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DSC study of chalcogenide glasses prepared under various gravity conditions

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Differential scanning calorimetry analysis was used to gain some insight into the thermal stability and calorimetric behaviour of $Ge_{20}Sb_{20}S_{60}$ glassy alloy prepared in various gravity conditions. The Earth-prepared glass retains its composition over all the bulk and DSC curves of as-quenched glass have similar shape. In the space glass, significant differences in the matter distribution inside the ampoule were observed. DSC curves of the material taken at the edge and inside of the bulk have different shapes. Significant density fluctuations in the space glass indicate a decreased homogeneity compared to the terrestrial glass. The driving force of the convection on Earth differs from that in space and has a strong influence on the mass transport towards the solidification front: on Earth it is the concentration-induced flow, whilst in space the Marangoni flow connected with changes of the free surface prevails. The surface tension seems to be the predominant force in the molten chalcogenide mixture, giving rise to decreasing homogeneity in the space glass.

1. Introduction

Attention has been paid to chalcogenide glassy alloys because they exhibit many useful and interesting physical properties [1, 2], which can be easily influenced by structural effects, e.g. by crystallization (degree of crystallization) or by stability of the crystalline phase. There is evidence that the chemical interaction between components of an alloy plays an important role in its glass-forming ability. One of the simplest ways to treat the interaction between atoms of components, giving a specific short-range order, is the thermodynamic investigation of the so-called associated complexes, pseudomolecules or even clusters, being in equilibrium with uncombined atoms. This suggests that in the liquid some atoms are free, while others associate into small groups [3, 4]. Such a group or complex may be considered as a molecular-like object. It differs, however, from a real molecule because it is likely to be formed by a group of bonds rather than by a group of atoms [5]. A rapid quenching of the melt freezes the liquid structure and is presumed to fix a definite chemical short-range order in the glass which could be responsible for nucleation and crystallization behaviour.

In the present work we carried out studies to determine whether any differences exist in structural inhomogeneity and/or in the thermodynamic behaviour of chalcogenide glasses prepared under different gravity conditions. Experiments performed in space have led to the conclusion that melts exhibit an increased tendency towards non-equilibrium solidification [6, 7]. It is supposed that the preparation of glasses under zero gravity may lead to an improvement of homogeneity, and to a decreased number of optical defects in the case of the infrared transmitting chalcogenide glassy alloys that largely originate due to the convection flow in the melt in a non-equilibrium temperature regime [8]. There are four broad areas in which reduced gravity plays a significant role [9]: (a) a reduction of natural convection, (b) containerless handling, (c) sedimentation, and (d) elimination of hydrostatic pressure. As far as the first case is concerned (which is also our case), if the role of buoyancy is substantially reduced, then surface-tension-driven flow may be the dominant mechanism for convection. Mass and heat transport are generally governed by diffusion and convection. The transport of species throughout the melt by pure diffusion only is gravity independent [10]. Thus, in many cases, the solidification of the melts is practically insensitive to the action of the external gravitational force, one of the weakest of the known fundamental force fields in nature [11].

Convection under terrestrial conditions follows the Bènard–Rayleigh flow where density and gravitational field are important quantities, while in space, under "low-g" conditions (g being reduced to about $10^{-3}g_0$–$10^{-6}g_0$ where g_0 is the acceleration due to gravity at the Earth's surface), the temperature dependence of free-surface changes play the most important role, which is expressed by the Marangoni flow. Further, the question of complex formation (or

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clusters or molecular-like objects) should perhaps be taken into account [12]. In other words, a coupled influence of gravity and complex formation may be expected. Such a phenomenon can be understood to be the succession of the usually non-linear chemical reactions. So it is possible that solid phases of different physico-chemical properties can be obtained from the given melt under identical technological conditions but at various levels of gravity. Here we suggest some possible mechanisms which would help in the understanding of the processes in the space.

2. Experimental procedure

The glassy alloy of composition $Ge_{20}Sb_{20}S_{60}$ was prepared from 99.999% pure germanium and antimony and from purified sulphur. The components were melted at 1120 K in an evacuated quartz ampoule for 10 h in a rotary furnace [13] and then cooled in water. The cooling rate was estimated to be 100 K min^{-1}.

