JOURNAL OF MATERIALS SCIENCE 21 (1986) 230–234

Effect of heat treatment and irradiation on electrical conductivity and crystallization in the $BaO–B_2O_3–Fe_2O_3$ glass system

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A glass system was prepared according to the formula 75 mol% B_2O_3–(25 − x) mol% BaO–x mol% Fe_2O_3, where $x = 0, 1, 2.5, 5, 7.5$ and 10. The glasses were subjected to heat treatment at 550° C for 2, 6, 12, 18 and 24 h. The glasses were also irradiated using γ-rays at a dose of $4.805 \times 10^4\,\mathrm{rad\,h^{-1}}$ for 12, 18 and 24 h. An X-ray diffraction technique was used to identify the separated crystalline phases. The electrical conductivity and activation energy of untreated, heat-treated and irradiated samples were measured and calculated. The rate and the dimensions of crystallization were also calculated by using the Avrami equation. It was found that α-Fe_2O_3 is the separated phase when a sample containing 7.5 mol% Fe_2O_3 is heat treated for 24 h; α-Fe_2O_3 and Fe_2O_3 are the separated phases when the sample containing 10 mol% Fe_2O_3 is heat treated for 6, 12 and 18 h, with the addition of BaO when the sample is heat treated for 24 h. A miminum value for the electrical conductivity of glass samples was found to occur around an Fe_2O_3/BaO ratio of 0.425. The rate of crystallization in the sample containing 10 mol% Fe_2O_3 is 1.30607×10^{-3} and the geometry of crystallization n is 1.2238, which indicates that the crystallization was in one dimension.

1. Introduction

Rawson [1] showed that, over a certain range of barium–borate composition and temperature, some two-component and multi-component melts are unable to form a homogeneous single-liquid phase. Instead they separate into two liquid phases differing markedly in composition from each other.

The heat treatment of glasses containing nucleating agents is often carried out in two stages. First the glass is given a nucleation treatment at low temperature, then it is crystallized at higher temperature. Some crystallization probably occurs during the nucleating treatment [2].

Kinser and Hench [3] studied the effect of heat treatment on the electrical conductivity of some glasses and concluded that the electrical conductivity decreased with heat treatment. Irion *et al.* [4] found that the conductivity of alkali borate glasses increases with the alkali content, and the conduction mechanism indicates that the structure consists of a covalent boron–oxygen network.

The main aim of the present work is to study the effects of the duration of heat treatment and irradiation on the electrical conductivity and crystallization of barium borate glass containing iron, and the control of such properties via controlled heat treatment.

2. Experimental details

Chemically pure materials were used to prepare a glass system according to the formula 75 mol% B_2O_3–(25 − x) mol% BaO–x mol% Fe_2O_3 where $x = 0, 1, 2.5, 5, 7.5$ and 10. The homogenous mixture was melted in an electric furnace at 1100° C for 2 h and quenched in air.

The glass samples obtained were heat treated at 550° C for 2, 6, 12, 18 and 24 h. The samples were also irradiated for 12, 18 and 24 h using γ-rays at a dose of $4.805 \times 10^4\,\mathrm{rad\,h^{-1}}$.

The samples were crushed into fine powder and examined by X-rays using Cu$K\alpha$ radiation. The separated crystalline phases were identified by comparison with ASTM cards.

The electrical conductivity of these samples was measured in the temperature range 160° to 250° C using a (VA–J–52) German type electrometer, and their activation energy was then calculated.

3. Results and discussion

3.1. The glassy state

Fig. 1 shows the electrical conductivity values for glass samples as a function of $1/T$. It can be observed that the conductivity of these samples increases as the temperature increases, due to thermal agitation which weakens the binding force between Ba^{2+} ions and the boron network. This explains the greater mobility of barium ions [3]. It was also observed that the conductivity of the samples increases with the increase of Fe_2O_3 content up to 5 mol%, then decreases at 7.5 mol% and then increases again. This may be due to the fact that the Fe_2O_3 at low concentrations up to 5 mol% enters in the network as a glass-former, and at higher concentrations begins to enter as a modifier so that the conduction is partly ionic and partly electronic.

