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The control of the electrical conductivity of germanium vanadate glasses by the admixture of chlorine during preparation

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The electrical conductivity of germanium vanadate glasses depends on the relative concentrations of V^{4+} and V^{5+} ions. It is found that by adding VCl_3 to the melt when the glass is formed, the added chlorine which acts as an oxidizing agent alters the ratio of concentration of vanadium ions and thus the conductivity. The optical absorption coefficients and d.c. conductivities of germanium vanadate glasses are measured as functions of VCl_3 content. It is found that the activation energy for conductivity increases with chlorine content, the increase of the activation energy corresponding to the change in optical gap energy. It is considered therefore, that the principle of the addition of a strong oxidizing agent to the glass to alter the reduced valency ion ratio may have general application in the control of electrical conductivity in transition metal ion glasses.

1. Introduction

Oxide glasses containing transition metal ions were first reported in 1954 [1]. Several transition metal oxides when heated with glass-forming substances such as P_2O_5, TeO_2 and GeO_2, form glasses on quenching from the melt. The loss of oxygen from the melt produces lower valency transition metal ions. Electrical conduction in these glasses occurs by electron hopping from an ion of the low valency state (V^{4+}) transition metal to an ion of the high valency state (V^{5+}) [2]. Murawski *et al.* [3] have suggested that although the thermal activation energy for conduction appears to be the dominating factor which controls the conductivity, it has recently been shown [4] that the admixture of chlorine has a great influence on the conductivity has been shown to be related to the ratio and relative concentrations of the ions in the different valency states (Mott [5], Linsley *et al.* [6], Moridi and Hogarth [7]). The electrical conductivity of these glasses is sensitive to the ratio $(V^{+})/(V_{\text{total}})$ where (V_{total}) represents the total concentration of vanadium in glass [5].

It is found that a maximum in the electrical conductivity of such glasses is observed for sample in which the concentrations (V^{4+}) and (V^{5+}) are of the same order of magnitude. For this reason a method which could control the value of (V^{4+}) is of great importance in controlling the conductivity of the glasses.

In general, glassy and amorphous materials cannot be doped to desired values of conductivity by the addition of small amounts of donors or acceptor impurities as in the normal procedure for crystalline semiconductors. We report here a process for the control of the electrical conductivity of vanadate glasses containing a fixed proportion of vanadium.

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The method proposed and tested in these experiments involves the incorporation of chlorine into the glass by the addition of vanadium chloride during the glass preparation process. Chlorine was chosen in preference to fluorine because of its atomic size and its lower chemical activity and it was anticipated that it would disperse evenly through the glass and not form localized clusters.

The oxidizing effect of the chlorine ions is expected to alter the ratio $[V^{4+}/V^{5+}]$ and thus to control the transition probabilities of the conduction electrons and hence the conductivity. It is believed that the principle involved is one which could be applied to a range of glasses involving electron transitions between ions of different valency, e.g. between Cu^+ and Cu^{2+}, and between Mo^{5+} and Mo^{6+} ions in molybdate glasses.

2. Experimental work

2.1. Glass preparation

Glasses in the system having the composition expressed in mol% $(GeO_2)_{50}(V_2O_5)_{50-x}(VCl_3)_x$ where x varied from 0 to 10 mol% where prepared from chemically pure grades of material, according to their molar composition. The melt was stirred from time to time to time using an alumina rod and was molten at 1000° C. By slow heating it was hoped to reduce mechanical and volatilization losses. The melt was finally poured on to a clean stainless steel plate and cast into a disc shape. The disc was immediately transferred to another furnace which was already maintained at 300° C. The furnace was kept at this temperature for 2 h and then was switched off to cool down to room temperature. The glass samples were polished using diamond paste, down to a minimum grit size of 0.1 μm. The thin glassy samples of specified compositions (the VCl_3 content varied from 0 to 10 mol%) were prepared by blowing in air using an alumina tube. Specimens in the thickness range from 5 to 12 μm were obtained, as measured using a Sigma comparator. All thin films were un-annealed when used for optical absorption measurements.

