Optical absorption in praseodymium germanate glass

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The optical absorption of binary praseodymium and cerium phosphate glasses has recently been reported [1–3]. In such materials, including a significant content of lanthanide oxide, the fundamental absorption edge is sharp, much more like crystalline than the usual glassy materials. The sharp absorption peaks at 445, 468, 479 and 589 nm are due to relevant transitions between $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$. The behaviour of rare earth ions in glasses is similar to that of rare earths in inorganic crystals of low symmetry. This different spectral behaviour, that is shown by ions of the d-block transition elements, lies in the fact that the $4f$ orbitals penetrate well in towards the nucleus and the $4f$ electrons are therefore well shielded by the outer $5s$ and $5p$ electrons. Consequently their energies and the energies of the f–f transitions are only little affected by the external fields. The visible spectra due to such transitions, therefore, are both sharp and almost independent of the medium in which the ions are immersed.

Reisfeld [4] 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 coordination of the rare earth ions. The overall coordination number is 8, the most common coordination of rare earth oxides.

In the present letter we report the optical absorption of praseodymium germanate glass, a material whose properties have not previously been reported in the literature.

The binary 5 mol % Pr_6O_{11}–95 mol % GeO_2 glasses were prepared from analytical reagent grades of Pr_6O_{11} and GeO_2 in 20 g batches, melted in an alumina crucible at 1530° C for 3 h. Homogeneity of the melt was ensured by stirring with an alumina rod from time to time. The melt was quenched by pouring into a disc-shaped depression in a steel plate. The glass samples were annealed at 300° C for 1 h to relieve mechanical stress.

The optical absorption measurements were made using a Perkin-Elmer Lambda-3 spectrophotometer in the wavelength range 200 to 900 nm and a sample of polished glass 0.74 mm thick.

The Pr^{3+} ion has a normal electronic configuration $4s^2$, $4p^6$, $4d^{10}$, $4f^2$, $5s^2$, $5p^6$, and a ground state $^3H_4$ with a well-defined value of total angular momentum $J = 4$. Fig. 1 shows the optical absorption as a function of wavelength for praseodymium germanate glass and it is clear that the fundamental optical absorption edge is sharp, much more like crystalline than the usual glassy materials, as observed earlier in praseodymium phosphate [1] and cerium phosphate glasses [2]. Sharp absorption peaks are observed at 442, 469, 482 and 590 nm, and these peaks are due to the transitions [5] $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$, respectively, as reported in praseodymium phosphate glasses [1] and the same sharp peaks are observed in sodium silicate [5] and ZnF_2 glasses [6] doped with Pr^{3+} ions.

According to Davis and Mott [7] the absorption in many amorphous semiconductors obeys the quadratic relation for interband non-direct transitions, i.e.

$$\alpha(\omega) = B(\hbar\omega - E_{opt})^2/\hbar\omega$$

where B is a constant, ω is the angular frequency and E_{opt} may be defined as an optical gap.

The value of E_{opt} is obtained by extrapolation of the plot of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ as shown in Fig. 2 to

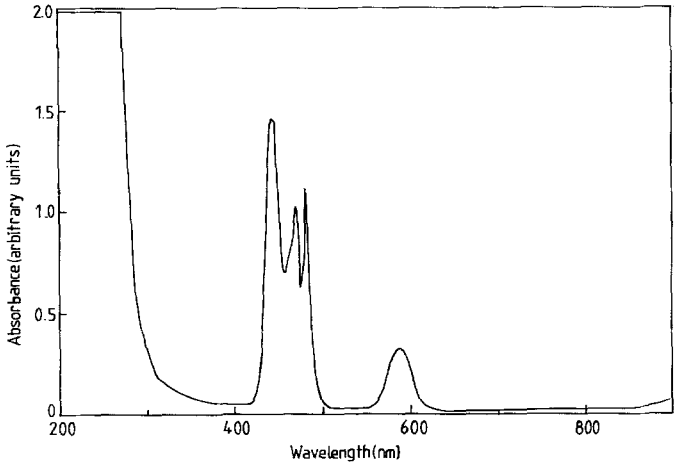

Figure 1 Optical absorption spectrum for a praseodymium germanate glass.

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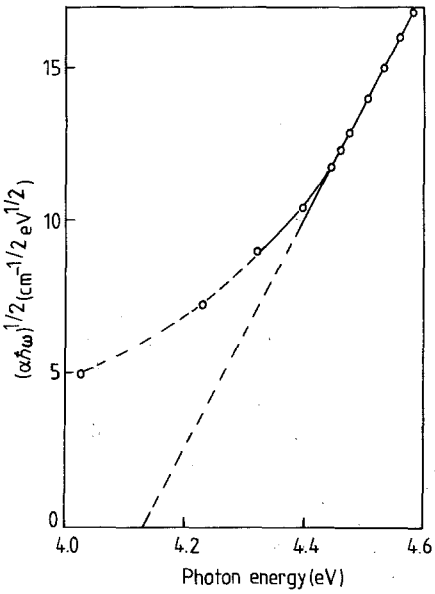

Figure 2 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy $\hbar\omega$ for a praseodymium germanate glass.

$(\alpha\hbar\omega)^{1/2} = 0$ and E_{opt} for the Pr_6O_{11}–GeO_2 glass is found to be 4.13 eV.

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