Two samples were prepared from this alloy. Both were placed into quartz ampoules of inner diameter 8 mm, and the ampoules with the samples were then evacuated and sealed. Each ampoule of total length 6 cm was wrapped in silver foil to improve temperature homogeneity and enclosed in evacuated stainless steel capsules.

The samples were subjected to further heat-treatment procedures under different conditions. One sample was treated in the Soviet Orbital Laboratory "MIR" in frame of the Intercosmos experiment and, the second one under terrestrial conditions in the Institute of Space Research, Academy of Science of the USSR, Moscow [14].

The heat procedures, identical for both samples, were performed using the CSK-1 equipment [15]. The treatment consisted in heating to temperature (1120 K), holding at this temperature for 2 h, cooling simultaneously to 998 K in 1 h, and annealing at this temperature for 3 h. Then the heating was turn off and the capsule was removed from the furnace and left to cool. The cooling rate was estimated to be 10 K min^{-1} in this case. The distribution of matter in the ampoules is shown in Fig. 1.

The terrestrial sample was received as a crescent-shaped bar adhered to both ends of the ampoule, the total mass being ~ 7 g. After opening the ampoule, the entire bulk was cracked into three pieces (Fig. 1). The majority of the following measurements was carried out using piece 2. The space glass was completely different; the bulk was situated in the rear end of the ampoule (with respect to the drawing direction) with a thin layer of a matter in the front part. On opening the ampoule we obtained a bulk which spontaneously broke into four pieces, as schematically shown in Fig. 1. Mostly piece 5 was used for further measurements. The whole piece was cut into two symmetrical halves along the axis of the ampoule. From one half, plates were cut perpendicular to this axis. Both the terrestrial and space materials, respectively, from the pieces mentioned above, were annealed at 673 K for various times (100, 150 and 200 h) so that the crystallization could be studied. The varied distribution of matter in both samples could be related to the different values of adhesion, surface tension and different types of convection occurring in the diverse gravitational fields (i.e. $g \geqslant 0$ and $g = 1$).

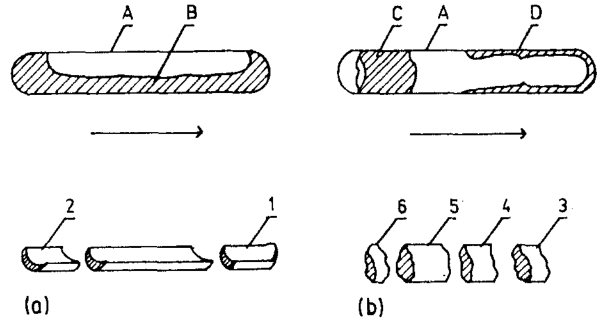

Figure 1 $Ge_{20}Sb_{20}S_{60}$ glassy samples after the Intercosmos procedure. (a) Terrestrial: A, quartz ampoule; B, glass. (b) Space: A, quartz ampoule; C, bulk in the back part; D, cracked layer along the front part. At the bottom, the pieces of the samples (drawn schematically) used for density measurements are shown (Table III). The arrow indicates the direction of movement in the furnace.

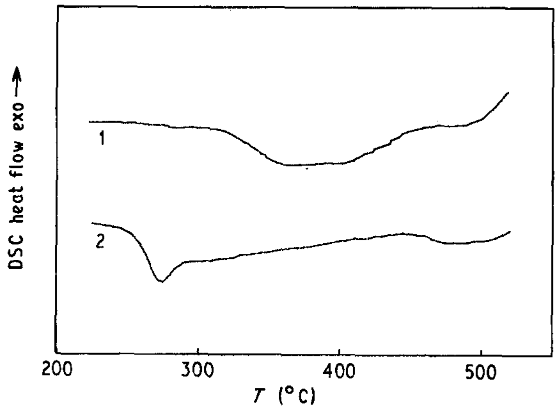

Figure 2 DSC curves of space as-quenched glass from the piece 5 (see Fig. 1): (1) from the outer surface, (2) from the centre.

