Journal of Non-Crystalline Solids 52 (1982) 227–233
North-Holland Publishing Company

COLOURING MECHANISM OF PbX IN GLASSES

WANG Shizhuo and YANG Quangzhi

Changchun Institute of Optics and Fine Mechanics, Academia Sinica, Changchun, China

This paper describes a series of glasses which are coloured by lead compounds of S, Se and Te. These glasses can absorb the entire visible spectrum and have a steep rise in transmission at various wavelengths in the 0.7–2.5 μm near-infrared region.

We have observed that the forbidden band gap of some semiconductors in glass is very close to that in crystals, and the location of the front edge of the absorption band of the glass is determined by the energy required for electronic transition from the valence band to the conduction band. We have obtained glasses with steep front edges at various wavelengths in the near-infrared region by introducing Pb*X* semiconductor into the glasses.

During the process of heat treatment, the lead and cadmium compounds of S, Se and Te in glass formed a continuous solid solution and its forbidden band gap was determined by the different composition of the aggregation just as in mixed crystals. We also found that the effect of temperature on the edge shift of the semiconductor in the glasses is similar to that of the corresponding crystals. Both the lead and cadmium compounds of S, Se and Te have such characteristics.

1. Introduction

Research on the colouring mechanism of glasses coloured by adding both Se and CdS has been carried out by many glass research workers for many years. Rooksby [1] demonstrated that differences in the relative amounts of CdS and CdSe in a solid solution produced colours ranging from yellow to deep red. The colloidal particles in the deep red glasses contained relatively more CdSe than the yellow glasses and it was suggested that the colour of the glass was due to the colloidal composition. The work of Begelow and Siverman agreed with that of Rooksby.

The traditional theory of colloidal colouration has been well known among glass workers for a long time. However, Huang Xihuai [2] proposed another point of view about the colouring mechanism of ruby glasses. He pointed out that the colour of ruby glasses might be due to the semiconductor properties of CdS and CdSe crystals in glasses and the theory of colloidal colouration had only described the superficial phenomena rather than the essence.

0022-3093/82/0000–0000/$02.75

2. Experimental method

2.1. How to introduce PbS, PbSe and PbTe into the glasses

It is well known that the lead compounds of S, Se and Te are widely used semiconductors. They are used in highly sensitive infrared detectors. Considerable difficulty has been experienced in interpreting the electrical properties of these materials and the determination of the true values of the activation energies mainly rely on optical and photoelectrical measurements. Gibson's curves of the room temperature absorption spectra of PbS, PbSe and PbTe are shown in fig. 1(a, b, c) [3].

The absorption coefficients of the three semiconductors change rapidly in the short wavelength region. This corresponds to the transition of an electron from the filled valence band to the conduction band or to an excited state. The forbidden band gaps of these three materials are: PbS 1.04 eV, PbSe 0.83 eV and PbTe 0.62 eV. These values change from high to low regularly. In order to introduce the semiconductor into the base glass, we adopted the glass compositions shown in table 1.

The glass batch was melted in a globar furnace in a clay pot; after stirring the homogeneous glass melts were poured into an iron mold and shaped into a glass block (100 × 80 × 10 mm). The homogeneously melted glass blocks were coarsely annealed in a muffle furnace. After the cooling was completed, the ingot was cut into small pieces (33 × 20 mm) and then subjected to a colour heat treatment (striking).

Because the temperature of striking is in the transformation region, the colourants may change their states in the glasses. After heat-treating and cooling, all the glasses became dark black. They were polished into 30 × 20 × 4 mm plates for spectral transmission measurements. This was performed using a type Sp-700 spectrophotometer.

Experimental results indicated that the glasses containing lead have a deep dark colour as a result of introducing Se or Te powder into the glass batches, but the colours obtained in the glass containing PbS were very faint. In order

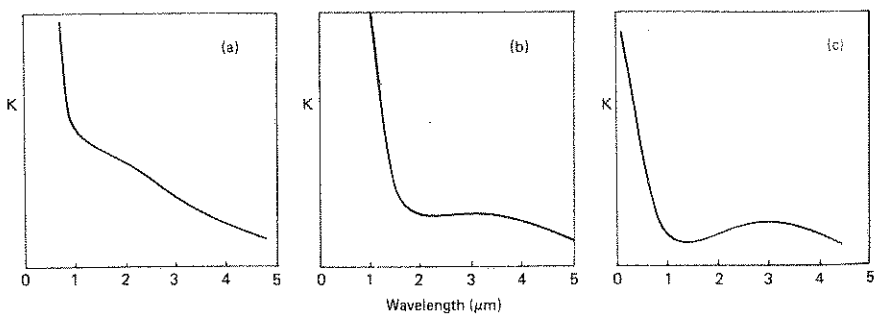

Fig. 1. (a) PbS; (b) PbSe; (c) PbTe.

