

PURIFICATION OF  $\text{As}_2\text{Se}_3$  BY DECOMPOSITION OF UREA

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*Dedicated to Professor S. Škramovský on the occasion of his 70th birthday.*

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A method of purification and preparation of oxygen-free chalcogenide glass  $\text{As}_2\text{Se}_3$  without some metal impurities is described. The method is based on pyrolytic decomposition of urea. The complete desoxidation takes place within the range of temperatures 700–750°C. Residual gases and structural defects are removed by subsequent vacuum remelting. The infrared absorption spectra and d.c. conductivities of the purified samples, prepared at different temperatures, are reported.

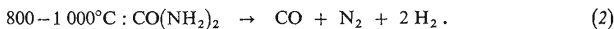
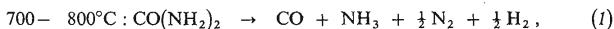
At present, a great deal of attention is concentrated on the peculiar physical properties of the amorphous glassy substances. These studies can only be performed with perfectly homogeneous and pure materials, which makes demands on their synthesis and, especially, on their purification. Amorphous glassy substances, such as  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ , Ge + Se, Ge + As + Se and others, have to date been studied mainly from the point of view of their technical importance as optical materials for infrared spectral region. For this reason the main goal of the technology of preparation of these materials was to ensure the removal of traces of impurities, especially those containing oxygen, since their presence brings about strong parasite absorption in the 480–1200  $\text{cm}^{-1}$  region. Electrical properties of these materials have so far attracted little attention. It was found that small amounts of oxygen seriously affect d.c. conductivity of these substances<sup>1,2</sup>. It can be expected that admixtures of other elements would exert similar effect.

So far, chalcogenide glass has usually been prepared by melting a mixture of stoichiometric amounts of starting elements of high purity in a quartz ampule without purification of the material so prepared. Only Savage and Nielson<sup>3</sup>, when working with a Se + Ge system, have used a desoxidation method based on distillation in a stream of hydrogen. Another method has recently been disclosed in a patent<sup>4</sup>, in which the desoxidation is effectuated by gaseous products of pyrolytic decomposition of a paraffin wax. The disadvantage of this procedure lies in the fact that the hydrogen, evolved in large amounts during pyrolysis, reacts immediately with selenium to give hydrogen selenide, whose presence manifests itself by a strong IR absorption band at 2200  $\text{cm}^{-1}$ . The carbon formed by pyrolysis is finely dispersed in the material, which non-selectively reduces its transmission in infrared region. Furthermore, because of gaseous decomposition products, the pressure in the ampule is quite high, which unfavourably affects the amount

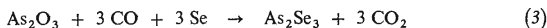
of defects in purified materials. In a previous work<sup>5</sup> dealing with preparation of samples of systems  $\text{As}_2\text{Se}_x$  and  $\text{Se} + \text{Ge}$ , we described a new method for preparing oxygen-free glassy materials, making use of a modified ampule. However, when starting materials contained larger amounts of oxygen, which was present not only in the form of surface oxide layer but also dispersed in the material, this method has not always yielded reproducible results. In this case, purification of the starting arsenic prior to its application was necessary, preferably by distillation from the melt with lead<sup>6</sup>, which inevitably complicated the whole process.

In the present work we aimed at working-up a new desoxidation method which would be simpler and would give reproducible results, irrespectively of whether the oxygen contained is fixed on the surface or dispersed in the volume of the material. We further assumed that such a method could also be used to remove admixtures of other elements from  $\text{As}_2\text{Se}_3$ .

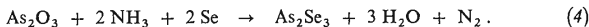
This method consists in heating either a mixture of stoichiometric amounts of the elements or impure glassy  $\text{As}_2\text{Se}_3$  with urea in a sealed quartz ampule, evacuated to  $10^{-4}$  Torr, to 700–750°C. When heated to 700–1000°C, urea undergoes decomposition, giving first ammonia and biuret<sup>7</sup>, which is subsequently decomposed to ammonia and cyanuric acid. On the ground of experimental evidence, we assume that the cyanuric acid undergoes decomposition on further heating, giving rise to the final products, carbon oxide, nitrogen and hydrogen. The course of the decomposition of urea depends on temperature. Dissociation of ammonia to nitrogen and hydrogen increases with increasing temperature. The decomposition of urea within the 700 to 1000°C temperature range can then be described by the following equations:



