Scanning Calorimetry (DSC) temperatures: the glass transition temperature (Tg), the first crystallization temperature (Tc_1) and the first melting temperature (Tf_1). Variations of the above parameters indicate that the studied glasses can vitrify easily and become increasingly stable when the concentration of As_2Se_3 increases. Good correlations between ΔT_r and K_h and between ΔT_r and parameters (K_w, ΔT and K_l), 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_2Se_3-As_2Se_3-Sb_2Te_3 glasses.

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Keywords: Glass transition temperature, First crystallization temperature, First melting temperature, Glass forming ability, Glass stability, Degree of undercooling

1. 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 whith 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)[1-5]. 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)[6, 7]. One is the reduced glass transition temperature $T_{rg} = Tg/Tf_1$ which is the ratio between the glass transition temperature Tg and the first melting temperature Tf_1 of the corresponding glass-forming system (Kumar et al, 2006; Chol-Lyong et al, 2006)[8,9]. Another parameter $K_h = (Tc_1\text{-}Tg)/(Tf_1\text{-}Tc_1)$, where Tc_1 is the first crystallization temperature, is also used as a measure of the glass-forming tendency of materials by (Farid, 2002)[10], (Aljihmani et al, 2003) [11] and (Nikhil Sur et al, 2006) [12].

Once a glass is made for instance by fast quenching a melt, its stability can be easily investigated. Thus the supercooled liquid range $\Delta T = Tc_1\text{-}Tg$ (Kumar et al, 2006) [8], the parameter $K_w = (Tc_1\text{-}Tg)/Tf_1$ (Avramov et al, 2003; Nasciemento et al , 2005) [13, 14] and a new criterion $K_l = Tc_1/(Tg+Tf_1)$ of (Lu and Liu 2002, 2003) [6, 7] are used to evaluate the glass stability against crystallization on heating.

The thermal stability of the metastable supercooled liquid obtained at temperatures between Tg and Tf_1 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

*Corresponding author; lehdeli@netcourrier.com

on the degree of undercooling $\Delta T_r = (Tf_l - Tc_1)/Tf_l$ 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_l) of the ternary system Sb_2Se_3-As_2Se_3-Sb_2Te_3 as function of As_2Se_3 concentration. Correlation between these parameters will be made in order to show the importance 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.

2. Materials and method

Glasses of Sb_2Se_3-As_2Se_3-Sb_2Te_3 system were prepared by our vitreous semiconductors group in << Laboratoire de Chimie des Matériaux Inorganiques>> by union of arsenic, selenium, tellurium and antimony of guaranteed purity (99,999%), introduced in stoechiometric proportions into sealed vacuum silica bulbs (10^{-3} Torr). Those are carried to 130°C during 24 hours, then to 900°C (at a speed of 3°C/mn approximately) and are maintained at this temperature during 24 hours. They, are finally soaked brutally in water-ice mixture. The x-rays diffractograms on powders made it possible to establish the vitreous state of the samples when they do not present any line but the very large waving characteristic to the vitreous state.

The thermal characteristic temperature such as the glass transition (T_g), the first crystallization temperature (Tc_1) and the first melting temperature (Tf_l) were measured in << Laboratoire de Chimie Physique, Minérale et Bioinorganique de la Faculté de Pharmacie de l'Université Paris XI (France)>> by using DSC 121 Setaram apparatus at a heating rate of 1°C mn^{-1} in the (25 to 650°C) temperature range. For the studied glasses, glass-forming ability was estimated using the following numerical parameters: the reduced glass transition temperature $T_{rg} = Tg/Tf_l$ and $K_h = (Tc_1-Tg)/(Tf_l-Tc_1)$ parameters. The glass stability parameters were also estimated by $K_w = (Tc_1-Tg)/Tf_l$, $K_l = Tc_1/(Tg+Tf_l)$ and $\Delta T = Tc_1-Tg$. The degree of undercooling was evaluated by $\Delta T_r = (Tf_l-Tc_1)/Tf_l$ (Komatsu et al, 1997) [15]. In this study we calculated the values of glass-forming ability and glass stability parameters given by the above expressions.

3. Results and discussion

3.1 Glass-forming ability parameters

Using the data shown in Table 1, the reduced glass transition temperature (T_{rg}) values for glasses of Sb_2Se_3-As_2Se_3 system vary little from 0.5 (50 mol% As_2Se_3) to 0.47 (100 mol% As_2Se_3). On the ternary system Sb_2Se_3-As_2Se_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 0.53 (50 mol% As_2Se_3) and decreased values are observed when the As_2Se_3 concentration increases up 50 mol% (Table 1).

The parameter $K_h(Tc_1)$ calculated with the onset temperature Tc_1 (Table 1), increases from 0.17 to 1.79 on Sb_2Se_3-As_2Se_3 system (fig 1).

For Sb_2Se_3-As_2Se_3-Sb_2Te_3 glasses containing a constant Sb_2Te_3 concentration of 20 mol%, $K_h(Tc_1)$ parameter increases from 0.20 to 2.33 as shown in Fig. 2.

