

# Gamma-ray dosimetric properties of molybdenum phosphate glasses

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In the present work, a study of the temperature dependence of the d.c. electrical conductivity and conduction activation for a series of  $\text{MoO}_3\text{-P}_2\text{O}_5$  glass systems has been carried out. The conductivity measurements of the unirradiated glass specimens proved to be mainly dependent on both temperature and transition metal ion content in the glass matrix. The results of the present investigation have shown that the conduction mechanism would be due to the electron exchange between the low and high valency states of the  $\text{MoO}_3$  oxide ( $\text{Mo}^{5+}$  and  $\text{Mo}^{6+}$ ). The radiation-induced conductivity of the glass system studied, produced by gamma rays, has also been measured experimentally. The d.c. electrical conductivity has proved to be dose dependent, which showed a decrease with increasing  $\gamma$ -dose. The results reflect some evidence of the  $\gamma$ -ray dosimetric potential of the glass specimens studied.

## 1. Introduction

Many metal oxides form glasses when melted with a basic glass former oxide such as  $\text{P}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$ , etc. The glass compositions investigated up to 1964 have been reviewed by Mackenzie [1]. The conduction processes in the amorphous materials are an interesting subject and have been extensively studied over a long period of time.

Phosphate glasses containing transition metal oxides have received a great deal of attention due to their capability of existing in more than one valence state. The vanadium glass system has been studied most thoroughly [2-4]. Electrical properties data are also available on phosphate glasses containing  $\text{CuO}$ ,  $\text{WO}$  and  $\text{MoO}$ , see [5-9]. The conduction process [10] in such glasses is believed to take place by the transfer of an electron from the ion in the low valence state to that in the high valence one.

The interaction mechanism of gamma radiation with the glass samples mainly occurs by means of electronic excitation, electronic ionization and primary atomic displacement. The free electrons thus created would attain sufficient energy and then be able to bounce through the network and might be trapped at various sites in the glass matrix. As a result, a change in the mobility of these charge carriers would take place, and one would expect that the d.c. conductivity measurement of the irradiated specimens should be affected by the passage of such ionizing radiation ( $\gamma$ -rays). The induced change in d.c. measurements is essentially related to the energy absorbed in the glass sample due to the exposure to the radiation.

In recent years, radiation dosimetry has been a subject of great importance and sometimes an emotional one [11]. Electrical dosimetry is based on the determination of the radiation dose from the induced changes in the d.c. electrical conductivity produced in the absorbed materials. Glassy materials, as well as

some organic ones, mainly polymers, have been increasingly tested for dosimetry purposes and successfully used as detectors for different kinds of radiation [12-16]. It has recently been reported that zinc [17] and cobalt [18] phosphate glasses could be used as  $\gamma$ -dosimeters in the megarad range.

The purpose of the present work was two-fold: (i) to study the d.c. electrical conductivity of the binary  $\text{MoO}_3\text{-P}_2\text{O}_5$  glass system having 37 to 70 mol %  $\text{MoO}$  compositions; (ii) to investigate the effect of  $\gamma$ -radiation on the above-mentioned glass specimens and then to discuss the validity of using such glass samples as  $\gamma$ -ray dosimeters.

## 2. Experimental procedure

### 2.1. Preparation of glasses

The glass specimens were prepared by melting an appropriate mixture of Analar metal oxide ( $\text{MoO}_3$ ) with  $\text{P}_2\text{O}_5$  in alumina crucibles (of  $\sim 100\text{ cm}^3$  capacity). The mix was heated first at  $500^\circ\text{C}$  for 1 h and then the temperature was raised to  $1200^\circ\text{C}$  using an electric furnace for 1 h. The melt was quenched at  $400^\circ\text{C}$ , and a glass formation range from 30 to 70 mol %  $\text{MoO}_3$  (starting compositions) was obtained. The samples were rod-shaped with diameter 1.6 cm and thickness  $\sim 5$  mm. All prepared glass samples, used in this investigation, are listed in Table I together with chemically analysed  $\text{MoO}_3$  (mol %). The densities of the glass samples were also measured by the Archimedes method using toluene as the immersion liquid; these are also given in Table I.

