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An assessment of Ge-Sb-Se glasses as 8 to 12µm infra-red optical materials

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This paper presents measured data on glass transition temperature, thermal expansion coefficient, density and hardness of some Ge–Sb–Se glasses. A method of purifying the elements Sb and Se from surface oxides is reported which enables low absorption glass to be synthesized. Suitable compositions for bulk synthesis are identified.

1. Introduction

In a recent paper [1] the suitability of Ge–As–Se glasses for use as 8 to 13 μm infra-red optical materials was discussed. Glasses from the Ge–Sb–Se system represent an alternative source of such materials and indeed Texas Instruments have already manufactured such a glass (TI 1173). However, there is insufficient published information on the physical properties of Ge–Sb–Se glasses to enable an optimum choice of materials to be made for any particular requirement or for comparisons to be made between glasses in this system and the Ge–As–Se system. It was the aim of the present work to provide sufficient measurements on the physical properties of Ge–Sb–Se glasses to enable such choices and comparisons to be made.

2. Experimental procedures

2.1. Glass preparation

Glasses were prepared from Hoboken polycrystalline germanium (50 ohm cm) Johnson Matthey spectrographically standardized antimony or MCP semiconductor grade antimony, and Johnson Matthey or MCP semiconductor grade selenium shot. Immediately before use the germanium and antimony were broken inside individual steel percussion mortars in an air atmosphere to a particle size of less than 3 mm to allow entry into necked down Vitreosil transparent silica glass tubes, and the selenium pellets were used as supplied. Melts of 25 g were made in the Vitreosil tubes of wall thickness 3 mm designed when sealed to withstand 10 atmospheres pressure with a safety factor of 10. The interior of each tube was rinsed with 50% V/V HCl then thoroughly washed with distilled water before drying in an air oven. Each tube was evacuated to 10^{-5} torr and out gassed by a prolonged heating of the tube with an oxy-hydrogen torch. After cooling under vacuum, each tube was filled with argon gas at atmospheric pressure, removed from the vacuum system and filled with the previously weighed germanium, antimony and selenium, and then repumped to 10^{-5} torr and held at this pressure for $1\frac{1}{2}$ h before sealing with an oxy-hydrogen torch.

In order to study the effect of oxygen impurity on the optical absorption of these glasses the melt tube design was changed and the raw material handling procedures and tube out gassing procedures were improved. To avoid unnecessary crushing and therefore contamination of the raw materials, a melt tube design retaining the full bore of the tube for the loading of the raw materials was adopted as shown in Fig. 1. This consisted of an outer tube plus a small insert onto which the outer tube was sealed after loading and evacuation. Each tube was evacuated as before but out gassed with a heating tape resistance heater at 450° C for 1 h. After cooling under vacuum, the valve A of Fig. 1 was closed and the

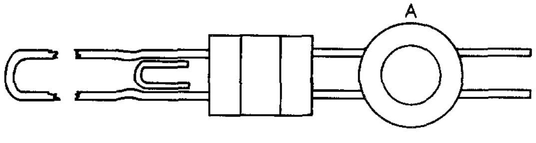

Figure 1 Melt tube, insert, and vacuum tap, A.

whole tube assembly transferred through a vacuum entry port into a glove box continuously flushed with argon. The germanium and antimony were crushed inside individual steel percussion mortars in this glove box to a particle size of 8 to 10 mm, while the selenium was used in pellet form. The raw materials were weighed in pyrex beakers on a top loading balance, and then transferred to the melt tube after the removal of tap A and insert. After reassembly, the filled melt tube with tap A closed was passed through the entry port of the glove box and re-evacuated to 10^{-5} torr. The tap A was then opened and the contents of the tube were evacuated to 10^{-5} torr for $1\frac{1}{2}$ h, after which the outer melt tube was sealed onto the insert by means of an oxy-hydrogen torch.

