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Fast ionic conduction via site percolation in AgI-AgPO$_3$ glasses

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The measured electrical conductivity of $(\mathrm{AgI})_x(\mathrm{AgPO_3})_{1-x}$ glasses for $0<x<0.6$ follows a power-law characteristic of site percolation. The percolation threshold is 0.3, the critical exponent 3.3, the vulnerability 4.8, and the number of contact sites 2.7. In an atomically disordered solid, the conductivity of the insulating matrix itself increases as the clusters grow in size, but this has little effect on the percolation threshold.

The dc conductivity of $(\mathrm{AgI})_x(\mathrm{AgPO_3})_{1-x}$ glasses at 298 K increases from $10^{-7}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ for pure AgPO$_3$ glass to $10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ for its 60 mol.% AgI containing glass. The high conductivity of the mixed glasses is attributed to the fast diffusion involving low-energy barriers for the motion of Ag$^+$ ions in the microdomains of α-AgI, which are embedded in a macroscopically rigid AgPO$_3$ matrix. The Ag$^+$ ions of the AgPO$_3$ chains remain relatively immobile at $T<T_g$. Thus, it seems that electrical conduction occurs through the connecting paths between the microdomains, which in turn are randomly distributed within a relatively less conducting amorphous matrix.

We suggest that the electrical transport in the AgI-AgPO$_3$ glass occurs by site percolation,[1,2] which leads to a remarkably high conductivity in a macroscopically homogeneous, positionally disordered, ionic solid. Most experiments for testing the percolation theories are done on macroscopically heterogeneous, insulator-conductor, phases[2] in which the presence of one phase does not alter the property of the other. We also show that when the atomic interactions between the phases are significant enough to affect the conductivity of the other, as in the AgI-AgPO$_3$ glass, the concept of percolation threshold is still justifiable.

With an increase in the x for the $(\mathrm{AgI})_x(\mathrm{AgPO_3})_{1-x}$ glass, the number of microdomains increases, and, at the threshold concentration x_c, the larger cluster of the (α-AgI) conducting elements merges to continuously connect the terminal ends of a conduction path, or form an "infinite" cluster. As x increases above x_c, the infinite cluster grows rapidly, and the conductivity σ is given by the power law[1,2]

$$\sigma(x)/\sigma_0 \propto (x-x_c)^{\mu}\ , \qquad (1)$$

where σ_0 is the conductivity for $x=1$ and μ is known as the critical exponent. x and x_c refer to the volume fraction of the cluster and the volume fraction of an infinite cluster at the percolation threshold, respectively.

In the structure of AgI-AgPO$_3$ glasses, there is a disorder in the composition of the two components in a matrix that itself is disordered in atomic positions. Since theoretical treatments of percolation give similar results for random and periodic arrays[2], only the disorder of composition plays a crucial role in percolation. Therefore, we ignore the topology of the disordered matrix of AgI. Specific volume measurements of the $(\mathrm{AgI})_x(\mathrm{AgPO_3})_{1-x}$ glasses have shown them to be thermodynamically ideal mixtures.[3] Therefore, the volume fraction of a component is proportional to its mole fraction and Eq. (1) may be expressed in mole fraction. The normalized conductivity $\sigma(x)/\sigma_0$ of the $(\mathrm{AgI})_x(\mathrm{AgPO_3})_{1-x}$ glasses at 298 K for $0<x<0.6$ measured by us and by others[4] is plotted against x in Fig. 1. For $x>0.6$, the mixtures do not readily form a glass and for $x=1$, i.e., for pure α-AgI, the composition is unstable at 298 K. Therefore, the conductivity for higher x values could not be measured. The value of σ_0, i.e., for $x=1$, is $0.63\ \Omega^{-1}\,\mathrm{cm}^{-1}$. This value was obtained from a linear extrapolation to $x=1$ of a plot of $\log_{10}\sigma$ against $\log_{10}(x-x_c)$ seen in Fig. 2. It is clear from Fig. 1 that despite the limited range of composition, the plot of σ against x shows an approach towards the percolation threshold, as is suggested by the theories.[1,2]

The electrical conductivity of a material does not become zero for any composition (insulators do have a nonzero conductivity) and therefore x_c cannot be obtained from the plot in Fig. 1. Therefore, in order to determine x_c, $\log_{10}\sigma$ was plotted against $\log_{10}(x-x_c)$ for different values of x_c, and the x_c value was obtained from the line which had the least deviation from the data. This plot, shown in Fig. 2, is the same as that used to determine σ_0.

