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EFFECTS OF HEAT TREATMENTS AND ACTIVE MINERALIZERS ON THE ELECTRONIC CONDUCTIVITY AND RELATED PROPERTIES OF SILICATE GLASSES

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ABSTRACT

An extensive study has been made of the behavior of electrical and spectral properties during the nucleation and crystallization of active mineralizer-doped silicate glasses, comprising DC electrical conductivity, thermopower, IR absorption spectra and UV absorption spectra. Analysis of the results obtained strongly suggests the hopping conduction mechanism traversing the barrier boundary between the amorphous-crystalline phases explaining the observed change in conductivity and values of activation energy during the stages of nucleation and crystallization. Finally, a useful tool for controlling the desired quality of silicate semiconductors to suit their application has been put forward for industry.

INTRODUCTION

The term pyroceram includes devitrification or recrystallization of glass by heat treatment. Recently, pyroceram has found great industrial application in the production of various color shades and for jewels. Thus, Pazin and Glushkov [1] studied the effect of low-temperature annealing on the electrical conductivity of glasses in the system $GeSe_2$—As_2Se_3—Sb_2Se_3. It has been found that compositions containing maximum Ge exhibit the greatest effect. Shkol'nikova et al. [2] investigated the effect of the nature of chalcogen and the deviation from stoichiometry on the crystallization kinetics of glass-forming $TlAsX_2$(X-S, Se, Te) compounds. Glasses with excess 1.8 at. % As crystallized considerably slower than the stoichiometric glasses. The replacement of Te—Se—S and excess As increased the activation energy of nucleation and crystal growth in $TlAsX_2$ glasses. Hayward [3], studying the electrical conductivities and cation mobilities of Na_2O—Al_2O_3—SiO_2 glasses, indicated that for Na: Al $\simeq$ 1 and glasses within the Na_2O—SiO_2 immiscibility boundaries and extending into the aluminous field, the electrical behavior is influenced by anion modifications. Tsuchiya et al. [4] worked on the electrical properties of silver-containing oxide glasses in the temperature range 20—130°C. In the case of conductivity, an anomaly was found for boric oxide at the composition 16 mole% Na_2O in the Na_2O—B_2O_3 glasses, but no anomaly was found in the Ag_2O—B_2O_3 glasses. Miroshvichenko and

Mobelli [5] examined the IR spectra and structure of $BaO—WO_3—P_2O_5$ system glasses. Based on the frequency and intensity of IR absorption bands, the effect of each component on the structure of glass was studied. Buffy and Bach [6] used UV spectroscopy for studying interdiffusion reactions of PbO on vitreous surfaces.

As far as the author is aware, no reference has been found in the literature data concerning the effect of various active mineralizers and heat treatments on the spectral and electrical properties of silicate glasses during their nucleation and crystallization. Since silicate glasses constitute the backbone of the glass industry, the aim of the present study is to solve this problem.

EXPERIMENTAL

Material preparation

Two silicate glasses in the system

$Li_2O—CaO—SiO_2—Al_2O_3—MO$ (M = Mn, Zn for samples I and II)
3% 5% 80% 10% 2%

were prepared from pure reagent-grade Li_2CO_3 (99.8%), $CaCO_3$ (99.97%), SiO_2 (99.8%) (Dutch silver sand was used for silica), Al_2O_3 (99.80%), $MnCO_3$ (99.78%), and $ZnCO_3$ (99.7%). Batch compositions (20 g) were dry-mixed in an agate mortar for 3 h, melted in Pt crucibles in an electric muffle furnace at 1500° C, stirred with a Pt rod, allowed to stand for 3 h as a soaking period until bubble-free and poured into a hot stainless steel mould (preheated at 600° C) in the form of rectangular disks of 0.2 × 0.4 × 0.8 cm.

Heat treatments

The prepared glass samples were subjected to different schedules of heat treatment in an electrically-heated muffle furnace provided with a temperature control unit. The heat-treatment schedule is diagramatically given in Fig. 1. The first step (part B) and second step (part D) are chosen as corresponding to the nucleation and crystal growth of silicate glasses [7]. In this respect, part B involves heating of both samples at 800° C and part (D) involves heating of both samples at 900° C for 8 h. In each case, the materials were slowly cooled (annealed to room temperature for 24 h) for possible elimination of the induced internal lattice strain.

