The presence of double T_g and phase separation in $Te_{80}Si_{20-x}Pb_x$ glasses

The occurrence of phase separation is of importance for preparation of materials with definite properties by controlled crystallization of glass [1–3]. In chalcogenides the phenomenon of phase separation has not been widely studied. Recently, the phase separation manifesting itself by double T_g has been found for Pb–Ge–As–Se glasses by calorimetric measurements and was confirmed by microscopic studies [4, 5]. The co-existence of two glassy phases has been also detected for $Te_{80}Ge_{12.5}Pb_{7.5}$ [6] and $Te_{77}Al_{23}$ [7] glasses. The possibility of phase separation in $Te_{80}Si_{20-x}Pb_x$ glasses has been shown by Lasocka [8]. The aim of this work was to confirm this prediction.

For preparation of alloys, high-purity elemental solids were used (5 N, 6 N). Weighed samples (20 g) were melted by induction for 3 min at about 1073 K, in evacuated quartz ampoules. A high-frequency generator was used. Small amounts of alloys thus prepared were remelted and then rapidly cooled by the gun technique [9] to produce a glass. Glassy samples of 10 mg were studied calorimetrically using a Perkin-Elmer DSC-2 unit. All glasses had the same thermal history. DSC curves taken for the first run exhibited only one glass transition temperature, T_{g_1} (Fig. 1a). In order to read the second glass transition temperature, T_{g_2}, the procedure proposed in [6] was used. Namely, samples were heated in a calorimeter at a rate of 20° min^{-1} to the temperature of the end of the first exothermic transformation, cooled at a rate of 320° min^{-1} and re-heated at a rate of 20° min^{-1}. T_{g_2} appeared within the temperature range of the previous peak of the first exothermic transformation.

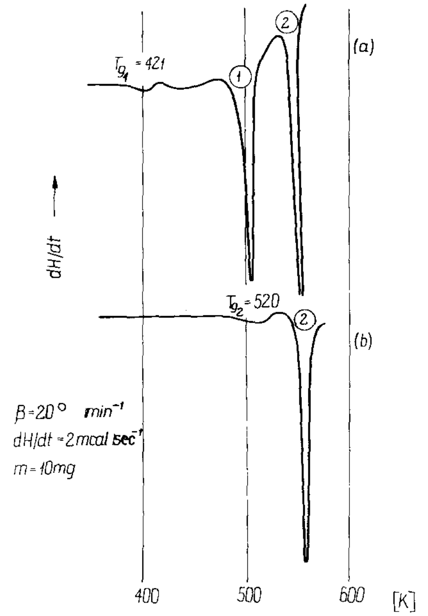

Figure 1 DSC traces taken for $Te_{80}Si_{17.5}Pb_{2.5}$ glass, as an example of double T_g occurrence: (a) first run, (b) second run, after previous heating to completion of the first exothermic transformation.

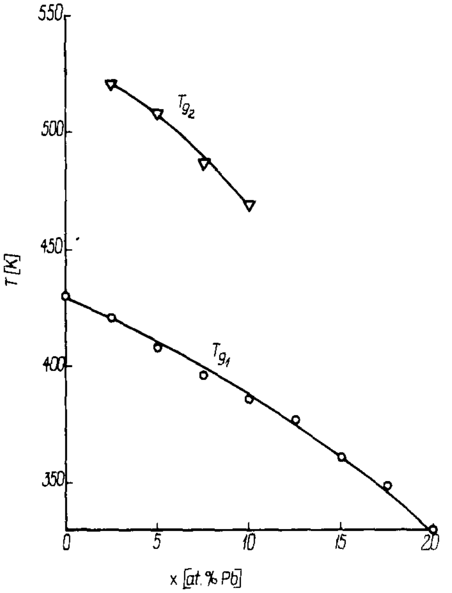

Figure 2 T_g of ternary glasses as a function of Pb concentration.

We used a series of $Te_{80}Si_{20-x}Pb_x$ glasses (at%) with values of x changing every 2.5%. For each composition of glass, five replicate samples were studied and the mean values of T_{g_1} and T_{g_2} were calculated. The reproducibility of the results was better than 1°. Full experimental data are recorded in Table I and plotted in Figs. 1, 2 and 4.

