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Correlation between mechanical and electrical losses in transition metal oxide glasses

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Abstract

The internal friction in iron phosphate glasses containing various glass modifiers has been studied in the temperature range from 120 to 700 K. The low frequency torsion pendulum technique has been employed. The dielectric loss has been investigated by two independent methods: the absorption current method and with an a.c. transformer bridge.

The internal friction spectra exhibit a low temperature peak that can be related to the electron transfer between iron atoms in different valence states. It is confirmed that the dielectric loss peak and d.c. conductivity reveal a similar activation energy to the internal friction peak.

The obtained data have been interpreted in the framework of a new model of relaxation in glasses recently proposed by Hunt.

1. Introduction

Many glasses containing transition metal ions *e.g.* iron or vanadium, are electronically conducting semiconductors [1]. A general condition for semiconducting behaviour is that the transition metal ion be capable of existing in more than one valence state, *e.g.* Fe(II) and Fe(III), so that conduction can take place by the transfer of electrons from low to high valence states. The charge transport in these glasses is usually termed "small polaron hopping" [2, 3]. One interesting property of these materials is that the dielectric and mechanical relaxation processes have the same activation energy as their d.c. conductivity [4]. This suggests that the same mechanism, associated with electron hopping between transition metal ions, is responsible for all three phenomena. In this paper we report the results of dielectric and internal friction measurements in a number of iron phosphate glasses. These results are discussed in terms of a new theory of relaxation in glasses that has recently been published by Hunt [5, 6].

2. Experimental details

Glasses of composition (in mole per cent) $50P_2O_5$–$50[(1-x)FeO$–$xMO]$ ($M \equiv Mg$, Ca, Ba; $x=0$, 0.2, 0.4, 0.6, 0.4) were prepared using the conventional method. The d.c. conductivity and dielectric measurements were performed on button-shaped samples. A capacitance bridge (Gen. Rad. 1615A) has been used for a.c. measurements in the frequency range from 20 Hz to 100 kHz. At frequencies near the relaxation peak the dielectric loss current is usually much smaller than the conduction current. This makes it difficult to observe the dielectric relaxation spectra, since it is impossible to separate the dielectric loss current from the total current measured by the a.c. bridge. To avoid such difficulties, we have applied the absorption current method. The dielectric loss is then obtained from the discharge current and no separation from the conduction current is necessary. The dielectric relaxation spectra can be observed at very low frequencies down to 10^{-4} Hz.

Measurements of the internal friction have been done by the torsion pendulum method at frequencies from 0.1 to 20 Hz. Fibre samples (20–50 mm in length) were used which had been drawn straight from the melt.

3. Results

Figure 1 shows typical dielectric loss spectra obtained for a transition metal oxide glass. The loss factor $\epsilon_1''(\omega)$ is calculated from the results of the absorption current measurements by means of the Hamon approximation [7]. The results of the a.c. bridge measurements are shown in Fig. 2. We used the electric modulus representation [8] in which the complex electrical modulus $M^* = 1/\epsilon^*$, where ϵ^* is the complex permittivity, is given

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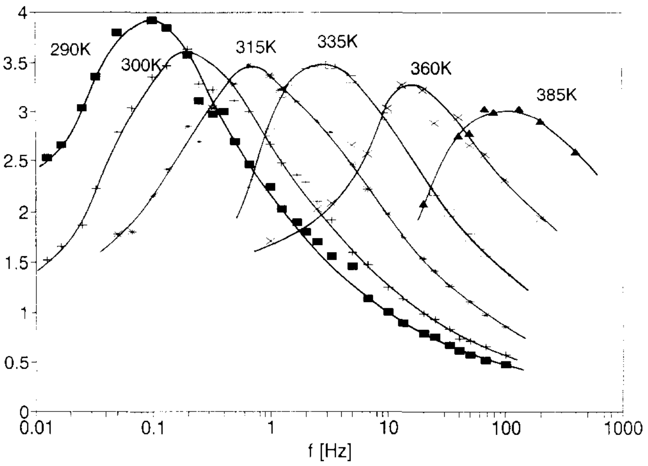

Fig. 1. Dielectric loss factor $\epsilon_1''(\omega)$ *vs.* frequency at various temperatures for 50P$_2$O$_5$–30FeO–20CaO glass.