DC electrical conductivity measurements

The DC electrical conductivity was measured using the two-probe method under vacuum. The circuit used is very similar to that previously described [8]. Measurements were made at room and elevated temperatures up to 476 K and the readings were taken at 15 min after each temperature equilibration.

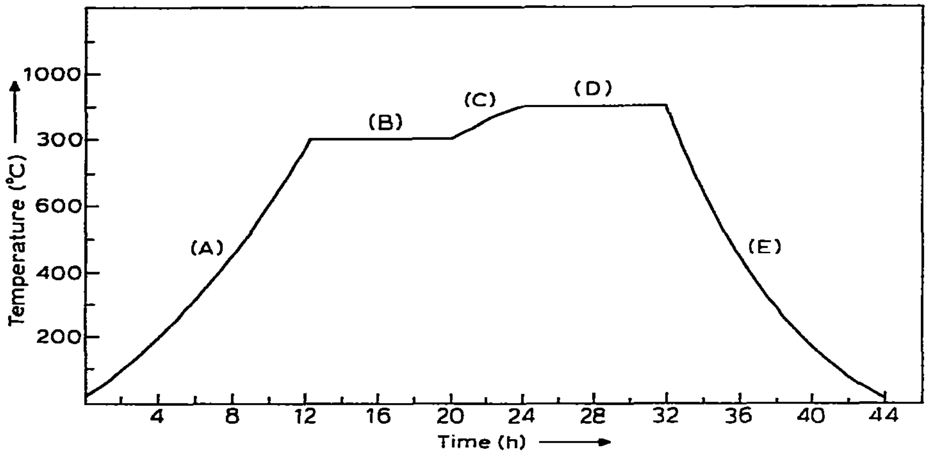

Fig. 1. A representation or heat treatment schedules.

Thermoelectric power measurements

This measurement was made as a rapid means of checking the sign of current carrier and to confirm the suggested mechanism for the variation of DC conductivity as a function of nucleation and crystallization. Thermopower measurements were taken against a Pt sheet using a K_3-potentiometer (U.S.A.), spot galvanometer and a temperature gradient of 10°C cm^{-1}. The circuit used was well shielded with copper.

IR absorption spectra measurements

In the present investigation, it is of significance to investigate the behavior of IR and electronic absorption spectra of different doped and heat-treated silicate glasses since the behavior of the X-ray diffraction patterns of similar silicate glasses have been previously investigated by several authors [7] on other glasses.

In this investigation, the room-temperature IR absorption spectra were carried out using the potassium bromide disk technique in the range 1800—625 cm^{-1}. A Pye Unicam (Ltd.), Cambridge, England SP 1000 spectrophotometer of Cat. No. 614211 was employed.

UV absorption spectra measurements

The UV absorption spectra were carried out using the Nujol mull solid technique. A Unicam SP 8000 spectrophotometer in the range 200—400 μm was employed. In each case, measurements were taken before and after each heat treatment and checked several times in order to attain reproducible and reliable data.

RESULTS AND DISCUSSION

Measurements of electrical conductivity were undertaken over a selected relatively low temperature range in order to avoid excessive heat treatments during measurements. Figures 2 and 3 represent the variation of electrical conductivity as a function of temperature [log σ vs. ($1000/T$ K^{-1})] for MnO-doped glass (sample I) and ZnO-doped glass (sample II), respectively. Measurements were conducted before heat treatment (curve a), after heat treatment at 800° C for 8 h (curve b) and after heat treatment at 900° C for 8 h (curve c).

Since there is a positive temperature coefficient of electrical conductivity ($d\sigma/dT$) for each straight line curve, the investigated materials possess semiconducting behavior in both cases. The investigated temperature range was chosen in order to avoid further heat treatment (excessive heating) and this temperature range corresponds to electronic conductivity.

The conductivity varies exponentially with temperature according to the well-known relation [9]

$$\sigma = \sigma_0 \, e^{-\Delta E/2KT}$$

The relatively slight response of σ with temperature variation involves ΔE values which can be interpreted by a simple single band model in most cases. Values of ΔE are calculated (Table 1) and assumed to correspond to the activation energies of defect mobilities.

