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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	26
page range	101-106
year	1976
URL	<a href="http://hdl.handle.net/10097/27795">http://hdl.handle.net/10097/27795</a>

# Far-Infrared Investigation on Structure of Amorphous Selenium\*

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(Received September 3, 1976)

## Synopsis

The structural ordering in various forms of amorphous selenium has been studied by means of far-infrared measurements on the two types of spectrum, corresponding to the Se<sup>8</sup>-ring component and the polymeric chain. The chemical extraction method of the Se<sup>8</sup>-ring component by CS<sub>2</sub> is re-examined in terms of the spectroscopic analysis which shows that the ring component can not be extracted entirely from the mixture of the ring and the chain. A polycrystalline trigonal selenium is obtained from the component extracted from the vitreous selenium quenched at a high temperature above 700°C. Black amorphous selenium is obtained by heat treatment of red one. The spectra for both of the amorphous states show that they consist of similar mixtures of the ring and the chain components, so that the transition from red to black does not correspond to the structural change from the ring to the chain nor *vice versa*.

## I. Introduction

The structure of amorphous selenium is characterized by the mixture of Se<sup>8</sup>-ring and polymeric chain. Two types of structural ordering has been investigated by Lucovsky et al.<sup>(1)</sup> by means of far-infrared and Raman measurements. There is a considerable difference in chemical solubility in CS<sub>2</sub> solution between the Se<sup>8</sup>-ring component and the polymeric chain. The former dissolves, whereas the latter does not. Using this chemical characteristic, Briegleb<sup>(2)</sup> has studied the weight fraction of Se<sup>8</sup>-ring in vitreous selenium formed at different quenching temperature. The experimental result shows that the weight fraction of Se<sup>8</sup>-ring decreases with increase in quenching temperature. There is some quantitative ambiguity, however, in this chemical extraction method in the sense that some Se<sup>8</sup>-ring component remains in the residue even after the extraction. Viscosity measurement<sup>(3)</sup> shows that the length of polymeric chain decreases with increase in quenching temperature. Ueno et al.<sup>(4)</sup> claim that even the chain component may dissolve in CS<sub>2</sub> if the chain length is short enough. If this is the case, the short

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\* The 1662th report of the Research Institute for Iron, Steel and Other Metals.

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(1) G. Lucovsky, A. Mooradian, W. Taylor, G.B. Wright and R.C. Keezer, *Solid State Comm.*, **5** (1967), 113.

(2) G. Briegleb, *Z. Physik. Chem.*, **A144** (1929), 321.

(3) R.C. Keezer and M.W. Bailey, *Mat. Res. Bull.*, **2** (1967), 185.

(4) T. Ueno, S. Muraoka, T. Shimada and A. Odajima, *Bulletin of the Faculty of Engineering, Hokkaido University No. 74* (1974), 19.

chain component in the vitreous selenium which is made by quenching from high temperature may also dissolve in  $\text{CS}_2$ . To the best of our knowledge, however, this phenomenon has not been detected so far.

There is little evidence for the presence of definite form of structure in red amorphous selenium and black one. Red amorphous selenium is readily soluble in  $\text{CS}_2$  and its structure has been considered to consist of  $\text{Se}^8$ -ring molecule.<sup>(5)</sup> Exothermic measurements in the process of crystallization show that red amorphous selenium is different from vitreous selenium.<sup>(6)</sup> X-ray spectroscopy also shows the difference between red amorphous selenium and vitreous one.<sup>(7)</sup> If red amorphous selenium is slowly heated, an endothermic transition takes place within the sample, so that it turns black at this transition temperature of approximately  $40^\circ\text{C}$ .<sup>(6)</sup> The sample after the transition is named black amorphous selenium. The structure of black amorphous selenium is also unknown. The present report on the far-infrared measurement shows that the spectra exhibit definite difference between red amorphous selenium and black one. Further spectral study here indicates that the difference between red state and black one does not give one-to-one correspondence with the difference between  $\text{Se}^8$ -ring and chain structure.

## II. Sample preparation

About 3 g of high purity (99.999%) selenium is sealed at the pressure of  $5 \times 10^{-6}$  torr in a quartz ampoule of about 10 cm in length, 5 mm I.D. and 0.5 mm thick. Then the ampoule is heated for about 50 hours at some temperature above the melting point of  $217^\circ\text{C}$ , from which it is quenched into a water bath kept at room temperature. This vitreous selenium is crushed into powder in a mortar of agate. Then the  $\text{Se}^8$ -ring component is extracted with  $\text{CS}_2$  solvent from other component at room temperature.