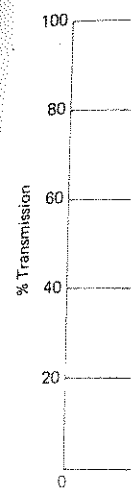

Fig. 2. Transn

to decreas
powder int
this metho
coloured b

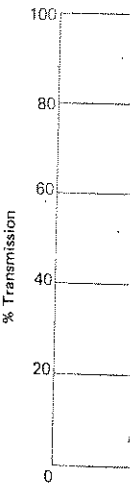

Fig. 3. Transmi

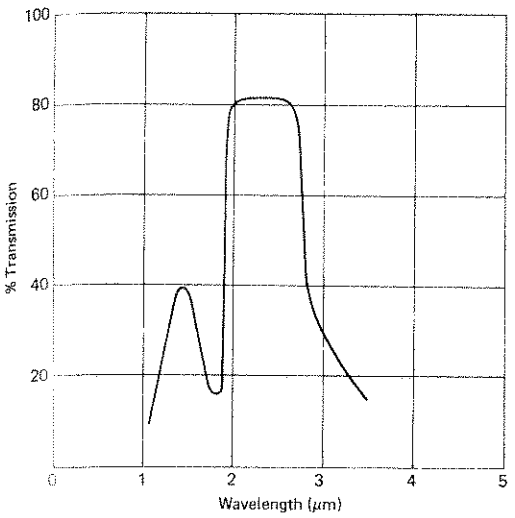

Fig. 2. Transmission of glass coloured by PbSe, $d = 4$ mm.

to decrease the burning out of sulphur we added both Na_2SO_4 and carbon powder into the batch. Carbon is used to reduce the sulphate into sulphur. But this method was not too successful. The spectral transmissions of glasses coloured by PbSe and PbTe respectively are shown in figs. 2 and 3.

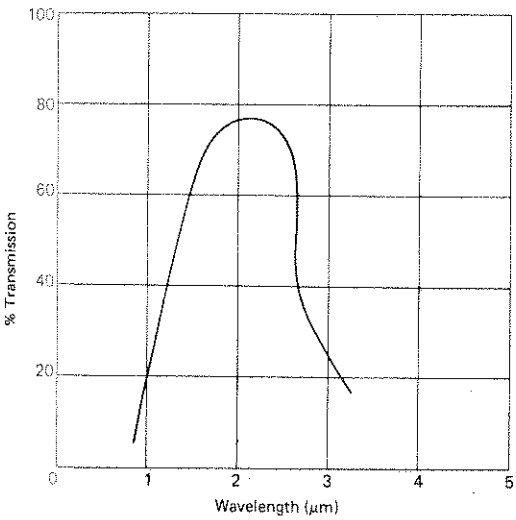

Fig. 3. Transmission of glass coloured by PbTe, $d = 4$ mm.

Table 1
Glass composition

No.	SiO_2	PbO	ZnO	B_2O_3	Na_2O	K_2O	Se	Te	S	Na_2SO_4	C
H001	60	24	13	3	8	11	2	–	–	–	–
H002	60	24	13	3	8	11	–	4	–	–	–
H003	60	24	13	3	8	11	–	–	2	–	–
H004	60	24	13	3	8	11	–	–	–	0.5	0.2

Table 2
Glass composition

No.	SiO_2	ZnO	B_2O_3	Na_2O	K_2O	Se	CdS	$CdCO_3$	Co_2O_3	Na_2SO_4	C
H005	46	20	12	18	4	1	0.5	11	0.4	–	–
H006	46	20	12	8	4	0.6	–	1	0.2	0.2	0.1

2.2. Glass containing PbSe and CdSe

Based on the successful introduction of PbSe into glasses, we further introduced both PbSe and CdSe into the glasses to see if we could obtain glasses coloured by PbSe + CdSe continuous solid solution and shift the front edge of the absorption towards longer wavelengths. Our idea was confirmed by experiments and the influence of heat treatment on colour is similar to that on CdSe + CdS coloured glasses.

During the process of heat treatment, colourants can be formed according to the following equation:

$$ZnSe + CdO \rightarrow CdSe + ZnO,$$
$$ZnSe + PbO \rightarrow PbSe + ZnO.$$

Because a PbSe · CdSe continuous solid solution is formed in the glass after striking and the variation of the forbidden band gap changes with the ratio of PbSe to CdSe in the coagulation, we can obtain a series of glasses with different properties from the same glass composition by choosing the striking temperature and governing the soaking time at the striking temperature. The transmission curves of these glasses are shown in fig. 4.

2.3. Glass containing PbTe and CdTe

The spectral transmission of these glasses is shown in fig. 5.

It has been shown in our work that PbTe · CdTe can also form a new continuous solid solution in the glass. Because the forbidden band gap of PbTe · CdTe is smaller than that of CdS · CdSe, the front edges of absorption of these glasses shift to longer wavelengths approaching 2.5 μm.

