JOURNAL OF MATERIALS SCIENCE 21 (1986) 3571–3574

Some optical properties of germania glasses containing praseodymium and chlorine

A. A. KUTUB
Department of Physics, Umm Al-Qura University, Makkah Al-Mukarramah, Saudi Arabia
A. E. MOHAMED-OSMAN, C. A. HOGARTH
Department of Physics, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

A range of germanate glasses containing praseodymium and chlorine was prepared. The optical absorption edges and infrared absorption spectra were measured. It is found that a small addition of $PrCl_3$ to GeO_2 glasses decreases the optical energy gap, but further addition of $PrCl_3$ increases the optical energy gap. The main infrared absorption bands in the GeO_2–$PrCl_3$ glasses are related to those characteristic of the GeO_2 component.

1. Introduction

Although the properties of glasses have been traditionally discussed in terms of chemical bonding they are now interpreted in electronic terms rather than simply from the chemical point of view.

The understanding of the amorphous and glassy state as described by Mott and Davis [1] and by Borisova [2] and in particular the relationships between structure and properties, has led to an increased application of glasses and glassy complexes in systems in which their electronic properties are involved.

In recent years several papers have appeared reporting the properties of glassy and amorphous semiconductors doped with small quantities of rare-earth oxides [3–9]. The spectra of rare-earth ions are characterized by absorption bands which are very sharp, indeed almost line-like. These sharp bands are due to forbidden transitions involving the $4f$ levels, and these $4f$ orbitals are very effectively shielded from interaction with external forces by the overlying $5s^2$ and $5p^6$ shells. Hence, the states arising from the various $4f^n$ configurations are only slightly affected by the surroundings of the ions and remain practically invariant for a given ion in various compounds. Reisfeld [10] proposed that the rare-earth ion in glass occupies the centre of a distorted cube which is made of four tetrahedra of borate, phosphate, silicate or germanate, whichever system is being considered, and each tetrahedron contributes two oxygens to the co-ordination of the rare-earth ions. The overall co-ordination number is 8, the most common co-ordination of rare-earth oxides. From the literature it appears that some investigations have been made on germanate glasses doped with Pr_6O_{11}, but there is no such study on germanate glasses doped with $PrCl_3$. It has already been found that the incorporation of a strong oxidizing agent such as chlorine can substantially affect the reduced valency ratio and hence the electronic properties of transition metal phosphate glasses.

In the present paper we report the optical absorption and infrared absorption spectral measurements made in order to study the effect of $PrCl_3$ added to germanate glasses, and noting that two different ions were being introduced into the glass simultaneously.

2. Experimental procedure

2.1. Glass preparation

Glasses in the system having the composition expressed in mol% $(GeO_2)_{100-x}(PrCl_3)_x$ where x varied from 0 to 10%, were prepared from chemically pure grades of material according to their molar compositions, in an alumina crucible. The melt was stirred from time to time using an alumina rod and was molten at 1570° C for 3 h. By slow heating it was hoped to reduce mechanical and volatilization losses. The melt was finally poured into an indentation in a clean stainless steel plate and cast into a small disc shape. The samples to be annealed were transferred to an annealing furnace maintained at 400° C for 1 h and were then allowed to cool slowly. The X-ray diffraction examination of the glass samples showed no discrete lines or structure and confirmed that our samples were essentially non-crystalline.

2.2. Optical measurements

The glass samples used for ultraviolet and visible spectroscopy were polished to about 1.5 mm thick. The measurements were carried out at room temperature in the wavelength range 190 to 900 nm using a Perkin–Elmer 402 spectrophotometer.

For infrared measurements, samples were ground in a clean mortar to a fine powder. A few milligrams of glass powder were mixed and ground with a large quantity of KBr. KBr pellets transparent to infrared were formed by pressing the mixture at 12 ton for a few minutes under vacuum. The infrared absorption spectra of these samples were determined by using a Unicam SP 2000 double-beam recording infrared spectrometer in the range 400 to 4000 cm^{-1}.

