# Control of electrical conductivity with the admixture of chlorine in copper tellurite glasses

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Copper tellurite glasses containing $CuCl_2$ with composition $65TeO_2$–$(35 - x)CuO$–$xCuCl_2$ (mol %) with $x = 0, 1, 2, 3, 4, 5$ were prepared by quenching the melt. An increase in density with the addition of $CuCl_2$ and with a corresponding decrease in molar volume, has been observed. The d.c. conductivity of copper tellurite glasses is found to be very sensitive to the reduced valency ration $C = [Cu^+]/[Cu_{total}]$ and depends on the relative concentrations of $Cu^+$ (reduced valency state) and $Cu^{2+}$ (higher valency state) ions. It is found that by adding cupric chloride to the melt when the glass is formed, the chlorine in the salt which acts as an oxidizing agent alters the ratio of the concentrations of $Cu^+$ and $Cu^{2+}$ ions in the glass and hence the conductivity. It is found that more than 2 mol % of cupric chloride reduces the conductivity very sharply due to the formation of chlorine clusters in the form of local $TeCl_4$ whereas less than 2 mol % of $CuCl_2$ leads to an increase in conductivity due to the $Cu^+ \rightarrow Cu^{2+}$ transition which is negligibly affected by the chlorine due to the formation of $TeCl_2$ which is amorphous in nature. The increase and decrease of electrical conductivity of glasses containing less or more than 2 mol % $CuCl_2$ is also interpreted in terms of the electronic transitions between the orbitals of tellurium 3d electrons, their binding energies and peak widths on the basis of XPS (X-ray Photoelectron Spectroscopy) study, and it was found that the increase in bandwidth supports the idea of clustering of chlorine above 2 mol % $CuCl_2$ and causing a decrease in the conductivity. Overall the conductivity is found to be somewhat uncontrollable in these glasses because it is not simply dependent on the concentration of $Cu^{2+}$ ions.

## 1. Introduction

Recently several studies on oxide glasses containing two transition metal (TM) oxides have been reported. These glasses consist of inorganic oxides containing appreciable amounts of TM ions which may enter the glass structure in two or more valency states. The loss of oxygen from the melt produces low valency TM ions and the conduction occurs by the movement of electrons from the low valency state to the higher valency state (e.g. $Cu^+$ to $Cu^{2+}$). The electrical conductivity has been shown [1–4] to be related to the ratio and the relative concentration of ions in the different valency states [5–7]. The concept of mixed valency electron conduction [8] has become generally accepted and can also be applicable to this class of semiconductors. Although the activation energy for conduction appears to be a very important factor in controlling the electrical conductivity [9] it is found that the electrical conductivity of these glasses is sensitive to the ratio $[Cu^+]/[Cu_{total}]$ where $[Cu^+]$ (diamagnetic) is the concentration of reduced valency sites and $[Cu_{total}]$ is the total concentration of copper ions in the glass [10]. This ratio can be altered by annealing [11] and also by the incorporation of an oxidizing agent in the glass as reported by Hogarth and Popov [12] in $P_2O_5$–$CuO$–$CuCl_2$ glass and by Kutub *et al.* [13] in the $GeO_2$–$V_2O_5$–$VCl_3$ glassy network, who showed that the addition of $CuCl_2$ in copper phosphate glasses and $VCl_3$ in germanium vanadate glasses in the melt during preparation caused a significant change in the ratio $[Cu^+]/[Cu_{total}]$ and $[V^{4+}]/[V_{total}]$ respectively. Novikov and Hogarth [15] have also shown the effects of another oxidizing agent such as iodine as well as of an annealing treatment during the study of switching phenomena in $CaO$–$CuO$–$P_2O_5$–$CuI$ glasses.

