Mixed Transition Ion Effect in Certain Polaronic Semiconductors

Biprodas DUTTA and Ian L. PEGG

Vitreous State Laboratory, The Catholic University of America, Washington, D.C. 20064, USA

The presence of vanadium and iron in phosphate glasses has been found to exhibit properties similar to the mixed alkali effect observed in oxide glasses. While conduction in the latter is caused by a classical barrier crossing mechanism of alkali ions, a quantum-mechanical process, comprising hopping of small polarons, is generally accepted to be the mechanism of charge transport in phosphate glasses containing transition metals. The substitution of one transition ion by another significantly increases dc resistivity activation energy for dc conduction and glass transition temperature, reaching maxima at an intermediate transition ion ratio.

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Introduction

Phosphate glasses containing iron and vanadium ions in more than one oxidation states are known semiconductors. At room temperature and above, the transport mechanism is generally accepted to be on account of hopping of small polarons, which travel from a reduced transition ion (TI) site, to a site occupied by an oxidized TI.\(^1\)\(^-\)\(^10\)

In the impurity bands of crystalline solids, localization of states is caused by the random occupation of the donor and acceptor ions.\(^1\)\(^1\)\(^1\)\(^1\) In melt-quenched glasses, localization is caused by the disorder of the lattice as well as the random occupation of the transition ions, giving rise to tail states in the forbidden band. An electron in such a localized state is almost always expected to distort the surrounding lattice. The carrier and the associated distortion of the lattice form a ‘pseudoparticle,’ which is termed polaron. When the radius of localization is of the order of atomic distances, it is called a small polaron.\(^1\)\(^2\) For larger radii, the pseudoparticle is termed large polaron, though a sharp distinction does not exist.

Anderson\(^1\)\(^2\) treated diffusion of carriers in random lattices and laid out the criteria for localization. The scatter in the atomic potential, as a result of disorder, was quantified as \(V_0\) and \(B\) was taken to be the bandwidth of the carriers. It was established that, at a limiting ratio of \(V_0/B\), all the carriers will be trapped in their potential wells such that there will be no conduction at the zero of temperature and the ensemble will behave as a perfect insulator. In other words, even though the band is partially filled and sufficient overlapping of electronic orbitals exists, carriers will not diffuse under the influence of an electric field. This is in contrast to crystalline lattice where only completely filled or completely empty bands lead to insulating behavior. The absence of diffusion at 0K, brought about by the randomness of lattices is known as Anderson localization.

When there is a finite density of states at the Fermi energy, \(E_F\), in a material whose atomic structure is sufficiently disordered for states there to be localized, the material is called a Fermi glass. An Anderson transition occurs if the position of the Fermi energy and/or the mobility edge, \(E_C\), is varied in such a way that \(E_C-E_F\) changes sign; a transition will occur from insulating (\(\sigma\rightarrow0\) as \(T\rightarrow0\)) to metallic behavior with \(\sigma\) tending to a finite value known as minimum metallic conductivity, \(\sigma_{\text{min}}\). Mott and Davis\(^1\)\(^1\) have demonstrated that in three-dimensional systems, at high temperatures, conductivity (\(\sigma\)) follows the relationship

\[
\sigma = \sigma_{\text{min}} \exp \left(- \frac{(E_C - E_F)}{kT}\right)
\]

and at low temperatures, variable range hopping pre-dominates following the relationship

\[
\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T}\right)^{1/4}\right]
\]

where, \(\sigma_0\) and \(T_0\) are constants. It was also demonstrated that the disorder parameter, \(V_0/B\), may increase as a result of increasing disorder (\(V_0\)) or decreasing bandwidth (\(B\)), the latter on account of increasing effective mass of carrier. It was also demonstrated that conductivity decreases while its activation energy increases with increasing \(V_0/B\).

