Mössbauer study of the dynamical properties of some lead borate glasses near their transformation temperature

A. G. MOSTAFA*, R. M. AWADALLAH
Faculty of Science in Aswan, Aswan, Egypt

A. M. SANAD, S. H. SALAH
Department of Physics, Faculty of Science, Al-Azhar University, Nasr-City, Cairo, Egypt

Calcium–lead-borate glasses containing iron were thoroughly studied by Mössbauer effect spectroscopy aiming to determine both their Debye temperature and their transformation temperature during heating. The obtained Mössbauer effect parameters at room temperature exhibit dispersion of iron ions in a low spin ferric state as modifying cations in a pure amorphous glass matrix. The electric field gradient due to the lattice was stabilized at moderate and high lead oxide content glasses. The high-temperature measurements were carried out between 300 and 750 K under vacuum. It can be concluded that the recoil-free fraction decreased and the mean square amplitude of the Mössbauer atom increased as the temperature was increased. From the $\ln f$ against T curve, the Debye temperature of the solid glass can be calculated ($\theta_D = 373.8$ K). The experimentally determined transformation temperature from this study was found to be 665 K, which may be slightly less than the real value.

1. Introduction

Glasses containing lead oxide are of special scientific interest due to their high refractive index as well as their shielding effect. These glasses are also of high technological importance due to their low maturing temperature and their high electrical resistivity [1]. Accordingly, many papers dealing with their structure have been published, from which it was found that the addition of lead oxide to B_2O_3 converts the BO_3 into BO_4 groups [2, 3]. It also appeared that Pb^{2+} ions occupy two different coordinations in borate glasses [4, 5].

More accurate information about the structure of a glass can be obtained during the study of the transitions that occur near its transformation temperature [6]. The earlier publications in this field were carried out to determine the softening points of various glasses using tempering methods [7–9], but over the last decades the method of the recoilless nuclear resonance absorption of gamma rays (the Mössbauer effect) has been extensively used to disclose much information about the structure of the transition metal sites in various inorganic glass systems [10–12]. It has been also used to investigate the structural changes at higher temperatures in some polymeric [13] and non-polymeric [14] systems. Other workers have applied Mössbauer spectroscopy to study the structural changes of some solidified liquids around their glass transition points [15, 16].

Accordingly, Mössbauer effect spectroscopy has been adopted here to obtain information about the structure, as well as the lattice dynamics of some lead borate glasses containing iron atoms (as Mössbauer probes) near their transformation temperature.

2. Experimental details

Chemically pure grade materials were used to prepare glasses having a molecular composition: 52% B_2O_3 · 28% CaO · X% PbO · $(20 - x)$ Fe_2O_3, (where $X = 0, 1.5, 3, 4.5 \ldots$ and 15). The batches were finely pulverized and were melted in platinium crucibles in an electrically heated furnace at $1000 \pm 10°$C for 3 h. Melts were then poured on to a heated stainless steel plate, and after setting they were directly placed in the annealing furnace at 300° C. The glass samples were then left to cool to room temperature at a cooling rate of $\frac{1}{5}°$ C min^{-1}. The annealed glasses were powdered and the Mössbauer absorbers were then prepared from the sieved powders to less than 160 mesh size.

The Mössbauer effect spectra were obtained using a constant acceleration spectrometer with a 20 mCi ^{57}Co radioactive source and a thallium-activated NaI scintillation detector. The high temperature measurements were carried out between 300 and 750 K under vacuum (10^{-2} mm Hg) using an automatically controlled oven directly attached to the system.