Table 1 Composition of glasses, thermal properties (Tg, Tc_1 and Tf_1) from DSC curves, values of glass-forming ability parameters (T_{rg}, and K_h), values of glass forming stability parameters (K_w, K_l and ΔT) and degree of undercooling ΔT_r for studied glass in the binary system Sb_2Se_3-As_2Se_3.

Composition of glass to As_2Se_3	Tg	Tc_1	Tf_1	T_{rg}	$K_h(Tc_1)$	$K_w(Tc_1)$	$K_l(Tc_1)$	$\Delta T(Tc_1)$	$\Delta T_r(Tc_1)$
0.5	185	212	366	0.5	0.17	0.07	0.38	27	0.42
0.55	185	216	366	0.5	0.2	0.08	0.39	31	0.41
0.6	183	230	366	0.5	0.34	0.13	0.42	47	0.37
0.65	182	237	366	0.5	0.42	0.15	0.43	55	0.35
0.7	181	242	366	0.49	0.44	0.17	0.44	61	0.34
0.75	182	264	366	0.5	0.6	0.28	0.48	104	0.28
0.8	182	291	367	0.5	1.43	0.3	0.51	109	0.21
0.85	178	285	368	0.48	1.29	0.29	0.52	107	0.22
0.9	180	274	370	0.48	0.98	0.25	0.5	94	0.26
0.95	170	283	367	0.46	1.34	0.31	0.53	113	0.23
1	177	304	375	0.47	1.79	0.34	0.55	127	0.19

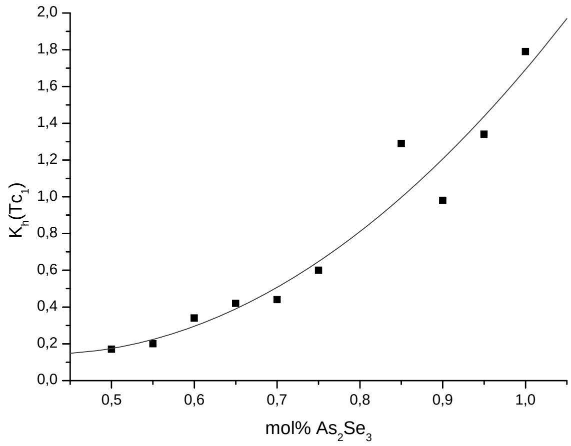

Fig. 1 Variation of K_h (Tc_1) with the As_2Se_3 concentration in the Sb_2Se_3-As_2Se_3 binary system.

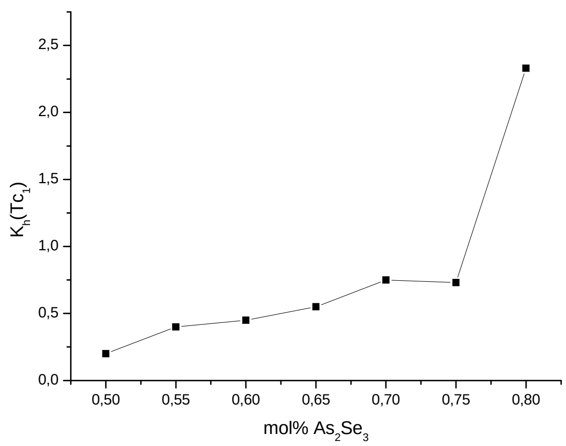

Fig. 2: Variation of K_h (Tc_1) with the As_2Se_3 concentration in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 20 mol%

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) [16] and (Davies, 1975) [17]. 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) [18]. 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 (Tumbull, 1969) [19], these liquids are good glass formers. It is clearly shown that the two thirds rule holds well for the studied glasses of Sb_2Se_3-As_2Se_3-Sb_2Te_3 system.

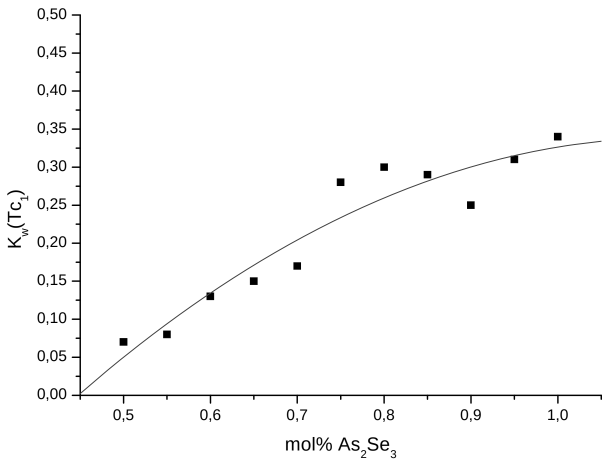

Fig. 3. Variation of $K_w(Tc_1)$ with the As_2Se_3 concentration in the Sb_2Se_3-As_2Se_3 binary system.