Following Mott,\(^1\)\(^1\) electronic conductivity in phosphate glasses containing transition metal ions is given by:

\[
\sigma = \sigma_0 \exp \left(- \frac{W}{kT}\right)
\]

where \(\sigma\) is the conductivity, \(W\) is the activation energy of dc conduction, \(k\) is the Boltzmann’s constant, \(T\) the absolute temperature, \(\sigma_0\) the pre exponential coefficient is given by:\(^1\)

\[
\sigma_0 = \left(\frac{\nu_0 n_0 e^2}{kT R}\right) C (1-C) \exp \left(-\alpha R\right)
\]

where, \(C\) is the fraction of reduced TI, \(n_0\) is the total number of sites, \(\nu_0\) is the phonon frequency, \(R\) is the mean distance between the transition ions and \(\alpha\) the rate of decay of the wave function \([\Psi=\exp(-\alpha r)]\) of an electron on the reduced transition ion. The activation energy, \(W\), is given by:

\[
W = W_H + 1/2 W_D
\]

where \(W_H\) is the energy for hopping and \(W_D\) is the difference in energy between two localized states. For phosphate glasses at room temperature and above, \(W_H < W_{th}\) implying that the activation energy for dc conduction is virtually equal to the small polaron hopping energy. The electron gains the hopping energy via lattice vibrations and the process may be either adiabatic or non-adiabatic, depending upon the probability of successful “jumps” of the carrier from one center to the other and the mobility is strongly dependent on the activation energy\(^1\)\(^1\)\(^1\) \(^1\) which has been demonstrated to be half the energy involved during the formation of the small polaron. It follows that the energy involved during the formation of small polarons in a rigid lattice would be higher than that in a relatively more elastic surrounding. Consequently, the activation energy of polaron transport would be expected to be higher in the former.

Day and coworkers\(^5\)\(^6\) have worked on the electrical and structural properties of binary iron phosphate, alkali iron phosphate and mixed alkali iron phosphate glasses. Moustafa and co-workers\(^7\)\(^1\)\(^0\) have studied electronic conduction and structural properties of iron containing barium vanadate and
lead borate glasses. The general conclusion of all these studies confirms that small polaron hopping (SPH) is the transport mechanism in these glasses with activation energies of around 0.4–0.6 eV.

Most of the previous work investigated the effect of vanadium or iron concentration on the structure and/or electrical properties of glasses. The present work was initiated to study the effect of varying the relative proportions of V and Fe ions in phosphate glasses keeping the total Ti concentration fixed at 50 mol%.

Experimental procedure

Glasses, in the series $x$V$_2$O$_5$·$(50-x)$Fe$_2$O$_3$·50P$_2$O$_5$, were prepared from reagent grade P$_2$O$_5$, V$_2$O$_5$ and Fe$_2$O$_3$. The batches were melted in Pt/Al crucibles at 1200°–1325°C for 30 minutes and quenched between thick aluminum plates. The glasses were not annealed after quenching. X-ray diffraction of glass powders did not reveal the presence of crystalline phases. The compositions of the glasses were analyzed by x-ray fluorescence spectroscopy.

DC conductivity was measured by the Van der Pauw four-probe method using a computerized apparatus, capable of scanning between 82 K and 700 K (MMR Technologies). A miniaturized Joule-Thomson refrigerator cooled the sample from room temperature to 82 K and kanthal strips, mounted at the bottom of the sample platform, heated the sample. The temperature was monitored to an accuracy of 0.5 K.

The samples were polished, co-planar wafers, 300–1500 μm thick, having arbitrary shapes. The current fed to the sample was varied between 10⁻⁶ and 10⁻¹¹ amperes, depending on the sample resistance and temperature. Silver electrodes were attached to the top edges of the samples (as point contacts) with silver paste and sample conductivity data were acquired under ohmic conditions. Pairs of electrical contacts on the sample, in different permutations and combinations, were used as current and voltage probes. The reciprocal of the average of twenty four conductivity measurements comprises each of the reported resistivity (ρ) data. All electrical measurements were performed under 8–10 millitorr vacuum, in a dark chamber. The error in conductivity measurements has been estimated at ±2%.

Glass transition temperatures were determined from differential thermal analyses performed at a scan rate of 10 K/min. The error in $T_g$ values is ±5 K. Density was measured (error limit ±0.010 gm/cc) in standard pycnometers, using deionized water and applying temperature corrections where necessary. Redox equilibria of iron in the glasses, as indicated by the Fe$^{2+}$/Fe$^{3+}$ ratios, were determined by Mössbauer spectroscopy. The error in the determination of reduced fraction of iron in the glass is estimated at ±0.03.