To study the properties of the samples, various methods were used. Differential scanning calorimetry (DSC) measurements were performed in Du Pont 990 thermal analyser with a 910 DS calorimeter. For each run, 15–20 mg powdered material were sealed in an aluminium pan. DSC curves are shown in Figs 2–4.

X-ray diffraction (XRD) using CuK_α radiation was used to check the amorphous state or crystallinity in as-quenched as well as in annealed glasses. In as-quenched glasses, no crystalline phases were found. In the terrestrial sample, small peaks of Sb_2S_3 appeared after annealing for 150 h at 673 K. XRD investigations of the annealed space material had to be abandoned due to lack of material.

Electron microscopy examinations were performed on a Link 860/2 Edax Microanalyser, scanning microscope Jeol 773 and Kevex Delta Class V. As can be seen in the photographs of both as-quenched glasses (Fig. 5) holes in the glassy matrix were observed. A typical photograph of the annealed space glass is shown in Fig. 6. The analyses of both as-quenched glasses are presented in Table I and those of annealed

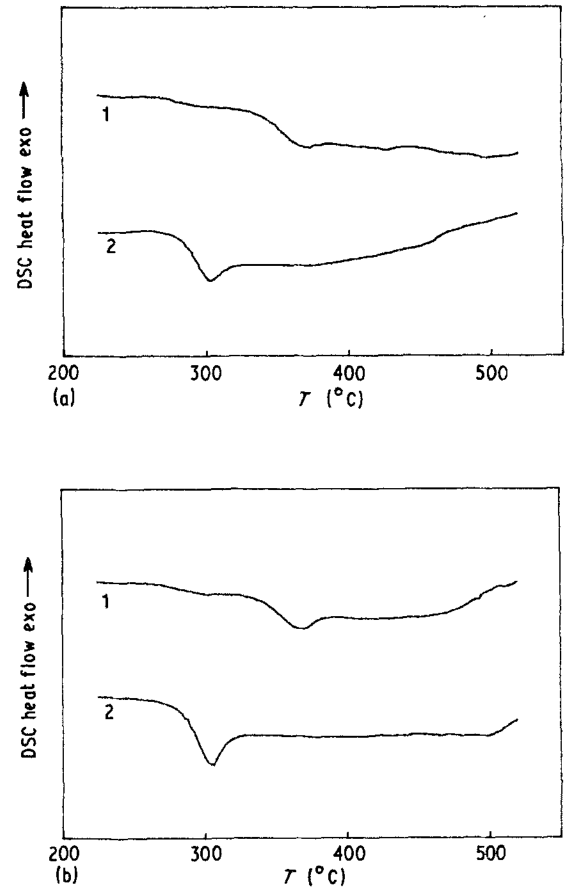

Figure 3 DSC curves of glassy $Ge_{20}Sb_{20}S_{60}$ (a) as-quenched, (b) heat-treated. (1) Space, (2) terrestrial. The powdered space sample was prepared from the layer near the centre of the ampoule. Heat-treated samples were annealed at 673 K in the DSC for 18 h, slowly cooled (2 K min^{-1}) to room temperature and then measured.