Each tube was loaded into a rocking rotation furnace described previously [2]. The furnace temperature was programmed up to 970° C at 5° C min^{-1} and after an overnight melting period of 19 h the temperature was reduced to 850° C for 1 h, after which each tube was air quenched into an insulated container at room temperature. This resulted in sufficient annealing to enable whole boules or boules fractured into two parts to be removed from the melting tubes. The glass transition temperature, T_g, of each of the glasses was measured and this was assumed to occur at a viscosity of approximately 10^{13} Pa. The annealing of the boules was achieved by heating them in an argon atmosphere at 5° C min^{-1} to $T_g + 5°$ C, holding them at this temperature for 1 h, and then cooling them slowly to room temperature. Specimens for physical property measurements were cut from the boules with a slow speed diamond saw and were polished as necessary by conventional techniques.

2.2. Thermal measurements

A Du Pont 900 thermal analyser console, a differential scanning calorimeter cell and a thermomechanical analyser were used in these measurements. Immediately before DTA measurement a sample of each glass was ground in an agate mortar in an air atmosphere. The glass transition temperature, T_g, the metastable melt crystallization temperature, T_x, and the onset of melting T_m, were determined on 25 mg of the powdered glass (240 mesh or less) heated at 5° C min^{-1} in an argon atmosphere. The measurement technique and the interpretation of data have been described elsewhere [3]. The linear thermal expansion coefficient of a single sample of each glass composition was measured on the thermomechanical analyser. This instrument was calibrated with samples of lead and aluminum of known thermal expansion coefficient and the precision of measurement was $\pm 0.15 \times 10^{-6}$. Each specimen was cut to a size of 5 mm x 8 mm by 10 to 20 mm long depending upon the size of annealed boule piece available, and the ends were ground smooth and parallel. A weight of 2 g was placed on the sample probe and each sample was heated at 5° C min^{-1} to $T_g - 25°$ C. At least three separate determinations were made on each sample.

2.3. Optical measurements

General visual examination of selenide glasses was carried out on a Nippon Electric Co. infra-red microscope type NB-11B. The transmittance of the glasses was measured on a Unicam SP1200 spectrophotometer in the range 2.5 to 24.0 μm through two different plane parallel samples of thickness 3 mm and 15 mm to allow determination of absorption coefficients.

2.4. Density and hardness measurements

Density measurements were made on annealed samples of average weight 10 to 12 g by the Archimedes method using freshly boiled water at room temperature (19° C). Six separate determinations were made on each sample and the average of these was corrected for the bouyancy of air [4]. The precision of measurement was ± 0.005 Hardness was determined by the Vickers diamond indentation method upon polished glass surfaces. The average results of six identations under a load of 20 g on each glass was taken as the final hardness number and the precision attained was ± 5.

2.5. Oxygen analysis

Determination of oxygen was made by Harwell Analytical R and D Unit using a gamma photon activation technique [5]. Samples of glass 5 mm x 5 mm x 3 mm were initially analysed in duplicate until a procedure had been established which yielded a precision of ±0.5 to ±1.0 p.p.m. by weight. Thereafter single samples were analysed.

3. Results

3.1. Glass-forming region and thermal properties

The glass-forming area enclosed by the dashed line in Fig. 2 is that reported by Hilton, Jones and

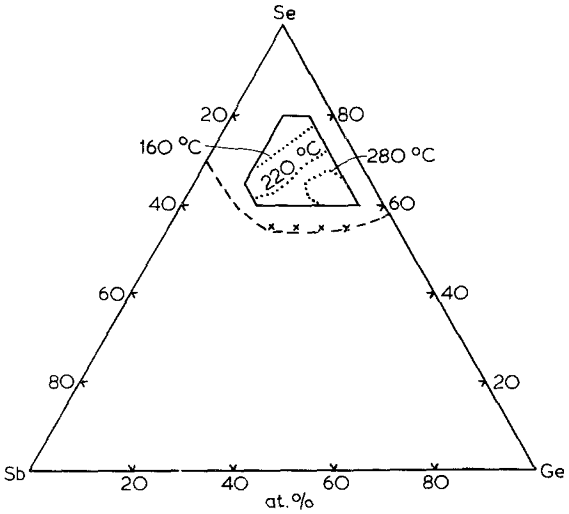

Figure 2 Glass-forming region of Hilton, Jones and Brau [6] – – –. Region studied in present work. ——— Glass transition temperature isotherms . . . . . .