From Figs. 2 and 3 and Table 1, it can be seen that the activation energy

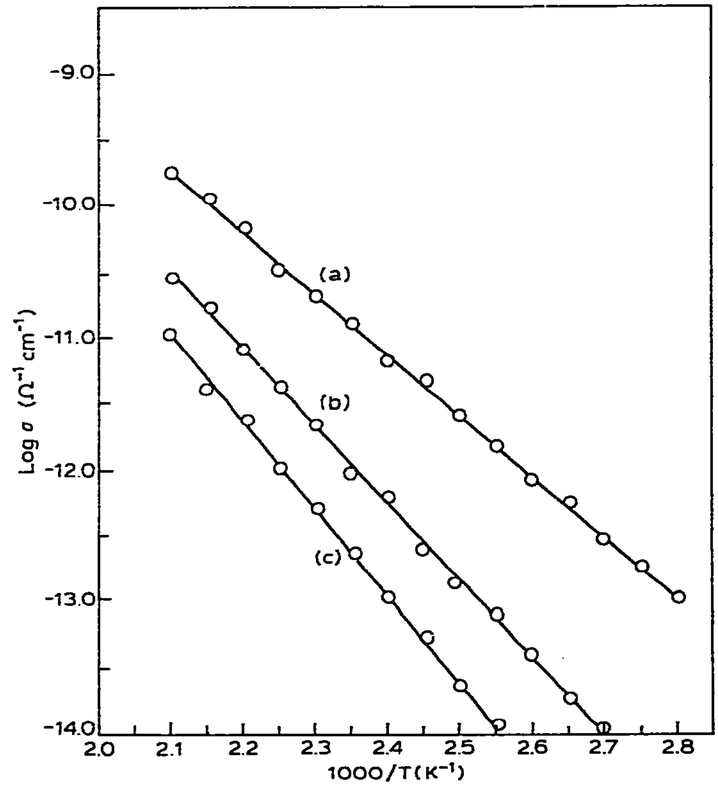

Fig. 2. A plot showing the temperature dependence of electrical conductivity for Mn-glass. (a) Before heat treatment; (b) after heat treatment at 800°C for 8 h; (c) after heat treatment at 900°C for 8 h.

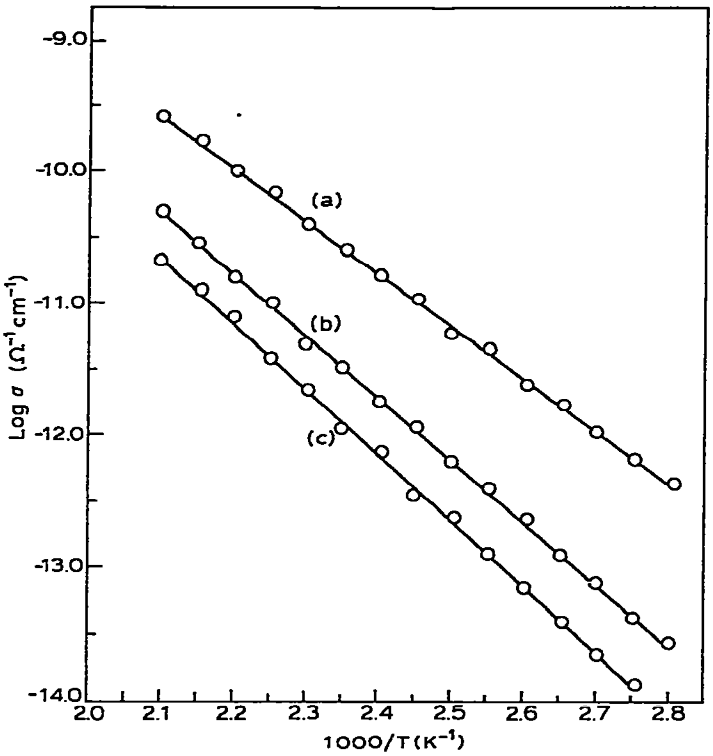

Fig. 3. A plot showing the temperature dependence of electrical conductivity for Zn-glass. (a) Before heat treatment; (b) after heat treatment at 800°C for 8 h; (c) after heat treatment at 900°C for 8 h.

and electrical resistivity gradually increase as a function of heat treatment for both samples, an effect which is more pronounced for MnO-doped silicate glass particularly at the second stage of heat treatment (D). This is in agreement with that previously given by Hanafi et al. [10] on working with other materials. This may be attributed to the nucleation of the two different doped silicate glasses at the initial stage of heat treatment and their subsequent crystallization at the second stage. This may lead to the formation of the crystalline phase at the expense of the present amorphous (glassy)phase. Besides, at elevated temperature (during the course of heat treatments), the creation of lattice defects may take place exponentially via Frenkel and/or Schottky mechanisms [8]

$$n = N \exp^{-W/2KT}$$

where n is the number of the formed defects, N is the number of possible defects, W is the activation energy for defects (very high for the Frenkel defect), K is the normal gas constant, and T is the absolute temperature.