### 2.2. The d.c. electrical conductivity measurements

For measurements of d.c. electrical conductivity, electrodes were formed by brush painting silver conducting paste. The method used for such measurements, which was previously described [16], depends on

TABLE I Composition and activation energy values of the molybdate glass system

| Sample | MoO <sub>3</sub> *<br>(mol %) | Density<br>(g cm <sup>-3</sup> ) | Activation energy <sup>†</sup> (eV) |                   |                  |                  |                  |                  |
|--------|-------------------------------|----------------------------------|-------------------------------------|-------------------|------------------|------------------|------------------|------------------|
|        |                               |                                  | W <sub>0</sub>                      | W <sub>0.25</sub> | W <sub>0.5</sub> | W <sub>1.0</sub> | W <sub>2.0</sub> | W <sub>5.0</sub> |
| A      | 37.04                         | 2.840                            | 0.715                               | 0.775             | 0.819            | —                | —                | —                |
| B      | 41.52                         | 2.892                            | 0.695                               | 0.728             | 0.748            | —                | —                | —                |
| C      | 50.05                         | 3.009                            | 0.648                               | 0.770             | 0.737            | —                | —                | —                |
| D      | 57.53                         | 3.142                            | 0.620                               | —                 | 0.662            | 0.670            | 0.682            | 0.716            |
| E      | 70.00                         | 3.382                            | 0.558                               | —                 | —                | —                | —                | —                |

\*MoO<sub>3</sub> mol % chemically analysed.

<sup>†</sup> W<sub>0</sub> activation energy for unirradiated glass specimens; W<sub>0.25</sub>, W<sub>0.5</sub>, W<sub>1.0</sub>, W<sub>2.0</sub> and W<sub>5.0</sub> the activation energies for glass samples exposed to 0.25, 0.5, 1.0, 2.0 and 5.0 Mrad γ-dose, respectively.

measuring the d.c. conductivity (σ) of each specimen using the formula

$$\sigma = L/RA$$

where L is the thickness of the sample (cm), A is the cross-sectional area of the electrodes (cm<sup>2</sup>), and R is the resistance (Ω).

### 2.3. Irradiation facilities

For gamma irradiation, the glass specimens were exposed in air to various γ-doses up to 5.0 Mrad at room temperature using a <sup>60</sup>Co gamma cell. Measurements were carried out before and after irradiation.

### 3. Results and discussion

Semilogarithmic plots of d.c. electrical conductivity against the reciprocal of the absolute temperature for all prepared unirradiated MoO<sub>3</sub> phosphate glasses is shown in Fig. 1. It is clear from Fig. 1 that all glass specimens (37.04 to 70.00 mol % MoO<sub>3</sub>) show a smooth variation with temperature. In addition, the d.c. conductivity (σ) of all glass samples of different MoO<sub>3</sub> content was found to be mainly dependent on the glass compositions; σ increases with temperature

and also with increasing transition metal oxide concentration. The present results are consistent with those recently obtained [9] for a molybdate system over a percentage range from 60 to 85% MoO<sub>3</sub> content (starting compositions).

The variation of the activation energy (W) of the unirradiated glass specimens with percentage of the total metal oxide content is shown in Fig. 2 (see also Table I). W was obtained from the slopes of the straight lines representing log σ-1/T, using a least square fit method. The activation energy shows a decrease with increasing MoO<sub>3</sub> concentration in the glass specimens studied and ranges from 0.558 to 0.715 eV.

The conduction mechanism of the transition metal oxides glass has been discussed by Mott [10] in terms of the hopping process between localized states, and a general formula was given for the d.c. conductivity (σ) of the form

$$\sigma = \frac{v_{ph} N e^2 R^2}{kT} C(1 - C) \exp(-2\alpha R) \times \exp(-W/kT)$$

where R is the average atomic spacing, N is the total number of sites per unit volume, C is the fraction of sites occupied by an electron in the lower-valence state (Mo<sup>5+</sup>/Mo total), α is the tunnelling probability and v<sub>ph</sub> is the phonon frequency.