Results

The target and actual compositions of all the glasses are listed in Table 1. Minor impurities (0.5–1 wt%) comprising the oxides of various metals such as Na, Al, Si etc., were determined in XRF analyses. Reported values of mol% P$_2$O$_5$, V$_2$O$_5$ and Fe$_2$O$_3$, ignored the presence of such impurities. The activation energy for dc conduction and $\rho$ of nine glasses along with published values of glasses similar to the binary compositions are provided in Table 2. The conductivity decreases as Fe is added to a binary vanadium phosphate glass, reaching a minimum at a Ti ratio, $V/(V + Fe)$, of 0.4. The latter is 250 times smaller than the former.

The activation energy, $W$, which was found to decrease with temperature, was calculated from the linear segment of the conductivity vs 1/T plot (Fig. 1) in the temperature range 330°–375 K. Initially, $W$ increases from 0.35 eV (PV glass) as Fe is added until it reaches a maximum at 0.54 eV (PVF-5) glass, which has a target Ti ratio of 0.40. On further Fe additions, $W$ decreases to 0.48 eV for the binary PF glass. Variations of $\rho$ and $W$ as functions of Ti ratio are exhibited in Fig. 2 and the data listed in Table 2. Variation of glass transition temperature ($T_g$) with Ti ratio is depicted in Fig. 3. Table 2 lists density as a function of Ti ratio. Whereas density increases with increasing Fe concentration, $T_g$ is found to increase as the second transition ion is added to a binary glass and reaches a maximum at Ti ratio ~0.4. The non-linear variation of $\rho$, $W$ and $T_g$ as functions of Ti ratio, in glasses containing multiple transition ions, has been termed the ‘mixed transition-ion effect’ or MTE.

The pre-exponential factor, $\sigma_0$, which appears in equations (iii) and (iv) has been determined from the intercepts of the Arrhenius plots of Fig. 1 and are listed in Table 2. The values of $\sigma_0$ are found to be in the range 0.01–0.70 (Ω.cm)⁻¹. The

<table>
<thead>
<tr>
<th>Glass</th>
<th>V/(V + Fe) Target</th>
<th>P$_2$O$_5$ Target</th>
<th>Actual</th>
<th>V$_2$O$_5$ Target</th>
<th>Actual</th>
<th>Fe$_2$O$_3$ Target</th>
<th>Actual</th>
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<tbody>
<tr>
<td>PV</td>
<td>1.00</td>
<td>50.00</td>
<td>47.63</td>
<td>50.00</td>
<td>52.37</td>
<td>0.00</td>
<td>Trace</td>
</tr>
<tr>
<td>PVF-1</td>
<td>0.90</td>
<td>50.00</td>
<td>46.66</td>
<td>45.00</td>
<td>47.86</td>
<td>5.00</td>
<td>5.49</td>
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<td>PVF-2</td>
<td>0.80</td>
<td>50.00</td>
<td>44.68</td>
<td>44.00</td>
<td>44.19</td>
<td>10.00</td>
<td>11.13</td>
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<tr>
<td>PVF-3</td>
<td>0.70</td>
<td>50.00</td>
<td>46.56</td>
<td>35.00</td>
<td>30.08</td>
<td>15.00</td>
<td>23.36</td>
</tr>
<tr>
<td>PVF-4</td>
<td>0.50</td>
<td>50.00</td>
<td>47.30</td>
<td>25.00</td>
<td>26.51</td>
<td>25.00</td>
<td>26.19</td>
</tr>
<tr>
<td>PVF-5</td>
<td>0.40</td>
<td>50.00</td>
<td>46.26</td>
<td>20.00</td>
<td>21.43</td>
<td>30.00</td>
<td>32.31</td>
</tr>
<tr>
<td>PVF-6</td>
<td>0.20</td>
<td>50.00</td>
<td>47.01</td>
<td>10.00</td>
<td>11.32</td>
<td>40.00</td>
<td>41.67</td>
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<td>PVF-7</td>
<td>0.10</td>
<td>50.00</td>
<td>47.00</td>
<td>5.00</td>
<td>5.60</td>
<td>45.00</td>
<td>47.41</td>
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<tr>
<td>PF</td>
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<td>50.00</td>
<td>47.36</td>
<td>0.00</td>
<td>Trace</td>
<td>50.00</td>
<td>52.64</td>
</tr>
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</table>
Table 2. Variation of Electrical and Structural Parameters with Ratio of Transition Ions V/(V + Fe)

