STUDY OF THE DENSITY OF GLASSES IN THE TERNARY SYSTEM Sb_2Se_3-As_2Se_3-Sb_2Te_3 AND THEIR STABILITY BY SLOW COOLING

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The study of the density of glasses and that of their stability by slow cooling in the ternary system Sb_2Se_3-As_2Se_3-Sb_2Te_3 show that glasses obtained have a density (ρ) ranging between 5.29 and 4.56 g/cm^3 and that most stable are located side of As_2Se_3.

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1. Introduction

The present study consists in determining the density of glasses in the ternary system Sb_2Se_3-As_2Se_3-Sb_2Te_3 and studying the influence of the addition of constant contents of Sb_2Te_3 (10%, 20% and 30%), on the structural order of glasses of the binary system Sb_2Se_3-As_2Se_3.

The study of the stability of these glasses by slow coolings, watch which the stable compositions are on the side of As_2Se_3, coming to confirm that the covalent character of this compound supports vitrification.

2. Synthesis and characterization of glasses

2.1 Synthesis of glasses

The samples were prepared by union of arsenic, selenium, the tellurium and the 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 with 900°C (at a speed of 3°C/mn approximately) and are gradually maintained at this temperature during 24 hours. They, are finally soaked brutally in an water-ice mixture. The diffractograms of X-rays on powders made it possible to establish the vitreous state of the samples when they do not present any line, but halations characteristic of the vitreous state.

2.2 Measurements of the density of prepared glasses

We used the automatic pycnométrique method for the determination of the densities and real volumes by measurement of a variation of helium pressure in a volume gauged with the room temperature (25°C). The principle is the following: the ACCUPYC 1330 is a pycnometer with displacement of gas, type of instrument which measures the volume of the solid objects of regular or irregular form, of the powders, the pastes, the parts. A very simplified diagram of the instrument is shown by the Figs. 1a and 1b. By supposing that volumes of cells and expansion are with environmental pressure Pa, and with room temperature Your, and that the valves are closed: the volume of cell is then subjected to a higher pressure P_1 **.**

The equation for the cell sample is:

$$P_1 (V_{cell.} - V_{éch.}) = n_c RTa \quad (1)$$

with n_c = many moles of gas in the cell sample
R = constant of the gas helium
Ta = room temperature
The equation for the volume of expansion is:
Pa. $V_{exp} = n_e RTa$ (2)
with n_e= many moles of gas in the volume of expansion.
When the valve of expansion is opened, the pressure will fall with an intermediate value P_2 and the equation becomes:

$$P_2 . (V_{cell.} - V_{éch} + V_{exp}) = n_c RTa + n_e RTa \quad (3)$$

In substituent the equations (1) and (2) in (3):

$$P_2 . (V_{cell.} - V_{éch} + V_{exp}) = P_1 (V_{cell.} - V_{éch.}) + PaV_{exp} \quad (4)$$

$$\text{Ou} \quad (P_2 - P_1)(V_{cell.} - V_{éch}) = (Pa - P_2) V_{exp} \quad (5)$$

$$\text{Then} \quad V_{cell.} - V_{éch} = (Pa - P_2) V_{exp} / (P_2 - P_1) \quad (6)$$

The addition and the subtraction of Pa to the denominator and after back in shape give us:

$$V_{éch} = -V_{cell} + (Pa - P_2) V_{exp} / (P_2 - Pa) - (P_1 - Pa) \quad (7)$$

while dividing by ($Pa-P_2$) with the numerator and the denominator:

$$V_{éch} = V_{cell} - V_{exp} [-1 - (P_1 - Pa)/(Pa - P_2)]^{-1} \quad (8)$$

$$V_{éch} = V_{cell} - V_{exp} [-1 + (P_1 - Pa)/(P_2 - Pa)]^{-1} \quad (9)$$

Like P_1, P_2 and Pa are expressed in the equations (1) to (9) in absolute pressure and as in the equation (9), Pa is deduced from the P_1 pressures and P_2, we can redefine new pressures P_{1g} and P_{2g} as follows:

$$P_1 g = P_1 - Pa \quad (10) \qquad P_2 g = P_2 - Pa \quad (11)$$

And the equation (9) becomes:

$$V_{éch} = V_{cell} - V_{exp} [-1 + (P_{1g}/P_{2g})]^{-1} \quad (12)$$

The equation (12) is that used to calculate volumes starting from the pycnometer. The procedure of calibration makes it possible to determine V_{cell} and V_{exp} and the pressures are measured by a pressure pick-up.