Brau [6]. The present investigation was limited to glasses with Sb contents of $\geqslant 5\%$ and Ge contents $\geqslant 10\%$ within this area since a practical optical material is required to possess good thermal stability, a $T_g \geqslant 150°$ C and a thermal expansion coefficient $\leqslant 17 \times 10^{-6}\,°\mathrm{C}^{-1}$, and it was thought that these desirable physical properties were most likely to be found within the specified area of the Hilton, Jones and Brau glass-forming region. Glass compositions near the dashed edge of the glass-forming region in Fig. 2 were found to be crystalline or partially crystalline after synthesis, but the remainder listed in Table I and contained within the area bounded by the continuous line in Fig. 2 were found to be vitreous. After synthesis, samples from all of the compositions listed in Table I were subjected to differential thermal analysis in order to determine T_g and T_x. The results gave sufficient information to allow the glass boules to be annealed and to assess the relative thermal stability of the Ge–Sb–Se glasses. The glasses 1 to 7 in Table I, containing $\leqslant 15\%$ Ge, either showed large exothermic peaks at T_x, indicating problems for bulk production, or possessed inadequately low glass transition temperatures. The remainder of the glasses in Table I showed a low to moderate exothermic peak at T_x and hence are not ideal for bulk production. Nevertheless this degree of thermal instability could probably be tolerated especially since one of these glasses, Ge:Sb:Se 28:12:60 (TI 1173) has already been commercially manufactured. T_g isotherms obtained from graphical plots of the data in Table I are shown as dotted lines in Fig. 2. Within the area of the currently explored portion of the glass-forming region the range of glass transition temperature ranges from 121 to 311° C. From Table I it is seen that the thermal expansion coefficient ranges from 28.2 to 12.6 x 10^{-6} ° C.

The densities and hardness values of the Ge–Sb–Se glasses shown in Table I were measured to enable comparisons to be made with other infra-red

TABLE I

No.	Composition (Ge:Sb:Se)	T_g (° C)	T_x (° C)	Thermal expansion (X 10^6) 30 → 180° C	Density (kg m^{-3} X 10^{-3})	Vickers hardness number (kg mm^{-2})
1	10:10:80	121	285	28.2	4.61	–
2	10:20:70	159	286	20.5	4.90	–
3	10:25:65	192	312	18.4	5.04	–
4	15:5:80	138	–	26.5	4.48	–
5	15:10:75	159	459	19.2	4.62	–
6	15:15:70	183	466	20.1	–	–
7	15:25:60	232	336	–	5.04	184
8	20:5:75	186	–	24.91	4.50	–
9	20:10:70	215	521	20.2	4.60	182
10	20:15:65	264	425	16.8	4.70	185
11	20:20:60	248	383	15.4	4.90	209
12	25:5:70	248	–	18.5	4.46	–
13	25:10:65	308	415	15.55	4.51	207
14	25:15:60	268	521	14.7	4.75	205
15	28:12:60	277	522	13.79	4.68	206
16	30:10:60	287	410	14.7	4.62	206
17	35:5:60	311	432	12.6	4.51	–

optical materials. The range of hardness values found, 180 to 210, should be compared with values of 81 to 265 for the Ge–As–Se system and with a value of 1002 for single crystal germanium of orientation 100.

3.2. Optical properties

The handling procedure for making melts in order to assess the optical absorption has been given in Section 2.1. Using this procedure the results on optical absorption were not impressive. This was thought to be due to oxide impurity and a simple binary glass Ge:Se 20:80 was chosen for initial investigation of the raw materials and the synthesis techniques. The germanium raw material and the glass were analysed for oxygen by the technique described in Section 2.5, but the selenium pellets were not in a suitable physical form. The oxygen concentration found in the Ge raw material was <0.1 p.p.m. w/w so that oxygen in bulk germanium was not a problem. However a level of 8.8 p.p.m. w/w of oxygen was found in the Ge: Se 20:80 glass made from this germanium raw material correlating with an oxide absorption coefficient at 800 cm^{-1} of 0.95 cm^{-1} as illustrated by the dashed curve in Fig. 3.