<table>
<thead>
<tr>
<th>New Glass</th>
<th>V/(V + Fe) (Target)</th>
<th>Activation Energy (eV, W)</th>
<th>Pre-exponential Term (Ω.cm)(^{-1}), (\sigma_0)</th>
<th>Resistivity at 375 °K (Ω.cm), (\rho)</th>
<th>Density (g/cm(^3))</th>
<th>(R) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV</td>
<td>1.00</td>
<td>0.35</td>
<td>0.04</td>
<td>1.20E+06</td>
<td>2.778</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.40(^1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVF-1</td>
<td>0.90</td>
<td>0.39</td>
<td>0.01</td>
<td>2.10E+06</td>
<td>2.798</td>
<td>0.28</td>
</tr>
<tr>
<td>PVF-2</td>
<td>0.80</td>
<td>0.46</td>
<td>0.01</td>
<td>1.75E+07</td>
<td>2.830</td>
<td>0.28</td>
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<tr>
<td>PVF-3</td>
<td>0.70</td>
<td>0.48</td>
<td>0.14</td>
<td>2.10E+07</td>
<td>2.848</td>
<td>0.28</td>
</tr>
<tr>
<td>PVF-4</td>
<td>0.50</td>
<td>0.53</td>
<td>0.12</td>
<td>1.10E+08</td>
<td>2.929</td>
<td>0.28</td>
</tr>
<tr>
<td>PVF-5</td>
<td>0.40</td>
<td>0.54</td>
<td>0.04</td>
<td>3.75E+08</td>
<td>2.930</td>
<td>0.28</td>
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<tr>
<td>PVF-6</td>
<td>0.20</td>
<td>0.54</td>
<td>0.38</td>
<td>4.90E+07</td>
<td>3.024</td>
<td>0.27</td>
</tr>
<tr>
<td>PVF-7</td>
<td>0.10</td>
<td>0.52</td>
<td>0.38</td>
<td>2.20E+07</td>
<td>3.133</td>
<td>0.27</td>
</tr>
<tr>
<td>PF</td>
<td>0.00</td>
<td>0.48</td>
<td>0.70</td>
<td>4.30E+08</td>
<td>3.235</td>
<td>0.26</td>
</tr>
</tbody>
</table>

\(^1\) Ref. 1 - \(\rho\) extrapolated from data
\(^2\) Ref. 14 - \(\rho\) of 45 Fe\(_2\)O\(_3\)-55 P\(_2\)O\(_5\) glass

Fig. 1. Conductivity vs 1/T plots for glasses in the series xFe\(_2\)O\(_3\), (50-x)V\(_2\)O\(_5\), 50P\(_2\)O\(_5\).

R = 1/(4\pi N/3)\(^{1/3}\)  \(\text{(vi)}\)

where \(N\) is the concentration of transition ions in unit volume of glass.

The effect of the furnace ambience (O\(_2\), N\(_2\), Air) on Fe\(^{2+}\)/ (Total Fe) and the corresponding values of \(\rho\) at 375 K are presented in Table 3. The conductivities of the PF and PV glasses under different melting conditions show marginal dependence on melt atmosphere. Even though the redox equilibrium of the V ions in the PV glass was not determined, the TI ratio in the PF glass showed little variation. The conductivity, likewise, did not change appreciably. However, the redox ratio of iron in the PVF-5 glass varies by an order of magnitude with melt atmosphere. The redox ratio of the PVF-5 glass was 0.28 when it was melted in flowing nitrogen.
Fig. 2. Activation energy and resistivity at 375°C vs ratio of transition ions $V/(V+Fe)$.

Fig. 3. Glass transition temperature $(T_g)$ vs $V/(V+Fe)$.

Table 3. Effect of Redox Equilibrium on the Resistivity of PV, PVF-5 and PF Glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\rho_{375}^1$ (melted in $N_2$) $(\Omega\cdot cm)$</th>
<th>$Fe^{3+}/(Total\ Fe)$ (melted in $N_2$)</th>
<th>$\rho_{378}$ (melted in Air) $(\Omega\cdot cm)$</th>
<th>$Fe^{2+}/(Total\ Fe)$ (melted in Air)</th>
<th>$\rho_{378}$ (melted in $O_2$) $(\Omega\cdot cm)$</th>
<th>$Fe^{2+}/(Total\ Fe)$ (melted in $O_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV</td>
<td>1.27E+06</td>
<td>-</td>
<td>1.20E+06</td>
<td>-</td>
<td>5.20E+05</td>
<td>-</td>
</tr>
<tr>
<td>PVF-5</td>
<td>1.15E+08</td>
<td>0.280</td>
<td>3.75E+08</td>
<td>0.095</td>
<td>9.60E+07</td>
<td>0.034</td>
</tr>
<tr>
<td>PF</td>
<td>5.90E+06</td>
<td>0.480</td>
<td>4.30E+06</td>
<td>0.520</td>
<td>5.25E+06</td>
<td>0.420</td>
</tr>
</tbody>
</table>