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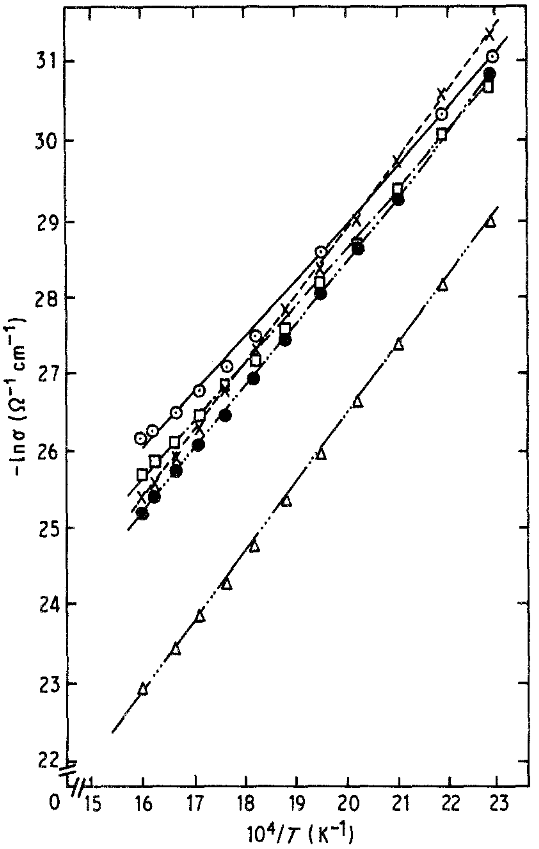


Figure 1 The relation between the electrical conductivity and $1/T$ for the glass samples. Concentrations of Fe_2O_3: (⊙) 0, (□) 2.5, (●) 5, (×) 7.5, and (△) 10 mol %.

Fig. 2 shows the electrical conductivity measured at 250° C as a function of Fe_2O_3/BaO concentration ratio. It can be seen that the electrical conductivity shows a minimum value around an Fe_2O_3/BaO ratio of 0.425. This means that the mobility of barium decreases with substitution of iron, and the glass structure would be modified to accommodate the type of the substitution ions. Upon comparing the ionic radius of Fe^{3+} and Ba^{2+}, it is found that the Fe^{3+}/Ba^{2+} ratio is equal to 0.477, and the Fe/Ba molecular weight ratio is 0.407. The mobility of barium was found to increase when the ratio Fe_2O_3/BaO is greater than 0.425, which indicates that the mobility increases with the addition of Fe_2O_3.

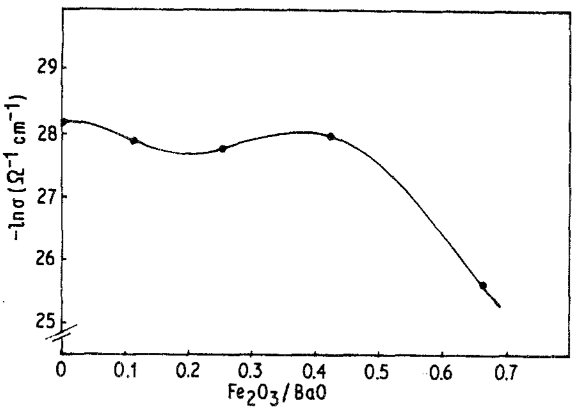


Figure 2 The relation between the electrical conductivity of glass samples at 250° C and the Fe_2O_3/BaO concentration ratio.