Thus, as crystallization takes place during the course of heat treatments (see Figs. 2 and 3), lattice defects are created and proceed as a function of heat treatments, leading to the increase of stoichiometric impurity content [11,12]. Further explanation of this phenomenon is that either Mn^{2+} or Zn^{2+} ions may induce positive vacancies in the lattice structure of silicate glasses throughout the course of preparation. This was established by the

TABLE 1

Values of the obtained activation energy (E, eV) for MnO- and ZnO-doped silicate glasses as a function of nucleation and crystallization

MnO-doped silicate glass		ZnO-doped silicate glass	
Heat treatment	ΔE	Heat treatment	ΔE
Before heat treatment	1.92	Before heat treatment	1.68
At 800°C for 8 h	2.20	At 800°C for 8 h	1.88
At 900°C for 8 h	2.60	At 900°C for 8 h	2.05

strong deflection of the generated thermoelectric power (as indicated by using the K_3-potentiometer and spot galvanometer) towards the p-type direction (by comparison with reference material). As the materials are subjected to heat treatments, the Mn^{2+} or Zn^{2+} ions may diffuse through the whole materials, filling up vacancy holes present and decreasing the p-type character of the investigated materials. This was established by the decreased intensity of the galvanometer deflection in the same previously mentioned p-type direction. This finding is further proved by the increased DC resistivity and the increased activation energy for conduction as a function of heat treatment. We can say that, in the investigated temperature range, the predominant conduction mechanism probably occurs by hopping via localized states near the Fermi level [13]. Thus, in accordance with that previously deduced by Limb and Davis [14], MnO and ZnO induced microstructural changes which dramatically affected the electronic conductivity and activation energy for conduction.

Comparison of the IR absorption spectra of the investigated samples as shown in Figs. 4 and 5 reveals that they all have one feature in common,

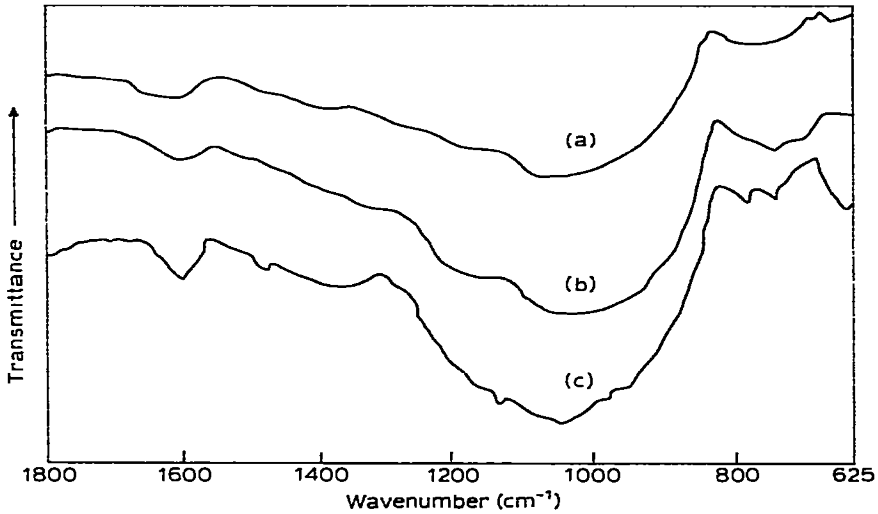

Fig. 4. Room temperature IR absorption spectra of Mn-glass. (a) Before heat treatment; (b) after heat treatment at 800°C for 8 h; (c) after heat treatment at 900°C for 8 h.

