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# Short Communication

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## Phase separation in glass melts with liquid-liquid immiscibility after rapid cooling under terrestrial conditions and at microgravity

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Dedicated to Prof. Dr. Günther Heinz Frischat on the occasion of his 60th birthday

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Glass melts with a stable (liquid-liquid) miscibility gap tend to form two layers by a sedimentation process. The heavier phase forms the lower layer, the other the upper layer, in which droplets of the heavier phase become deposited. Cooling of glass melts with stable miscibility gaps under microgravity conditions prevents the sedimentation. The structure (texture) of glasses cooled under microgravity conditions is compared with that of glasses cooled on earth.

### Phasentrennung in Glasschmelzen mit stabiler Mischungslücke bei schneller Unterkühlung unter irdischen Bedingungen und bei Mikrogravitation

In Glasschmelzen mit stabiler Mischungslücke treten bei der Abkühlung Sedimentationsprozesse auf. Diese können zu geschichteten Proben führen. Die untere Schicht besteht aus der schweren, die obere Schicht aus der leichteren Glasphase, in die Teile der schwereren tropfenförmig eingelagert sind. Durch Unterkühlung einer derartigen Schmelze bei Mikrogravitation kann die Sedimentation verhindert werden. Die dabei entstehenden Phasentrennungsstrukturen werden mit denen verglichen, die sich in einer gleichartigen Schmelze unter irdischen Bedingungen bilden.

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### 1. Introduction

The transition of a melt to a glass is determined by chemical, thermodynamical and kinetic aspects. The processes controlling the structure take place in the range between the melt temperature and the glass transformation temperature  $T_g$ . This range is partially characterized by the cooling rate  $dT/dt$ , which holds for glass forming systems with phase separation, too.

Due to the sedimentation of the heavier glass phase, a complication arises in glass forming melts with stable immiscibility under terrestrial conditions [1 to 3]. Therefore, it is nearly impossible to predict the influence of the chemical composition on the function (matrix or droplet) of the coexisting phases.

### 2. Investigations under "terrestrial conditions"

A fast and defined cooling of  $PbO-B_2O_3$  melts [4] should suppress the sedimentation to a large extent. A cooling device was developed which consists of two copper plates to press the glass forming melt between them. It enables temperature measuring at different sites of the sample and allows the adjustment of sample thickness. Due to the shape and the effect of the cooling plates, the phase separation proceeds symmetrically in relation to the middle line of the sample (direction of pressing is

parallel to gravity). A temperature gradient occurs between surface and inside of the sample. The cooling rate varies depending on sample thickness and distance between the distinct site and the copper plate (cooling rate near the surface is assumed to be up to 20 000 K/min).

Light and scanning electron microscopic investigations of the samples show three different textures:

- a) glass matrix with microdroplets (either  $PbO$ -rich matrix with  $B_2O_3$ -rich droplets or  $B_2O_3$ -rich matrix with  $PbO$ -rich droplets),
- b) interconnected (spinodal-like) microphases, and
- c) a very small area which is completely clear ('heart' of the sample).

These textures are shown in figure 1. The texture can be explained by time and temperature dependence of the chemical composition of the coexisting phases, their viscosity, diffusion coefficients, heat transport, and by theoretical considerations on thermodiffusion. Despite the fast cooling, the texture is modified by gravitation (due to the density differences of the coexisting phases). An 'upper'  $B_2O_3$ -rich matrix with  $PbO$ -rich drops and 'lower'  $PbO$ -rich matrix with  $B_2O_3$ -rich drops was found. Consequently, quantitative statements are only possible with experiments under microgravity.

### 3. Experiments at "microgravity"

The experiments mentioned above were repeated with identical glass forming melts and temperature/time re-

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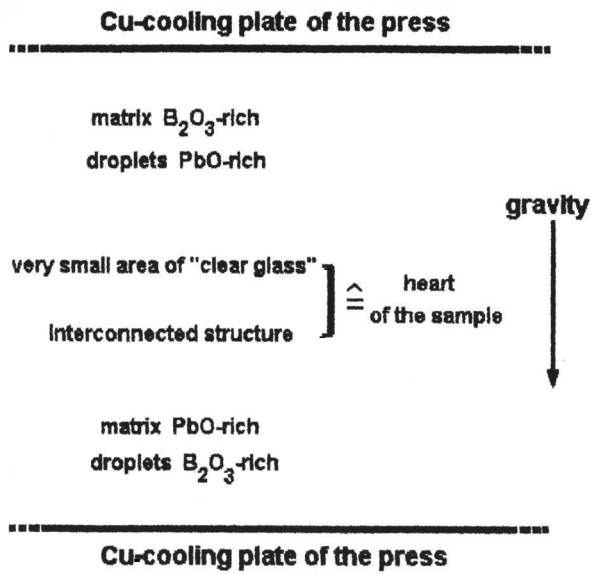


Figure 1. Scheme of the texture after the 1 g experiments.