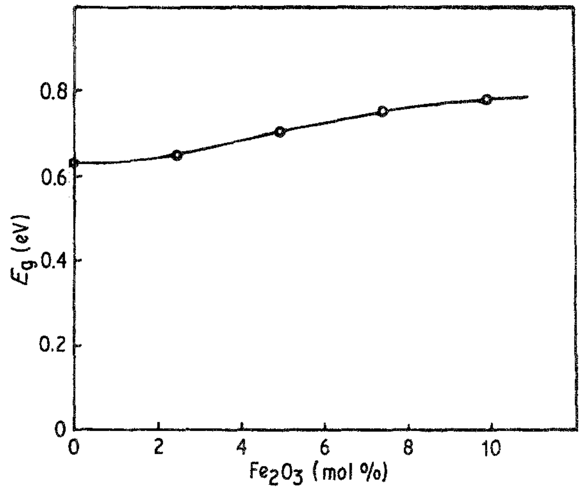


Figure 3 The relation between the activation energy E_g of glass samples and the concentration of Fe_2O_3.

Fig. 3 shows the relationship between the activation energy E_g of glass samples and the concentration of Fe_2O_3; it indicates that the activation energy increases with an increase of Fe_2O_3 content. The increase in the activation energy with increase in Fe_2O_3 concentration may be due to the change of BO_3 to BO_4, since E_g is the energy needed to activate the ion diffusion and the energy to separate one configuration of the borate unit from another. This means that E_g is the energy of the interaction that couples the borate unit motion with the diffusion of the ions [5].

3.2. The effect of heat treatment

The results of X-ray diffraction patterns for heat-treated glass samples are summarized in Table I. It shows that no crystallization process was detected in all the heat-treated samples containing iron oxide less than 7.5 mol % Fe_2O_3. While the crystallization process was detected in samples containing 7.5 mol % Fe_2O_3 only after heat treatment for 24 h, in the glass containing 10 mol % Fe_2O_3 the crystallization process was detected in the samples heat treated for 6, 12, 18 and 24 h.

From the results it is observed that up to 5 mol % Fe_2O_3 no crystallization was observed. It is expected that at low concentrations of iron oxide the iron ions may be taken in the network as a glass-former, which increases the nucleation temperature range. Also it can be expected that the change of B^{3+} to B^{4+} at

TABLE I The relation between the time of heat treatment and the separated phases

Fe_2O_3 (mol %)	Time of heat treatment (h)	Phases
0, 1, 2.5 and 5	2, 6, 12, 18 and 24	In glassy state
7.5	2, 6, 12 and 18	In glassy state
	24	α-Fe_2O_3
10.0	2	In glassy state
	6	α-Fe_2O_3 + Fe_2O_3
	12	α-Fe_2O_3 + Fe_2O_3
	18	α-Fe_2O_3 + Fe_2O_3
	24	α-Fe_2O_3 + Fe_2O_3 + BaO