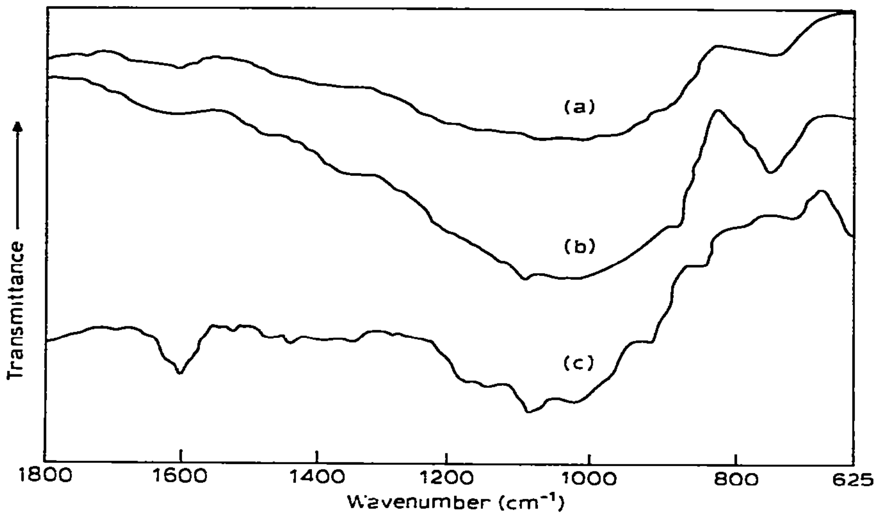

Fig. 5. Room temperature IR absorption spectra of Zn-glass. (a) Before heat treatment; (b) after heat treatment at 800°C for 8 h; (c) after heat treatment at 900°C for 8 h.

namely, the number, intensity and sharpness of the absorption bands increase as a function of nucleation and crystallization. This is more pronounced in the case of MnO than for ZnO dopants — a behavior which could be explained by the role played by the dopant ions as active mineralizers inducing nucleation and subsequent crystallization of the investigated materials which run linearly as a function of heat treatments [15—17]. Besides, the bands located in the region 900—1500 cm^{-1} suffer from gradual shifts towards shorter wavelength (blue shift), i.e. towards higher energy as a function of heat treatment. This could be attributed to the increased M—O bond strength [18] as a function of heat treatment and/or formation of a new compound with the dopant oxide. Thus, results of the temperature dependence of electrical conductivity and IR absorption spectra are in good agreement.

From Figs. 6 and 7, it can be seen that the UV absorption bands have one feature in common, namely, an increase in their number and degree of sharpness as a function of MnO or ZnO dopants (curve a) and heat treatments (curves b and c). MnO has a greater effect on the spectral properties of the investigated materials than does ZnO (see Fig. 6). Thus, in all the results of measurements taken, the greater mobility of Mn^{2+} ion than Zn^{2+} ion is clear cut. In both cases observed, the increased sharpness and number of the absorption band could be correlated with the increased degree of crystallinity and M—O bond strength in the same direction. This was established from the present results of DC electrical conductivity and IR absorption spectra measurements. The initially broad UV absorption envelope changes with heat treatment in accordance with that previously reported by Buffy and Bach [6] and other workers [19—21] for other glasses. The explanation is most probably that MnO- and ZnO-containing glasses nucleate readily because of the tendency of MnO/ZnO to segregate and/or form a two-phase glass comprising droplets of one glass dispersed in a matrix of