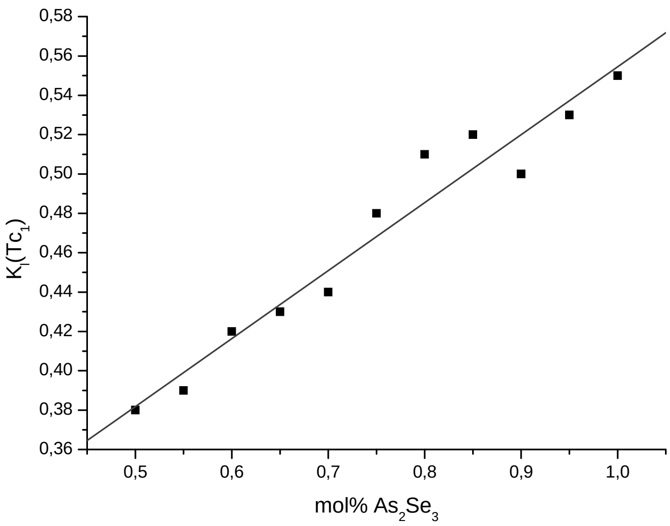

Fig. 4. Variation of $K_l(Tc_1)$ with the As_2Se_3 concentration in the Sb_2Se_3-As_2Se_3 binary system.

The increase of $K_h(Tc_1)$ and T_{rg} (except of T_{rg} of 20% Sb_2Te_3) with increasing As_2Se_3 (covalent compound) incorporation supports the Glass-Forming Ability (GFA). In other words, GFA increases with increase in As_2Se_3 concentration. For these glasses $K_h(Tc_1)$ and T_{rg} reflect the GFA effectively. GFA in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 system is conditioned by the presence of a glass forming compound As_2Se_3. This indicates that As_2Se_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 system to form glasses. T_{rg} evolution of Sb_2Se_3-As_2Se_3-Sb_2Te_3 glasses containing 20 mol% Sb_2Te_3 is not linear like $K_h(Tc_1)$ 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) [16] and phosphate glass systems (Ouchetto et al, 1991) [20].

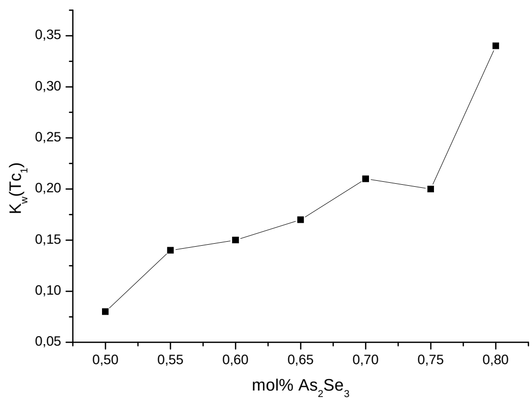

Fig. 5. Variation of $K_w(Tc_1)$ with the As_2Se_3 concentration in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 20 mol%

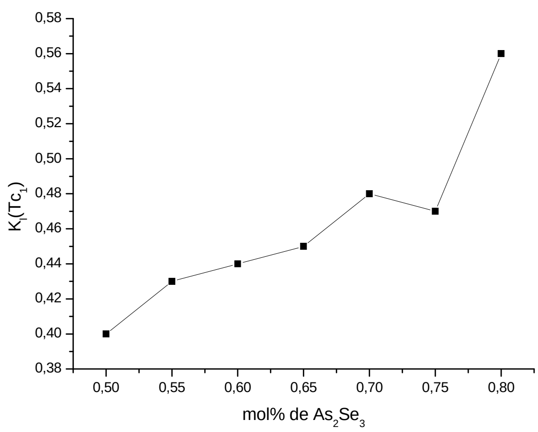

Fig. 6. Variation of $K_l(Tc_1)$ with the As_2Se_3 concentration in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 20 mol%

3.2 Glass stability parameters

In this study, values of the supercooled liquid region $\Delta T(Tc_1)$ parameter and Lu-Liu parameter $K_l(Tc_1)$ used for stability assessment of Sb_2Se_3-As_2Se_3-Sb_2Te_3 glasses, Table 1 and 2. Generally, the difference $\Delta T(Tc_1) = Tc_1\text{-}Tg$, gives a measure of thermal stability of the glass (Kamboj and Thangaraj, 2003) [21]. For the present study, its values are found to be in the range 27-127°C on the binary system Sb_2Se_3-As_2Se_3 and 24-105°C on the ternary system Sb_2Se_3-As_2Se_3-Sb_2Te_3 (containing 20 mol% Sb_2Te_3). Values of $K_w(Tc_1)$ parameter and Lu-Liu parameter $K_l(Tc_1)$ increase when As_2Se_3 concentration increase on the binary system Sb_2Se_3-As_2Se_3 (fig 3) and on the ternary system Sb_2Se_3-As_2Se_3-Sb_2Te_3 with 20 mol% Sb_2Te_3 (fig 4). Even if K_w and K_l obtained at Tc_1 don't give the width of the temperature interval like $\Delta T(Tc_1)$, they can be suggested to represent the glass stability because they have similar trends when they are plotted versus As_2Se_3 concentration (fig 3-6). It is obvious that the thermally stable glasses in the above systems are obtained when the As_2Se_3 concentration increase. In other words, the thermal stability of these glasses against crystallization increases with increase in As_2Se_3 concentration. As can be shown in tables 1 and 2 the increases in $\Delta T(Tc_1)$ in the two systems mainly result from the increase of Tc_1. This implies that the added As_2Se_3 acts effectively as an inhibitor of crystallization. The onset-crystallization Tc_1 can serve as an important factor estimating the stability of glass (Hen et al, 1991) [22]. On the other hand, it is reasonable to assign that As_2Se_3 a covalent compound, acts as network breaking agents to decrease Tg because it decrease with increasing As_2Se_3 concentration as shown in Table 1.