The material allows a filling and a handing-over the atmosphere optimized of gases and a precise seizure of the data to correctly calculate volumes of the rooms samples and expansion and to clean the samples of their vapors.

We weighed beforehand the sample using a balance SARTORIUS R 180 D-^{H}F1 monoplateau which give a precision about 1/100ème mg.

The density of the samples is then given by the relation:

$\rho = m_{éch}/V_{éch}$ with $m_{éch}$ = mass of the sample

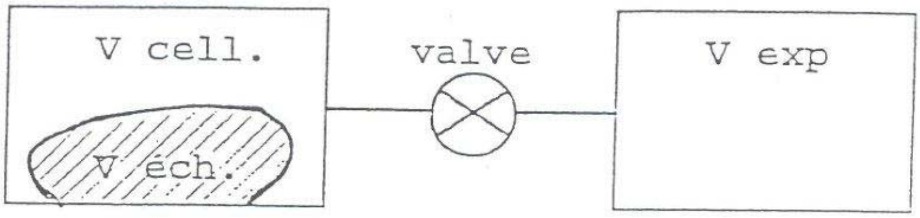

Fig. 1a. Simplified diagram of the block analyzes

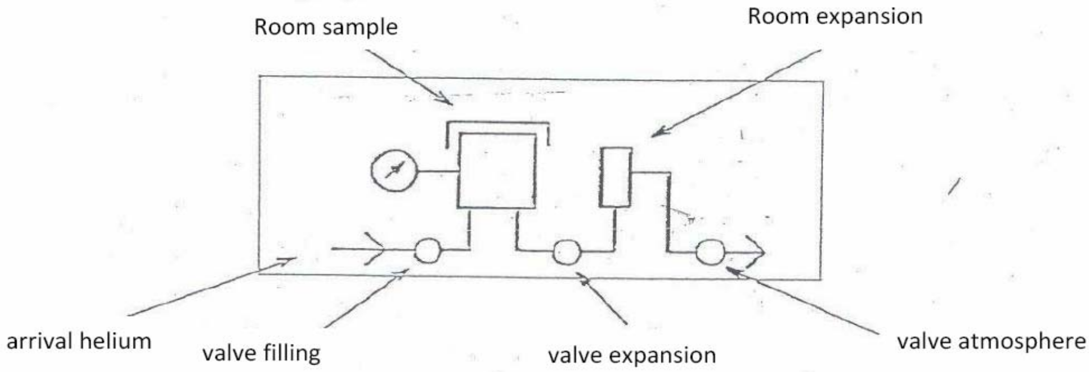

Fig. 1b. Synoptic diagram

2.3 Preparation of glasses by slow cooling

Glasses which we prepared were obtained by hardening starting from the liquid state with 900°C.

The stability of these glasses can be studied by the variation the speed of cooling.

This study is carried out while subjecting to each vitreous sample a heating at the speed of 1°C/min until 500°C following slow coolings at speeds of 20°C/min, 15°C/min, 10°C/min, 5°C/min, 3°C/min and 1°C/min in the apparatus of differential calorimetry.

3. Results and discussion

3.1 Evolution of the density of glasses

For the same composition being able to exist in a crystallized state (order with long distance) or in a vitreous state (order at short distance), one can expect that the vitreous compound is less dense than the compound crystallized because of its more open structure, which had with the larger disorder. The measurement of the density can be also a measurement of the disorder and degree of crystallinity. Thus an increase in the total disorder inside and a reduction in the degree of crystallinity involve a reduction in the density.

3.1.1 Case of As_2Se_3

The densities ρ (g/cm^3) of As_2Se_3 published by various authors are given in table 1.