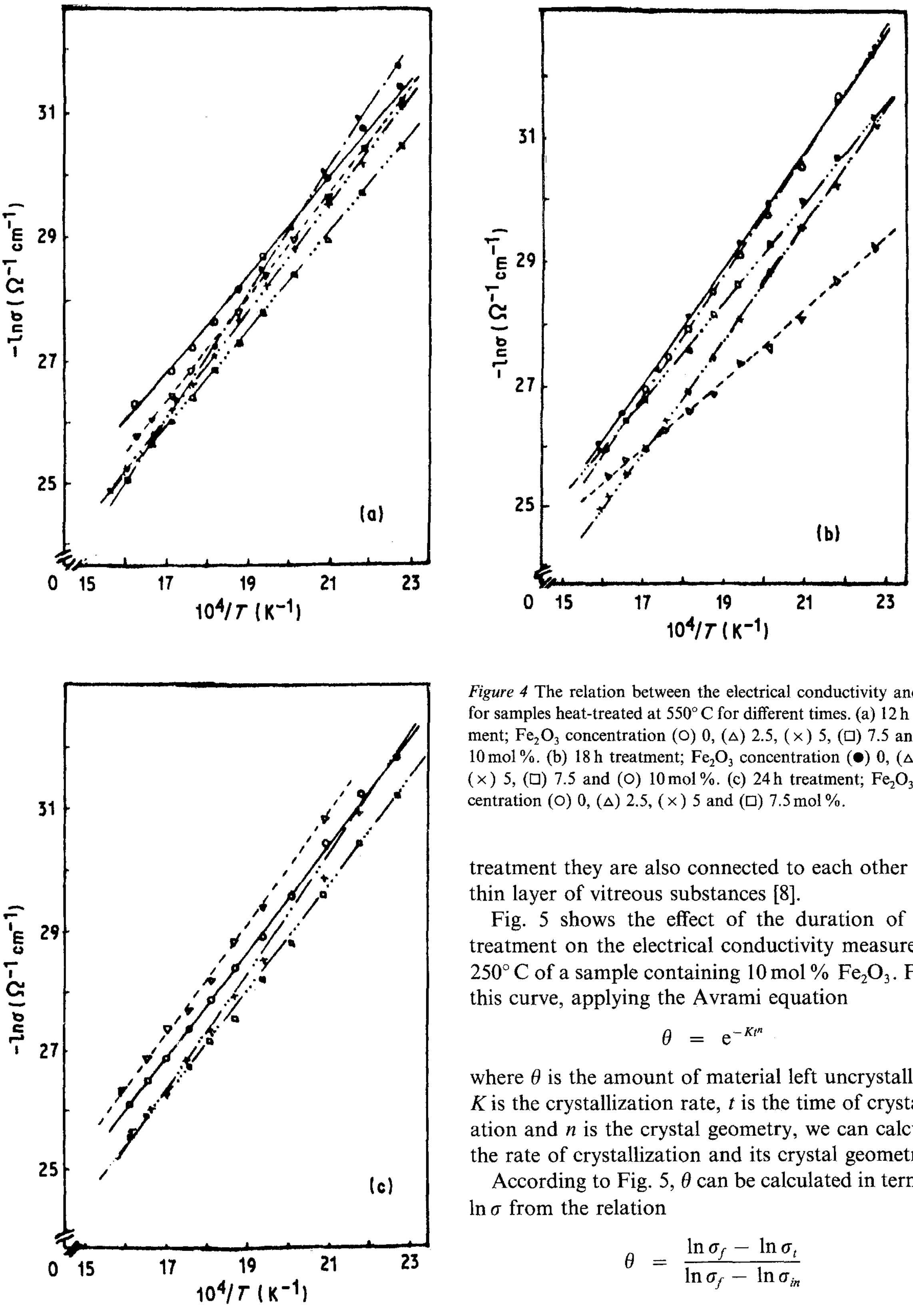


Figure 4 The relation between the electrical conductivity and $1/T$ for samples heat-treated at 550° C for different times. (a) 12 h treatment; Fe_2O_3 concentration (○) 0, (△) 2.5, (×) 5, (□) 7.5 and (●) 10 mol %. (b) 18 h treatment; Fe_2O_3 concentration (●) 0, (△) 2.5, (×) 5, (□) 7.5 and (○) 10 mol %. (c) 24 h treatment; Fe_2O_3 concentration (○) 0, (△) 2.5, (×) 5 and (□) 7.5 mol %.

concentrations up to 5 mol % causes a decrease in the immiscibility region, which in turn decreases the probability of phase separation [6].

Fig. 4 shows the electrical conductivity values obtained for heat-treated samples as a function of $1/T$.

The decrease in conductivity with the increase in time of heat treatment could be attributed to a change in the structure of samples. From a study of the structure using X-ray and IR techniques [7], we have shown that the boron ions are coordinated to three oxygens in a triangle, and the barium ion surrounds itself with non-bridging oxygens of the network. Due to heat treatment they are also connected to each other by a thin layer of vitreous substances [8].

Fig. 5 shows the effect of the duration of heat treatment on the electrical conductivity measured at 250° C of a sample containing 10 mol % Fe_2O_3. From this curve, applying the Avrami equation

$$\theta = e^{-Kt^n}$$

where θ is the amount of material left uncrystallized, K is the crystallization rate, t is the time of crystallization and n is the crystal geometry, we can calculate the rate of crystallization and its crystal geometry.