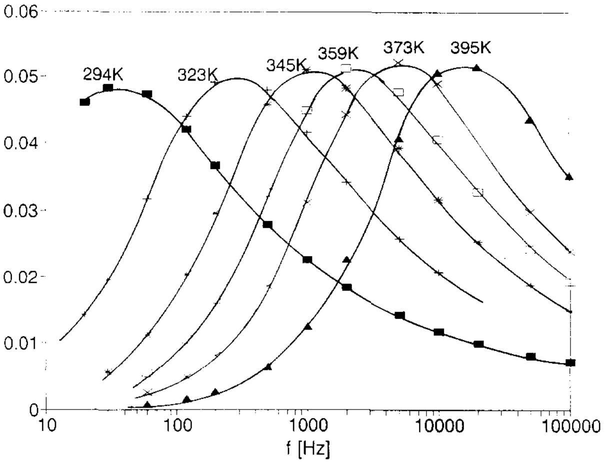

Fig. 2. M'' as a function of frequency at various temperatures for 50P$_2$O$_5$–50FeO glass.

by

$$M^* = \frac{1}{\epsilon^*} = \frac{\epsilon'}{(\epsilon')^2+(\epsilon'')^2} + \mathrm{j}\,\frac{\epsilon''}{(\epsilon')^2+(\epsilon'')^2} = M' + \mathrm{j}M'' \qquad (1)$$

The conductivity σ_t is related to ϵ^* by

$$\epsilon^* = \epsilon' - \mathrm{j}\epsilon'' = \epsilon' - \mathrm{j}\,\frac{\sigma_t}{\omega\epsilon_o} \qquad (2)$$

and

$$\epsilon'' = \frac{\sigma_t}{\omega\epsilon_o} = \frac{\sigma_{dc}}{\omega\epsilon_o} + \epsilon_1''(\omega) \qquad (3)$$

where

$$\sigma_t = \sigma_{dc} + \sigma_{ac} \qquad (4)$$

and

$$\sigma_{ac} = \omega\epsilon_o\epsilon_1''(\omega) \qquad (5)$$

Representative internal friction spectra for an iron phosphate glass are presented in Fig. 3. There are two distinct peaks in the internal friction spectrum. The low temperature peak depends on the iron ion content in the glass. It disappears for glasses without iron oxide. Accordingly, the height of this peak decreases and the peak shifts to higher temperatures with decreasing iron content. It is confirmed [4] that this peak is caused by a relaxation mechanism due to the presence of iron ions in the matrix of the glass. The high temperature peak is usually observed in alkaline earth phosphate glasses and can be explained by the migration of protons [9].

The temperature dependences of the peak frequencies for the dielectric relaxation ϵ_1'', the electric modulus M'' and the internal friction Q^{-1} are shown in Fig. 4. The plot of $\log f_m$ vs. 1/T indicates a linear relationship within the temperature and frequency range investigated, so we expect f_m to be given by the simple Arrhenius formula

$$f_m = f_{m0}\exp\left(\frac{-W}{kT}\right) \qquad (6)$$

As seen in Table 1, the activation energies W of the d.c. conductivity, the dielectric relaxation and the internal friction are all of the same value within experimental error.

We have found that the dielectric loss peaks obey the Barton–Nakajima–Namikawa (BNN) [10–12] relation

$$\sigma_{dc} = 2\pi f_{mD}\epsilon_o(\epsilon_s - \epsilon_\infty)p \qquad (7)$$

where p is constant. Namikawa has shown [13] that in an electronically conducting glass $p = 1$. If we assume that this is also true in our glasses, then the BNN

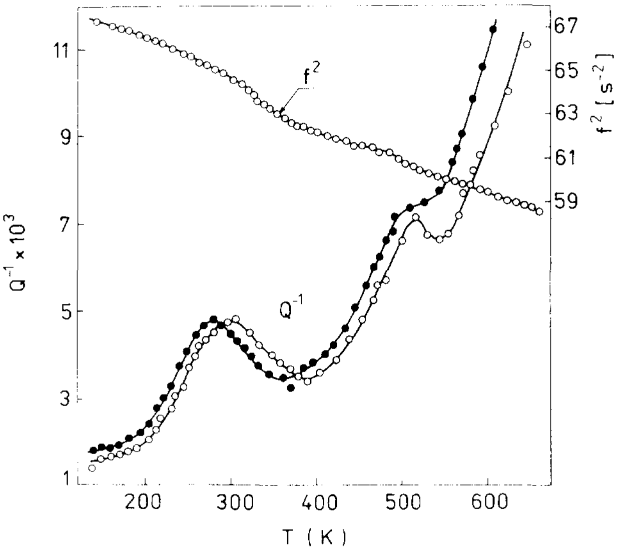

Fig. 3. Internal friction at frequencies of 0.8 Hz (●) and 8 Hz (○) for 50P$_2$O$_5$–50FeO glass.