Red and black amorphous selenium samples are prepared as follows. Selenium in a quartz ampoule is heated above  $1000^\circ\text{C}$ , then the vapour of selenium passes through the liquid nitrogen. Thus the powder of red amorphous selenium is obtained. Black amorphous selenium is prepared by heat treatment of red amorphous selenium at  $45^\circ\text{C}$  for 5 minutes.

The powder thus obtained is mixed with fluid paraffin to insure homogeneity. Such mixture of sample and paraffin is sandwiched between sheets of polyethylene.

## III. Experimental results and discussion

Figure 1 shows the far-infrared transmission spectrum of extracted powder and residual one of vitreous selenium quenched from  $270^\circ\text{C}$ .<sup>(8)</sup> The main absorp-

(5) G. Briegleb, *Z. Physik. Chem.*, **A144** (1929), 340.

(6) G. Gattow and M. Draeger, *Z. anorg. u. allg. Chem.*, **343** (1966), 55.

(7) S.M. Karal'nik, A.P. Nesenyuk and V.D. Dobrovolskii, *Ukr. Fiz. Zh.*, **10** (1965), 668.

(8) M. Kawarada and Y. Nishina, *Jap. J. Appl. Phys.*, **14** (1975), 1519.

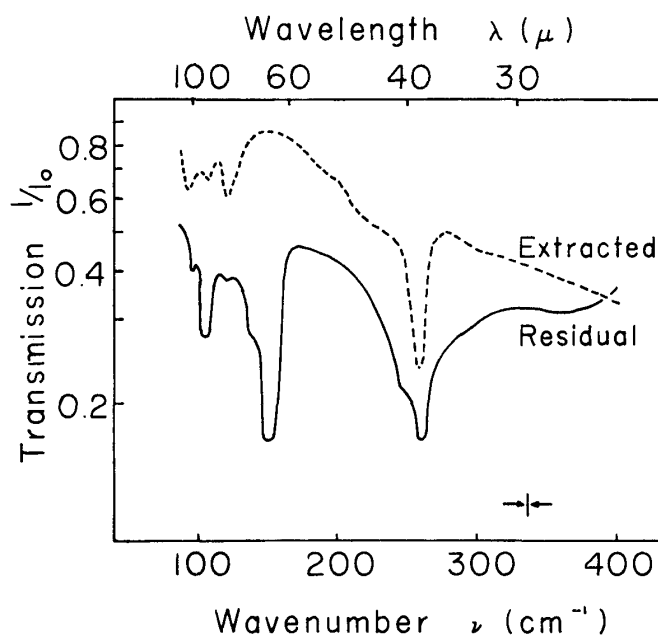


Fig. 1. Transmission spectrum of the  $\text{Se}^8$ -ring powder extracted by a  $\text{CS}_2$  solution and the residual powder at room temperature. The solid line denoted by "Residual" is the spectrum for the sample 270R in Table 1, which is the remaining component after the extraction of  $\text{Se}^8$ -ring component by a  $\text{CS}_2$  solution. The dashed line, "Extracted", corresponds to the sample 270E which is recrystallized from the  $\text{CS}_2$  solution used in extraction of the  $\text{Se}^8$ -ring component.

Table 1. Spectral characteristics of selenium deduced from the far-infrared measurement

Sample	Wavenumber for absorption peak ( $\text{cm}^{-1}$ )									
	96	103	120	140			254			364
270R	96	103	120	140			254			364
270E	95	102	120				254			
730R (A)*		102		144	175					378
730E-I (B)*	94	103		145				278		370
730E-II (C)*	97	102	120	142			253			
Red	92			132		217	256		303	364
Black	92			132			256		303	345
Assignment <sup>1)</sup>	R-E <sub>1</sub>	C-A <sub>2</sub>	R-B <sub>2</sub>	C-E		R-2B <sub>1</sub>	R-E <sub>1</sub>	C-2E	C-3A <sub>2</sub>	C-2E

\*) This notation is given in the curves of Figure 2.

tion peak of extracted powder (dashed line) is observed at  $254 \text{ cm}^{-1}$  which is associated with the  $\text{Se}^8$ -ring<sup>(1)</sup> as shown in Table 1. Residual powder (solid line) has two strong absorption peaks at  $140 \text{ cm}^{-1}$  and  $254 \text{ cm}^{-1}$ . The former absorption peak is associated with the polymeric chain according to Lucovsky et al.<sup>(1)</sup>