2.2. Electrical measurements

Disc-shaped samples were made by casting and polishing, and electrodes of gold were evaporated to form a guard-ring to eliminate surface leakage current and then central electrodes to ensure good ohmic contacts. A simple measuring circuit was used similar to that described by Hogarth and Khan [8]. A stabilized power supply was used to provide a constant voltage source and the circulating currents were measured using a Keithley 610C electrometer.

The temperature of the samples was monitored using a chromel–alumel thermocouple attached to the sample. The measurements of d.c. conductivity were carried out using the device similar to that described by Khan *et al.* [9], which could employ five samples at a time. This ensured the accurate comparison of five samples under similar conditions.

As shown in Fig. 1 all samples showed ohmic behaviour and the results of temperature variations of σ showed that $\log \sigma$ is a linear function of $1/T$ for all samples and the activation energy lay in the range 0.29 to 0.40 eV. The values for the glass containing no chlorine agreed closely with the results for similar glasses examined earlier by Janakirama-Rao [10]. The addition of VCl_3 to the glasses showed that the electrical conductivity was reduced as the admixture of chlorine was increased The results of a typical series of measurements are shown in Fig. 1.

2.3. Optical measurements

The specimens used for ultraviolet and visible spectroscopy were prepared by blowing thin films from the molten glass. The measurements were carried out at room temperature in the wavelength range 390 to 610 nm by using a Perkin-Elmer spectrophotometer. The optical absorption coefficient $\alpha(\omega)$ was calculated by using the fomula:

$$\alpha(\omega) = \frac{1}{d}\log(I_0/I_t)$$

where I_0 and I_t are the intensities of the incident and transmitted beams, respectively, and d is the thickness of the specimen. The absorption spectra for a series of glasses as a function of wavelength are given in Fig. 2, and show that the optical absorption edge is not sharp, and this is a typical characteristic of glassy materials. The values of optical gap, E_{opt}, are obtained by extrapolating from the linear region of the plots of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ and are seen to be dependent in a systematic manner on the glass composition as shown in Fig. 3. The graph shows straight lines with some deviation at the lower photon energies. The deviation from linearity as suggested by Redfield and Afromowitz [11] may be due to imperfections in the material.

