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An assessment of the technique of hydrogen distillation as a production process for Ge-As-Se glasses

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The hydrogen distillation of glasses of composition Se–40As, Se–20Ge and Se–30Ge–15As from elemental raw materials in a 200 g scale horizontal tube furnace and in a 1.5 kg capacity vertical silica still and condenser, is described. The results demonstrate that inclusion-free and oxide-free glass can be prepared from cheap impure arsenic and selenium raw materials in the vertical still. The germanium selenide binary glass cannot be prepared by this technique due to fractionation into selenium glass and germanium selenide crystalline products. The ternary composition is capable of being manufactured by this process but an unacceptably high loss of arsenic and selenium can occur.

1. Introduction

There is interest in the manufacture of Ge–As–Se glasses for use in 8 to 13 μm infra-red optical equipment requiring components such as windows or lenses. These glasses are sensitive to oxygen contamination which produces unacceptable 12 to 14 μm absorption bands at concentrations greater than 1 to 2 ppm wt. There are two basic approaches that may be considered for the commercial manufacture of such materials. One is to scale up the usual laboratory synthesis technique of sealing elements in an evacuated silica tube and react these at 1000° C followed by a cooling and annealing heat-treatment. This sealed tube process [1] has the merit of retaining compositional integrity, but has the disadvantage of needing oxide-free starting materials. The alternative technique is that of distillation of the glass or of the elemental raw materials in hydrogen gas [2] which permits the removal of oxide during the synthesis but does not necessarily maintain compositional integrity. It was the aim of this work to assess the potential of the distillation technique as a process for bulk production. The first part of this account describes the results obtained from a small scale (150 to 200 g) horizontal distillation apparatus. The second part describes the evaluation of a 1.5 kg capacity vertical distillation unit and the results obtained from it. Finally, an attempt is made to forecast the probable usefulness of the technique.

2. Horizontal distillation

2.1. Apparatus

Previous work [2] has shown that a 10 g sample of selenide glass contaminated with oxygen impurity could be distilled in flowing hydrogen gas inside a horizontal silica tube. There was some loss of arsenic and selenium but the resulting glass contained a much reduced oxygen content as deduced from the reduction in infra-red absorption between 12 and 14 μm. In any commercial process it would be necessary to start from the individual raw materials rather than the already reacted ones in the form of a glass. Therefore, it was decided

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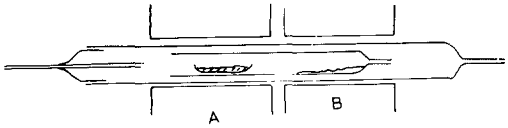

Figure 1 Schematic diagram of the horizontal distillation apparatus showing the source boat at position A, and the distillate collection at position B.

to scale up this horizontal apparatus [2] to distil 150 to 200 g batches of raw materials to further assess the potential of the process. A schematic diagram of the apparatus is shown in Fig. 1. This consisted of an outer silica tube 7 cm i.d. and 120 cm long fitted with a gas inlet cone and socket joint at one end, to provide access to an inner distillation tube, and a gas outlet at the other end. The inner tube as shown in Fig. 1 was designed for convenient collection of the distillate without contamination from powder sublimate or volatile oxides which would be swept into the outlet end of the outer silica tube. A two-zone furnace of zone length 12 cm was positioned over the outer tube relative to the boat of raw materials and the inner distillation tube as shown in Fig. 1. After each experiment the apparatus was cleaned by physical removal of the loose distillate and sublimate followed by a bake in hydrogen prior to the next distillation. In these experiments pure hydrogen without further purification was used directly from a cylinder. In operating the apparatus, the charge was loaded into the source boat, the gas flow was established and the furnaces were run up to the operating temperature. After completion of the distillation, the furnaces were switched off and the apparatus was allowed to cool naturally.

2.2. Assessment

Because of the considerable variation in composition within each distillate it was found necessary to homogenize each distillate by melting under vacuum at 500 to 520° C. Part of the homogenized distillate was then chemically analysed for selenium content. The residues in the source boats were also chemically analysed to determine their composition. Slices from the homogenized distillates were examined for inclusions on a Nippon Electric Co infra-red microscope type NB-11B, and thin chips of the unhomogenized distillate were also examined for inclusions and bubbles.