3. Results and discussion

The usual feature of all Mössbauer spectra obtained at room temperature is the presence of a broadened paramagnetic quadrupole doublet with a small diffused peak which can be observed on the right-
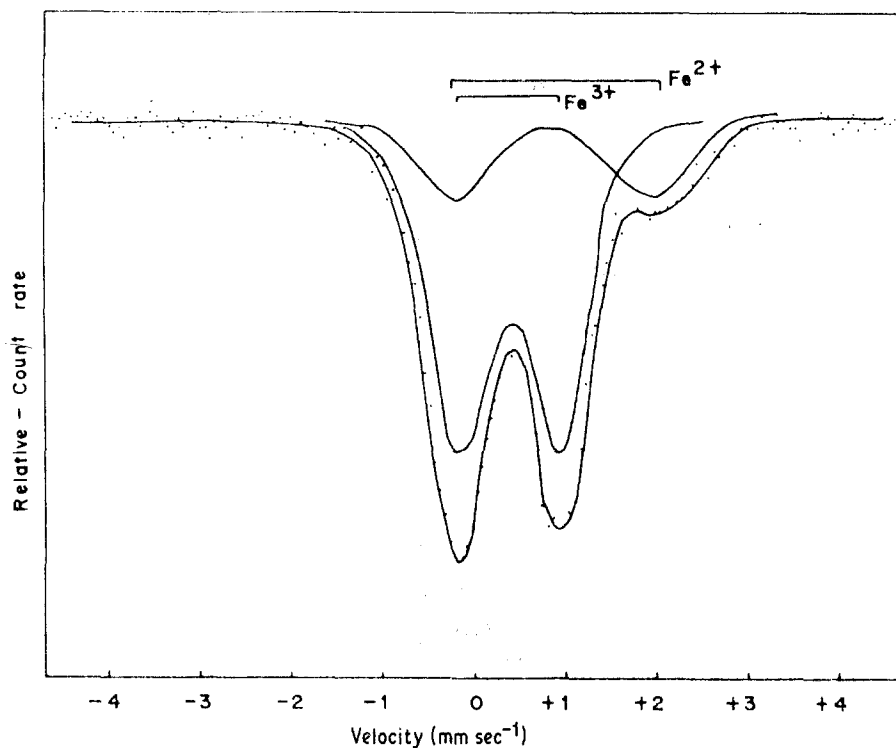
Figure 1 The analysis of the Mössbauer effect spectrum obtained for the sample containing 11% Fe_2O_3 at room temperature.

hand side of the spectra. This small peak was found to decrease as the iron oxide content was gradually increased until it became vanishingly small in the spectra of the samples which contained a high iron oxide content. Assuming the Lorenzian line shape for all peaks, the spectra were analysed into two quadrupole doublets. The least squares fit method showed that both lines were identical, and Fig. 1 represents both doublets obtained for the sample which contained 11% Fe_2O_3 and 9% PbO. The quadrupole splitting (QS) and the isomer shift (IS) energies of one of these two doublets is approximately twice that of the other. Since the Fe^{2+} cations have one more d-electron than the Fe^{3+} cations, the s-electrons of the Fe^{2+} are, therefore, more screened from the nucleus than those of Fe^{3+}. Accordingly a lower electron density at the nucleus results and hence the ferrous cations are characterized by the largest IS and QS energies [10]. Hence the doublet of the larger QS and IS values indicates the presence of an amount of ferrous ions, which can be attributed to the reduction effect of the

platinium crucibles used, as was previously discussed by Baak and Hornyak [17]. It was seen that the amount of the ferrous ions depends mainly on the concentration of the iron oxide in the batches and it decreases as the total iron content was increased [12].

The isomer shift and the quadrupole coupling values, calculated for the Fe^{3+} state are represented in Fig. 2 as a function of PbO content. It appears that as the lead oxide content is gradually increased to reach 3 mol%, replacing the iron oxide, the quadrupole splitting energy shows a maximum value of 1.3 mm sec^{-1}. The continuous increase of the lead oxide to 7.5 mol% shows a gradual decrease in the quadrupole splitting value to 1.02 mm sec^{-1}, and then it stabilizes around this value. The first observed increase in the QS values with increasing PbO content may be due to the radius differences between the Fe^{3+} ions ($r_{Fe^{3+}} = 0.064$ nm) and the Pb^{2+} ions ($r_{Pb^{2+}} = 0.128$ nm), which forms the basic valences in the glasses studied. When the amount of PbO is increased, there will be a large distortion of the iron
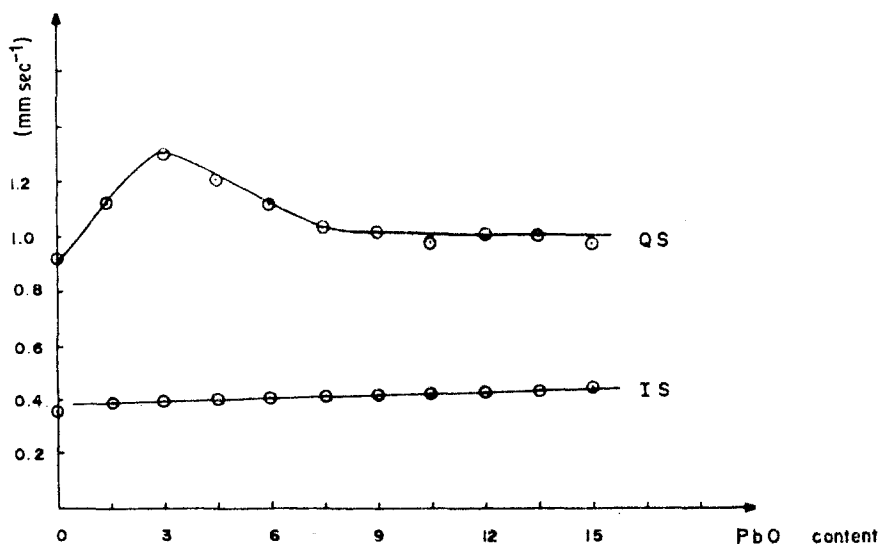