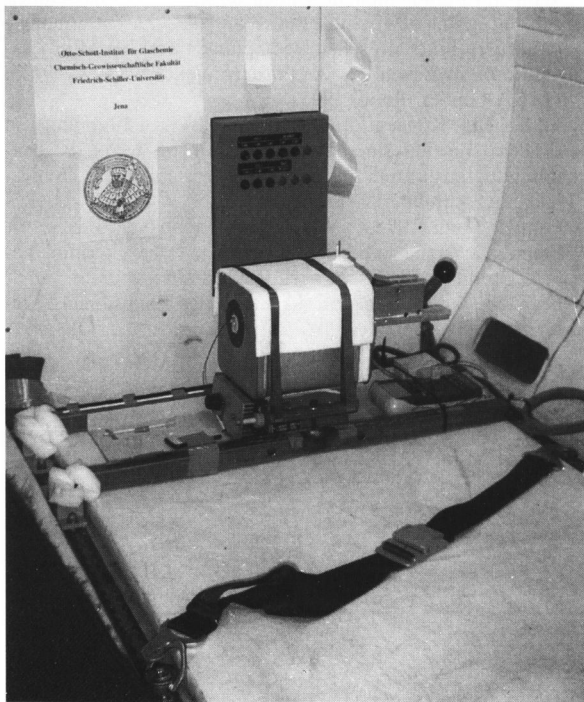


Figure 2. Cooling device on board the aircraft.

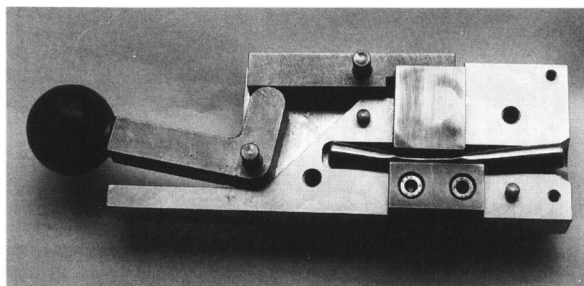


Figure 3. Cross-section through the lever press with "squeezed" platinum ampoule.

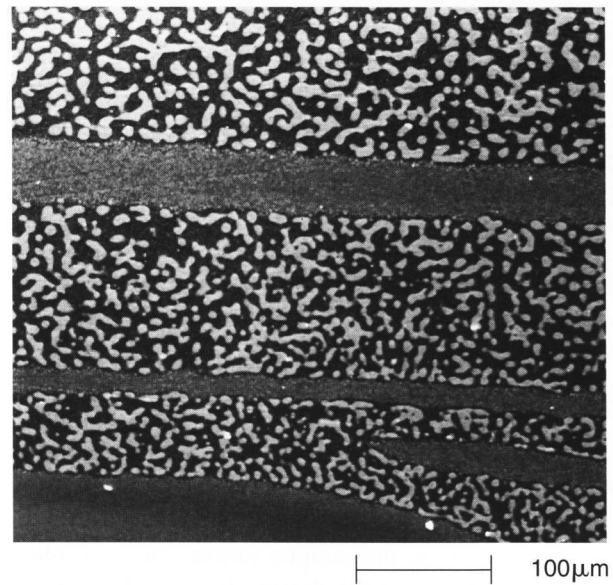
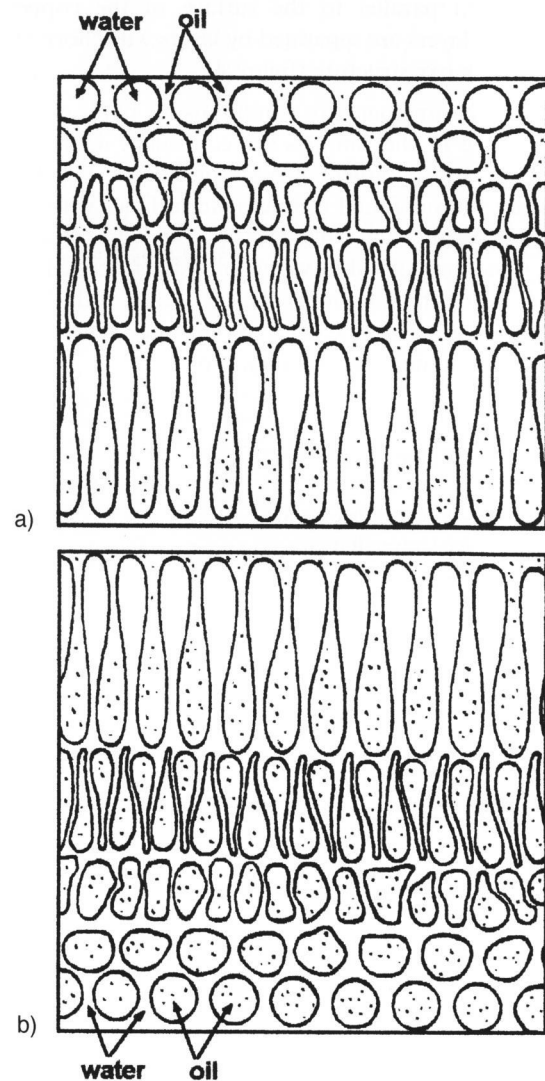