As the pyrolysis slowly proceeds, mixtures containing different amounts of individual components ( $\text{CO} + \text{NH}_3 + \text{N}_2 + \text{H}_2$ ) are formed. The necessary condition for the removal of small amounts of oxygen from a purified glass is the presence of the efficient desoxidation components, CO and  $\text{NH}_3$ , in the melt. Ammonium can also be effective in removing other impurities like traces of Al, In, by converting these to insoluble nitrides. The course of the desoxidation itself is temperature-dependent, too. We describe it in the following way:



respectively



According to literature<sup>8</sup>, the desoxidation by CO is limited by the temperature 700°C at which the equilibrium between CO and  $\text{CO}_2$  is practically attained. The dependence

of the composition of the products of pyrolytic decomposition of urea on temperature influences also the total pressure of gases in the ampule. The large pressure in the ampule unfavourably affects macrostructure of the glass being prepared, since it increases the amount of gases soluted in it. When the temperature of the melt decreases, the gases contained in the melt evolve as bubbles of different size, which markedly reduces transmission of the glass in the near and medium infrared regions. From the foregoing discussion it follows that the suggested method of purification of  $As_2Se_3$  by means of decomposition of urea is considerably affected by temperature. For this reason, a more detailed study of this effect has been undertaken.

## EXPERIMENTAL AND RESULTS

### *Effect of Temperature on the Removal of Traces of Oxygen from $As_2Se_3$*

Glassy  $As_2Se_3$  was purified by decomposition of urea at 700–1000°C. The glassy  $As_2Se_3$  containing oxygen in the form of glassy  $As_2O_3$  (ref.<sup>9</sup>) and exhibiting significant absorption bands at 630 and 800  $cm^{-1}$ \* (Fig. 1) was used as a starting material. A 10 ml quartz ampule (14 mm across) was charged with 10 g of the glassy  $As_2Se_3$  and 0.01 g urea. Then the ampule was evacuated to  $10^{-4}$  Torr, sealed and placed into a tube furnace provided with a swinging speed selector. The required temperature was maintained for 8 hours. During first three hours the furnace was allowed to swing from the vertical to horizontal position, then the swinging was stopped and the furnace was kept in vertical position for another five hours. The cooling rate of the melt, which corresponded to that of spontaneous cooling of the furnace, equaled to 35°C per min. After cooling to room temperature, the ampule was taken out from the furnace and the ingot so prepared was cut into 1.2 to 1.4 mm thick plates. Their surfaces were polished till the

TABLE I

Positions of Parasite Absorption Bands for the Glassy  $As_2Se_3$  Prepared at Different Desoxidation Temperatures

Temperature, °C	Wavenumber, $cm^{-1}$ <sup>a</sup>						
1 000	635 m	1 285 vw	1 385 vw	2 200 vs	2 820 w	—	4 300 w
900	635 m	1 285 vw	1 385 w	2 200 s	2 820 w	—	4 300 w
800	635 w	1 285 vw	1 385 m	2 200 m	2 820 w	3 140 w	4 300 w
750	—	1 285 vw	1 385 m	2 200 m	2 820 w	3 140 w	—
700	—	1 285 vw	1 385 m	2 200 w	2 820 w	3 140 m	—

<sup>a</sup> vs very strong, s strong, m medium w weak, vw very weak.

\* The IR measurements have been performed on Zeiss UR-10 spectrometer.

optical quality of the surfaces was achieved. The infrared absorption spectra and d.c. conductivity measurements were made on the so prepared plates. Their homogeneity was checked by infrared microscopy. The results of the spectral and conductivity measurements are summarized in Tables I and II.

At the temperature of  $1000^\circ\text{C}$  decomposition of urea proceeds according to Equation (2), the gas pressure being equal to approximately 5.5 atm if there is 0.001 g urea per 1 ml volume of the ampule. As observed by infrared microscopy, a great number of bubbles remain in the ingot of  $\text{As}_2\text{Se}_3$ , which results in decreased transmission, especially in near IR region (Table I). The analysis of IR absorption spectrum of the so prepared glass shows that at this temperature desoxidation does not take place; the  $630\text{ cm}^{-1}$  absorption band, corresponding to the glassy  $\text{As}_2\text{O}_3$ , can unambiguously be identified. Along with this band, the infrared spectrum shows a very intense band at  $2200\text{ cm}^{-1}$  which can be assigned to  $\text{H}_2\text{Se}$ . No evidence of the presence of ammonia among gaseous products has been observed; the gases did not smell, did not react with hydrochloric acid, nor did they change the colour of litmus paper.