Double T_g occurred for glasses containing 2.5 to 10 at% Pb. Depending on the composition, T_{g_1} and T_{g_2} were present within the temperature ranges 330 to 430 K and 469 to 520 K, respectively (Fig. 2). Glasses with lead concentration higher than 10 at% exhibited no double T_g.

The occurrence to two glass transition temperatures, T_{g_1} and T_{g_2}, points to the co-existence of two glassy phases in the as-quenched sample. The question arises which T_g corresponds to which

0022–2461/80/061586–03$02.30/0

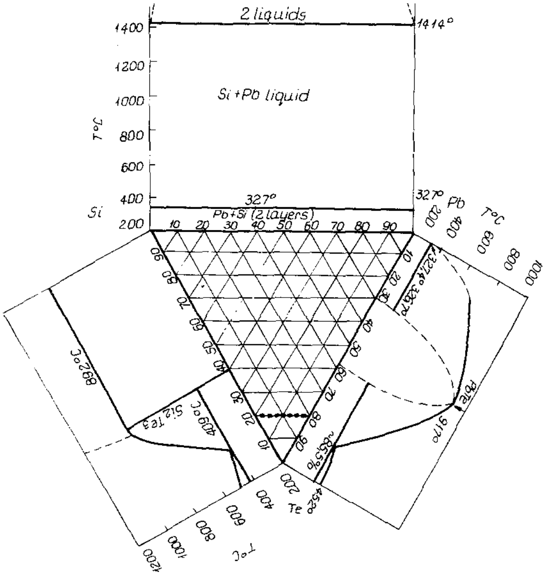

Figure 3 Compositions studied, shown in the concentration triangle of system Te–Si–Pb. Binary Te–Si, Te–Pb and Si–Pb diagrams were taken from refs. [10], [11], and [12], respectively.

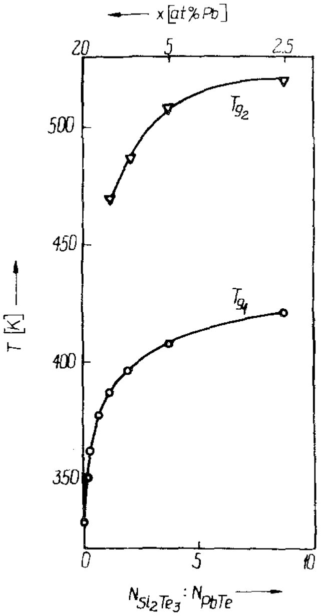

Figure 4 T_g as a function of molar ratio Si_2Te_3:PbTe.

phase. At equilibrium, the studied system Te–Si–Pb can be considered to be composed of Te, Si_2Te_3 and PbTe species (Fig. 3). In the glassy state, the existence of two super-saturated solid solutions PbTe(Te) and Si_2Te_3(Te) may be assumed. Calorimetric results indicate that T_{g_1} corresponds to the first exotherm, and T_{g_2} to the second one. X-ray studies performed for two different samples heated to just above the first and second exotherms, respectively, indicate the occurrence of Te plus PbTe crystals in the first, and Si_2Te_3 in the second sample. The co-existence of two glassy phases, PbTe-rich and Si_2Te_3-rich, also seems to be confirmed by the nature of the changes in T_g plotted as a function of the molar concentration ratio $N_{Si_2Te_3}:N_{PbTe}$ (Fig. 4). The slope of the line within the range of low values of this ratio (high Pb concentrations) points to a strong dependence of T_{g_1} on the Pb concentration. In the case of lower Pb concentrations (2.5 to 7.5 at%), even a great change in the ratio fails to affect T_{g_1} to any great extent. The occurrence of T_{g_2} within the range of high concentrations of Si_2Te_3 seems to be due to the existence of a Si_2Te_3-rich glass.

TABLE I Glass transition temperatures, T_{g_1}, T_{g_2}, and molar fractions of Te, Si_2Te_3, PbTe in $Te_{80}Si_{20-x}Pb_x$ glasses

	x (at%)								
	0	2.5	5	7.5	10	12.5	15	17.5	20
Molar fraction									
N_{Te}	0.5000	0.5125	0.5250	0.5375	0.5500	0.5625	0.5750	0.5875	0.6000
$N_{Si_2Te_3}$	0.5000	0.4375	0.3750	0.3125	0.2500	0.1875	0.1250	0.0625	0
N_{PbTe}	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
$N_{Si_2Te_3}$: N_{PbTe}	–	8.75	3.75	2.08	1.25	0.75	0.42	0.18	0
Glass transition temperature (K)									
T_{g_1}	430	421	408	396	386	377	361	349	330
T_{g_2}	–	520	508	487	469	–	–	–	–

Acknowledgements

The financial support of this work by the US National Science Foundation under Grant no. GF 421 76 is greatly appreciated. Thanks are due to Professor Henryk Matyja for his stimulating interest in this study.