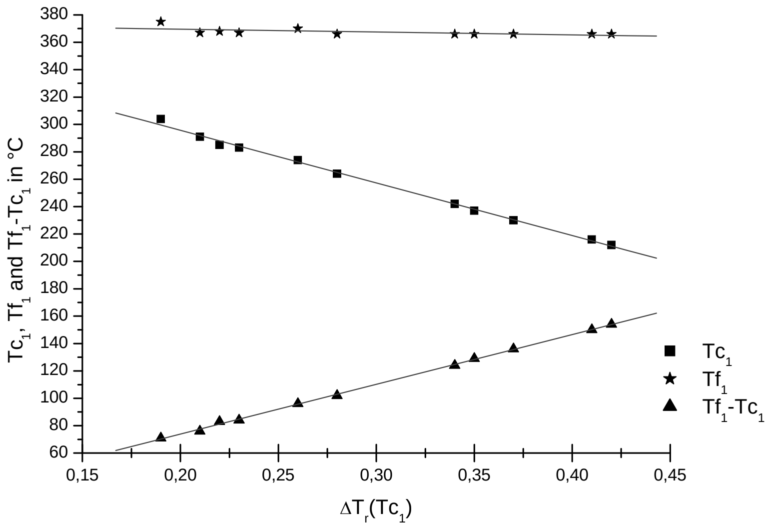

Fig. 7. Evolution of the onset crystallization temperature Tc_1, the first melting temperature Tf_1 and undercooled liquid region Tf_1-Tc_1 versus the degree of undercooling $\Delta T_r(Tc_1)$ on the Sb_2Se_3-As_2Se_3 binary system

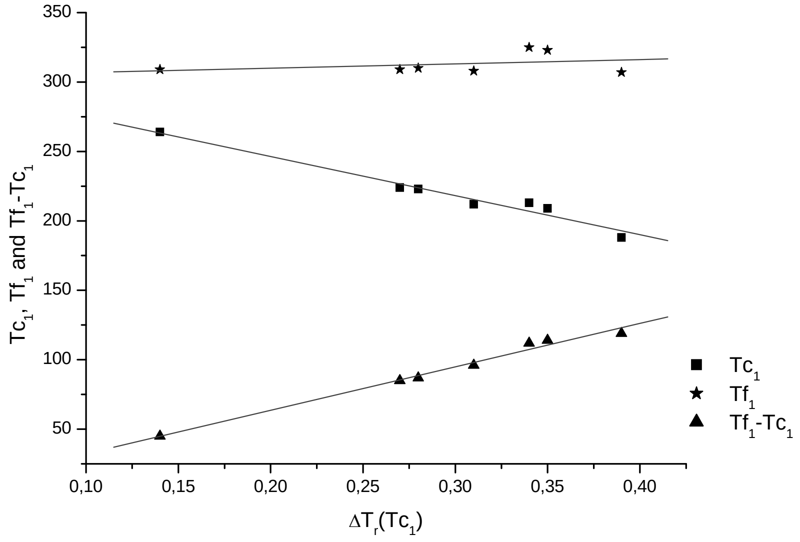

Fig. 8. Evolution of the onset crystallization temperature Tc_1, the first melting temperature Tf_1 and undercooled liquid region Tf_1-Tc_1 versus the degree of undercooling $\Delta T_r(Tc_1)$ on the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 20 mol%

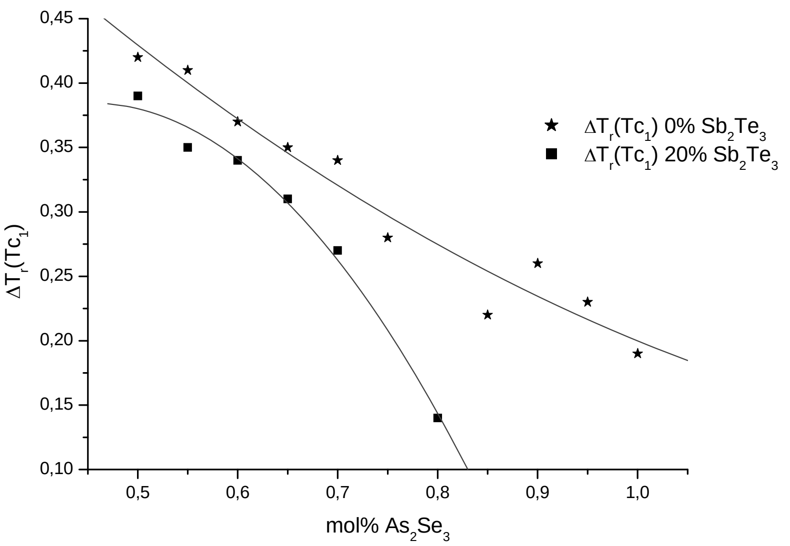

Fig. 9. Variation of $\Delta T_r(Tc_1)$ with the As_2Se_3 concentration in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 0 and 20 mol%