3. Results and discussion

3.1. Optical absorption

Optical absorption measurements were made as a

0022–2461/86 $03.00 + .12 © *1986 Chapman and Hall Ltd.*

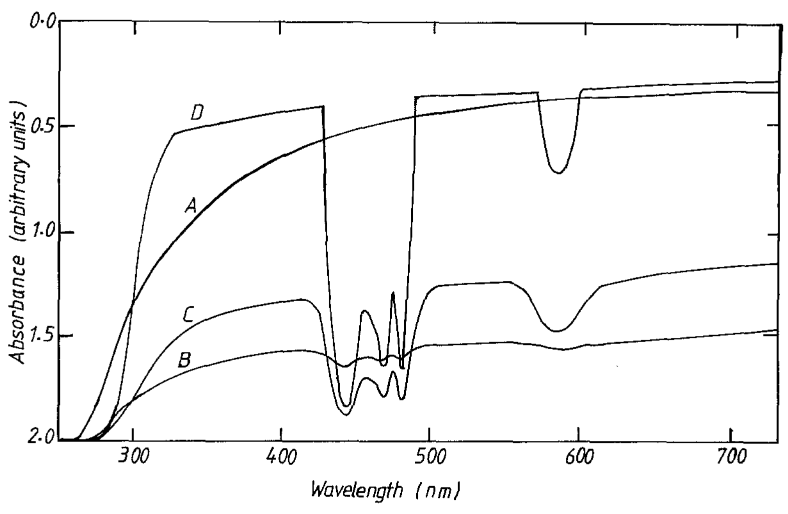

Figure 1 Absorption as a function of wavelength for glasses of different thicknesses and composition as given in Table I. Thickness: A, 1.02 mm; B, 1.2 mm; C, 1.73 mm; D, 2.00 mm.

function of photon energy at room temperature for a series of unannealed glasses and the compositions are listed in Table I. Fig. 1 shows the absorption in arbitrary units as a function of wavelength. It is clear from this figure that the region of high absorption of undoped germanate glass is in the ultraviolet while it is transparent in the visible region.

The absorption characteristic in these glasses may be described on the generally accepted qualitative understanding that the absorption edge is determined by the oxygen bond strength in the glass-forming network. Any change of oxygen bonding in the glass network, for instance the formation of non-bridging oxygens, changes the absorption characteristic [11].

The general appearance of the absorption spectrum of germanate glasses doped with $PrCl_3$ is similar to those observed from other glasses doped with praseodymium, for example P_2O_5–Pr_6O_{11} glass [8, 9], GeO_2–Pr_6O_{11} [7] and germanate glass doped with Eu^{3+} [4]. Two general regions of absorption are of interest in the glasses. Firstly, the fundamental optical absorption edge becomes sharper as the $PrCl_3$ content is increased and is much more like crystalline than glassy materials. Secondly, sharp absorption peaks are observed at 442, 469, 482, and 590 nm and these peaks became sharper as the $PrCl_3$ content is increased. These peaks are due to the transitions [12] $^3H_4$–$^3P_2$, $^3H_4$–$^3P_1$, $^3H_4$–$^3P_0$ and $^3H_4$–$^1D_2$, respectively, as reported for the praseodymium phosphate glasses [8, 9] and the same sharp peaks are observed in sodium silicate [12] and ZnF_2 glasses [13] doped with Pr^{3+} ions. Annealed glass samples showed no change in the absorption spectrum. The optical absorption coefficient $\alpha(\omega)$ has been derived and the result may be displayed in a number of ways as a function of photon energy, $\hbar\omega$. The most satisfactory results were obtained by plotting the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$ as suggested by Davis and Mott [14] for materials in which the optical transitions are indirect. The coefficient $\alpha(\omega)$ for many amorphous materials is found to obey the relation

$$\alpha(\omega)\,\hbar\omega \;=\; B(\hbar\omega - E_{\text{opt}})^2 \qquad (1)$$

where E_{opt} is the optical energy gap and B is a constant. Fig. 2 shows the plot of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ for the glass samples and the values of E_{opt} determined by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{1/2} = 0$ are shown in Table I.