References

1. D. R. UHLMANN and A. G. KOLBECK, *Phys. Chem. Glasses* **17** (1976) 146.
2. P. F. JAMES, *J. Mater. Sci.* **10** (1975) 1802.
3. W. VOGEL, in "Glass 77", Vol. 1 edited by J. Götz (CVTS Dum Techniky, Praha, 1977) pp. 172–214.
4. C. T. MOYNIHAN, P. B. MACEDO, I. D. AGGARWAL and U. E. SCHNAUS, *J. Non-Cryst. Solids* **6** (1971) 322.
5. J. J. MECHOLSKY, C. T. MOYNIHAN, P. B. MACEDO and G. R. SRINIVASAN, *J. Mater. Sci.* **11** (1976) 1952.
6. M. LASOCKA, *ibid* **13** (1978) 2055.
7. J. COLMENERO and J. M. BARANDIARÁN, *J. Non-Cryst. Solids* **30** (1979) 263.
8. M. LASOCKA, *Phys. Letters* **65A** (1978) 256.
9. M. CHYCZEWSKI and H. MATYJA, Report IBJ No. 1343/XIV/PS, Warszawa (1971).
10. L. G. BAILEY, *J. Phys. Chem. Solids* **27** (1966) 1593.
11. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys", 2nd edn. (McGraw-Hill, New York, 1958) p. 1111.
12. E. G. ROCHOW, "The Chemistry of Silicon" (Pergamon Press, Oxford, 1975) p. 1343.

Received 24 September
and accepted 19 October 1979

M. LEONOWICZ
M. LASOCKA
Institute for Materials Science and Engineering,
Warsaw Technical University,
Narbutta 85,
02-524 Warszawa,
Poland

Preparation of copper-coated titania particles for composites

In recent years, various methods for production of metal ceramic particulate composites have been developed based on powder and liquid metallurgy techniques [1–5]. Frequently, non-wettability between oxide particles and metals results in segregation of metal and ceramic phases and poor interfacial bonding in metal–ceramic particulate composites [6–7]. To improve the wettability, the ceramic particles are frequently coated with metals. Various coating techniques have been developed [8] of which electroless deposition is the method most commonly used [9]. Deonath and Rohatgi [10] have used this procedure to coat copper on mica particles. The major steps involved in the electroless method are: (a) activation of the surface of the ceramic particles by deposition of a noble metal such as Pd, Pt and Ag; (b) deposition of metal on the activated surface from a reducing bath containing metal ions.

Owing to the large surface area of ceramic particles, uniform activation throughout the surfaces can be achieved only with a large amount of activator. As a result, the process frequently becomes uneconomical with conventional activators. In this communication, we report a new method for coating titania (TiO_2) particles with copper (thickness range 2 to 15 μm) employing a relatively inexpensive activator – copper tartrate (CuT). Experiments were also carried out to coat copper onto TiO_2 particles using conventional activator $SnCl_2/PdCl_2$ solution [6]. The results obtained from both techniques are compared.

TiO_2 powder of particle size 1 to 20 μm was supplied by M/s Travancore Titanium Products Ltd, Trivandrum. Copper tartrate (CuT) solution was prepared by mixing sodium potassium tartrate

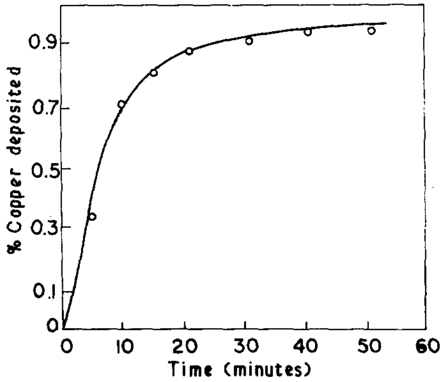

Figure 1 Copper tartrate adsorption on TiO_2 particles as a function of time.