Figure 2 The change of both IS and QS as a function of the PbO content.

sites leading to the gradual lowering of the octahedral symmetry of Fe^{3+} ions which results in a large QS. A further addition of PbO will lead to the formation of non-bridging oxygen atoms in the BO_4 and FeO_4 polyhedra, and hence a decrease in the values of QS.

The isomer shift values were found to fall into a narrow range of 0.4 to 0.44 mm sec^{-1} (relative to metallic iron) which coincides with the range of IS of the octahedrally coordinated ferric ions in glass [18]. Both the IS and the QS energies exhibit dispersion of iron ions in a low spin ferric state in a pure amorphous glass matrix. This explanation can be acceptable assuming that the present Ca^{2+} ions act as bridges between the glass building units (BO_4, BO_3). The replacement of Fe_2O_3 by PbO reduces the oxygen supplied to the glass network. Accordingly, lead cations may act as a bridges in the glasses which

contain a lower lead content, while Ca^{2+} cations act as modifiers replacing the Fe^{3+} ions. This disturbs the electric field gradient in the glass network around the iron ions, which in turn increases the QS values.

After the PbO reached 7.5 mol %, a stabilization of the building groups may achieved and hence the added Pb^{2+} cations also participate as modifying cations and the disturbance of the electric field around the iron becomes negligible. According to this the suggestion that the replacement of a monovalent modifying ion by Pb^{2+} does not modify the ligand field, the charge state and the coordination of iron [19] is not strictly true for different glasses, but it may depend mainly on the glass composition.

The slight increase in the IS values as the iron oxide content was increased coincides with the results obtained by Burzo and Ardeleon [20]. This can be
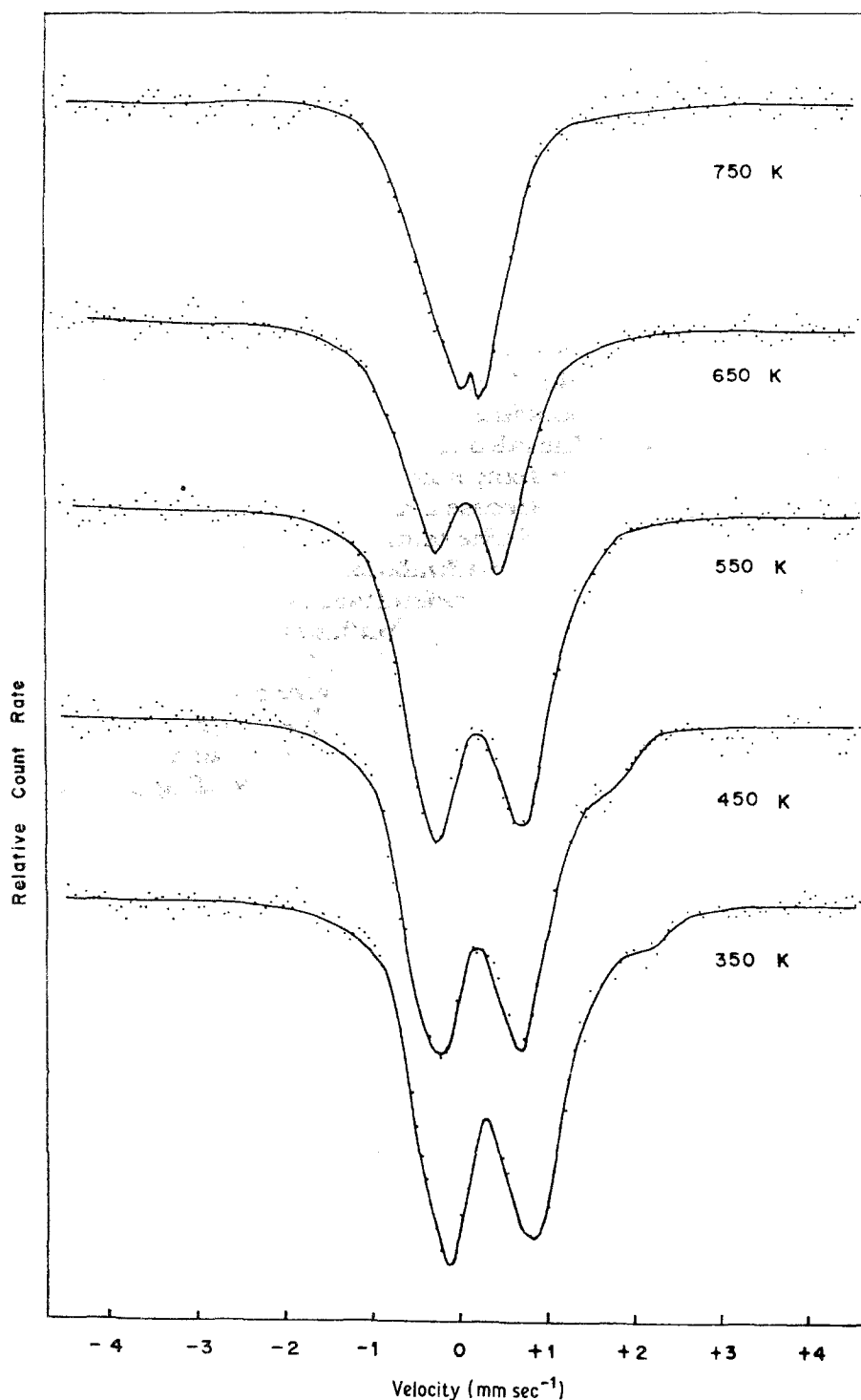