At the temperature of  $900^\circ\text{C}$  urea is also decomposed according to Eq. (2). The pressure in the ampule amounts to c. 5 atm. The gas bubbles in the ingots and the amount of the subsequently evolved gas are smaller than in the preceding case. The desoxidation of  $\text{As}_2\text{Se}_3$  does not take place, as proved by the occurrence of the  $630\text{ cm}^{-1}$  absorption band. The observed  $2200\text{ cm}^{-1}$  band indicates the presence of  $\text{H}_2\text{Se}$ . No ammonia has been found in the gaseous phase.

At the temperature of  $800^\circ\text{C}$  decomposition of urea proceeds by two pathways (Eq. (1) and Eq. (2)). The pressure of gases in the ampule for the ratio 0.001 g urea: 1 ml volume of the ampule amounts to c. 4 atm. As observed by infrared microscope, the size and number of gas bubbles decreases. The total transmission of the plates slightly increases, the intensity of the  $630\text{ cm}^{-1}$  absorption band, which is assigned to vibrations of As—O bonds, is substantially lowered, as well as the intensity of the band of hydrogen selenide (at  $2200\text{ cm}^{-1}$ ). The infrared spectra of some samples showed a new band at  $1390\text{ cm}^{-1}$  which is likely to belong to  $\text{NH}_4^+$  ion. The presence of ammonia can be detected by smell.

TABLE II  
Specific Resistances of Samples of  $\text{As}_2\text{Se}_3$  Purified by Decomposition of Urea at Different Temperatures

Glassy $\text{As}_2\text{Se}_3$	Spec. resis., $\Omega\text{ cm}$
Starting $\text{As}_2\text{Se}_3$	$2 \cdot 10^{12}$
Purified at $1000^\circ\text{C}$	$1.25 \cdot 10^{12}$
Purified at $900^\circ\text{C}$	$1.30 \cdot 10^{12}$
Purified at $800^\circ\text{C}$	$1.50 \cdot 10^{12}$
Purified at $750^\circ\text{C}$	$6.8 \cdot 10^{11}$
Purified at $700^\circ\text{C}$	$7.6 \cdot 10^{11}$
After purification remelted <i>in vacuo</i> at $450^\circ\text{C}$	$9.0 \cdot 10^{11}$
Distilled <i>in vacuo</i> after purification	$2.0 \cdot 10^{11}$

At the temperature of 750°C the decomposition of urea proceeds according to Eq. (1). The pressure in the ampule for 0.001 g urea per 1 ml volume of the ampule reaches c. 3.7 atm. Gas bubbles practically does not appear at all, the total transmission of the glass in infrared region is further increased. At this temperature the desoxidation of oxygen-containing impurities is practically completed, as proved by disappearance of the 630  $\text{cm}^{-1}$  band and by very low intensity of the 2200  $\text{cm}^{-1}$  band. Similarly as in desoxidation at 800°C, also here some samples show absorption band at 1390  $\text{cm}^{-1}$ . The gaseous products contain ammonia, as checked by smell.

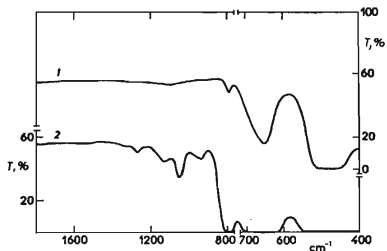


FIG. 1

Infrared Spectrum of Glassy  $\text{As}_2\text{Se}_3$  Contaminated by Different Amounts of Oxide Admixtures  
1 Planparallel plate of 2.39 mm thickness, 2 planparallel plate of 10.23 mm thickness.