TABLE 1. Activation energies of d.c. conductivity (W_{dc}), dielectric loss (W_{RD}), electric modulus (W_M) and internal friction (W_{IF}) in $50P_2O_5$–$(50-x)$FeO–xMO glasses, where M ≡ Ca, Ba

x (mol%)	10CaO	20CaO	30CaO	10BaO	20BaO	30BaO	0
W_{dc} (eV)	0.64	0.72	0.76	0.58	0.71	0.70	0.63
W_{RD} (eV)	0.68	0.69	0.70	0.62	0.68	0.74	0.63
W_M (eV)	0.64	0.72	–	0.65	0.66	–	0.61
W_{IF} (eV)	0.67	0.70	0.74	0.48	0.52	0.68	0.59

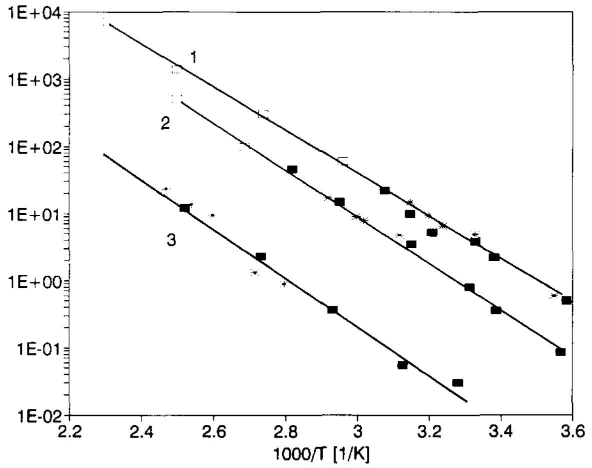

Fig. 4. Temperature dependences of dielectric relaxation (■), electric modulus (□) and internal friction (*) for (1) $50P_2O_5$–40FeO–10BaO, (2) $50P_2O_5$–30FeO–20BaO and (3) $50P_2O_5$–20FeO–10CaO glasses.

relation is fulfilled for $\Delta\epsilon = \epsilon_s - \epsilon_\infty = 11.4$–$13.4$ in the system with CaO and for $\Delta\epsilon = 17.6$–18.7 in BaO-containing glass. The magnitude of the dielectric relaxation $\Delta\epsilon$ is very close to its value obtained from the Kramers–Kronig analysis assuming that the relaxation spectra in these glasses are symmetrical.

4. Discussion

Recently Hunt [5, 6] has published a new theory of dielectric relaxation in electronic and ionic conducting glasses. His basic concept is to distinguish two relaxation processes in two frequency ranges: below and above the dielectric loss peak. In the high frequency range (above the peak) the relaxation processes have a local (parallel) character, which means that carrier hopping takes place between pairs of centres in close proximity. In this range a distribution in relaxation time with an exponential dependence on a random variable, *i.e.* the hopping distance R, is known to give a non-Debye behaviour with $\sigma_{ac} \propto \omega^s$, $s < 1$ [14]. The cross-over frequency is the peak frequency ω_m, at which individual (parallel) pair processes percolate and thus necessitate the consideration of series processes. The series processes in the low frequency range are non-local and can be treated as the percolation of individual particles over macroscopic distances in clusters or chains. For $\omega < \omega_m$ a fractal structure of clusters is responsible for relaxation currents and the conductivity has the form

$$\sigma_t(\omega) = \sigma_{dc}\left[1 + K(d)\left(\frac{\omega}{\omega_m}\right)^r\right] \tag{8}$$

where $r = 1 + d - d_f > 1$, d is the dimensionality of the space containing relevant clusters, d_f is the fractal dimensionality of such clusters and $K(d)$ is a dimensionally dependent constant related to the statistics of the contributing clusters. For $\omega > \omega_m$ the pair approximation holds and the conductivity is given by

$$\sigma_t(\omega) = \sigma_{dc}\left[1 + A\left(\frac{\omega}{\omega_m}\right)^s\right] \tag{9}$$

where $s < 1$ and A is constant.