The value of N increases with increasing glass compositions, while R varies as (1/N)<sup>1/3</sup> and v<sub>ph</sub> can be

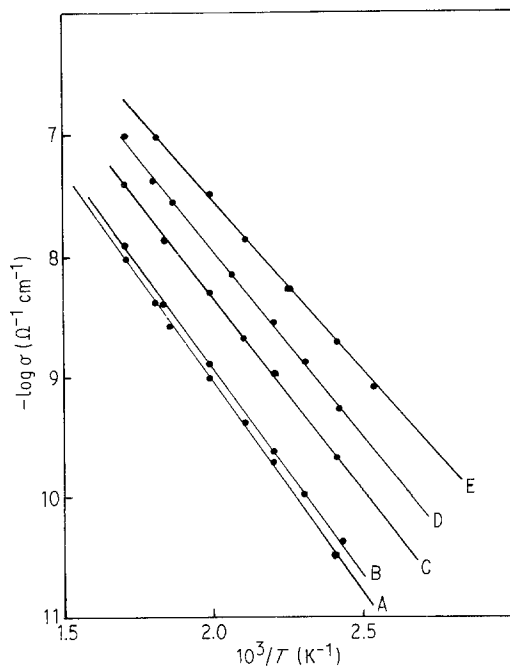


Figure 1 Variation of d.c. electrical conductivity of unirradiated MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> glasses with absolute temperature. Glasses A, B, C, D and E represent 37.04, 41.52, 50.05, 57.53 and 70.00 mol % MoO<sub>3</sub>, respectively.

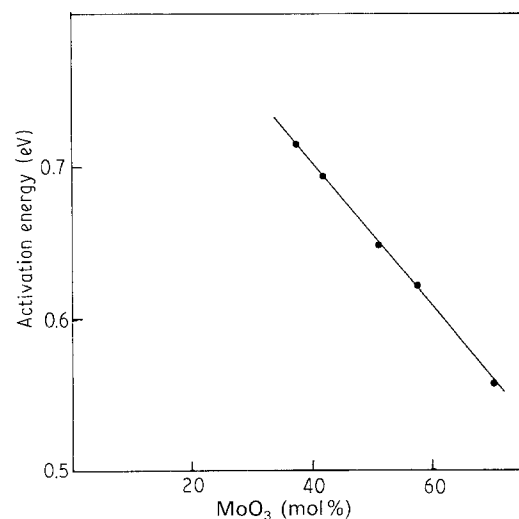


Figure 2 The variation of the activation energy of unirradiated glasses as a function of mol % MoO<sub>3</sub>.

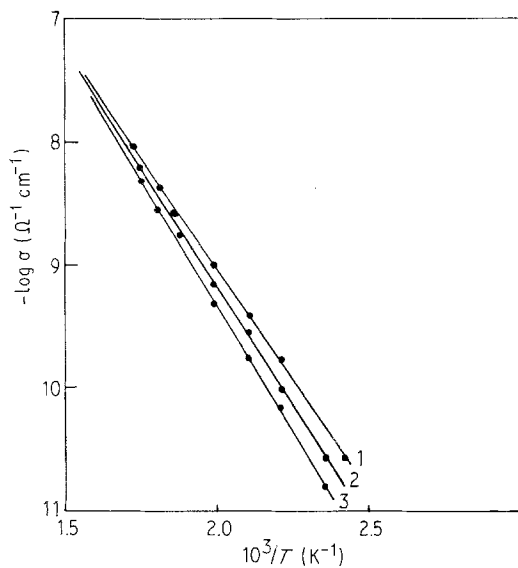


Figure 3 D.c. electrical conductivity of unirradiated and irradiated 37.04 mol % glass sample A. 1, 2 and 3 represent unirradiated, 0.25 and 0.5 Mrad  $\gamma$ -dose, respectively.

taken as  $\sim 10^{13}$  Hz for all glasses. It was found [9] that the variation of  $\alpha$  for the molybdate glass system with composition was difficult to explain.

From electron spin resonance measurements [9], the reduced valence ratio ( $C$ ) for the glass system studied was found to decrease with increasing transition metal oxide content. As a result, from the present data as well as from previous work [9], one can conclude that the d.c. conductivity of the molybdate glass system increases as the  $\text{MoO}_3$  content increases; even so the ratio ( $C$ ) showed a decrease and the number of unoccupied  $\text{Mo}^{6+}$  site increases.

Therefore, it is difficult to interpret the variation of the conductivity with glass composition. However, one can argue that the last expression can only qualitatively explain the molybdate data.