Table 1. Density (ρ) of As_2Se_3 published by various authors

AUTHORS	ρ (g/cm³)	Method of measurement
D. HOUPHOUET BOIGNY [1]	4.57	Pycnometer with immersion in benzene
BORISOVA et al [2]	4.51	Pycnometer with immersion in benzene
KASAKOVA et al [3]	4.51	Pycnometer with immersion in benzene
C.DEMBOVSKI et al[4]	4.8	Hydrostatic with immersion in toluene
Our study	4.56	Automatic pycnometer (Accupyc 1330)

The density ρ (g/cm^3) given for the composition x = 1 (As_2Se_3) is of the same order of magnitude as that of these authors [1-3]. This enables us to check the reliability of the results obtained by the method of the automatic pycnometer (Accupyc 1330) which we used in comparison with that of the pycnometer with immersion in benzene used by these authors [1-3]. We are in perfect agreement with D. HOUPHOUET BOIGNY [1] because of the fact that the method of preparation of the samples is the same one. We are in dissension with the others owing to the fact that we do not have the same method of preparation of the samples. The particularly high value of ρ = 4.8 g/cm3 for C.DEMBOVSKI and collar [4] is justified by the fact that they used the hydrostatic method with immersion in toluene.

3.1.2 Case of glasses of the binary systems Sb_2Se_3-As_2Se_3 et Sb_2Te_3-As_2Se_3

Fig. 2 shows the evolution of the values of the density from **Table 2** according to the content of As_2Se_3.

Table 2. Density (ρ) of glasses of the binary systems Sb_2Se_3-As_2Se_3 et Sb_2Te_3-As_2Se_3

	System Sb_2Se_3-As_2Se_3	**System Sb_2Te_3-As_2Se_3**
Molar fraction of As_2Se_3 (x)	**ρ (g/cm³)**	**ρ (g/cm³)**
0,60	4,93	
0,65	4,90	
0,70	4,86	5,16
0,75	4,79	5,01
0,80	4,73	4,95
0,85	4,66	4,84
0,90	4,64	4,75
0,95	4,61	4,66
1	4,56	4,56

On the whole of the binary systems, the density ρ presents a decrease of the values:
- from 4.93 to 4.56 g/cm^3 when the content of As_2Se_3 increases x = 0.60 to x = 1 on the Sb_2Se_3-As_2Se_3 binary system;
- from 5.16 to 4.56 g/cm^3 when the content of As_2Se_3 increases x = 0.70 to x = 1 on the Sb_2Te_3-As_2Se_3 binary system.

The evolution is similar on the two binary systems i.e. decreasing when the content of As_2Se_3 increases.

This decrease of the values indicates that the tendency to vitrify i.e. the disorder in these vitreous compositions of the binary systems increase with the content of As_2Se_3. It is also justified by the substitution of heavy elements Sb (M = 121.75 g/mol) or Te (M = 127.60 g/mol) by elements less heavy As (M = 74.92 g/mol) or (M = 78.96 g/mol). This substitution explains the stronger decrease for the binary system Sb_2Te_3-As_2Se_3 in which Te (M = 127.60 g/mol) is substituted by (M = 78.96 g/mol).

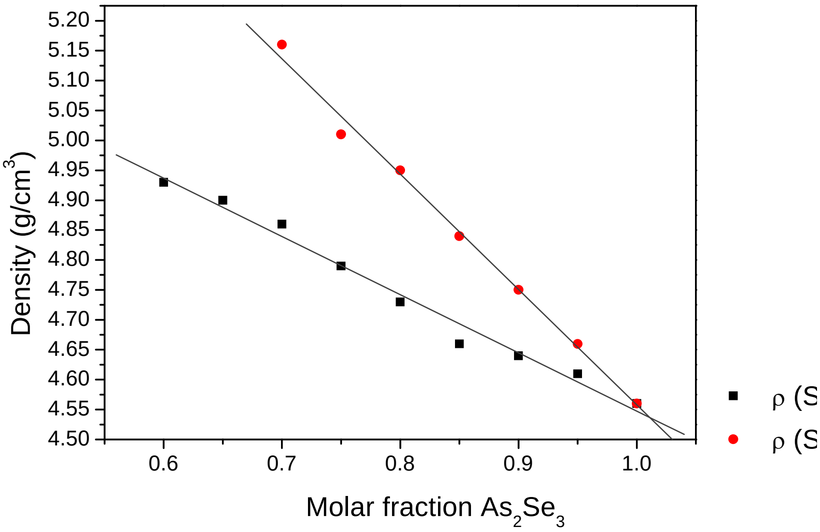

Fig. 2. Evolution of the density of glasses of the systems binary Sb_2Se_3-As_2Se_3 et Sb_2Te_3-As_2Se_3 according to content of As_2Se_3

3.1.3 Case of the ternary system Sb_2Se_3-As_2Se_3-Sb_2Te_3

Fig. 3 shows the evolution of the values of the density gathered in table 3 according to the content of As_2Se_3.