$^1$ Resistivity at 375°C

Atmosphere. When melted in an atmosphere of flowing oxygen, the ratio was determined to be 0.034. The corresponding variation of $\rho$ is only limited to a factor of 1.25 (Table 3) which is considered marginal compared to the 2-3 orders of magnitude change in $\rho$, observed in the mixed transition ion effect (Fig. 2).
Discussion

Conductivity and activation energy for dc conduction of PV and PF glasses (Fig. 1 and Table 2) agree well with those of similar compositions reported earlier.\(^{1,14}\) Binary vanadium and iron phosphate glasses are universally considered SPH conductors.\(^{1,10}\) As discovered for SPH conductors in previous studies,\(^{2,10}\) the conductivity and activation energy of the binary and ternary phosphate glasses containing one or two transition ions tend towards maximum values at low temperatures. The similarity of the activation energy and conductivity data and low temperature conductivity characteristics of the ternary glasses (Table 2) to those of previously reported indicate that SPH conduction is prevalent in all the glasses listed in Table 1.

Conductivity and activation energy for dc conduction (Table 2), as plotted against \(V/(V + Fe)\) ratio in Fig. 2, exhibit a trend similar to the mixed alkali effect,\(^{13}\) observed in ionically conducting glasses. \(\rho\) and \(W\) increase with the addition of a second Ti even though the total Ti concentration remains constant, reaching maxima at \(V/(V + Fe) \approx 0.4\). As Ti is increased beyond 0.4, \(\rho\) and \(W\) monotonically decrease to reach minimum values at \(V/(V + Fe) = 1\), which corresponds with the composition of the binary vanadium phosphate glass, PV. The glass transition temperature (\(T_g\)), also shows a similar trend, Fig. 3.

An important factor that may influence the conductivity is \(\sigma_o\), the pre-exponential term in equation (iii), which is dependent on a number of variables such as \(R\), \(C\), \(n_0\) and \(v\). As described earlier, the pre-exponential term is found insensitive to the Ti ratio (Table 2). Moreover, \(n_0\) and \(v\) are assumed to remain constant among all the glasses examined. The fact that \(\sigma_o\) remains constant indicates that the combined influence of the redox equilibria of the Fe and V ions, \(R\), \(n_0\) and \(v\) in equation (iv) does not have any major effect on the conductivity of the MTI glasses. Hence, the effect of all these variables contributing to \(\sigma_o\), may be ruled out as possible sources of the MTE. However, the roles of \(R\) and \(C\) have been further tested.

The average distance between transition ions, \(R\), the average of \(V-V\), \(V-Fe\) and \(Fe-Fe\) distances, calculated from density measurements (Table 2) and composition, does not vary appreciably with Ti ratio (Table 2). In order to evaluate the effect of redox equilibrium (\(C\)) on the conductivity of the MTI glasses, the PVF-5 glass was subjected to melting at 1325 \({\degree}\)C for 1/2 hour in \(N_2\), \(O_2\), and air atmospheres. \(\rho\) and the corresponding Fe\(^{2+}\)/\(\text{Total Fe}\) are tabulated in Table 3. Even though the fraction of Fe\(^{2+}\) ions for the PVF-5 glass varies by almost one order of magnitude, \(\rho\) remains largely unchanged. Hence, a shift in the redox equilibrium and/or change in inter-transition ion distance, \(R\), do not appear to cause the MTE.