2.3. Results

Noranda 4N8 selenium and Vieille–Montagne 5*N* arsenic were taken as standard raw materials and the distillation parameters for glass Se–40As were first established. It was observed that when a mixture of arsenic and selenium was heated in a hydrogen flow of 400 $\mathrm{cm^3\,min^{-1}}$ a melt of uniform appearance with a grey surface scum was obtained. This was not appreciably volatile below about 700° C, but above this temperature the rate of distillation rapidly increased but levelled off in the region of 730 to 740° C. The rate of recovery of the distillate initially increased rapidly and reached a maximum at 730° C for a condensing temperature of 250° C and then decreased at higher distillation temperatures, suggesting that at these higher temperatures incomplete condensation occurred. It was also anticipated that the distillate collection temperature would influence the distillate quality, especially with regard to avoiding the condensation of volatile oxides. In early runs the collection temperature was set at 250° C, but it was obvious that condensation took place higher up the tube at a temperature of 400 to 500° C and then ran down the tube to the lower temperature section at 250° C. The collection zone was therefore set to 400° C which also ensured a more efficient removal of volatile oxides [2].

The effect of variation of hydrogen flow rate was also studied. The rate of distillation reached a maximum at about 400 $\mathrm{cm^3\,min^{-1}}$ of hydrogen flow. At lower flow rates, distillation was accompanied by the formation of a film of material above and around the boat. At high flow rates the cooling effect of the gas flow probably resulted in the observed reduced distillation rate.

Having established the basic conditions for producing Se–40As glass from an initial raw material ratio of As/Se = 2/3.8 at 400 $\mathrm{cm^3\,min^{-1}}$ hydrogen flow, 730° C distillation temperature and 400° C collection temperature, a series of runs was carried out to test the reliability of the procedure for consistently producing material of composition Se–40As. Seventeen distillations were completed and eleven yielded distillate analysing within 1 at.% of the target composition. The reason for the wider variation in the other seven runs was probably that small temperature and flow fluctuations led to relatively large compositional variations. The boat residues consisted largely of carbon (~ 50%) with silicon (1%) and boron (100 ppm) and other trace metal constituents. Microscopic examination of small chips of distillate revealed that bubbles varied in size from 25 to 150 μm and varied widely from run to run but these were not thought to be a serious defect since they would be removed during any subsequent homogenization. The most serious observation arising from the evaluation programme was the high inclusion content of the glass distilled in the horizontal system. Even after a homogenization process in a sealed silica tube at 800° C there appeared to be no significant reduction in the inclusions which were as large as 0.05 mm as shown in Fig. 3a. It is most likely that these were carbon particles carried over during the distillation process and attempts to reduce these by means of baffles were unsuccessful.

To summarize, the distillation experiments carried out on a 200 g scale showed that distillate of fairly predictable composition could be obtained, and a greater consistency of composition could probably be achieved by a simple scaling up operation. Effort was then turned to a vertical distillation system where baffling could be expected to be more effective in eliminating carry over of insoluble impurities.

3. Vertical distillation

3.1. Apparatus

A silica glass distillation apparatus was built to produce boules of unhomogenized glass weighing up to 1.5 kg. The apparatus, shown schematically in Fig. 2a consisted of a silica glass boiler at the base of a vertical column in which a removable silica baffle system was situated. A silica gas lead tube projected through the centre of the baffle system into the boiler and a second gas lead tube enabled the dead space at the top of the boiler column to be continuously flushed. A heated side arm carried the distillate away from the boiler and into a heated pyrex or silica receiver attached to the boiler side arm by means of a dry cone and socket joint. As a safety precaution forming gas ($N_2 + 3H_2$) was used effectively in these larger scale experiments and the exhaust gases were burnt off at the exhaust outlet which consisted of a short extension to the boiler side arm as shown in detail in Fig. 2b. The early runs in this system indicated that back diffusion of oxide into the distillate could occur, hence in later runs this exhaust section was modified to include a baffle and initially a room temperature nitrogen blanket flow. This ambient temperature gas flow resulted in vapour condensation which partially blocked the exhaust so that a final modification shown by the dashed lines in Fig. 2b incorporated a heated nitrogen blanket flow after the baffle plate.