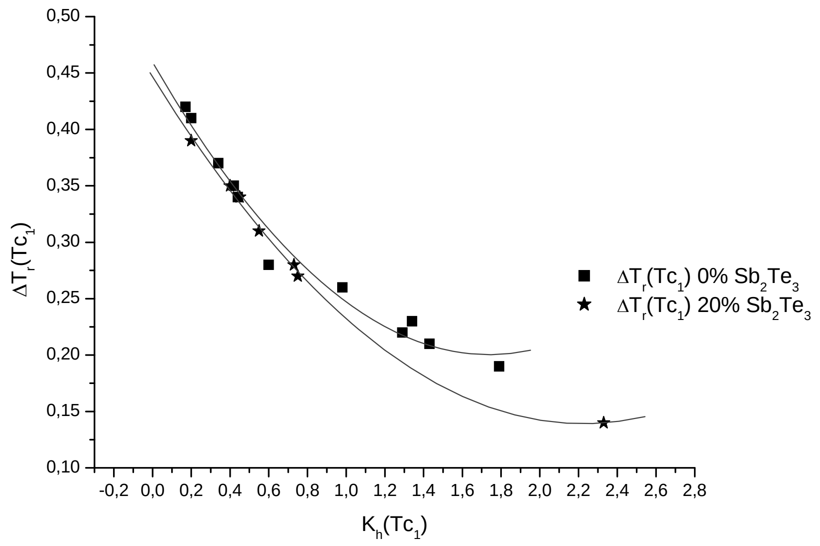

Fig. 10. Correlation between $\Delta T_r(Tc_1)$ and $K_h(Tc_1)$ in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 0 and 20 mol%

Increased values of $\Delta T(Tc_1)$ may indicate that the supercooled liquid can remain stable in a wide temperature range without crystallization. Thus, As_2Se_3 incorporation has a stabilizing effect because $\Delta T(Tc_1)$ becomes wide when its concentration increases. It is desirable to have ΔT as large as possible in oder to achieve a large working range during operations such as perform preparation for fibre drawing according (Feng et al, 1999) [23]. The partial replacement of Sb_2Se_3 (less covalent) by As_2Se_3 (covalent), on Sb_2Se_3-As_2Se_3 and Sb_2Se_3-As_2Se_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_2Se_3 involves probably the formation of high stable network structure which may be due to the presence of covalent bondings. That means that As_2Se_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) [24], The Raman and IR bands of Sb_2Se_3-As_2Se_3 glasses are attributed to $AsSe_3$ and $SbSe_3$, 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) [25] 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) [26], 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 -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 ($SbSe_3$). As there is no available information on the structure of Sb_2Se_3-As_2Se_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 $SbSe_3$ and $AsSe_3$ the trigonal pyramidal units as seen in the case of Sb_2Se_3-As_2Se_3 glasses. There is an obvious correlation between covalence and glass stability.

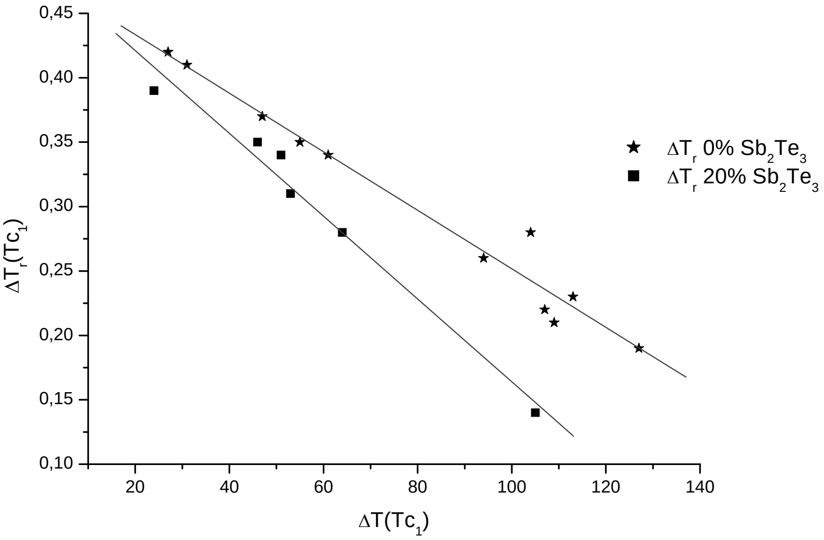

Fig. 11. Correlation between $\Delta T_r(Tc_1)$ and $\Delta T(Tc_1)$ in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 0 and 20 mol%