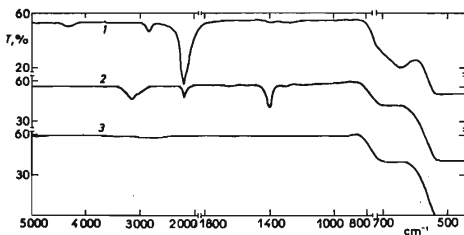


FIG. 2

Infrared Spectrum of Glassy  $\text{As}_2\text{Se}_3$  after Vacuum Remelting with Urea

1 At temperature 950°C, planparallel plate of 8.81 mm thickness; 2 at temperature 700°C, planparallel plate of 5.43 mm thickness; 3 at temperature 700°C, with subsequent vacuum remelting at 450°C, planparallel plate of 6.64 mm thickness.

At the temperature of  $700^\circ\text{C}$  urea is exclusively decomposed according to Eq. (J). The pressure in the ampule amounts to c.  $3.5$  atm the same experimental conditions as described in the preceding paragraph. IR microscopy reveals no gas bubbles in the samples. The complete desoxidation of  $\text{As}_2\text{O}_3$  can be inferred from the disappearance of the  $630\text{ cm}^{-1}$  band. Also the  $2200\text{ cm}^{-1}$  band is very weak. In the infrared spectra of some samples the  $1390\text{ cm}^{-1}$  band has been observed. The gaseous phase contains ammonia.

#### Removal of Dissolved Gases Formed by Pyrolysis

As it is seen from the obtained results, admixtures of oxides can be completely removed from  $\text{As}_2\text{Se}_3$  at  $700$ – $750^\circ\text{C}$ . However, even in the so prepared materials, weak absorption bands at  $1390$  and  $2200\text{ cm}^{-1}$  can be sometimes detected. For this reason the  $\text{As}_2\text{Se}_3$  glass was further purified by remelting at  $450^\circ\text{C}$  for 2 hours under vacuum of diffusion pump. The ampule was then sealed and heated to  $900^\circ\text{C}$  for 1 hour. After cooling down to room temperature with the  $35^\circ\text{C}$  per min rate, the purified  $\text{As}_2\text{Se}_3$  glass did not show any parasite absorption bands in the infrared region. It had 60% transmission and, as shown by infrared microscopy, it was homogeneous, without any micro- or macroscopic defects, and proved to be suitable material for preparing optical equipments for infrared region. As an example, in Fig. 2 are shown the infrared spectra of samples prepared upon using different purification procedures.

#### Direct Current Conductivities of Samples of $\text{As}_2\text{Se}_3$

The results of d.c. conductivity measurements of the prepared samples are summarized in Table II. From the Table it can be seen that specific resistance of the samples somewhat increases with increasing temperature of purification. This fact can be accounted for by assuming that the number of macroscopic defects increases with increasing temperature, which reflects in a decrease of the effective surface of the measured sample. Furthermore it was proved that the samples prepared at higher temperature are contaminated by trace oxide impurities which increase<sup>1,2</sup> the resistance of the glassy  $\text{As}_2\text{Se}_3$ .

#### CONCLUSION

From the discussed dependences it follows that the removal of oxide impurities from  $\text{As}_2\text{Se}_3$  can be accomplished by decomposition of urea at  $700$ – $750^\circ\text{C}$ . As the so prepared material sometimes exhibits parasite absorption bands at  $1390\text{ cm}^{-1}$  ( $\text{NH}_4^+$  ion) and  $2200\text{ cm}^{-1}$  ( $\text{H}_2\text{Se}$ ) and defects caused by evolved gases, we recommend that the  $\text{As}_2\text{Se}_3$  be remelted *in vacuo* at  $450^\circ\text{C}$ . In this way, the gaseous residues can be completely removed. The  $\text{As}_2\text{Se}_3$  so obtained is homogeneous and does not show any parasite absorption bands. It is suitable material for production of optical equipments for infrared region.

It should be noted, however, that the amount of oxide admixtures which can be removed, depends on the ratio of  $\text{As}_2\text{Se}_3$  to  $\text{CO}(\text{NH}_2)_2$ . When using 0.01 g of  $\text{CO}(\text{NH}_2)_2$ , theoretically only 0.00267 g of  $\text{O}_2$  can be removed by CO. However, larger amounts of urea can be used if the volume of the ampule is appropriately increased. This makes it possible to decrease at the same time also the total pressure of gaseous pyrolytic products in the ampule. It is to be expected that the described method can also be used to remove other trace admixtures which would form nitrides with nitrogen or ammonia.

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