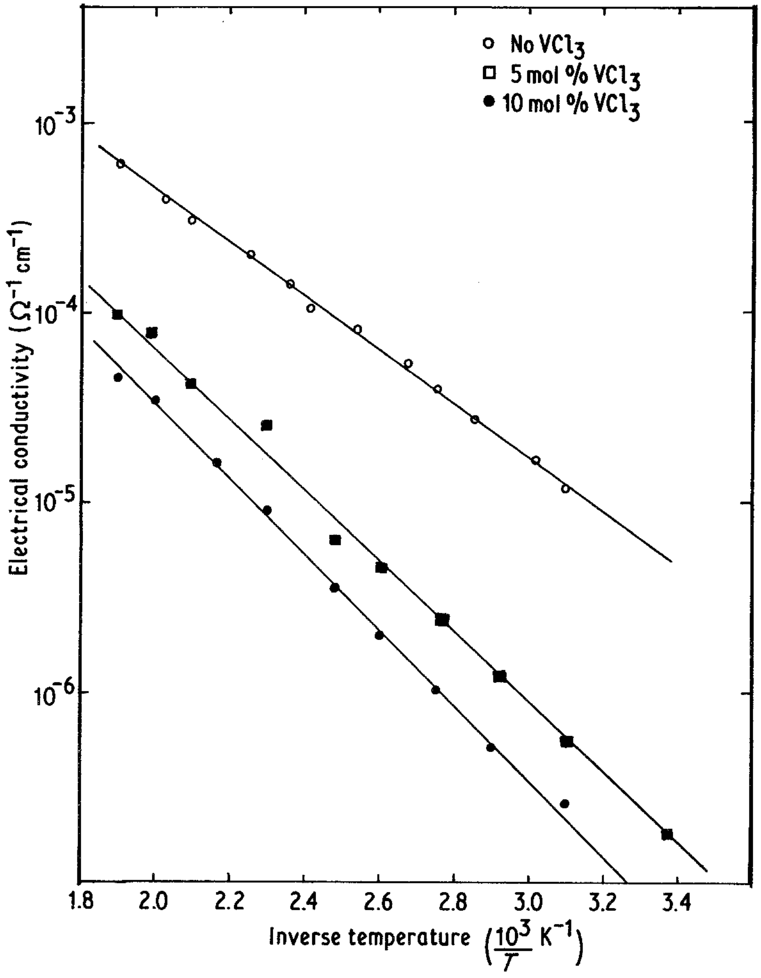

Figure 1 Electrical conductivity as a function of reciprocal temperature showing the dependence on the concentration of VCl_3 in the glasses.

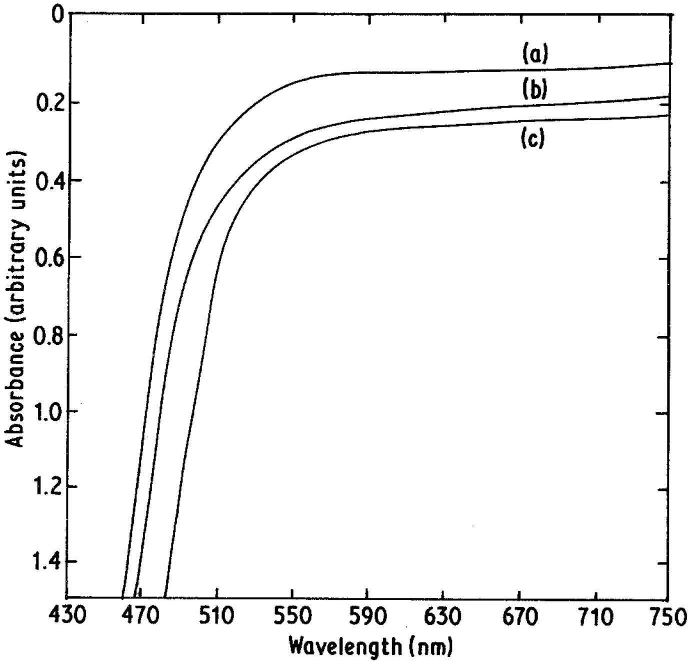

Figure 2 Optical absorption as a function of wavelength in the ultraviolet region with the concentration of VCl_3 in the glasses. (Figures indicate sample thickness.)