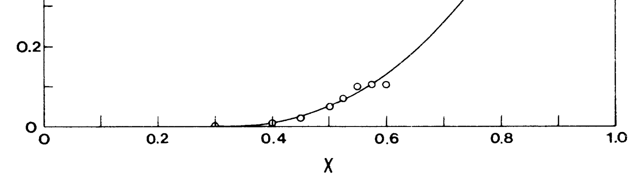

FIG. 1. A plot of the normalized dc conductivity at 298 K against the mole fraction of AgI for AgI-AgPO$_3$ glasses. Dashed line is the tangent on the curve as $x\rightarrow 1$.

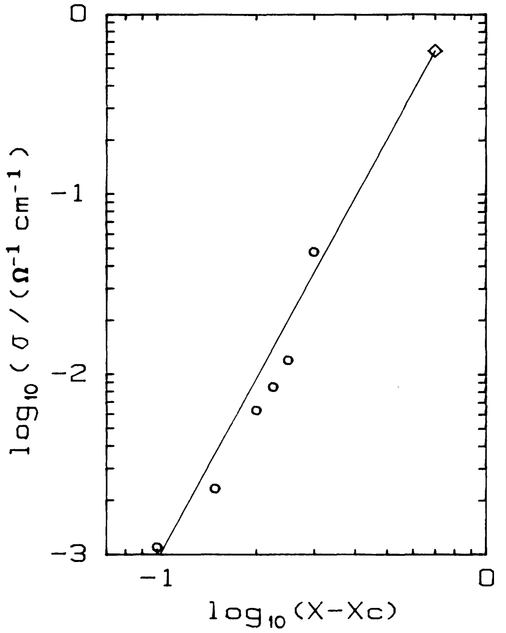

FIG. 2. A logarithmic plot of the dc conductivity at 298 K against $(x-x_c)$ according to Eq. (1) for the AgI-AgPO$_3$ glasses, $x_c=0.3$. ◇ represents an extrapolated value of σ_0 for $x=1$.

For the AgI-AgPO$_3$ glass, $x_c=0.3\pm0.05$ and $\mu=3.3\pm0.2$.

In the limit of $x\rightarrow1$, the plot of (σ/σ_0) against x reaches a limiting slope, given by

$$K=-\sigma^{-1}(\partial\sigma/\partial x)_{x\rightarrow1}\ , \tag{2}$$

where K is known as vulnerability.[1,2] It is a measure of the sensitivity of conductivity to the replacement of a small fraction of conducting elements. K is large when the coordination between the conducting elements in a site percolation model is small. For a regular two- or three-dimensional lattice, Ottavi *et al.*[5] have given an empirical relation,

$$K=2(z-1)/(z-2)\ , \tag{3}$$

where z is the number of contact sites. For AgI-AgPO$_3$ glasses, the plot in Fig. 1 gives $K=4.8$, which gives $z=2.7$ from Eq. (3). This value is close to the value obtained for a diamond site lattice.[5]

For an aperiodic lattice with bond percolation, Scher and Zallen[6] have obtained $zx_c\sim1.5$ in three dimensions. This means that an average of 1.5 bonds per site are active for percolation to occur if all sites were conducting. For $x_c=0.3$, this gives $z=5$, which is somewhat higher than the value of z obtained from Fig. 1. Nevertheless, it does not conflict with our suggestion for site percolation in the ionic glass.

The dc conductivity of AgPO$_3$ glass at 298 K is $3\times10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. This value, which corresponds to that of a poor insulator, is due to the Ag$^+$ ions occupying the deep potential wells in a configurational space. These ions are incapable of moving over the high-energy barriers in the glassy AgPO$_3$ matrix at 298 K. The presence of α-AgI domains in the matrix of the mixed glasses affects the potential energy contours in the configurational space of the matrix, as is evident from a change in T_g, and, therefore, affects the conductivity of the AgPO$_3$ matrix in the mixed glass. Thus the conductivity of the insulator itself is altered by the conducting inclusions in the atomically or molecularly disordered phases. For the AgPO$_3$ matrix, this appears as an increase in σ when x is increased from $x=0$.

When percolation theories are examined, this increase in σ of the insulating matrix may appear as a positive deviation of the data from a straight line in the $\log_{10}\sigma$ vs $\log_{10}(x-x_c)$ plots, when $x\rightarrow x_c$, as has been observed for mixtures of conducting and nonconducting spheres[5] and in (two-dimensional) films of superconducting-semiconducting, Pb-Ge and Al-Ge metals mixtures.[7] In our analysis, the observed increase in σ of the insulating matrix has little effect on the percolation threshold.

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