According to Fig. 5, θ can be calculated in terms of $\ln\sigma$ from the relation

$$\theta = \frac{\ln\sigma_f - \ln\sigma_t}{\ln\sigma_f - \ln\sigma_{in}}$$

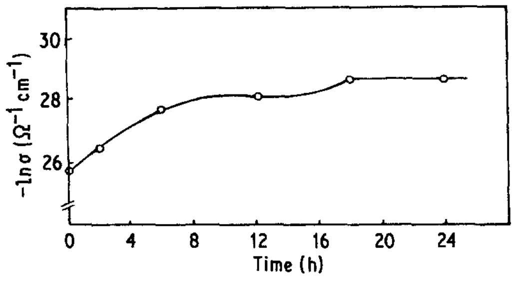


Figure 5 The relation between the electrical conductivity and time of heat treatment for a sample containing 10 mol % Fe_2O_3, measured at 250° C.

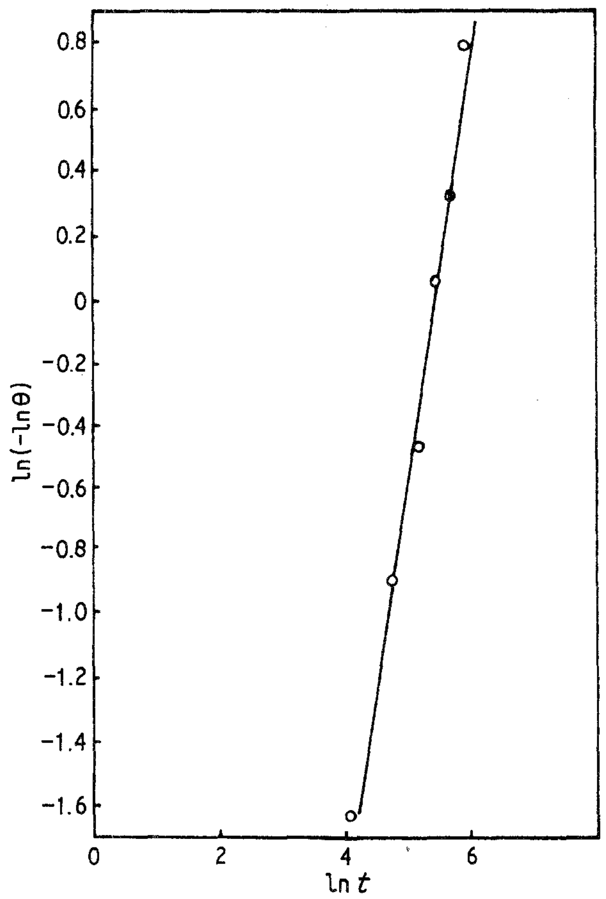


Figure 6 The relation between $\ln(-\ln\theta)$ and $\ln t$ for samples containing 10 mol % Fe_2O_3.

TABLE II The activation energy of irradiated samples for the 75 mol% B_2O_3–(25 − x) mol% BaO – x mol% Fe_2O_3 glass system

Fe_2O_3 (mol %)	Time of irradiation (h)	E_g(eV)
0	12	0.728
	18	0.778
	24	0.781
2.5	12	0.831
	18	0.738
	24	0.815
5.0	12	0.792
	18	0.809
	24	0.720
7.5	12	0.805
	18	0.805
	24	0.808
10.0	12	0.856
	18	0.783
	24	0.792

where t is the time at any point between the limits *in* and *f*. The calculated values of $\ln(-\ln\theta)$ were plotted against $\ln t$ as shown in Fig. 6, which is a straight line; from this graph the value of n can be directly computed. The value of n was found equal to 1.2238, which indicates that the geometry of crystallization is in one dimension, and the rate of crystallization was found equal to 1.30607×10^{-3}.

3.3. The effect of irradiation

X-ray diffraction patterns of the irradiated barium borate base glass and the glasses containing iron up to 10 mol % Fe_2O_3 show that all the samples are still in a glassy state. This means that the irradiation of these samples did not initiate any crystallization process.

Fig. 7 shows the effect of irradiation time on the electrical conductivity of samples. It can be observed that the conductivity decreases with increasing time of irradiation up to 18 h, and then increases.