To operate this vertical distillation system, a raw material charge was first loaded into the boiler, the baffle column was set in position, the boiler top cap was bolted in position and the gas flows started through the main and top gas leads. Boiler side arm and receiver temperatures were established and the product distilled into the receiver over a period of about 1½ h. When distillation

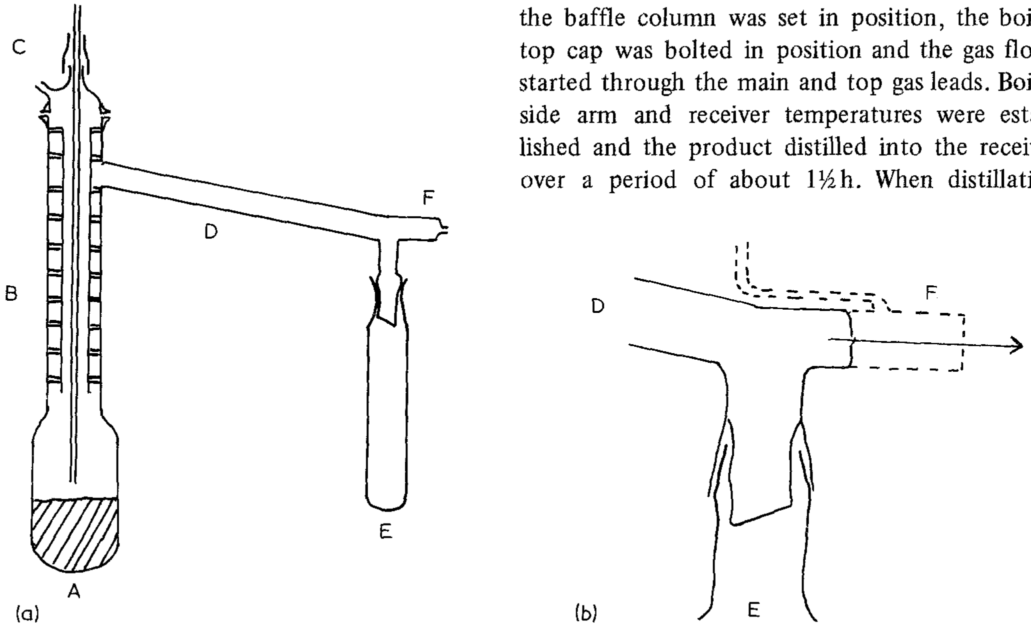

Figure 2 (a) Schematic diagram of the vertical distillation apparatus showing A, the boiler, B, the baffle system, C, the gas inlet, D, the side arm, E, the receiver and F, the exhaust. (b) Detail of the original exhaust system shown in continuous line. Detail of the final modification extension shown by a dashed line.

was complete all the heaters were switched off and the apparatus was removed from the furnace structure. The receiver with the gas flow maintained was allowed to cool naturally in air for an appropriate period of time, thus cooling the distillate rapidly through the crystallization temperature, and was then placed in an annealing furnace and cooled slowly to room temperature. This procedure gave an intact boule of glass ready for examination for inclusions and for assessment of infra-red transmission.

3.2. Assessment

On the completion of each distillation, boiler and baffle column residues were analysed by emission spectroscopy and each boule was sampled at the top, in the centre, and at the bottom for chemical analysis. Slices were cut from each boule for assessment of infra-red transmission on a Unicam SP1200 spectrometer and for assessment of inclusion content on an infra-red microscope.