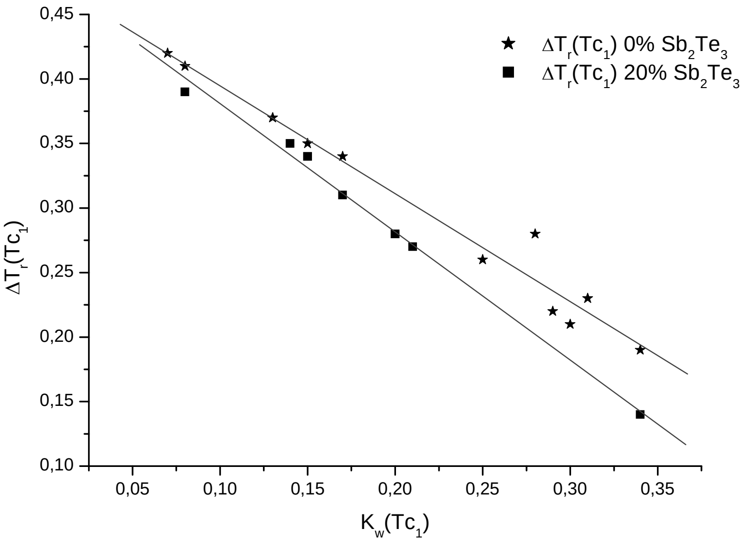

Fig. 12. Correlation between $\Delta T_r(Tc_1)$ and $K_w(Tc_1)$ in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 0 and 20 mol%

3.3 Degree of undercooling parameter

The calculated values of $\Delta T_r(Tc_1)$ at the onset crystallization temperature Tc_1 for examined glasses are reported in table 1 and 2. It is indicated that $\Delta T_r(Tc_1)$ values depend on the thermal characteristics such as Tc_1 and Tf_1 . Tc_1 increases but Tf_1 vary little when As_2Se_3 concentration increases on Sb_2Se_3-As_2Se_3 binary system and on 20 mol% Sb_2Te_3 section of Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system. As indicated in fig 7 and 8, Tc_1 decreasing and Tf_1 vary little imply the increasing of $\Delta T_r(Tc_1)$. So the higher value of Tc_1 (lower value of Tf_1) in each system corresponds the smaller value of $\Delta T_r(Tc_1)$ and a small undercooled region (Tf_1- Tc_1) is observed. At the smaller value of Tc_1 (higher value of Tf_1) corresponds to the higher value of $\Delta T_r(Tc_1)$ and a wide undercooled region is also observed. The degree of undercooling depends on the extended undercooled region which depends on Tc_1 and Tf_1. The variation of the degree of undercooling, $\Delta T_r(Tc_1)$, as a function of As_2Se_3 concentration is shown in Fig 9. $\Delta T_r(Tc_1)$ decreases exponentially on Sb_2Se_3-As_2Se_3 binary system and on 20 mol% Sb_2Te_3 section of Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system whith increasing of As_2Se_3 concentration. In the two cases, it is seen that small values of $\Delta T_r(Tc_1)$ are obtained when the concentration of As_2Se_3 increases. The decreased values of $\Delta T_r(Tc_1)$ can be explained by progressive substitution of Sb_2Se_3 by As_2Se_3 as it is seen above in the cases of glass-forming ability and glass stability. Thus, added As_2Se_3 can diminish the degree of undercooling and the undercooled region. These results imply that the glasses with high concentration of As_2Se_3 have a possibility of a low frequency of homogeneous nucleation because $\Delta T_r(Tc_1)$ decreases in respect to the classical theory of homogeneous nucleation. A similar trend was reported in (30-x)$K_2O_{-x}Nb_2O_5$-70TeO_2) glasses (Komatsu et al, 1997) [15] when Nb_2O_5 concentration increases.

Table 2 Composition of glasses, thermal properties (Tg, Tc_1 and Tf_1) from DSC curves, values of glass forming ability parameters (T_{rg}, and K_h), values of glass forming stability parameters (K_w, K_l and ΔT) and degree of undercooling ΔT_r for studied glass in the ternary system Sb_2Se_3-As_2Se_3-Sb_2Te_3 at constant Sb_2Te_3 concentration of 20 mol%.

Composition of glass to As_2Se_3	**Tg**	**Tc_1**	**Tf_1**	**T_{rg}**	**$K_h(Tc_1)$**	**$K_w(Tc_1)$**	**$K_l(Tc_1)$**	**$\Delta T(Tc_1)$**	**$\Delta T_r(Tc_1)$**
0.5	164	188	307	0.53	0.20	0.08	0.40	24	0.39
0.55	163	209	323	0.5	0.4	0.14	0.43	46	0.35
0.6	162	213	325	0.5	0.45	0.15	0.44	51	0.34
0.65	159	212	308	0.51	0.55	0.17	0.45	53	0.31
0.7	160	224	309	0.52	0.75	0.21	0.48	64	0.27
0.75	159	223	310	0.51	0.73	0.20	0.47	64	0.28
0.8	159	264	309	0.51	2.33	0.34	0.56	105	0.14

3.4 Correlation between the degree of undercooling, glass-forming ability and glass stability

Similar trends were observed when the glass-forming parameter, $K_h(Tc_1)$ and the glass-stability parameters, $K_w(Tc_1)$ and $K_l(Tc_1)$, are plotted versus As_2Se_3 concentration. So, we will use only values of $K_w(Tc_1)$ and $K_l(Tc_1)$ obtained with Tc_1 temperature during correlations in which these parameters are used.