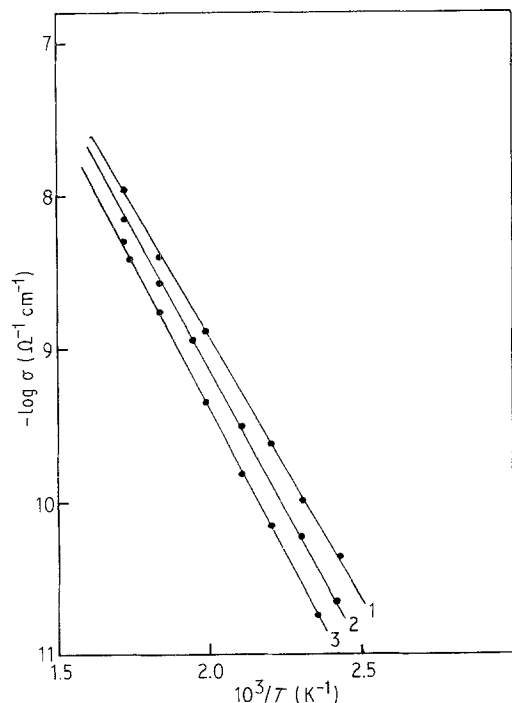


Figure 4 The variation of d.c. electrical conductivity with inverse temperature for unirradiated and irradiated 41.52 mol % glass sample B. 1, 2 and 3 represent unirradiated, 0.25 and 0.5 Mrad  $\gamma$ -dose, respectively.

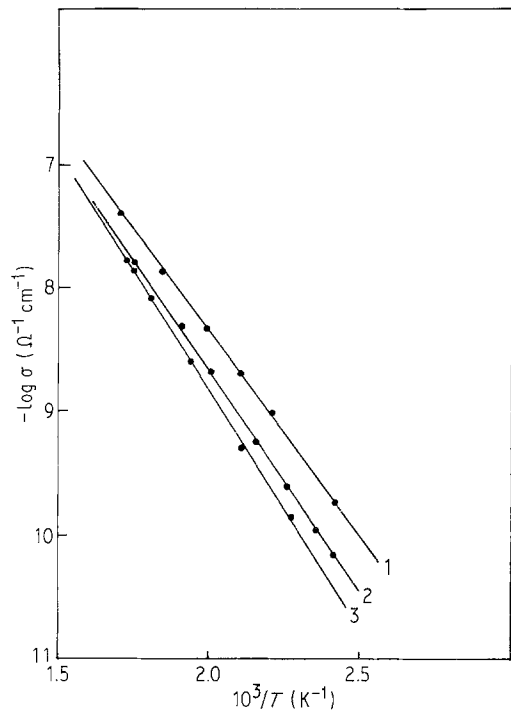
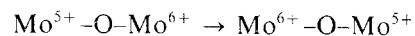


Figure 5 D.c. electrical conductivity as a function of inverse temperature for unirradiated and irradiated 50.05 mol % glass specimen C. 1, 2 and 3 represent unirradiated, 0.25 and 0.5 Mrad  $\gamma$ -dose, respectively.

It has been verified [9, 18] that the conduction mechanism of the transition metal oxides is due to the hopping process which involves the exchange of electrons from a low valence state ( $\text{Mo}^{5+}$ ) to that in the high valence one ( $\text{Mo}^{6+}$ ). This can be expressed as



and a small polaron would be produced as a result of the strong interaction between the electrons and the lattice.

The radiation-induced d.c. electrical change could, in principle, be used as a measure of the  $\gamma$ -ray absorbed doses. This induced d.c. electrical conductivity is carefully studied in the dose range up to 5.0 Mrad. Figs 3

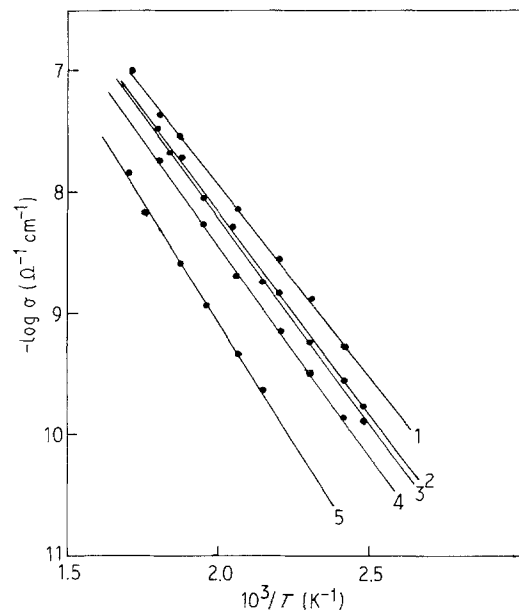


Figure 6 Conductivity-inverse temperature plots for unirradiated and irradiated 57.53 mol % glass specimen D. 1, 2, 3, 4 and 5 represent unirradiated, 0.5, 1.0, 2.0 and 5.0 Mrad  $\gamma$ -dose, respectively.