Figure 4. Texture after the  $\mu\text{g}$  experiment (SEM micrograph).



Figures 5a and b. Continuous phase transition in oil-in-water emulsion; a) water droplets in oil matrix [8], b) oil droplets in water matrix [8].

gime under microgravity conditions. This was done during the 21st ESA Parabolic Flight Campaign in 1995 [5 and 6].

A furnace and the cooling device (figure 2) were installed on board the aircraft. Glass forming melts were poured into platinum ampoules which were hermetically sealed before the flight. Ampoules were heated again during flight to temperatures above the critical miscibility temperature to obtain homogeneous melts. On onset of microgravity, the ampoules with the melt were pushed out and immediately pressed with the cooling device. Figure 3 shows the cross-section through the lever press with "squeezed" platinum ampoule.

The 'cooling time' is short, this is why these experiments are suitable for parabolic flights with microgravity periods of about 20 s.

The textures of the samples formed during cooling under microgravity differ drastically from the textures obtained during the terrestrial experiments: it shows interconnected microphases arranged in streaks which are orientated parallel to the surface of the copper plates. These layers are separated by layers with 'normal' droplets-in-matrix structure (figure 4).

Due to the microgravity conditions all parts of the entire volume of the samples are equivalent. Only the local temperature gradient decides on texture [7]. The texture the authors found is in total accordance with the scheme concerning the fluid transitions of droplets-in-matrix structures of oil-in-water emulsions derived by Ostwald [8] (figures 5a and b). This is shown with these findings for the first time for glass forming melts with stable (liquid-liquid) immiscibility, too.

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#### 4. References

- [1] Reiß, H.; Reiß, S.: Zur Sedimentation in glasig erstarrenden Schmelzen mit stabiler Mischungslücke. Köln: DLR (Deutsche Versuchsanstalt f. Luft- u. Raumfahrt), 1993.
- [2] Reiß, H.; Horn, L.; Vogel, W.: Elektronenmikroskopischer Nachweis des Funktionswechsels von Matrix- und Tropfenphase als Folge eines Temperaturgradienten in schnell abgekühlten Glasschmelzen. In: 11. Tagung Elektronenmikroskopie, Dresden 1984. Tagungsband. p. 204–205.
- [3] Mazurin, O. V.; Streltsina, M. V.; Shvaiko-Shvaikovskaya, T. P.: Handbook of glass data. Pt. B. Single-component and binary non-silicate oxide glasses. Amsterdam (et al.): Elsevier, 1985.
- [4] Levin, E. M.; Robbins, C. R.; McMurdie, H. F.: Phase diagrams for ceramists. Columbus, OH: Am. Ceram. Soc., 1964–1975. 1964 ed.: p. 115, fig. 281; 1969 suppl.: p. 91, fig. 2327; 1975 suppl.: p. 122, fig. 4349.
- [5] Reiß, H.: Vorbereitende Untersuchungen zum Einfluß eines Temperaturgradienten in schnell abgekühlten Glasschmelzen mit stabiler Mischungslücke auf die Phasentrennungsstrukturen unter irdischen Bedingungen und bei Mikrogravitation. Zwischenber. z. Förderprojekt 50 WM 9435, DARA GmbH, Bonn. 1993.
- [6] Reiß, H.: Konzentrationsabhängige Phasentrennung in Gläsern: Einfluß eines Temperaturgradienten auf die Entmischungsstrukturen in Gläsern mit stabiler Mischungslücke. Abschlußber. z. Förderprojekt 50 WM 9435, DARA GmbH, Bonn. 1995.
- [7] Kluge, G.; Neugebauer, G.: Grundlagen der Thermodynamik. Berlin: VEB Dtsch. Verl. Wiss., 1976.
- [8] Ostwald, W.: Beiträge zur Kenntnis der Emulsionen. Kolloid-Z. **6** (1910) p. 103–109.

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