We have applied this theory to our results of dielectric loss measurements in transition metal oxide glasses. The results of the numerical calculation of $K(d)$, r, A and s are given in Table 2. These parameters are obtained by fitting the theoretical expression for $\epsilon_1''(\omega)$ to the experimental curves of Fig. 1. From (7) and (8) $\epsilon_1''(\omega)$ can be deduced: for $\omega < \omega_m$

$$\epsilon_1''(\omega) = \sigma_{dc} K(d)\,\frac{\omega^{r-1}}{\epsilon_0\,\omega_m^{\,r}} \tag{10}$$

and for $\omega > \omega_m$

$$\epsilon_1''(\omega) = \sigma_{dc} A\,\frac{\omega^{s-1}}{\epsilon_0\,\omega_m^{\,s}} \tag{11}$$

TABLE 2. Parameters of numerical fitting for $50P_2O_5$–30FeO–20CaO glass

T (°C)	$K(d)$	r	A	s
17	–	–	0.045	0.67
27	0.001	1.44	0.065	0.665
42.5	0.0012	1.30	0.053	0.67
62	0.0019	1.4	–	–
86.5	0.0025	1.22	–	–

TABLE 3. Frequency prefactors f_{om} and $f_{o(dc)}$ in $50P_2O_5$–$(50-x)$FeO–xMO glasses

x (mol %)	10CaO	20CaO	30CaO	10BaO	20BaO	30BaO	0
f_{om} (10^{11} Hz)	1.04	0.95	0.45	2.7	1.06	0.16	5.85
$f_{o(dc)}$ (10^{11} Hz)	0.17	0.23	0.11	0.48	0.29	0.05	0.79

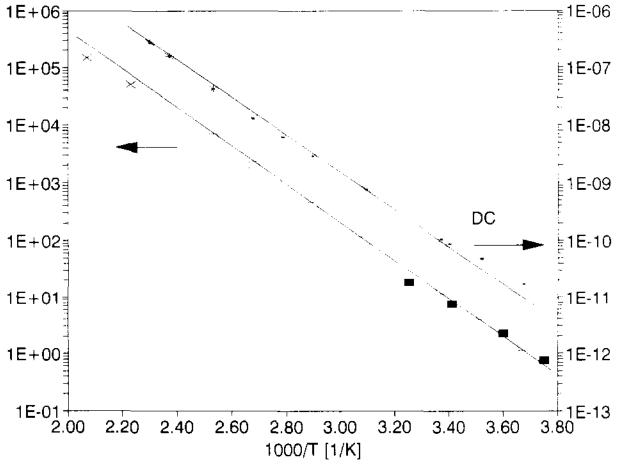

Fig. 5. Temperature dependences of d.c. conductivity (∗), frequency of peaks of internal friction (■) and dielectric loss (□); ×, results of Miller and Hansen [16].

The values s and r are reasonable and may confirm the applicability of Hunt's theory to our glasses. If transport takes place in three dimensions, it is possible to calculate d_f, which is the fractal dimensionality of clusters. Using the average values $r=1.4$ and $d=3$ (from Table 2), one obtains $d_f=2.6$. This means that in the clusters the percolation paths also have three-dimensional character.