Figure 3 Some of the obtained Mössbauer spectra at different temperatures for the sample containing 11% Fe_2O_3.

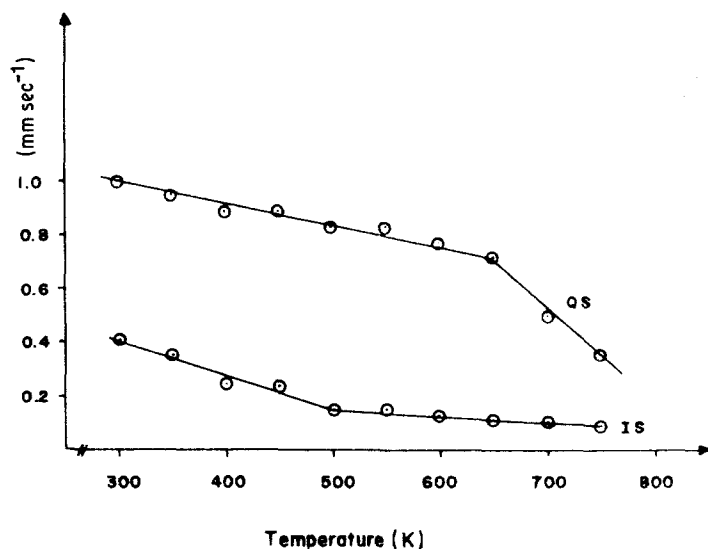attributed to the decrease in the covalence degree of the whole glass as a result to the replacement of Fe^{3+} by Pb^{2+}. At the same time some Pb^{2+} ions replace the positions of some Ca^{2+} cations in the glass matrix and the later cations may occupy some ionic positions.

The Mössbauer spectra measured at different temperatures between 300 and 750 K for the sample which had 9 mol % PbO and 11 mol % Fe_2O_3 are shown in Fig. 3. The spectra show a pronounced shoulder which represents the presence of some Fe^{2+} ions, and they decrease as the temperature increases, and have completely disappeared at 500 K. Fig. 4 represents the temperature dependence of the obtained QS and IS values. It is seen that the IS values decrease linearly from 0.41 to 0.15 mm sec^{-1} in the temperature range 300 to 500 K. It then continues to decrease at a smaller rate from 0.15 to 0.09 mm sec^{-1} until the temperature reaches 750 K. The QS values show a gradual decrease from 1.01 to 0.71 mm sec^{-1} as the temperature is elevated to 650 K. Above this temperature it continues to decrease to 0.36 mm sec^{-1} at 750 K.