3.3. Results

3.3.1. Se–40As glass

Noranda 4N8 selenium was used throughout these experiments in combination with Cominco (5*N*) arsenic containing the least nonvolatile particulate impurity, or Vieille–Montagne (5*N*) arsenic containing more particulate impurity, or cheap BDH reagent grade arsenic containing much particulate impurity. Thus the efficiency of the process in producing inclusion-free glass could be tested. The first three runs were abortive but served to establish initial operating parameters. These were 700 to 800° C for the boiler and side arm temperatures, 500° C for the receiver temperature, 800 $cm^3 min^{-1}$ of forming gas through the boiler and 100 $cm^3 min^{-1}$ of forming gas through the top of the boiler. Using these operating conditions and a 10% excess of selenium two distillations using Cominco arsenic and one using Vieille–Montagne arsenic were completed (runs 1 to 3, Table I). On removal of the first two boules from the pyrex receivers the surfaces were seen to contain some grey particulate matter and the third boule contained slightly more surface particulate matter. This was thought to result from carry over during the distillation process. To reduce this carry over changes were made during the next two runs in order to reduce the arsenic selenide distillation rate. It was found that lower boiler temperatures led to too drastic a reduction in the rate of distillation, but that by varying the gas flows some considerable control of distillation rate could be achieved. The next run (4, Table I) was completed with the boiler gas flow reduced from 800 to 500 $cm^3 min^{-1}$ and the top of the boiler gas flow reduced from 100 to 50 $cm^3 min^{-1}$. Little sign of surface contamination was seen on this boule. A further two distillation runs (5 and 6, Table I) were completed under these modified conditions using BDH reagent grade arsenic. This material of only 99% purity could provide an attractively priced raw material if technically suitable. The runs proceeded without incident yielding boules showing

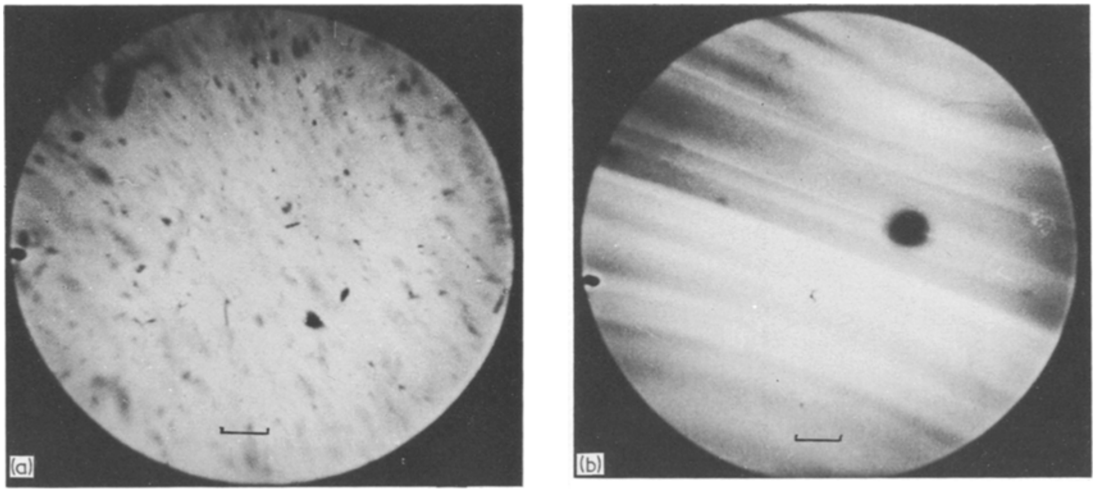

Figure 3 Infra-red microscope view of Se–40As glass after (a) horizontal distillation and remelting in a sealed tube at 800° C showing the presence of many inclusions (scale bar = 0.1 mm), (b) after vertical distillation showing inhomogeneity but no inclusions.

no surface contamination, although the non-volatile residues in the boiler and on the baffle column were much heavier than usual. A view through a slice of this material shown in Fig. 3b indicates that no inclusions were present. The large dark mass seen in the figure is an out of focus bubble. The infra-red transmissions of these distilled Se–40As materials were good considering the compositional inhomogeneities present and showed no sign of oxide contamination in the form of OH or As_2O_3. In this respect they were comparable to sealed tube melts [1] with the exception of the occurrence of the expected H_2Se absorption at 2200 cm^{-1}. In all of these distillations the grey residue found on the baffles was analysed to be silicon while the black boiler residue consisted of carbon and silicon. Chemical analysis also indicated that the boules were on average 1% rich in selenium. Full details of the six useful distillations of Se–40As glass are given in Table I and a typical transmission curve is shown in dotted line in Fig.4.