TABLE I Some derived glass parameters

Notation	Composition (mol %)	Optical gap, E_{opt} (eV)	Urbach energy, E_e (eV)
A	$(GeO_2)_{100}$–$(PrCl_3)_0$	4.03	0.6
B	$(GeO_2)_{99}$–$(PrCl_3)_1$	3.62	0.5
C	$(GeO_2)_{95}$–$(PrCl_3)_5$	3.70	0.6
D	$(GeO_2)_{90}$–$(PrCl_3)_{10}$	3.92	0.5

The graph shows straight lines with some deviations at the lower photon energies which were suggested by Redfield and Afromowitz [15] to be due to imperfections in the material. The variation of E_{opt} with the $PrCl_3$ content in the germanate glasses is shown in Fig. 3.

It is clear from this figure that the values of E_{opt} decrease with small increases in the concentration of $PrCl_3$ (1 mol %), but increase again for further additions of $PrCl_3$. Clearly, the addition of chlorine to the glasses does, as expected, modify the band

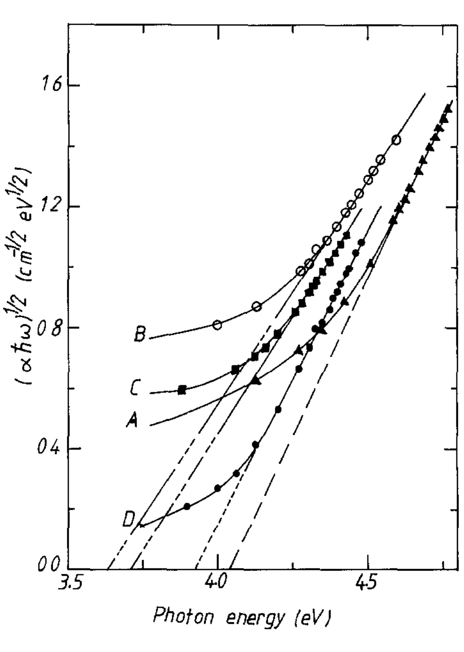

Figure 2 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for four different glass samples.

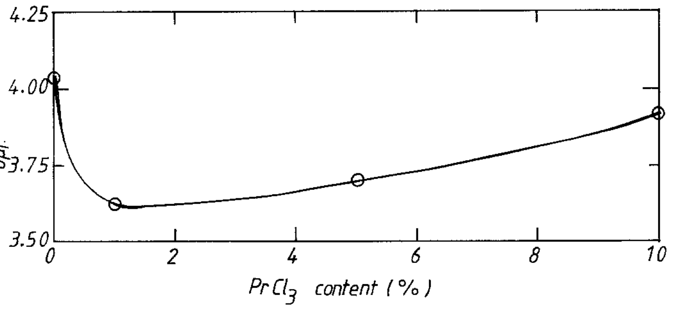

Figure 3 E_{opt} as a function of $PrCl_3$ content for GeO_2–$PrCl_3$ glasses.

characteristics in a systematic manner by reducing the concentration of Pr^{3+} ions. However, the increase for larger concentrations of added chlorine does not fit the general picture and it may well be that for more than 1 mol % of added chlorine, the chlorine is no longer widely and thinly dispersed but rather forms clusters which tend to aggregate as further chlorine is added and become therefore less effective in acting as a generally dispersed oxidizing agent and the role of Pr^{3+} ions becomes more dominant and effective in increasing the E_{opt} values. Hogarth and Popov [16] reported that all parameters measured including the Cu^{2+} concentration decreased with a small increase in $CuCl_2$ to the range 4 mol % in the copper–phosphate glasses, and increased again for further additions of $CuCl_2$.

The exponential dependence known as the Urbach rule [17] may be written in the form

$$\alpha(\omega) = A \exp \frac{\hbar\omega}{E_e} \tag{2}$$

where A is a constant and E_e indicates the width of the band tails of the localized states. The equation is found to fit the absorption edge data for a number of amorphous materials, particularly at the lower values of α. Tauc and Zanini [18] believe that the densities of states in the band tails arising from electronic transitions between localized states are exponentially dependent on energy. Dow and Redfield [19] suggested that the tailing may arise from the random fluctuations of the internal disorder in many amorphous solids. One possible reason suggested by Davis and Mott [14] is that the slopes of the observed exponential edges obtained from Equation 2 are very much the same as in many semiconductors and the values of E_e for a range of amorphous semiconductors lie between ≈0.045 and 0.67 eV. Fig. 4 shows the variation of log α with $\hbar\omega$ and the values of E_e in Equation 2 are calculated from the slopes of the straight lines and found to lie between 0.5 and 0.6 eV for the glass samples, rather higher than the value of 0.06 eV reported for Pr_6O_{11}–P_2O_5 glasses [9]. This confirms that the bonding in rare-earth germanate glass is different from that of the phosphate glasses.