The decrease in the IS values, as the temperature was gradually elevated, can be attributed to the increase in the covalent character of the whole glass matrix [10]. This may be due to both the gradual

change of Fe^{2+} into Fe^{3+} and the increase in the interatomic distances of the solid glass, where both factors are of realistic effect to decrease the electronic charge density on the iron nuclei. It can be remarked here that both factors affect the first decrease in the IS between 300 and 500 K, while the second factor is the only reason for its decrease between 500 and 750 K. The decrease of the QS values between 300 and 650 K reflects the decrease of the electric field gradient due to the matrix, which in turn can be attributed to the increase of the symmetrical distribution of the oxygens around the Fe^{3+} cations. Since the breadth of the interatomic distances increase as the temperature is gradually increased, the coordination of iron, therefore, appears to change to a higher coordination state. The observed sharp decrease in the QS values above 650 K indicates that there is an increase in the order/disorder ratio of the solid as a whole [6]. This is usual in this range of temperature due to the corresponding higher lattice dynamics.

The values of the recoil-free fraction (f) were calculated as the area under the Mössbauer absorption peaks and they are represented as a function of temperature in Fig. 5. The observed change in the values of (f) appear to be very similar to the trend of QS
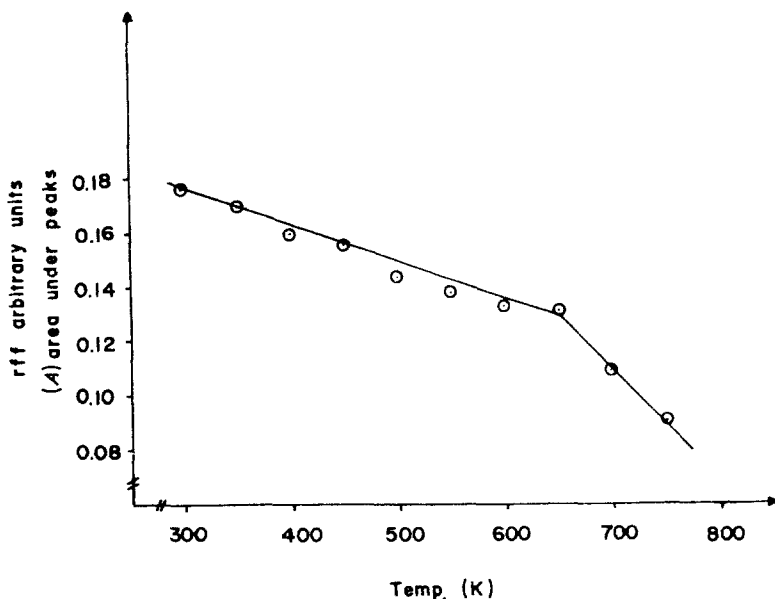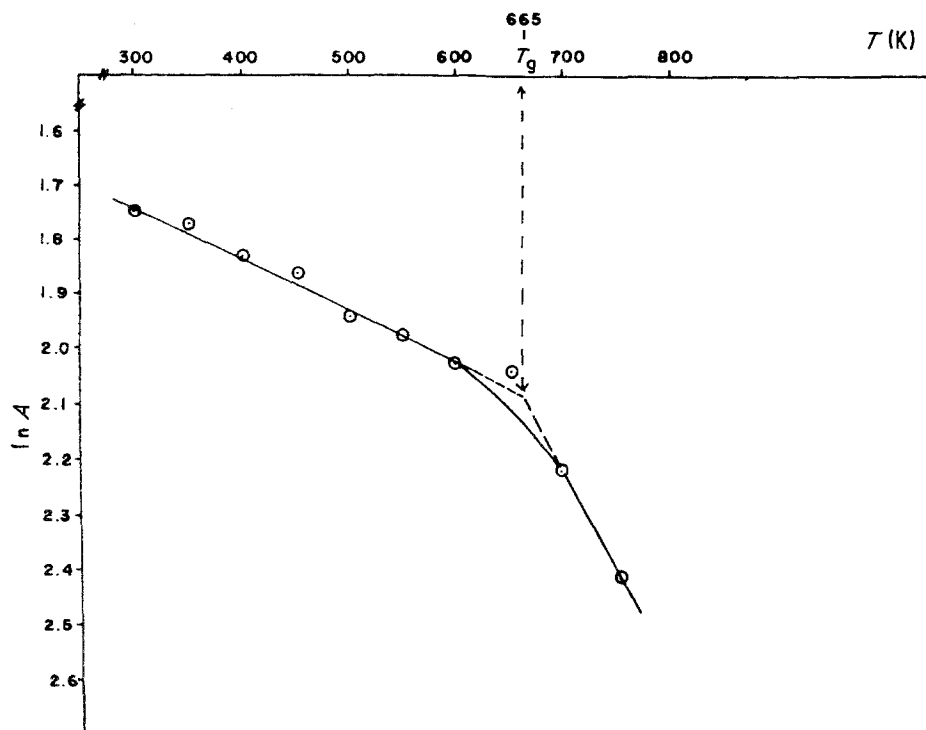
Figure 6 The temperature dependence of ln (f).