3.3.2. Se–20Ge glass

The distillation conditions were as before except that a silica glass receiver was used at a temperature of 650° C and the boiler and side arm temperatures were raised to 930 and 850° C respectively. In the first run complete reaction of the 99.95% purity germanium took place in the boiler and after distillation the residue contained no unreacted germanium. Crystalline germanium diselenide was recovered from the side arm and the distillate was partially crystalline. In a second run the germanium was added to the boiler in the form of germanium monoselenide and diselenide but again considerable separation of the constituents took place, with half of the germanium collecting in the side arm as crystalline germanium diselenide. It appears unlikely that an open flow gas distillation system will be successful in producing a uniform glass owing to the ease of fractional separation of selenium and germanium diselenide.

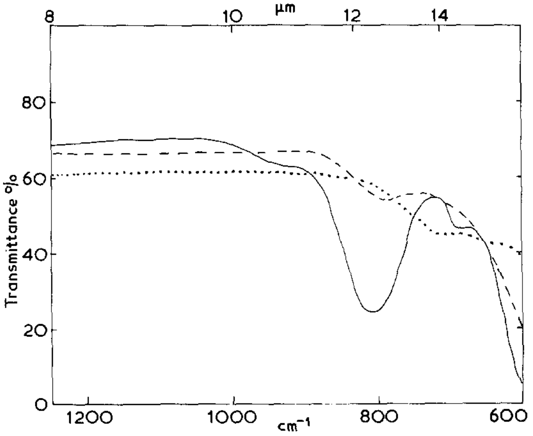

Figure 4 Infra-red transmission curves for (dotted line) the Se–40As distillate from run 6, Table I (specimen thickness 3.9 mm), (solid line) the ternary distillate from run 7, Table I showing oxide contamination (specimen thickness 4.0 mm), and a similar curve (dashed line) for run 8, Table I showing no oxide contamination (specimen thickness 5.7 mm).

3.3.3. Se–30Ge–15As glass

The first two distillation runs were attempted under similar conditions to those for the Se–20Ge glass. However, in both cases the charge incompletely distilled and the receiver entrance became blocked due to too low a temperature at this point. It was considered that a more effective distillation of the ternary mixture would be achieved if the temperature uniformity and distribution of the distillation unit were improved. The side arm heater was rewound to include the receiver connection and the baffle plate column was extended to reduce further the possibility of carry over of particulate matter. The third distillation run (7, Table I) using Cominco arsenic proceeded smoothly, the ternary mixture of elements completely distilled to give a boule containing no visible inclusions and of uniform composition with surprisingly good optical homogeneity considering that no agitation had been given to the distillate. Infra-red transmission revealed the presence of a high level of oxygen contamination in this boule as shown in Fig. 4. Another problem with this run was the difference in composition between the distillation charge and the distillate. It was anticipated that there would be a loss of selenium in the distillation of the ternary as occurred with the binary Se–40As. Therefore, a 10% excess of selenium was used but the distillate contained 64 at.% Se indicating a preferential loss of arsenic and/or germanium instead of selenium. In the next run the excess Se was reduced to 5% but due to a boiler furnace failure only part of the charge distilled. This distillate was found to be contaminated with oxide as indicated by absorptions at 35400 and 1600 cm^{-1} (OH) and at 810 cm^{-1} (GeO_2 or As_2O_3). It was decided to improve the exhaust section in order to reduce back diffusion of oxide by employing a baffle and ambient tem-

TABLE I

Run no.	Arsenic source*	Charge weight (g)			Gas flow (cm^3 min^{-1})			Temperature (° C)			Boule wt as % of charge weight	Average at.% of top, middle and bottom of each boule		Comments
		As	Se	Ge	Main	Top	Exhaust	Boiler	S-arm	Receiver		Se	Ge	
1	COM	600	1000	0	800	100	0	830	800–680	500	91	61.9	0	No oxide
2	COM	600	1000	0	800	100	0	850	810–670	500	94	62.3	0	No oxide
3	VM	600	1000	0	800	100	0	850	800–670	500	88	61.1	0	No oxide
4	VM	600	1000	0	500	50	0	830	760–610	500	88	58.9	0	No oxide
5	BDH	600	1000	0	500	50	0	830	800–670	500	88	61.9	0	No oxide
6	BDH	600	1000	0	500	50	0	830	820–700	500	91	58.6	0	No oxide
7	COM	101	500	195	500	50	0	800	930–650	650	85	64.0	–	Apparatus rebuilt oxide contamination
8	COM	147	608	296	500	50	1000	900	660–940	650	56	60.7	26.4	Reduced Se in charge heated exhaust gas flow. No oxide.
9	COM	147	608	296	500	50	1000	915	870	650	84	57.2	29.2	No oxide.
10	COM	147	608	296	500	50	1000	940	780	650	47	60.0	32.4	No oxide.
11	COM	147	608	296	500	50	1000	940	690–770	650	56	57.7	32.7	Receiver cracked
12	COM	147	608	296	500	50	1000	950	640–690	650	56	57.3	33.9	Receiver cracked