Correlation between $\Delta T_r(Tc_1)$ and $K_h(Tc_1)$, for studied glasses containing 0 and 20 mol% Sb_2Te_3 is shown in Fig 10 which indicates that $\Delta T_r(Tc_1)$ decreases when $K_h(Tc_1)$ increases.

Correlation between $\Delta T_r(Tc_1)$ and $\Delta T(Tc_1)$ of glasses with 0 and 20 mol% Sb_2Te_3 shows that $\Delta T_r(Tc_1)$ decreases when $\Delta T(Tc_1)$ increases (Fig 11). Supercooled liquid having wide supercooled liquid region ($\Delta T(Tc_1)$ is wide) is characterized by a low degree of undercooling ($\Delta T_r(Tc_1)$ is low). That means that the supercooled liquid is stable in a wide temperature range without crystallization and with high resistance to the nucleation and growth of crystalline phase (KapaKlis et al, 2003) [27]. The same behaviour is observed when $\Delta T_r(Tc_1)$ is correlated with the other glass stability parameter such as $K_w(Tc_1)$ (Fig 12). At the higher values of $\Delta T(Tc_1)$, $K_w(Tc_1)$ corresponds with lower value of $\Delta T_r(Tc_1)$. Thus, when the glass stability parameter become higher, the frequency of homogeneous nucleation becomes lower ($\Delta T_r(Tc_1)$ decreases) and vice versa. The relationship between $\Delta T_r(Tc_1)$ and parameters ($\Delta T(Tc_1)$ and $K_w(Tc_1)$) shown in Fig 11 and 12 indicates a good correlation $\Delta T_r(Tc_1)$ is one of key parameter for the glass stability of As_2Se_3 based glasses.

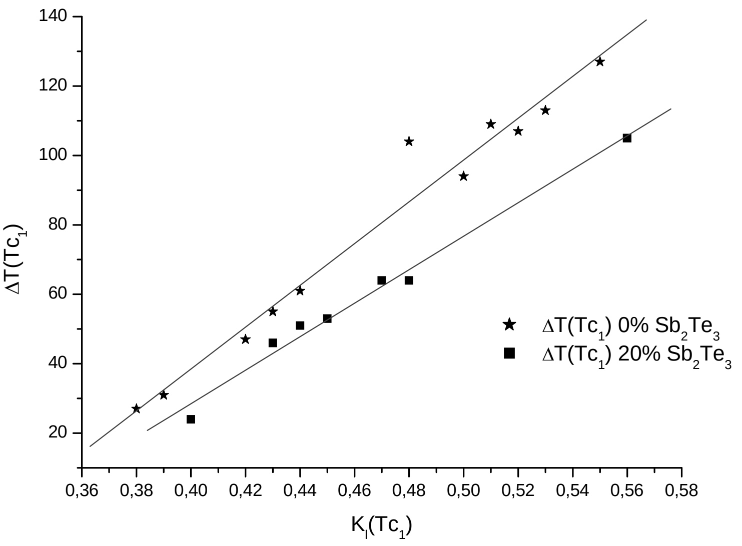

Fig. 13. Correlation between $\Delta T(Tc_1)$ and $K_l(Tc_1)$ in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 0 and 20 mol%

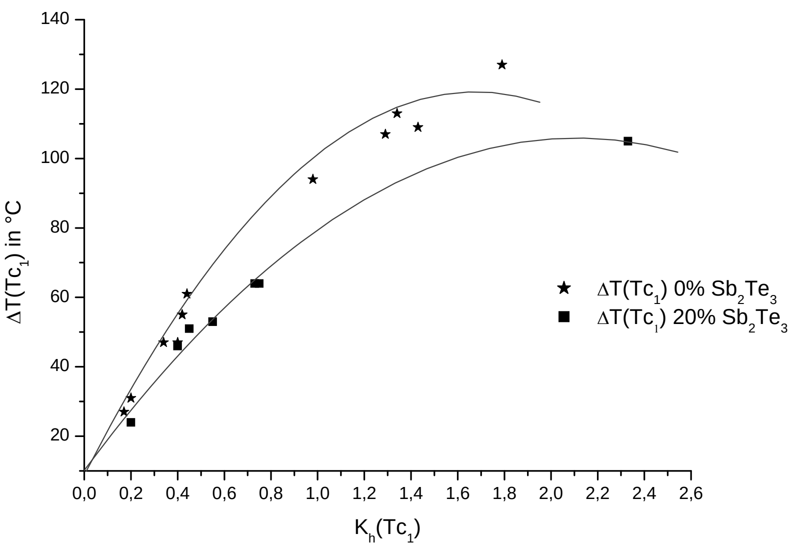

Fig. 14. Correlation between $\Delta T(Tc_1)$ and $K_h(Tc_1)$ in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 0 and 20 mol%