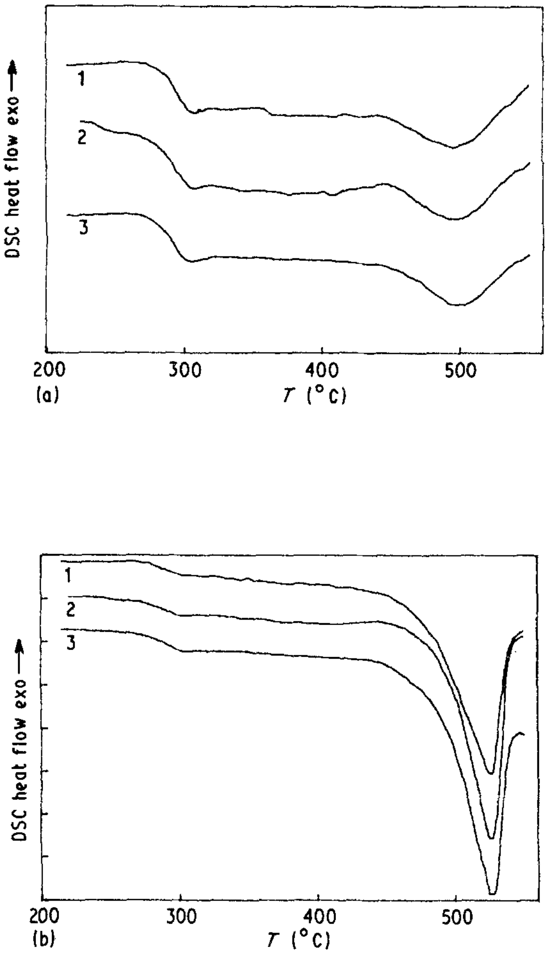

Figure 4 DSC curves of $Ge_{20}Sb_{20}S_{60}$ glassy samples annealed at 673 K; (a) terrestrial, (b) space (piece 3). (1) 100 h, (2) 150 h, (3) 200 h.

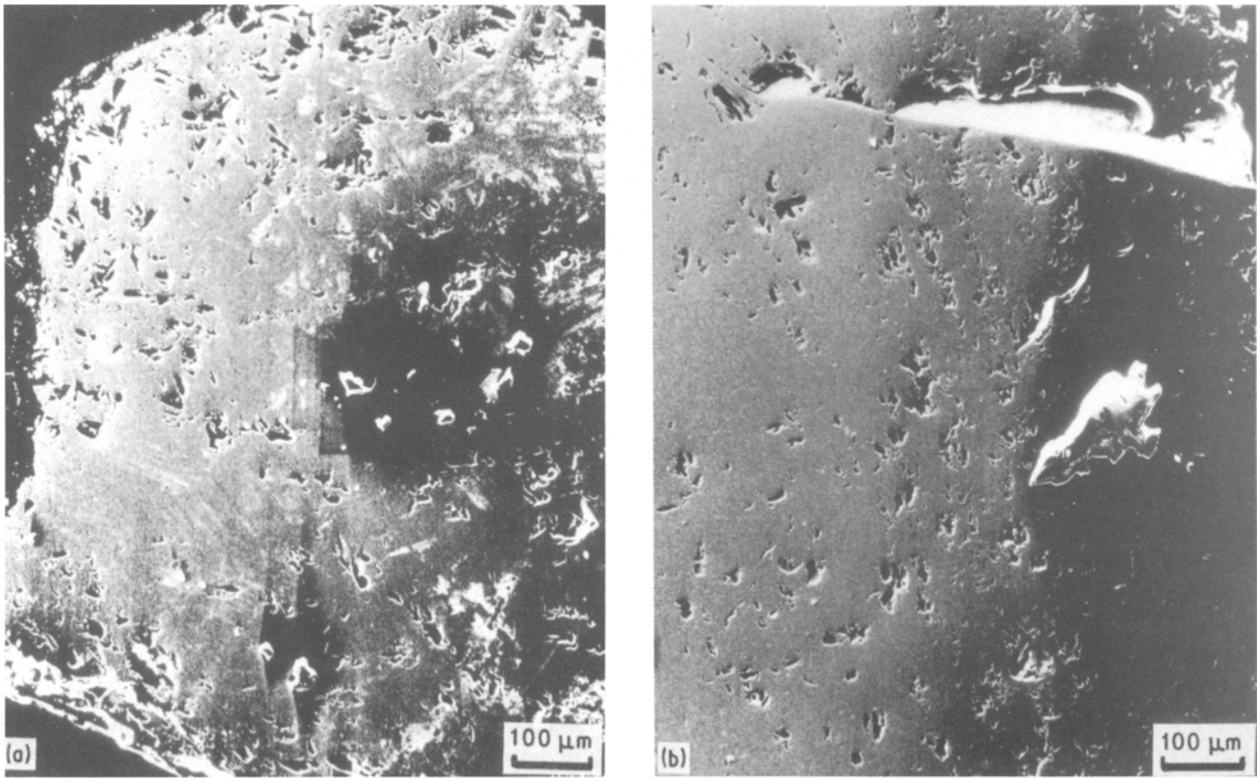

Figure 5 Electron micrographs of $Ge_{20}Sb_{20}S_{60}$ as-quenched glasses: (a) terrestrial, (b) space.