energy with temperature. That is, it decreases linearly from 0.176 to 0.13 when the temperature increases from 300 to 650 K. It then shows a sharp linear decrease to 0.09 at 750 K. Since the value of f correlates to the mean square displacement $\langle X^2 \rangle$ of a Mössbauer atom along the γ-ray direction (wavelength λ) by the formula [21]:

$$\ln f = -\langle X^2 \rangle / \lambda^2 \qquad (1)$$

and since $\langle X^2 \rangle$ is temperature dependent, it is, therefore, convenient to apply here an equation of the form:

$$\ln f = -\left(\frac{6E_r}{K\theta_D^2}\right) T \qquad (2)$$

i.e.

$$\mathrm{d}\ln f/\mathrm{d}T = -\left(\frac{6E_r}{K\theta_D^2}\right) \qquad (3)$$

where E_r is the free atom recoil energy, θ_D is the Debye temperature, and K is the Boltzmann constant.

Accordingly, ln f was plotted as a function of temperature in Fig. 6, from which a Debye temperature for the studied glass was calculated and it was found to be equal to 373.8 K.

Equation 1 was also used to calculate $\langle X^2 \rangle$ and it was plotted as a function of temperature in Fig. 7. The curve obtained is completely similar to that obtained thermodynamically during the study of the variation of the entropy with temperature for a glassy material [6].
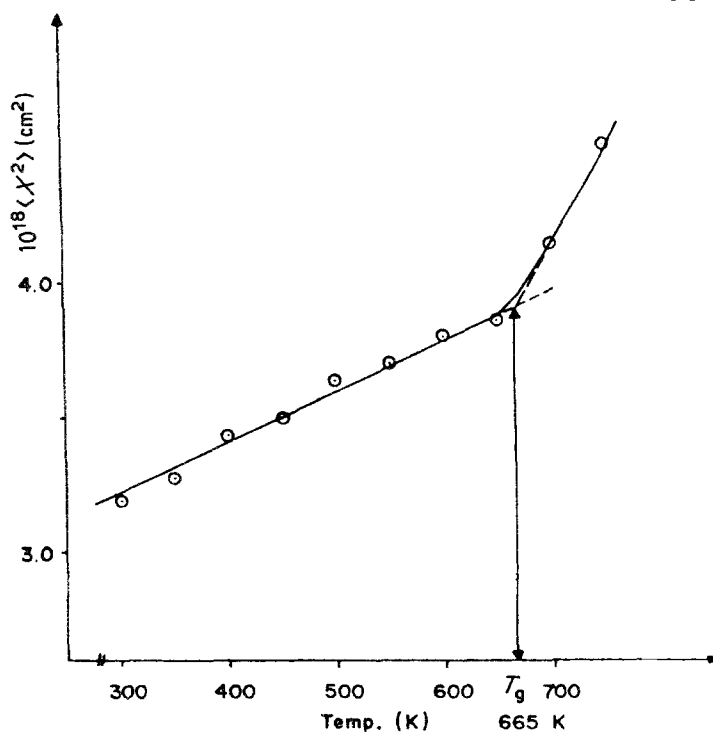

Figure 7 The temperature dependence of $\langle X^2 \rangle$.

According to the curves obtained for the change of QS and (f) (Figs 4 and 5), and according to the trends of both ln f and $\langle X^2 \rangle$ (Figs 6 and 7), it can be supposed that the transformation temperature of these glasses is approximately equal to 665 K (392° C). Since the rate of heating of the glass samples during measuring is slower than the rate of cooling during the glass preparation, the supposed value of the transformation temperature is, therefore, smaller than the correct value [15]. The obtained Mössbauer resonance after this temperature can be accompanied by a high-viscosity structural relaxation process which already occurs in order to approach a state of lower entropy [6]. This can be understood by referring to the fact that the glassy state is a metastable one, and that the transformation temperature is referred to as being the temperature of a second-order transition.

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