The effect of irradiation on the electrical conductivity has not been studied in detail for glasses except

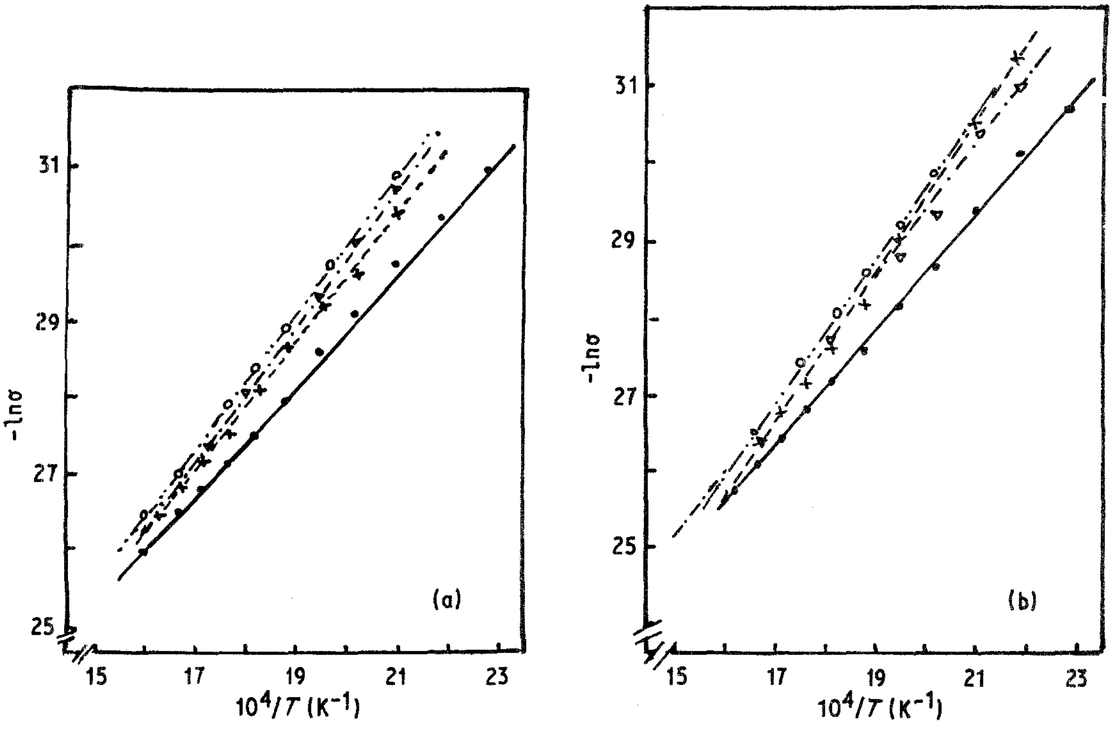
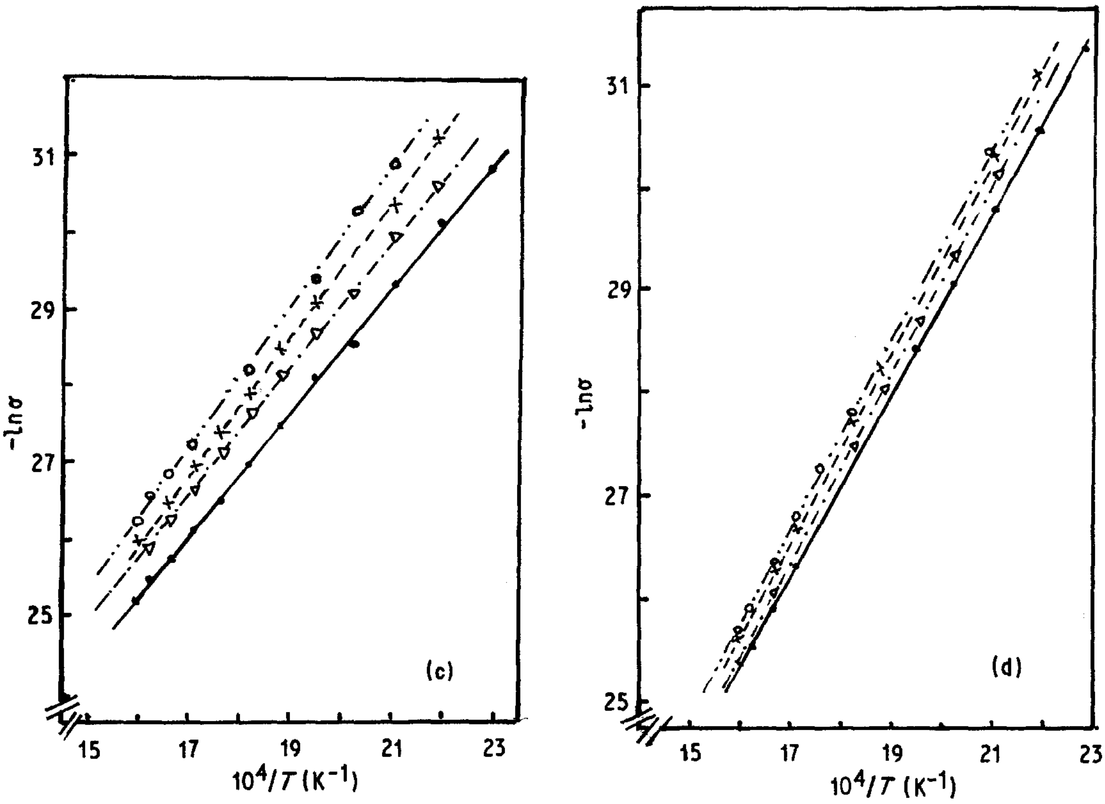