TABLE I Chemical composition of $Ge_{20}Sb_{20}S_{60}$ as-quenched glasses

Sample	Analysed spot	Found (at %)		
		Ge	Sb	S
Terrestrial 2	Inside	16.0	21.5	62.4
	At edge	16.4	21.3	62.4
Space 5	Inside	13.4	28.5	58.2
	At edge	23.3	16.3	60.4

TABLE II Chemical composition of $Ge_{20}Sb_{20}S_{60}$ samples annealed 150 h at 673 K

Sample	Analysed spot	Found (at %)		
		Ge	Sb	S
Terrestrial 2	Inside	17.97	19.78	62.25
	At edge	17.94	19.91	62.14
Space 3	Inside	15.37	23.11	61.52
	At edge	24.59	11.25	64.18
	White[a]	6.76	77.17	16.07

[a] Fig. 6, white spots.

TABLE III Density of $Ge_{20}Sb_{20}S_{60}$ glasses according to Fig. 1

Sample	Piece	Average ρ	Δ (±)
Terrestrial	1	3.514	0.016
	2	3.508	0.005
Space	3	4.32	0.04
	4	3.787	0.003
	5	3.819	0.002
	6	4.116	0.024

ones in Table II. In Fig. 7 the Ge–Sb–S diagram is shown.

3. Results and discussion

Starting from the density determination, one can see a considerable variation of density values, in particular in the space sample. Parts of the space sample near to the free surface (parts 3 and 6) have a higher density than those in the centre of the bulk (Table III). The density differences are apparently greater than deviations of the measurements. Compared with the density values calculated from those of GeS_2 and Sb_2S_3 ($\rho(GeS_2) = 2.7$ and $\rho(Sb_2S_3) = 4.8$) the values for $(GeS_2)_{0.6}(Sb_2S_3)_{0.4}$ and $(GeS_2)_{0.5}(Sb_2S_3)_{0.5}$ (the nearest to $Ge_{20}Sb_{20}S_{60}$, see Fig. 7) are 3.54 and 3.75, respectively.

In Table I we can see that the composition in piece 2 (terrestrial) is the same over the entire investigated cross-section and in certain limits it approaches $Ge_{20}Sb_{20}S_{60}$ or even better $(GeS_2)_{0.6}(Sb_2S_3)_{0.4}$ which is considered to be very close to a hypothetical eutecticum of a pseudobinary system GeS_2–Sb_2S_3. The analyses of a space glass plate cut from piece 5 give different values of element concentrations at the round border which had touched the ampoule wall, and in the centre of the bulk. The concentration inside the bulk approaches nearly $(GeS_2)_{0.5}(Sb_2S_3)_{0.5}$, but at the border an excess of germanium appeared and the composition could be considered to be nearly $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$. The difference in composition is reflected not only by the different colours of the powdered materials (from brownish to dark grey), but also by the results of the DSC measurements (Fig. 2). The glass transition temperature, T_g, of the sample