Table 3. Density of glasses of the cuts container 0 %, 10 %, 20 % and 30 % of Sb_2Te_3

	0 % of Sb_2Te_3 (Sb_2Se_3-As_2Se_3)	**10 % of Sb_2Te_3**	**20 % of Sb_2Te_3**	**30 % of Sb_2Te_3**
Molar fraction of As_2Se_3 (x)	**ρ (g/cm^3)**	**ρ (g/cm^3)**	**ρ (g/cm^3)**	**ρ (g/cm^3)**
0.50		5.15	5.25	
0.55		5.07	5.14	
0.60	4,93	5.02	5.14	5.29
0.65	4.90	4.99	5.08	5.15
0.70	4,86	4.93	5.02	5.16
0.75	4.79	4.83	4.96	
0.80	4.73	.	4.95	
0.85	4.66	4.78		
0.90	4.64	4.75		
0.95	4.61			
1	4.56			

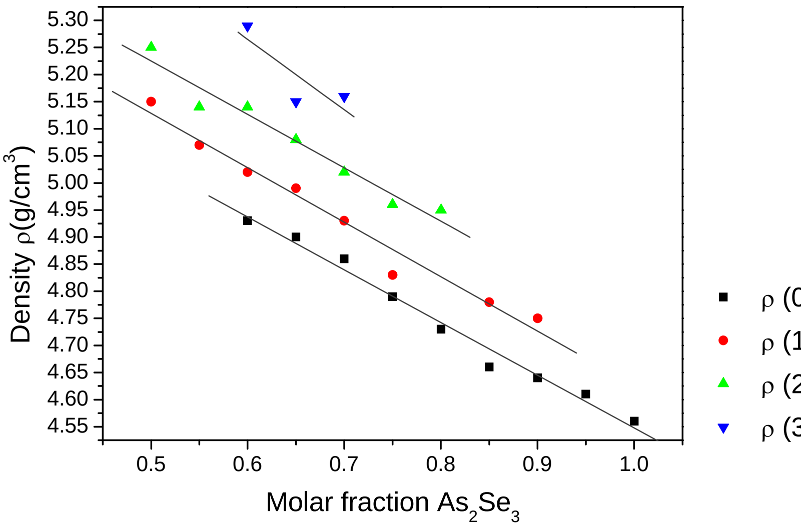

Fig. 3. Evolution of the density of the cuts containing 0%, 10%, 20% and 30% of Sb_2Te_3 of system ternary Sb_2Se_3-As_2Se_3-Sb_2Te_3 according to the content of As_2Se_3

On the whole of the ternary cuts, the density ρ presents a decrease of the values:
- from 4.93 to 4.56 g/cm^3 when the content of As_2Se_3 increases x = 0.60 to x = 1 on the cut containing 0% of Sb_2Te_3;
- from 5.15 to 4.75 g/cm^3 when the content of As_2Se_3 increases x = 0.50 to x = 0.90 on the cut containing 10% of Sb_2Te_3;
- from 5.25 to 4.95 g/cm^3 when the content of As_2Se_3 increases x = 0.50 to x = 0.80 on the cut containing 20% of Sb_2Te_3;
- from 5.29 to 5.15 g/cm^3 when the content of As_2Se_3 increases x = 0.60 to x = 0.70 on the cut containing 30% of Sb_2Te_3.

This decrease of the values shows that the tendency to vitrify, i.e. the disorder in these vitreous compositions of the ternary cuts, increases with the content of As_2Se_3.

This decrease also has another origin because it is also due to the substitution of antimony (Sb) by arsenic (As) less heavy.

