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STUDIES ON SELENIUM GLASS

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Introduction

Elementary selenium can exist in the glassy form, and the utilization of the chemical element as an optical material has recently attracted much attention due to its good transmittance in the infrared region[1,2].

Moreover, a certain transition occurs rather easily in glassy selenium, and it must be investigated closely in order to define the structure of the selenium glass[3].

The author prepared the selenium glass for the purpose of investigating on the conditions under which crystals are formed in the glassy form, and obtained the artificial selenium glass having broad transmission limits in the region of wavelength from 1 to 19 μ.

That the glass is softened at low temperatures is the defect of it, but it can be used as the excellent optical material in the infrared due to its good stability.

Experimentals

First, selenium is prepared by treating crude commercial selenium powder with concentrated hydrochloric acid, heating and filtrating the solution. Secondly, white selenium dioxide is obtained by boiling down the selenium in concentrated nitric acid in a casserole on a sand bath. Thirdly red selenium is obtained by paassing a slow stream of sulfur dioxide in the purified solution of white selenium dioxide. The red selenium is washed in plenty of water until no precipitate can be found in the filtrate by passing hydrogen sulfide. Washed selenium is spread on a tray and dried below 60°C in an air bath.

In case of necessity, the gray purified selenium thus obtained is sublimated in a big silica tube flowing nitrogen gas. Selenium is melted and cast as in the case of arsenic trisulfide glass mentioned in the previous report[4].

The measurements of the transmission in the infrared region are carried out with a Koken DS 301 infrared spectrometer with KBr optics.

Comparing with the other optical glasses, it is very troublesome to polish the soft selenium glass, but this glass can be polished on a deer-leather with alumina with scrupulous care.

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1) H. A. Gebbie, *J. Opt. Soc. Am.*, 42, 277 (1952)
2) R. Frerichs, *ibid.*, 43, 1153 (1953)
3) N. E. Brown, *J. Metals*, 7, 379, (1955)
4) S. Minomura, J. Matsuda, and M. Oura, *This Journal*, 29, 22 (1959)

Results and Considerations

As shown in the figure, the transmission of this pure glass is 65~70% between 2 and 19.5 μ.

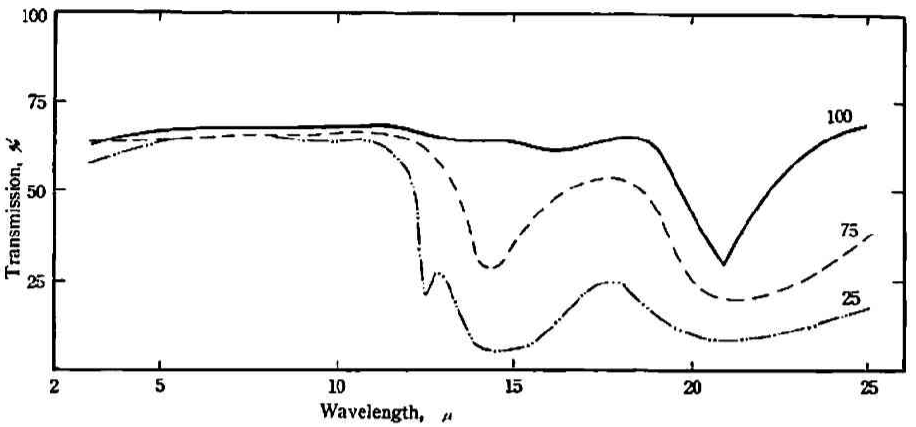

Figure Transmissions of various selenium glasses in 1 mm thickness
——, ------ and —·— are 100, 75 and 25% selenium glasses respectively.

that is, these values are fairly high to the wide range of the infrared region. On the other hand, the loss of transmission is chiefly due to the surface reflection, because of the high refraction index of this glass, as also observed in the case of arsenic trisulfide glass.

The selenium glass is very stable as compared with optical single crystals. This glass can be prepared more readily and not so easily etched with alkali as arsenic trisulfide glass. This is the reason why the selenium glass can be used as an excellent optical material. However, this glass has the defects: the softening at low temperatures, and the tendency of deformation in the air.

The polished selenium glass of 3 cm in diameter and 1 mm in thickness will warp a little in a few days at room temperature in summer, but scarcely change even during the course of two months at the constant humidity, 40% and temperature, 20°C in the room provided with the infrared spectrometer.

Selenium can form stable binary glasses with arsenic trisulfide and their transmissions are also shown in the figure.

Since the publication of the theory by Zachariasen and the introduction of the x-ray analysis by Warren, some investigators have insisted that the structure of glass is homogeneous polymer, but some others, that it is composed of microheterogeneous system by microcrystalline structure[5]. The difference of these opinions closely rests on the various accounts of the process of the transition of solids. The various physical properties of glass have frequently been studied on this point.

The author has studied the changes of thermal expansion of the selenium glass by the optical lever method. However, the softening temperature of this glass is too low to measure the thermal expansion by this method.

5) K. S. Evstropyev, *The Structure of Glass*, Consultants Bureau, Inc., New York, p. 9 (1958), F. C. Kracek, *Phase Transformations in Soids*, John Wiley & Sons, Inc., New York, p. 257 (1951).

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