3.2. The infrared absorption

Fig. 5 shows the spectra of GeO_2 and several GeO_2–$PrCl_3$ glasses, together with the spectrum of crystalline GeO_2.

Comparing the infrared spectra of germanate glass with those doped with $PrCl_3$, it appears that all the glasses show great similarity in their general shape of absorption spectra, with the exception that for glasses doped with 7 and 10 mol % $PrCl_3$, new weak peaks appeared at about 1450 and 1650 cm^{-1} instead of the broad peak at 1300 to 1900 cm^{-1}.

The undoped GeO_2 glass gave peaks at 590 and 900 cm^{-1} and these agree closely with the values reported by other investigators and they are attributed to the Ge–O–Ge stretching vibrations [4, 20] and the infrared spectrum of amorphous germania is similar to that of the hexagonal crystalline form [20]. By adding $PrCl_3$ the 590 and 900 cm^{-1} bands are broadened. It has been reported [21] that the glasses doped with praseodymium show absorption peaks between 260 and 635 cm^{-1}, while the bonds in the halides are, in general, much more ionic than in the oxides and consequently are less directional [22].

Therefore, it seems that the presence of the Pr^{3+} ion leads to a reduction in the Ge–O–Ge stretching frequency in the range from 500 to 650 cm^{-1}. Kolobkov *et al.* [5] reported that the germanate band becomes less intense when the GeO_2 concentration is decreased, and the presence of GeO_2 in the glass with high concentration dominates the characteristics of the spectrum.

Therefore, the strong and broad bands at 500 to 650 cm^{-1} and 800 to 1050 cm^{-1} in the more highly concentrated $PrCl_3$ germanate glasses, could be due to the combined effect of Ge–O–Pr–Cl vibrations.

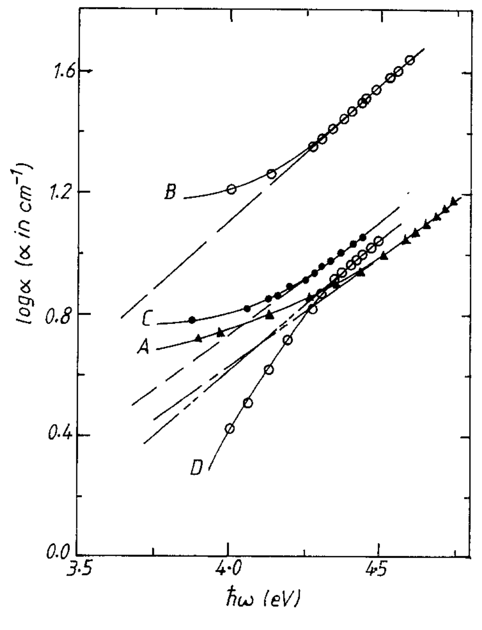

Figure 4 Absorption coefficient as a function of photon energy for germanate glasses containing $PrCl_3$.