* COM = Cominco 5*N*
VM = Vieille–Montagne 5*N*
BDH = BDH reagent grade

perature nitrogen blanket gas flow. However, during the next run the gas effluent was partially blocked as a result of distillate condensation near the ambient temperature nitrogen blanket flow. In a final equipment modification this blanket nitrogen flow was heated before entry into the exhaust section. The next run (8, Table I) with a reduced selenium content was successful in yielding a distillate of low oxide content as shown by the transmission curve in Fig. 4, but the distillate still possessed too high a selenium content and fractured badly presumably due to compositional variations within the distilled boule. Four more distillation runs (9 to 12, Table I) were completed with the same batch material ratio to establish the compositional consistency of the distillate with modified distillate cooling procedures to reduce cracking and thus facilitate the assessment procedures. The results of these six useful ternary distillations together with the operational parameters are shown in Table I. The main feature of the results of Table I is the low weight of distillate collected compared with the weight of batch materials. On average about 38 wt% was lost from the apparatus as vapour. At this point it was considered that sufficient information on this technique had been acquired to make judgements as to its likely usefulness and no further experiments were performed.

4. Discussion

It is quite clear from the above results that Se–40As glass can be distilled in the vertical system free from oxide and particulate impurity using cheap selenium and arsenic raw materials. The resulting inhomogeneous distillate would require a subsequent homogenization process which could also be carried out in an atmosphere of forming gas. However, it is not possible to distill a binary germanium selenide glass such as Se–20Ge owing to the fractional separation of selenium and germanium diselenide. On the other hand, a glass containing arsenic and germanium such as Se–30Ge–15As can be distilled free from inclusions and oxide. It is difficult to see how the high vapour loss could be reduced while collecting the distillate at a temperature above the liquidus of the glass (650° C) but some reduction in loss might result from a reduction in the proportion of hydrogen in the gas supply and perhaps by a reduction in the rate of distillation. The redesign of the exhaust section in the vertical equipment to reduce the oxide level in the ternary glass was probably necessary because of the high germanium content of the exhaust gases. Back diffusing germanium oxide would not be reduced by hydrogen at the temperatures of the receiver and side arm, and would, therefore, contaminate the distillate. In the case of the arsenic selenide binary the receiver and side arm temperatures would have been high enough to encourage hydrogen reduction of As_2O_3 and SeO_2 vapours which accounts for the fact that this glass could be produced oxide free in the unmodified equipment. The problem of germanium selenide segregation as experienced with the binary glass was not apparent during the distillation of the ternary glass. The presence of arsenic may have been an important factor in allowing the formation of germanium arsenide species [3] during the distillation thus helping to reduce the tendency for the distillate to segregate into selenium and germanium selenide fractions.

The control problems associated with the production of a high percentage germanium ternary glass plus the high cost of germanium raw material would ensure that glass made by the vertical distillation process would be as costly as glass made by a sealed tube process with the additional disadvantage of batch to batch compositional variations perhaps as high as 4 at.%. Hence this synthesis technique would be most suited to the volume production of material for low power infra-red windows, an application where batch to batch refractive index variations resulting from the compositional variations would not be a major problem. However, for the same application a much cheaper material to produce would be Se–40As glass. If the batch size were limited to 3 to 5 kg then the slight crystallization tendency of this glass [1] would not be a problem. From previous work in which the refractive indices of a number of glasses were measured [1] it is estimated that the batch to batch variation of refractive index resulting from a compositional variation of 1 at.% for Se–40As glass would be no more than 5×10^{-3}.

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