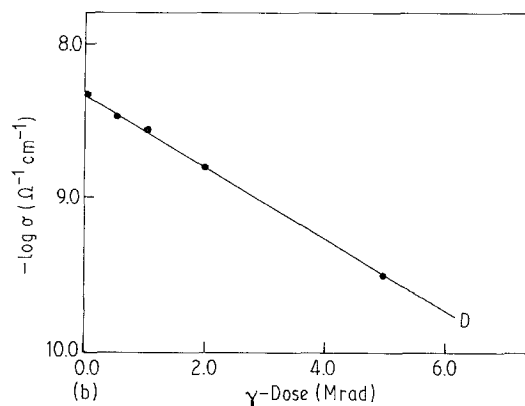
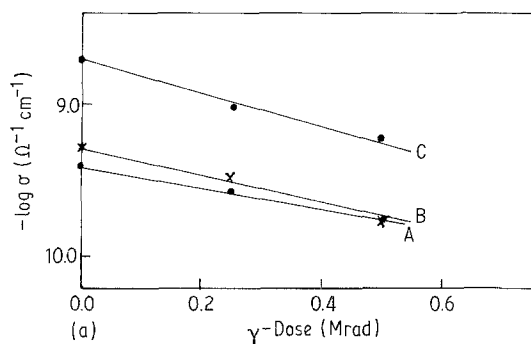
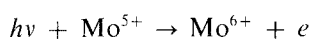


Figure 7 (a, b) The variation of d.c. electrical conductivity with the absorbed  $\gamma$ -dose at 475 K. A, B, C and D represent 37.04, 41.52, 50.05 and 57.53 MoO<sub>3</sub> mol %, respectively.

to 6 show the variation of  $\log \sigma$  as a function of reciprocal temperature at different  $\gamma$ -doses. From inspection of these figures, it is clear that the d.c. conductivity increases as the temperature increases while  $\sigma$  shows a decrease with increasing  $\gamma$ -doses. It is understood that the interaction of  $\gamma$ -radiation with the molybdate system would take place through the reaction process



The result of such a reaction will, of course, reduce the valence ratio ( $C$ ). Generally speaking, and for a certain glass composition, one could explain the induced change in the d.c. electrical conductivity as a result of  $\gamma$ -interaction, to the reduction of the ( $C$ ) value. The later factor might be expected as a predominant term affecting the value of  $\sigma$  in the  $\gamma$ -interaction process with each glass specimen. This explanation may not be enough, and further studies are being carried out in order to clarify such a mechanism. However, for dosimetry purposes, it is only necessary to relate the  $\gamma$ -doses to the induced changes in the d.c. conductivity measurements. Such a dose dependence would lead to a study of the validity of using the molybdate glass system as a  $\gamma$ -dosimeter.

The activation energy ( $W$ ) of the irradiated glass specimens was obtained from the slopes of  $\log \sigma$  against  $1/T$  using a least squares method;  $W$  shows an increase with increasing  $\gamma$ -dose at each particular composition (see Table I).

Figs 7a and b shows the variation of the d.c. conductivity as a function of  $\gamma$ -dose for different compositions and at 475 K; where glass samples A, B and C were exposed to 0.25 and 0.5 Mrad while glass sample D was exposed to 0.5, 1.0, 2.0 and 5.0 Mrad. Generally, it was found that a linearity is almost obtained. However, in the case of glass samples A and B (Fig. 7a) the two straight lines are very close to each other, especially for  $\gamma$ -doses greater than 0.25 Mrad. On the other hand, glass sample D (Fig. 7b) really does show the

best linear behaviour, also it possesses the highest d.c. conductivity values compared with the other specimens (i.e. A, B and C).

From the results of the present study, we conclude that the electrical conductivity response of glass specimen D to gamma dose could be used as a  $\gamma$ -dosimeter within the studied  $\gamma$ -dose range (0.5 to 5.0 Mrad).

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