Then this extracted powder should consist mostly of the  $\text{Se}^8$ -ring component. Residual powder, however, has an absorption peak at  $254 \text{ cm}^{-1}$ . Thus the  $\text{Se}^8$ -ring component still remains there to an appreciable degree. Hence there is some uncertainty in the quantitative aspects of the chemical analysis by Briegleb.<sup>(2)</sup>

Figure 2 shows the far-infrared transmission spectrum of two kinds of extracted

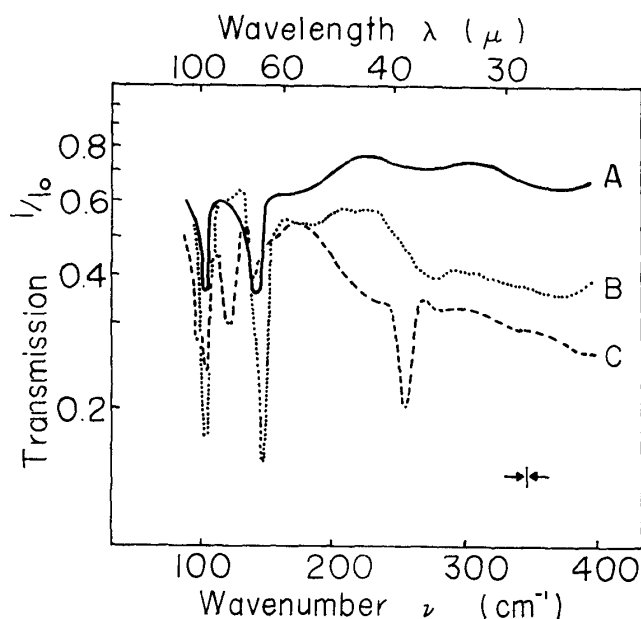


Fig. 2. Transmission spectra of the various phases of selenium at room temperature. The spectral resolution is  $\sim 1 \text{ cm}^{-1}$ . A: the powder which remains in the residue of vitreous sample after extraction by  $\text{CS}_2$ . The sample is quenched from  $730^\circ\text{C}$  (730R in Table 1). B: the precipitated polycrystal developed in the  $\text{CS}_2$  solution of vitreous selenium. The sample is quenched from  $730^\circ\text{C}$  (730E-I in Table 1). C: the polycrystal obtained through the vaporization of  $\text{CS}_2$  solution extracted from the vitreous selenium quenched from  $730^\circ\text{C}$  (730E-II in Table 1).

materials and residual powder of vitreous selenium quenched from  $730^\circ\text{C}$ . The spectrum A is obtained from the powdered sample in the residue after the chemical extraction of the  $\text{Se}^8$ -ring component. The spectrum shows two strong absorption peaks at  $102 \text{ cm}^{-1}$  and  $144 \text{ cm}^{-1}$ , respectively, both of which indicate the presence of polymeric chain structure. The spectrum B is obtained from the sample extracted out by  $\text{CS}_2$  and precipitated on the internal wall of a test tube and it has a form of thin film. The sample, exhibiting this type of spectrum, may not be extracted if the vitreous selenium is quenched at such a low temperature as  $270^\circ\text{C}$ . The spectrum B has strong absorption peaks at  $103 \text{ cm}^{-1}$  and  $145 \text{ cm}^{-1}$ , respectively, which are associated with polymeric chain.<sup>(1)</sup> X-ray diffraction measurement shows that this component is a polycrystalline of trigonal selenium. The main absorption peak of the spectrum C is observed at  $253 \text{ cm}^{-1}$  which is associated with the  $\text{Se}^8$ -ring as mentioned previously. It is noted here that the sample for the spectrum A does not give rise to an absorption peak at  $254 \text{ cm}^{-1}$  associated with the  $\text{Se}^8$ -ring. This result implies that vitreous selenium quenched from  $730^\circ\text{C}$  contains little weight fraction of the  $\text{Se}^8$ -ring, and it is consistent with the result of our previous report.<sup>(8)</sup>

The sample for the spectrum B is a polycrystalline form of trigonal selenium which does not dissolve in  $\text{CS}_2$ .<sup>(2)</sup> This film is formed by the following process: The vitreous selenium, quenched from rather high temperatures, consists of the

short chains which may dissolve in  $\text{CS}_2$ .<sup>(4)</sup> If the ordinary processes of crystallization applies to the present case,<sup>(9)</sup> one may expect the following mechanisms to take place: Some of the short chains, if dissolved in  $\text{CS}_2$ , is trapped by a heterogeneous nucleus on the surface of vessel or by a homogeneous one which is formed by the association of a few short chains. Thus the trapping would induce the crystallization of trigonal selenium. If the short chain crystallizes, it would become a long polymeric chain and would no longer dissolve in  $\text{CS}_2$ , but precipitates as trigonal selenium. The sample for the spectrum B has been formed possibly through this crystallization process. The sample for the spectrum C in Fig. 2 consists mostly of the  $\text{Se}^8$ -ring component. This sample, however, shows minor absorption peaks at  $102\text{ cm}^{-1}$  and at  $142\text{ cm}^{-1}$ , so that it certainly contains a little polymeric chain component. This spectrum suggests that short chain component dissolves in  $\text{CS}_2$  to form a mixture with the  $\text{Se}^8$ -ring.