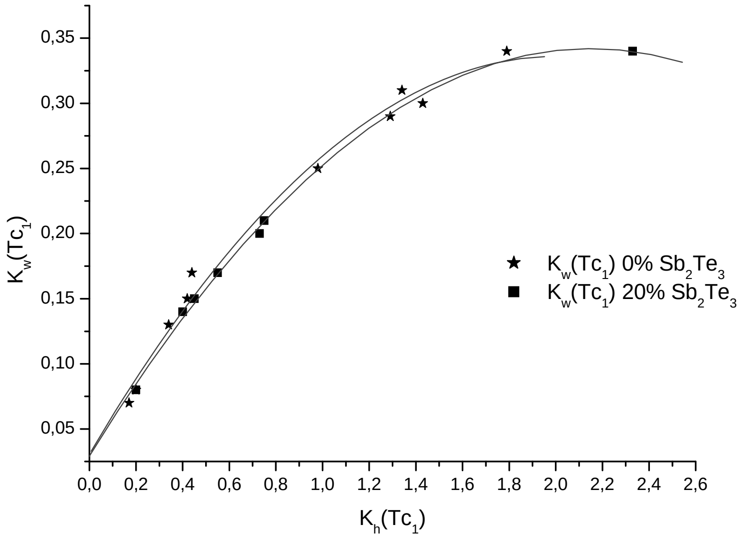

Fig. 15. Correlation between $K_w(Tc_1)$ and $K_h(Tc_1)$ in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 0 and 20 mol%

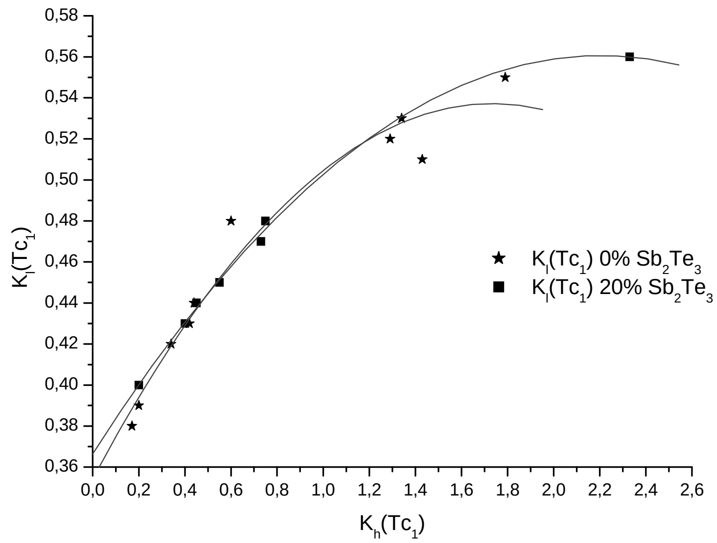

Fig. 16. Correlation between $K_l(Tc_1)$ and $K_h(Tc_1)$ in the Sb_2Se_3-As_2Se_3-Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 0 and 20 mol%

Correlation between $\Delta T_r(Tc_1)$ and $K_l(Tc_1)$ of glasses with 0 and 20 mol% Sb_2Te_3 shows that $\Delta T_r(Tc_1)$ increases when K_l (Tc_1) increases (Fig 13). Supercooled liquid having low glass stability parameter such as (K_l (Tc_1) is low) is characterized by a wide degree of undercooling ($\Delta T_r(Tc_1)$ is wide).

Both $\Delta T(Tc_1)$, K_h (Tc_1) of glasses with 0 and 20 mol% Sb_2Te_3 increase with the increasing in As_2Se_3 content (Fig 14). In another words, a wide supercooled liquid region showns a high glass-forming ability. A large $\Delta T(Tc_1)$ value may indicate that the supercooled is stable in a wide temperature without crystallization, this leads to a larger GFA of the alloy (Inoue et al, 1993) [28]. 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 $\Delta T(Tc_1)$ = Tc_1-Tg while the crystallization resistance is proportional to Tc_1. The increase of $\Delta T(Tc_1)$ 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 $\Delta T(Tc_1)$ for glasses of Sb_2Se_3-As_2Se_3-Sb_2Te_3 system. So K_h (Tc_1) can be used to represent $\Delta T(Tc_1)$ and vice versa for these glasses based on As_2Se_3. That means $\Delta T(Tc_1)$ 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) [29]. The same trend is observed between $K_h(Tc_1)$ and the other parameters of glass stability ($K_w(Tc_1)$ and $K_l(Tc_1)$) of 0 and 20 mol% Sb_2Te_3 (Fig 15 and 16). According to (Hruby, 1972) [30], 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 $K_h(Tc_1)$) is a thermally stable glass ($\Delta T(Tc_1)$). Glass forming ability $K_h(Tc_1)$ 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_2Se_3-As_2Se_3 binary system but not in the case of T_{rg} of 20 mol% Sb_2Te_3 in Sb_2Se_3-As_2Se_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.

4. Conclusions

Glass-forming ability parameters (except of T_{rg} of 20 mol% Sb_2Te_3) and glass stability parameters increase but the degree of undercooling decreases when the content of As_2Se_3 increases in Sb_2Se_3-As_2Se_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.

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