Figure 7 The relation between the electrical conductivity and $1/T$ for irradiated samples treated for different times and containing different amounts of Fe_2O_3. (a) 0 mol %; (○) glass, (×) 12 h, (●) 18 h and (▲) 24 h. (b) 2.5 mol % and (c) 5 mol %; (●) glass, (×) 12 h, (○) 18 h and (△) 24 h. (d) 7.5 mol % and (e) 10 mol %; (●) glass, (×) 12 h, (○) 18 h and (△) 24 h.



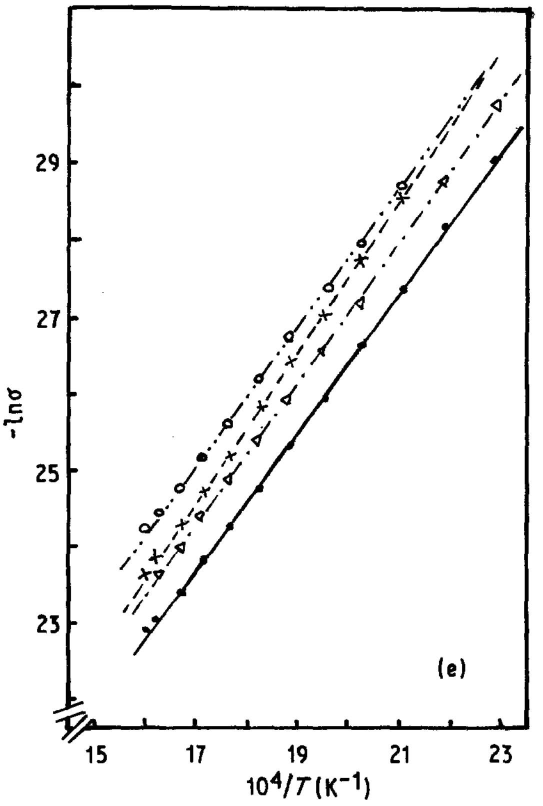


Figure 7 Continued.

the silicate glasses [9]. The decrease in conductivity as the time of irradiation increases may be due to the formation of compact structure. At higher doses of irradiation the increase in conductivity may be attributed to the breakage of the B–0 bond formed with non-bridging oxygens. The activation energies of irradiated samples are summarized in Table II.

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Received 18 September 1984
and accepted 28 February 1985