Figure 3 shows the transmission spectrum of red amorphous selenium and that of black amorphous selenium. Red amorphous selenium has absorption peaks at  $132\text{ cm}^{-1}$  and at  $256\text{ cm}^{-1}$  so that it is a mixture of the  $\text{Se}^8$ -ring with the polymeric chain in accordance with spectral assignment of these absorption peaks by Lucovsky et al.<sup>(1)</sup> Black amorphous selenium also has absorption peaks at  $132\text{ cm}^{-1}$  and at  $256\text{ cm}^{-1}$  and it is a similar mixture of the  $\text{Se}^8$ -ring and the polymeric chain.

There is no appreciable difference between red amorphous selenium and black

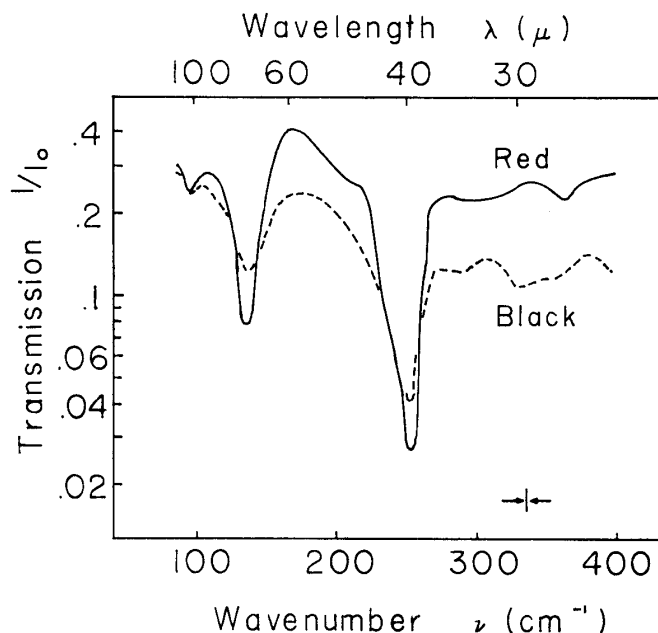


Fig. 3. Transmission spectra of red-amorphous selenium and black-amorphous selenium at room temperature corresponding to the samples "Red" and "Black" in Table 1, respectively.

(9) D. Turnbull, *Solid State Physics*, ed. F. Seitz and D. Turnbull (Academic Press, New York, 1956) Vol. 3, p. 225.

one in the relative intensity of absorption due to the Se<sup>8</sup>-ring with respect to that of the polymeric chain. The result suggests that the transition from red to black does not correspond to the transition from the Se<sup>8</sup>-ring component to the polymeric chain nor *vice versa*. The difference between red amorphous selenium and black one is as follows: Namely, the transmission in the neighborhood of 400 cm<sup>-1</sup> is clearly larger for the red amorphous selenium than that for the black. One may see a good possibility that there would be more significant differences in the shorter wavelength range down to the visible on account of the obvious difference in their colors.

### Conclusions

The far-infrared measurements have been carried out to investigate the structures of chemically treated vitreous selenium, red amorphous selenium and black amorphous selenium. The results show that the extraction of the Se<sup>8</sup>-ring by CS<sub>2</sub> from the vitreous selenium, still leaves detectable amount of the Se<sup>8</sup>-ring component in the residue.

A polycrystalline form of trigonal selenium precipitates in the CS<sub>2</sub> solution of the vitreous selenium quenched from a high temperature. This crystal transformation process may correspond to the polymerization of short chains in the solution. Both red amorphous selenium and black one consist of the mixture of the Se<sup>8</sup>-ring and the polymeric chain. The transition from red amorphous selenium to black one is not the consequence of the structural transition from the Se<sup>8</sup>-ring to the polymeric chain nor *vice versa*, but should be related to the fine detailed structural difference in rather long range order.

### Acknowledgement

Authors would like to acknowledge the assistance of Mr. Fumio Chida in taking data in far-infrared measurements.