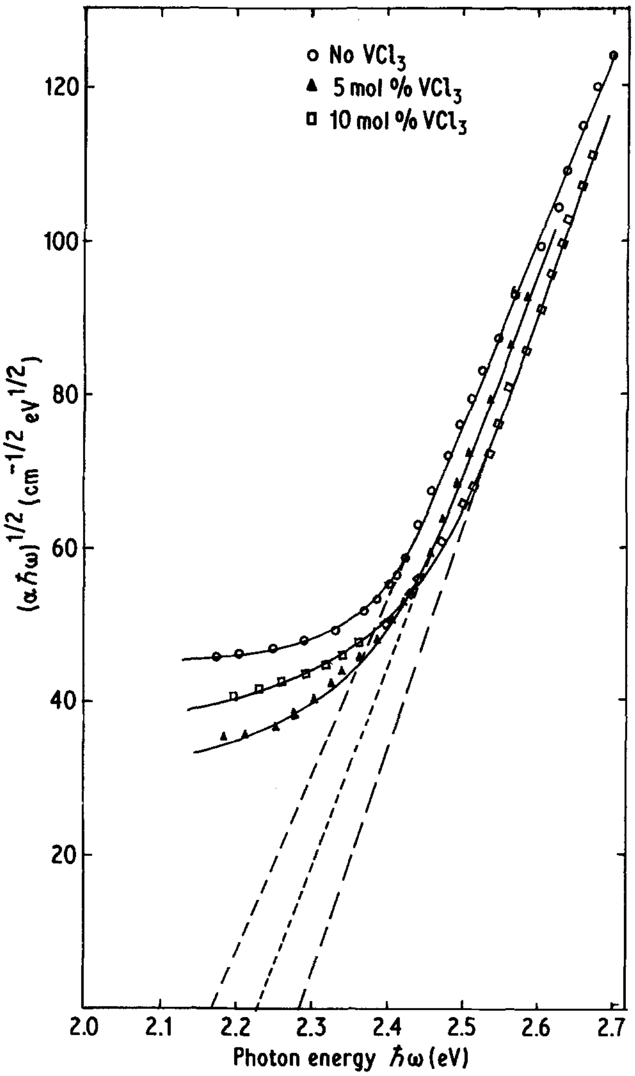

Figure 3 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for GeO_2–V_2O_5–VCl_3 glasses.

The absorption chacracteristic in these glasses may be described on the generally accepted qualitative understanding that absorption edge is determined by the oxygen bond strength in the glass-forming network. Any change of oxygen bonding in glass network, for instance the formation of non-bridging oxygen, changes the absorption characteristic [12]. By increasing the chlorine content, the absorption edges shift towards higher energies which range from 2.17 to 2.28 eV (as indicated by Fig. 4).

The linear relationship of $(\alpha\hbar\omega)^{1/2}$ with $\hbar\omega$ may be taken as evidence of internal indirect band transitions in the non-crystalline system being studied. Absorption changes depend upon the particular metal oxide incorporated in vanadate glasses. Thus the linear variation of E_{opt} with VCl_3 is mainly responsible for the optical absorption as described in the present work.

3. Discussion

Although the conductivities of amorphous semiconductors are generally much less sensitive to the presence of impurities than those of crystalline semiconductors, a large increase of conductivity has been found by the addition of silver in As_2Se_3 [13, 14]. Recently, Hogarth and Popov [4] showed that the admixture of chlorine during the preparation of copper phosphate glasses, affects the conductivity of glasses. But the control of the electrical conductivty of GeO_2–V_2O_5 glasses by the admixture of chlorine has not been investigated. It is found that the addition of chlorine to the melt when the glass is formed introduces an

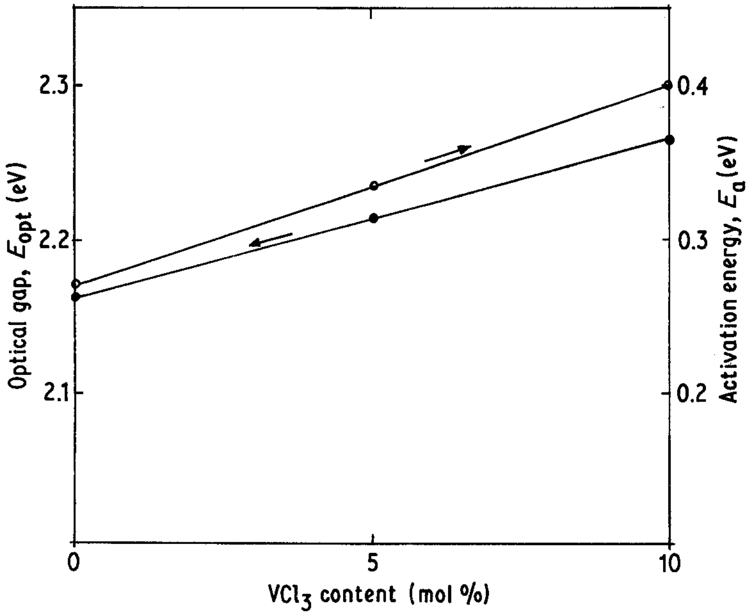

Figure 4 Dependence of activation energy and optical gap energy on the concentration of VCl_3 in the glasses.

oxidizing agent which alters the ratio of the concentrations of V^{4+} and V^{5+} ions and thus the conductivity.

The optical absorption measurement showed that by increasing the chlorine content of vanadate glasses, the absorption edges shift to higher energies which range from 2.17 to 2.28 eV. The absorption characteristic of these glasses may be described on the generally accepted 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 oxygen, changes the absorption characteristic. This could be ascribed to the added chlorine which acts as an oxidizing agent.

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