The evolution of the density (ρ) is parallel for the four cuts, which makes think that the introduction of tellurium into these cuts is done according to the same mechanism. The tellurium plays the same role in these cuts.

It is noted that the values of the density (ρ) increases when the proportion out of tellurium increases.

The density (ρ) being able to be related to the structural order in glass, its increase when the content of Sb_2Te_3 increases indicates that the disorder in these vitreous compositions decreases, but it should be added that the effect of mass is dominating.

3.2 Study of the stability of glasses by slow cooling

After the treatment above described the sample then passed to x-rays to identify the phases which crystallize.

Some of them remain vitreous after this treatment in the apparatus of differential calorimetry.

We indicate by stable glass any glass not presenting neither peak of crystallization on the thermograms to cooling and nor lines of diffraction on the diffractograms of x-rays after the treatment described above.

On the Sb_2Se_3-As_2Se_3 binary system, glasses of compositions x = 0.80; 0.90 and 1 remain stable. Glasses of compositions x = 0.60 and 0.70 crystallize partially.

On the Sb_2Te_3-As_2Se_3 binary system, glasses of compositions x = 0.80; 0.90 and 1 remain stable. Glass of compositions x = 0.70 crystallizes partially.

On the cut containing 10% of Sb_2Te_3, glasses of compositions x = 0.70; 0.80 and 0.90 remain stable. Glasses of compositions x = 0.50 and 0.60 crystallize partially.

On the cut containing 20% of Sb_2Te_3, glasses of compositions x = 0.70 and 0.80 remain stable. Glasses of compositions x = 0.50 and 0.60 crystallize partially.

Stable glasses are represented in the following diagram of the system Sb_2Se_3-As_2Se_3-Sb_2Te_3 (Fig. 4). The observation of figure 5 makes it possible to conclude that the stable compositions are side of As_2Se_3, coming to confirm that the covalent character of this compound supports vitrification.

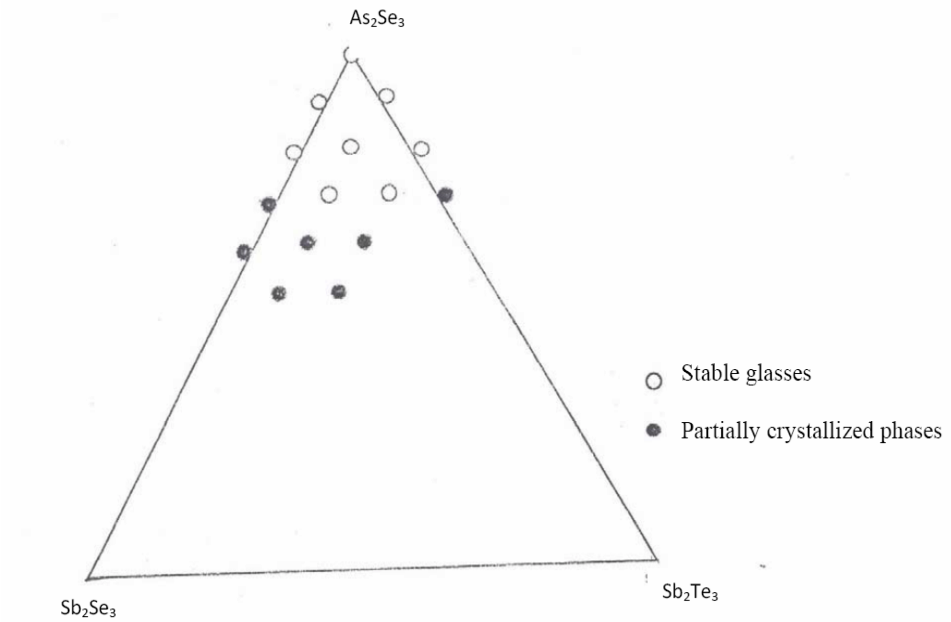

Fig. 5. Localization of stable glasses.

4. Conclusions

The density (ρ) being able to be related to the structural order in glass, its increase when the content of Sb_2Te_3 increases indicates that the disorder in these vitreous compositions decreases, but it should be added that the effect of mass is dominating.

The stable compositions of studied glasses are side of As_2Se_3, coming to confirm that the covalent character of this compound supports the vitrification.

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