The only other variable which may influence conductivity in equation (iii) happens to be \(W\), the activation energy. It has been demonstrated that\(^{1,11}\) the activation energy for polaron hopping and the energy of polaron formation are related as:

\[
W = W_p/2
\]  

\(W\), as described before, is the activation energy for SPH conduction and \(W_p\) is the energy of polaron formation. The effect of \(W\) on polaron mobility, \(\mu\), is given by

\[
\mu = (e/kT) \rho r^2 \exp (- W/kT)
\]

where, \(p\) is the jump probability of a carrier from one site to another, which may be either adiabatic or non-adiabatic in nature. Regardless of whether it is adiabatic or non-adiabatic, the invariance of \(\sigma_o\) indicates that the jump mechanism is the same in all the glasses. For the adiabatic regime, \(p\) is equal to the frequency of an optical phonon which may be assumed invariant in all the glasses while it is inversely proportional to \(\sqrt{W}\) for non-adiabatic jumps.\(^{1,11,12}\) In other words, the jump probability of a carrier is either constant for all the glasses or is a weak function of the activation energy. However, the exponential term in equation (viii) makes mobility a strong function of the activation energy, which may be related to the conductivity through the following relationship:\(^{16}\)

\[
\sigma = \mu e F^2 C
\]

where \(e\) is the electronic charge, \(F\) is the Faraday constant and \(C\) is the concentration of carriers. A simple calculation involving the substitution of experimentally obtained activation energy values for glasses PV and PVF-5 in equations (viii) and (ix) results in a conductivity difference of around 2.5 orders of magnitude, which agrees with the conductivity data presented in Table 2 and Fig. 2. Hence, the mixed transition ion effect can be adequately explained by reduced mobility of small polarons as a second Ti is added to a binary vanadium or iron phosphate glass.

The variation of \(W\) and \(T_g\) with Ti ratio (Figs. 2 and 3) appears to be complimentary. Addition of iron to barium vanadium glasses has been demonstrated to increase micro-hardness.\(^{10}\) Our results show increased \(T_g\) with the introduction of Fe in vanadium phosphate glasses and vice versa. Both micro-hardness and \(T_g\) are indicators of the rigidity of the glass network. A less rigid network is expected to exhibit lower \(T_g\) values in DTA test and larger elastic deformation and flow during micro-hardness measurement.\(^{13}\) \(W_p\), the energy of polaron formation of such a glass, is expected to be low since restructuring of the glass network will require less energy. On the other hand, an increase in \(W_p\) is associated with increased activation energy for dc conduction according to equation (vii).

The PVF-5 glass may be considered to have the highest cross linking of the network forming chains resulting in the most rigid structure, reflecting the highest \(T_g\) among the glasses in Table 1. A high \(T_g\) represents strong bonds connecting the constituents participating in the formation of the network structure of the glass. Apart from cross-linking of two-dimensional (chains) structural units, \(\text{V}^{4+}\) and \(\text{Fe}^{3+}\) have also been shown\(^{12,17}\) to exist in four-fold coordination of oxygen ions forming three-dimensional tetrahedral units. A two-dimensional network requires less energy to reconfigure than a three-dimensional network, simply because the number of bonds is less in the former. As the composition of the ternary glasses move towards \(V/(V + Fe) \approx 0.4\) from the binary compositions, the energy of polaron formation (\(W_p\)) increases, resulting in increased lattice distortion. Increased lattice distortion results in increased effective mass of the small polaron. A direct consequence of increased effective mass is a reduction in the bandwidth, \(W_0\).\(^{1,11}\)

The reduction in mobility of the small polarons which seems to be responsible for MTE appears to be the result of increased Anderson localization caused by an increase in the \(V_0/B\) ratio as discussed by Mott.\(^{11}\) The increase in the localization of carrier wave-functions is a result of an increase in the disorder parameter, \(V_0\). \(\text{V}_2\text{O}_5\) is a bonafide glass former whereas, \(\text{Fe}_2\text{O}_3\) is not. Only in certain favorable circumstances, does \(\text{Fe}_2\text{O}_3\) participate in network formation. When iron, for example, is added to a binary vanadium phosphate glass, the Fe ions do not necessarily occupy the positions occupied by the V ions. Hence, it is not difficult to visualize the increase in configurational disorder as one transition ion replaces another leading
to an increase in \( V_0 \). Hence, it appears that the mixed transition ion effect in phosphate glasses is a direct manifestation of increased Anderson localization of the charge carriers caused by enhanced configurational disorder of the network structure when two transition ions are mixed in phosphate glasses.

**Conclusion**

A mixed transition ion effect (MTE) has been shown to occur in semiconducting phosphate glasses containing V and Fe ions. The non-linear behavior of conductivity, activation energy for dc conduction and glass transition temperature bear resemblance to the mixed alkali effect in glasses containing mixed alkali ions. The MTE has been shown to be caused by a reduction in mobility of the small polarons which is a direct consequence of increased Anderson localization of the charge carriers.

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**References**