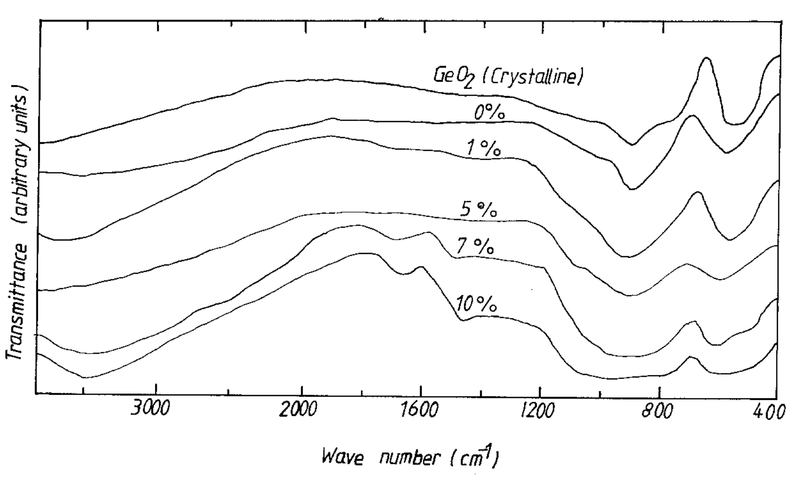

Figure 5 The infrared absorption spectra of five different samples ($PrCl_3$ content in mol% as indicated), and for crystalline GeO_2.

Qualitatively, the infrared spectra of germanate glasses doped with $PrCl_3$ would suggest that the germanate structure is dominant in these glasses and that a partially covalent Ge–O–Pr–Cl bond would be created at higher $PrCl_3$ content and would lead to the new weak bands which appeared at 1450 and $1650\,cm^{-1}$. The $3500\,cm^{-1}$ absorption is a weak band and is most probably due to overtones or to traces of water in the glasses. The infrared spectra of samples annealed at 300, 500 and 800° C were also recorded and no significant changes were observed in the absorption band positions as a result of the annealing.

References

1. N. F. MOTT and E. A. DAVIS, "Electronic processes in non-crystalline materials" (Oxford University Press, Oxford, 1979).
2. Z. U. BORISOVA, "Glassy Semiconductors" (Plenum Press, New York, 1981).
3. M. N. KHAN, R. HARANI, M. M. AHMED and C. A. HOGARTH, *J. Mater. Sci.* **20** (1985) 2207.
4. R. REISFELD and N. LIEBLICH, *J. Phys. Chem. Solids* **34** (1973) 1467.
5. V. P. KOLOBKOV, S. P. LUNKIN, I. A. ZHMYREVA, E. A. KOSHELEVA, P. I. KUDRYASHOV and I. N. MOROZOVA, *Sov. J. Glass Phys. Chem. USA* **9** (1983) 345.
6. A. K. AKULOV, I. V. KORICHEVA and A. K. PRZHEVOSKII, *Sov. J. Glass Phys.* **9** (1983) 333.
7. R. HARANI, C. A. HOGARTH, M. ROILOS and A. E. MOHAMED-OSMAN, *J. Mater. Sci. Lett.* **5** (1986) 275.
8. R. HARANI, C. A. HOGARTH, M. M. AHMED and D. F. MORRIS, *ibid.* **3** (1984) 843.
9. M. M. AHMED, R. HARANI and C. A. HOGARTH, *ibid.* **3** (1984) 1055.
10. R. REISFELD, *Structure and Bonding* **13** (1973) 53.
11. B. D. McWAIN, N. F. BORREL and S. U. GONGJEN, *Phys. Chem. Glasses* **4** (1963) 1.
12. H. L. SMITH and A. J. COHEN, *ibid.* **4** (1983) 173.
13. Y. OSHISHI, S. MITACHI, T. KANAMORI and T. MANABE, *ibid.* **24** (1983) 135.
14. E. A. DAVIS and N. F. MOTT, *Phil. Mag.* **22** (1970) 903.
15. D. REDFIELD and A. AFROMOWITZ, *Appl. Phys. Lett.* **11** (1967) 138.
16. C. A. HOGARTH and A. L. POPOV, *Int. J. Electron.* **54** (1983) 171.
17. F. URBACH, *Phys. Rev.* **92** (1953) 1324.
18. J. TAUC and M. ZANINI, *J. Non-Cryst. Solids* **23** (1977) 349.
19. J. D. DOW and D. REDFIELD, *Phys. Rev. B* **5** (1972) 594.
20. R. H. DOREMUS, "Glass Science" (Wiley, London, New York, 1973).
21. W. L. BAUN and N. T. McDEVIT, *J. Amer. Ceram. Soc.* **46** (1962) 294.
22. H. RAWSON, "Inorganic Glass-forming Systems" (Academic, London, New York, 1967).

Received 31 October
and accepted 20 December 1985