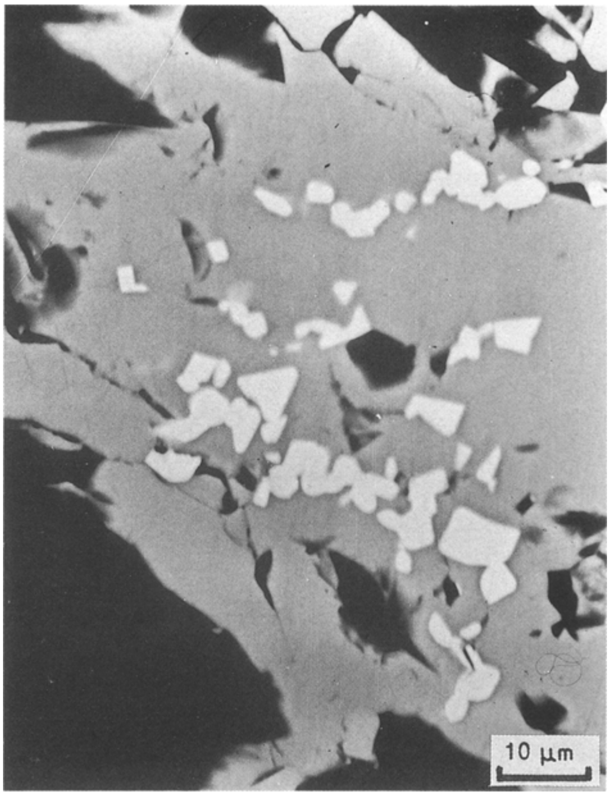

Figure 6 Electron micrograph of $Ge_{20}Sb_{20}S_{60}$ space glass annealed at 673 K for 150 h (see Table II). The white spots contain mostly antimony (see Table II).

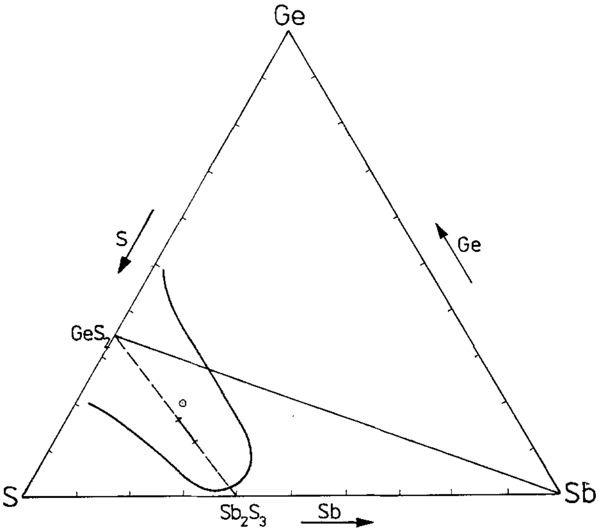

Figure 7 Ge–Sb–S diagram with a glass-forming region – $Ge_{20}Sb_{20}S_{60}$; the abscisa on the GeS_2–Sb_2S_3 line shows the region where the hypothetical eutectic should be found.

scraped from the outer surface of the bulk of piece 5 (Curve 1, Fig. 2) is 593 K, while that from the centre is 528 K. The shape of both curves is a consequence of a radial temperature gradient in the sample during quenching, slower cooling inside the bulk originating the so-called lambda peak on the T_g value. It is evident that different T_g values correspond to different phases, which is in accordance with the chemical analyses. According to our previous measurements [2], the T_g of $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$ is 593 K, and a $T_g = 528$ K lies in the interval $(GeS_2)_{0.4}(Sb_2S_3)_{0.6}$–$(GeS_2)_{0.5}(Sb_2S_3)_{0.5}$.

Table II summarizes the analyses of the annealed glasses. It is obvious that the elemental composition in the annealed terrestrial sample does not change very much from that in Table I and remains close to $(GeS_2)_{0.6}(Sb_2S_3)_{0.4}$. The space glass seems to be more difficult. Owing to a shortage of material, we had to study piece 3. The concentration changes, however, inside the bulk and at the border have the same character as those in the as-quenched glass, i.e. $(GeS_2)_{0.6}(Sb_2S_3)_{0.4}$ inside the bulk and $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$ near the border. Moreover, white spots appeared near the free surface (Fig. 6) which contained preferably antimony. Antimony had been observed before in the annealed $Ge_{25}Sb_{20}S_{55}$ [16].

By annealing the glassy samples at 673 K for 100, 150 and 200 h we tried to initiate crystallization. DSC curves of all the annealed samples are shown in Fig. 4a and b. During annealing the crystallization proceeded and hence a large endo effect always occurred. Only in DSC curves of the matter annealed for 150 h at 673 K did a suggestion of a small exo peak appear in both terrestrial and space glasses (Fig. 4). The endo effect could be connected with the formation of a phase of composition very near to the hypothetical eutecticum $(GeS_2)_{0.6}(Sb_2S_3)_{0.4}$. According to our experiences with the pseudobinary GeS_2–Sb_2S_3 system the melting temperature of such a composition should lie in the range 773–833 K. We are not able to explain the small indication of an exo peak proceeding the endo one after 150 h annealing. Only in the terrestrial sample annealed for 150 h were small peaks belonging to Sb_2S_3 found in the XRD measurements.