This pick up of oxygen could have originated from the selenium raw material, from the surfaces of the germanium raw material, from the silica tube during seal off, or from the silica tube during the melting process. To standardize the experimental procedure a batch of melting tubes and individual batches of the raw materials were retained for the experiments, but it was found that melts of the Ge:Se 20:80 glass using three different batches of selenium raw material yielded glass with three different but reproducible absorption coefficients of 0.84, 1.66 and 1.95 cm^{-1} at a wavelength of 800 cm^{-1}. Clearly the oxygen impurity was associated with the selenium raw material. It was found that all three batches of selenium could be purified from oxygen and standardized to yield glass of identically low absorption coefficient by vacuum baking for 1 h at 300° C and 10^{-2} torr prior to use. Some selenium was lost but a white deposit presumably SeO_2 was also present on the cooler parts of the vacuum baking tube. The lump selenium resulting from this purification was used as a raw material in the glove box as described in Section 2.1. A typical example, illustrated in Fig. 3 by the continuous curve, showed an absorption coefficient of 0.42 cm^{-1} with a measured oxygen content of 0.7 p.p.m. w/w. The absorption in the impure glass in the region of 700 to 800 cm^{-1} is likely to be due in part to oxide absorption centred at 800 cm^{-1} which is almost completely removed in the purified glass, and to be due in part to the third overtone at 760 cm^{-1} of the Ge–Se fundamental tetrahedral vibration at 245 cm^{-1} [7] seen clearly in the spectrum of the purified glass. Several melts of composition Ge:Se 20:80 were analysed for oxygen as described in Section 2.5 enabling the plot of absorption coefficient at 800 cm^{-1} against oxygen concentration to be produced as shown in Fig. 4.

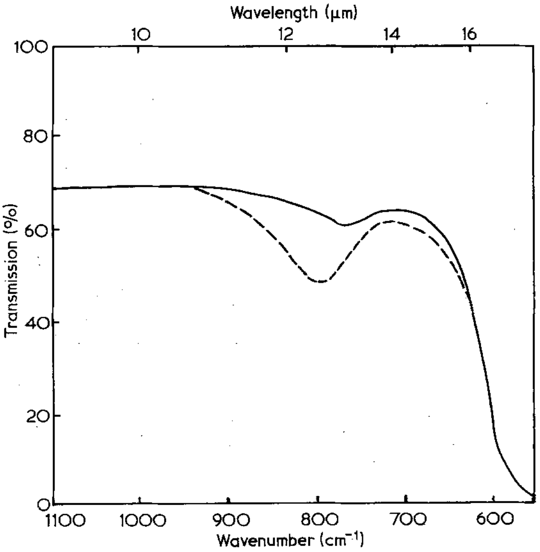

Figure 3 Transmission curve of a 3 mm thick sample of Ge:Se, 20:80 glass containing oxide purity – – –, and when purified ———.

In order to synthesize a ternary glass of the same purity level it was necessary to remove surface oxide from the antimony metal. If this was not done a glass showing a value of absorption coefficient of >1.0 cm^{-1} at a wavelength of 800 cm^{-1} was obtained. Table II quantifies the relative vapour pressures of Se, SeO_2, Sb and Sb_2O_3 at several temperatures. There is a large relative

TABLE II

Temperature (° C)	Vapour pressure (mm Hg)			
	Se	SeO_2	Sb	Sb_2O_3
200	0.004	1.89	–	–
275	0.096	74.0	–	–
300	0.24	200.07	–	–
550	–	–	0.01	0.41
600	–	–	0.06	1.94
630	–	–	0.16	4.50

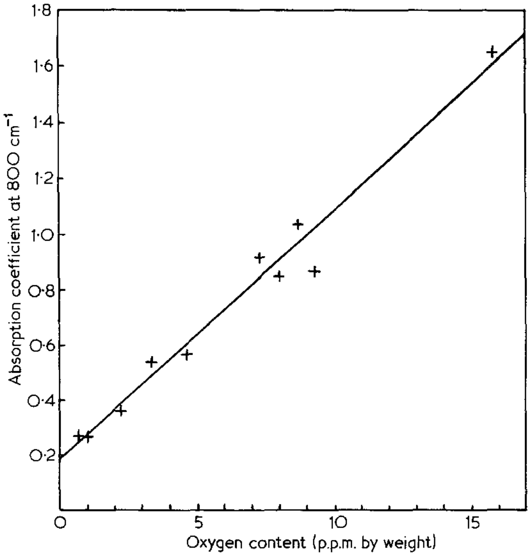

Figure 4 A plot of absorption coefficient at a wavelength of 800 cm^{-1} against oxygen content in p.p.m. wt for glass Ge:Se, 20:80.