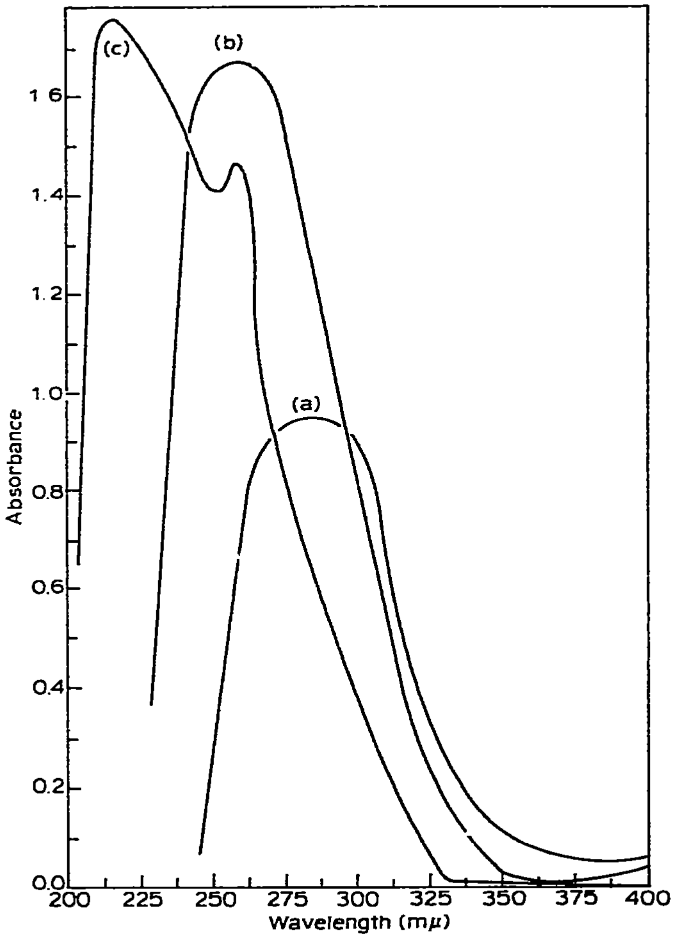

Fig. 6. Room temperature UV absorption spectra of Mn-glass. (a) Before heat treatment; (b) after heat treatment at 800°C for 8 h; (c) after heat treatment at 900°C for 8 h.

another. In the precipitation of MnO or ZnO from glass, the rate of nucleation is higher in comparison to the rate of crystallization. At high temperatures, MnO or ZnO assume a structure which has vacant anion sites which lead to distortion of binding forces which in turn lowers the activation energy of nucleation from the glassy phase. This may result in nucleation as a first stage and its subsequent crystallization as a second stage.

CONCLUSION

It is of interest to note that there is good agreement for all measurements taken on the two doped silicate glasses. Thus, it is concluded that either doping with MnO or ZnO as well as heat treatment of the test materials may bring about nucleation at the first stage followed by its subsequent crystallization which proceeds on further heat treatment and this may lead to the following:

(a) a gradual increase of the DC electrical resistivity and activation energy for conduction;

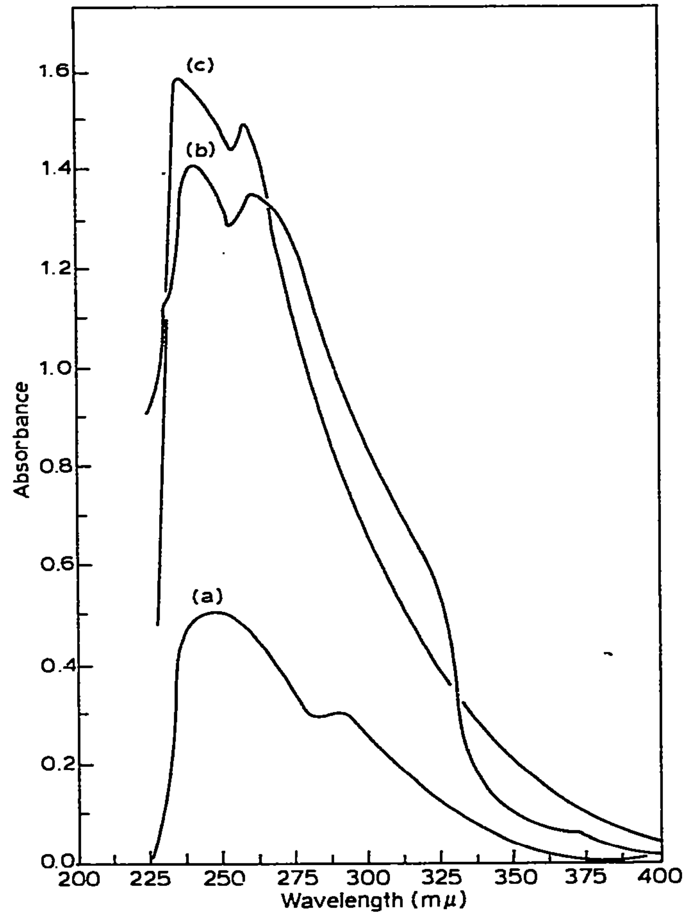

Fig. 7. Room temperature UV absorption spectra of Zn-glass. (a) Before heat treatment; (b) after heat treatment at 800°C for 8 h; (c) after heat treatment at 900°C for 8 h.

(b) the IR and UV absorption spectral bands are sharper, increase in number and suffer from gradual shifts towards shorter wavelength, i.e. higher energy.

These could be correlated with the increased degree of crystallinity and M—O bond strength in the same direction — a trend which is pronounced in the case of MnO doping. Thus, the greater mobility of Mn^{2+} than Zn^{2+} ions is clear-cut.

Accordingly, this provides us with a useful tool for evaluating the exact amount and type of dopants to control the desired final obtained electrical and spectral properties of silicate and other glasses to suit their uses and to be followed during their mass production and final application in industry.

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