4. Conclusions

The hypothesis is known [17] that material prepared under microgravity conditions will show a higher homogeneity, better internal ordering and fewer microdefects. In some works space-grown and Earth-grown crystals were compared [18, 19] but evidence indicating the superiority of space-grown crystals was not conclusive. Our experimental results seem to be rather in contradiction with the above hypothesis [17] because: (i) the terrestrial glass investigated in this paper retains its composition throughout the bulk, and all DSC curves of the as-quenched glass have similar shape; (ii) the space glass has significant differences in chemical composition at the edge of and inside the bulk, and consequently the DSC curves taken from these two parts of the glass have a very different shape. Moreover, significant density fluctuation in the space glass clearly indicates a decrease in homogeneity in comparison with the terrestrial glass. In order to study more accurately the problem of the solidification of a multicomponent melt under microgravity conditions the following important phenomena should be taken into account: (i) the mass transport towards the solid–liquid interface during solidification, (ii) complex or associate formation, and (iii) the position of the solidified phase inside the ampoule.

The mass transport may be provided by diffusion, which is considered to be gravity independent, and by convection. While on Earth it is the concentration-induced flow (Bénard–Rayleigh flow) that makes the melt homogeneous; in space the Marangoni flow, connected with changes in surface tension of the free surface, prevails over the concentration-induced one. The most recent crystal-growth theories (References 9–11 in [10]) explain the differences between the ground and space experimental data in terms of convection. As the driving force of the convection on Earth differs from that in space, the convective transport of the species in the liquid phase to the solidification front can strongly influence the results of the solidification process itself.

In the system where chemical reactions (in general, non-linear) are expected, such as in the molten mixture of germanium, antimony and sulphur, those reactions can be greatly influenced by the gravitational field, especially when the system is far from equilibrium. It is well known that some aspects of the Ge–Sb–S glasses can be interpreted using a molecular model with GeS_4 and SbS_3 structural units interconnected through bridging –S– atoms. The formation of clusters $(GeS_4)_x$ and $(SbS_3)_y$ should occur just in the melt in space, and when cooled, compositions close to the hypothetical eutectic $(GeS_2)_{0.6}(Sb_2S_3)_{0.4}$ could be formed. Because of radial temperature gradient inside the matter, a germanium-rich compound solidifies first along the ampoule wall, leaving that closer to the hypothetical eutectic in the centre.

The position of the space sample in the ampoule differs significantly from the matter distribution in the terrestrial one. Ignoring the fact that the ampoules cannot be completely full of material (when cooling the quartz ampoules should be cracked), the melt in the horizontal position on Earth spreads along the whole length of the ampoule because of the gravitational field. The capillarity and adhesion forces make the melt rise along the walls so that the typical shape is produced (Fig. 1). In the space sample, surface-tension-driven force plays the most important role. In the absence of the gravitation field, the melt assumes the smallest volume and also surface area (i.e. a ball), and such a formation could be situated in any position in the ampoule. If the ampoules were broad enough, the ball would be situated in the centre without touching the wall. As the inner diameter is quite small the molten ball is limited by the quartz wall. When starting the movement (pulling the ampoule out) the adhesion necessary to fix the molten matter in the same position need not be sufficient to retain it, and the greater part of the mass could be moved to the rear of the ampoule, leaving a thin layer of the melt at the front. The wall surface, in the role of heterogeneous nucleation centres, will be covered with a solidified layer. Surface force could be one reason for the diffusion of heavier particles towards the free surface, resulting in a higher density in those parts.

Contrary to previous work [17], the surface tension seems to be the predominant force in the molten chalcogenide mixture. Therefore, it would be useful to include, in future space flights, carefully chosen experiments with the aim to observe surface-tension-driven flows in melts.

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