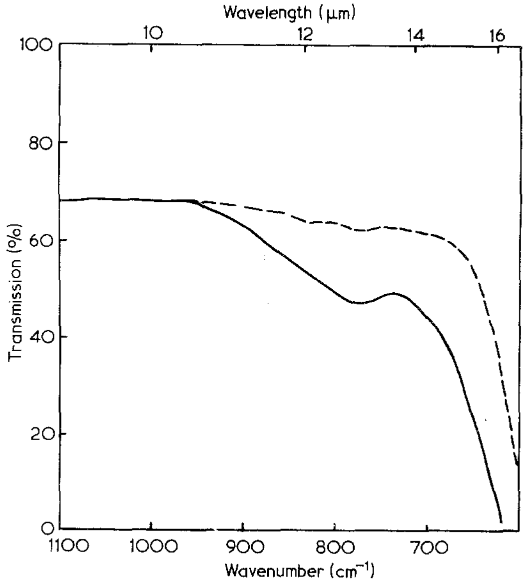

Figure 5 Transmission curve of a 3 mm thick sample – – –, and a 15 mm thick sample ———, of purified Ge:Sb:Se, 28:12:60 glass.

vapour pressure difference between selenium and its oxide enabling the metal to be readily purified by vacuum baking. However, the purification is a little more difficult to achieve in the case of antimony due to the smaller relative vapour pressure difference between antimony and its oxide close to the melting point of the metal. Nevertheless, this physical purification technique is viable if sufficient care is taken. Using the purified antimony an absorption coefficient of 0.23 cm^{-1} at a wavelength of 770 cm^{-1} was obtained for glass Ge:Sb:Se 28:12:60. A transmission curve for this glass is shown in Fig. 5.

4. Discussion

From the results given in Section 3.1, glasses with adequate thermal stability for commercial manufacture and of thermal expansion coefficient $\leqslant 17 \times 10^{-6}$ are to be found within the area of the Hilton and Brau phase diagram bounded by the continuous lines and to the right of the 220° C T_g isotherm shown in Fig. 2. These glasses potentially available for commercial manufacture from the Ge–Sb–Se system are smaller in number and less thermally stable than those reported to be available in the Ge–As–Se system [1].

Rechtin *et al.* [7] have studied the effects of compositional change and of impurities on the absorption coefficient of Ge–Sb–Se glasses in the range 400 to 900 cm^{-1}. Values obtained for high purity Ge:Sb:Se 28:12:60 glass were 0.013 cm^{-1} at a wavelength of 943.4 cm^{-1} (10.6 μm) and approximately 0.26 cm^{-1}* at a wavelength of 770 cm^{-1}, the latter not being significantly different from the value of 0.23 cm^{-1} obtained in the present work. The lowest values of absorption coefficient in the Ge–Sb–Se system were reported for high purity Ge 23.5:Sb 18:Se 58.5 glass and these were 0.008 cm^{-1} at a wavelength of 943.4 cm^{-1} (10.6 μm) and approximately 0.26 cm^{-1}* at a wavelength of 770 cm^{-1}.

Hilton *et al.* [8] have also studied the effects of impurities on the absorption of a Ge–As–Se glass of composition Ge:As:Se 33:12:55 and obtained values of absorption coefficient for the purified glass of 0.05 cm^{-1} at a wavelength of 943.4 cm^{-1} and 0.35 cm^{-1} at a wavelength of 780 cm^{-1}. In the present work an absorption coefficient of 0.27 cm^{-1} at a wavelength of 780 cm^{-1} has been obtained for a glass of composition Ge:As:Se 30:15:55. It would appear therefore that the intrinsic absorption levels in Ge–Sb–Se glasses are slightly lower than those in the Ge–As–Se glasses but it must be added that no attempts have been made to optimize the composition for minimum intrinsic absorption in the latter system. It is likely that in commercial production the ab-

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* Values marked were estimated from a plot of absorption coefficient against wavelength [7].

sorptions seen in the glasses from the two systems would be similar since it would be difficult to maintain the absorptions exactly at their minimum intrinsic levels.

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