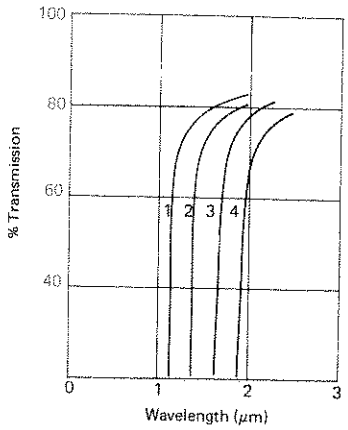

Fig. 4. The effect of striking temperature on the light transmission, $d = 4$ mm.

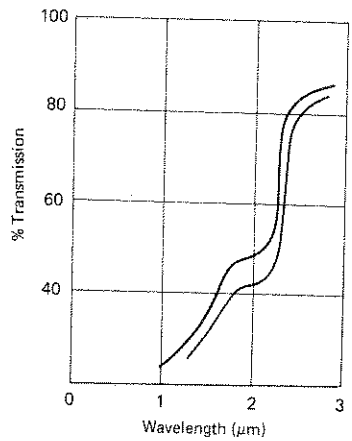

Fig. 5. Transmission of glass coloured by PbTe and CdTe, $d = 4$ mm.

2.4. Integrated effect on colouring of semiconductors and transition metal ions

In order to observe the correlation between the light absorption of transitional metal ions and semiconductors, we introduced cobalt oxide to semiconductor doped coloured glasses. The glass composition is shown in table 2.

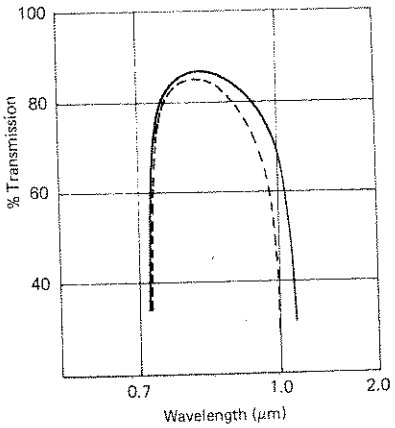

Fig. 6. Transmission of glasses coloured by transition metal ions and semiconductor colourants.

After melting and cooling, we obtained a cobalt coloured blue glass at first, but it turned to dark black after striking. This implies that the transition metal ion played an important role in the glass before heat treatment, but after striking, particles of semiconductor crystals of sub-microscopic dimensions formed in the glass absorbing visible light, so the glasses became dark black.

Visible absorption in this glass results mainly from the presence of semiconductor crystals in the glass, but the absorption near 1.2 μm is attributed to the cobalt ion. The transmission of these glasses is shown in fig. 6.

3. Discussion

In this paper we have studied the colouring mechanism of S, Se and Te compounds of Pb and Cd in glasses. The results are very similar to those glasses coloured by CdS and CdSe but the front edge of the absorption is shifted to the longer wavelength.

As far as we know, the ultraviolet absorption corresponds to the transition of electrons and the location of the UV absorption wavelength is determined by the energy required for electron transition from the valence band to an excited state.

Research on the colouring mechanism of PbX in glasses has shown that this theory is also suitable to explain the front edge of light absorption of

semiconductors in the visible and near infrared region. The front edge of light absorption of semiconductor doped glasses in this paper depends upon the properties of the semiconductors in the glass and it is due to the excitation of electrons of S, Se and Te anions. Therefore the activation energy of a valence electron of an anion in the sulfide is larger than that in the selenide. Their front absorption edge is decided by the affinity of anions. So the activation energy becomes smaller and smaller in the order of S, Se, Te. This is the reason why we can shift the front edge of absorption to longer wavelengths by introducing CdTe, PbSe and PbTe semiconductors into the glasses. Both the lead and cadmium compounds of S, Se and Te have the same characteristics.

4. Conclusion

(1) Using the semiconductor colouring mechanism, we have investigated the colouration of PbX in glasses. The colouring effect of PbSe, CdSe, PbTe and CdTe semiconductors in glasses are presented and it might be useful for studying new filter glasses.

(2) The colouring mechanism of lead compounds of S, Se and Te in glass belongs to the semiconductor doped colouration. When the dimensions of the semiconductor sub-crystals are in the range from 20–100 Å, they will display their semiconductor properties completely, then the front edge of light absorption will be decided by the properties of the semiconductors in glasses.

The glasses studied in this paper may be called semiconductor doped coloured glasses.

References

[1] Rooksby, H.P.J.S.G.T. 16 (1932) 171.
[2] Huang Xihuai, J. Chinese Silicate Soc. 1 (2) (1962) 98.
[3] A.F. Yoffe, Semiconductors in Recent Physics (Russian) (1955) p. 300.