The theory explains the correlation between internal friction, dielectric relaxation and d.c. conductivity. The mechanism of mechanical loss is associated with the migration of polarons. Hopping between pairs of centres is observed in the high frequency range, while at low frequencies the percolation in clusters is an appropriate mechanism. In both ranges of frequency the same value for the activation energy of dielectric relaxation is predicted. Mechanical stress as well as electric field may change the probability of hopping in a certain direction. It is confirmed [15] that polaron formation is limited by the strength of the electron–lattice interaction and by the material stiffness. The hopping rate depends on the wavefunction overlap, which can be described by a factor $\exp(-2\alpha R)$, where α is a measure of the spatial decay of the electron wavefunction and R is the average site spacing. Mechanical stress may change the distribution of electronic density of the polaron state. At low frequency this leads to diffusion within clusters in the direction induced by the mechanical stress. If the frequency of sample vibration decreases, this process comprises larger clusters and the internal friction peak is shifted towards lower temperatures. On the other hand, at high frequency the motion of polarons takes place between paired sites with a distribution in hopping distance. Consequently the peak of internal friction is observed at a higher temperature. According to Hunt's theory, the activation energy of dielectric relaxation in the domain of clusters and in pairs of centres is the same. This is also true for mechanical loss. Figure 5 shows the temperature dependence of the d.c. conductivity as well as the peak frequency of both the internal friction and dielectric loss for $50P_2O_5$–50FeO glass. It is clearly seen that all three processes exhibit the same activation energy. Even the results of Miller and Hansen [16] obtained from ultrasonic attenuation measurements at higher frequencies (150 and 50 kHz) are in good agreement. The frequency prefactors f_{om} for dielectric loss and internal friction are identical in this glass. Assuming the BNN relation with $f_m=f_{om}\exp(-W/kT)$ and $\sigma=\sigma_o\exp(-W/kT)$, one can deduce $\sigma_o=2\pi\epsilon_o f_{om}\Delta\epsilon$.

The d.c. conductivity is described by the Mott expression [17]

$$\sigma=C(1-C)\frac{e^2\nu_{el}}{RkT}\exp(-2\alpha R)\exp\left(-\frac{W}{kT}\right) \tag{12}$$

where $C=Fe^{2+}/Fe_{tot}$, ν_{el} is an electron frequency factor and

$$\sigma_o=C(1-C)\frac{e^2\nu_{el}}{RkT}\exp(-2\alpha R) \tag{13}$$

Hence the BNN relation becomes

$$\nu_{el}\exp(-2\alpha R)\frac{e^2C(1-C)}{kTR}=2\pi f_{om}\epsilon_o\Delta\epsilon \tag{14}$$

If we compare $f_{o(dc)}=\nu_{el}\exp(-2\alpha R)$ taken from the d.c. conductivity with f_{om} from the dielectric loss and internal friction (Table 3), it is seen that always $f_{om}>f_{o(dc)}$. The frequency prefactor f_{om} can be described in a similar form to $f_{o(dc)}$, namely $f_{om}=\nu_{el}\exp(-2\alpha R')$, where R' is the hopping distance between a pair of ions. It is confirmed that the maximal hopping distance determines the d.c. conductivity if we consider the sequences of series processes in the percolation paths between the electrodes; hence $R>R'$ and $f_{om}>f_{o(dc)}$.

References

1 L. Murawski, C.H. Chung and J.D. Mackenzie, *J. Non-Cryst. Solids, 32* (1979) 91.

2 N.F. Mott, *J. Non-Cryst. Solids, 1* (1968) 1.

3 I.G. Austin and N.F. Mott, *Adv. Phys., 18* (1969) 41.

4 W. Chomka and D. Samatowicz, *J. Non-Cryst. Solids, 57* (1983) 327.

5 A. Hunt, *J. Phys.: Condens. Matter, 2* (1990) 9055; *3* (1991) 7831; *4* (1992) 6957.

6 A. Hunt, *J. Non-Cryst. Solids, 134* (1991) 267; *144* (1992) 21.

7 B.V. Hamon, *Proc. IEE, 99* (1952) 115.

8 P.B. Macedo, C.T. Moynihan and B. Bose, *Phys. Chem. Glasses, 13* (1972) 171.

9 H.M.J.M. Van Ass and J.M. Stevels, *J. Non-Cryst. Solids, 16* (1974) 267.

10 J.L. Barton, *Verres Refr., 20* (1966) 328.

11 T. Nakajima, *Ann. Rep., Conf. on Electric Insulation and Dielectric Phenomena,* National Academy of Sciences, Washington, DC, 1972, p. 168.

12 H. Namikawa, *J. Non-Cryst. Solids, 18* (1975) 173.

13 H. Namikawa, *Res. Electrotech. Lab. (Tokyo), 757* (1975).

14 M. Pollak and G.E. Pike, *Phys. Rev. Lett., 28* (1972) 1449.

15 D. Emin and T. Holstein, *Phys. Rev. Lett., 36* (1976) 323.

16 R.A. Miller and K.W. Hansen, *J. Electrochem. Soc., 116* (1969) 254.

17 N.F. Mott and E.A. Davis, *Electron Process in Non-crystalline Materials,* Clarendon, Oxford, 1979, p. 142.