In general, glassy and amorphous materials cannot be doped to the desired value of conductivity by the addition of small amounts of donor or acceptor impurities as is the normal procedure in crystalline semiconductors. It is found that a maximum in the electrical conductivity of such glasses is observed for samples in which the $Cu^+$ and $Cu^{2+}$ concentrations are of the same order of magnitude. For this reason a method which controls the value of $[Cu^{2+}]$ is of importance in controlling the conductivity of the glasses which exhibit memory switching phenomena [14, 15]. Osman [16] has also investigated the effect of chlorine in the binary $GeO_2$–$PrCl_3$ glasses and concluded that the activation energy decreases by the addition of at least 1 mol % of $PrCl_3$ and with further addition, chlorine forms clusters and becomes less effective in acting as a generally dispersed oxidizing agent. In this communication, we present our experimental results concerning the control of electrical conductivity by keeping the total amount of copper fixed and using chlorine as an oxidizing agent in copper tellurite glasses.

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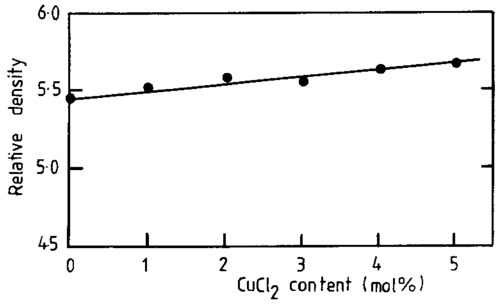


*Figure 1* Relative density of annealed $TeO_2$–CuO–$CuCl_2$ glasses as a function of $CuCl_2$ content.

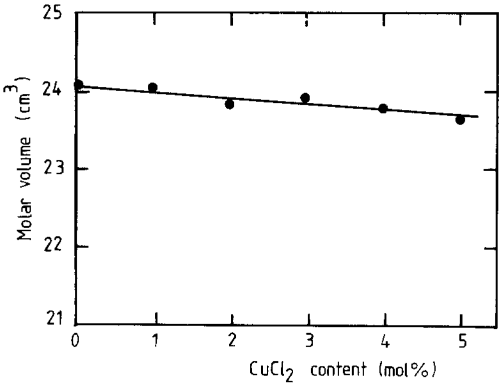


*Figure 2* Molar volume of $TeO_2$–CuO–$CuCl_2$ glasses as a function of $CuCl_2$ content.

### 1.2. Choice and incorporation of chlorine

Chlorine was chosen rather than fluorine because of its low chemical activity and large atomic size (~0.1 nm). It was believed that chlorine would disperse evenly through the glass and not form clusters. It was also expected that chlorine being an oxidizing agent would alter the ratio of $[Cu^+]/[Cu_{total}]$ and thus control the transition probabilities of hopping (conduction) electrons and hence the electrical conductivity. This principle could be applied to the range of glasses involving electronic transition between ions of different valency e.g. $V^{4+}$ and $V^{5+}$ in vanadate and between $Mo^{5+}$ and $Mo^{6+}$ ions in molybdate glasses. The chlorine was incorporated into the binary $TeO_2$–CuO glass by the addition of $CuCl_2$ (anhydrous).

## 2. Experimental work

### 2.1. Glass preparation

Glasses having the composition expressed in mol % $65TeO_2$–$(35 - x)$CuO–$xCuCl_2$ (where $x = 0, 1, 2, 3, 4, 5$) were prepared from pure grades of materials by the melt quenching technique using an electrically heated furnace at 950 to 960° C. The melt was cast on to a clean steel plate and disc-shaped samples were made. A few samples were immediately transferred to an annealing furnace maintained at a temperature of 300° C for 1 h to remove the mechanical stresses and then it was switched off to cool down to room temperature. The samples were polished using diamond paste, and gold electrodes were deposited by vacuum evaporation. One side had a gold circular electrode of diameter 0.5 cm surrounded by a guard-ring to eliminate surface leakage current while the other side had a slightly larger electrode of diameter 1.2 to 1.5 cm.

### 2.2. Density and molar volume measurements

The relative densities $\varrho_g$ of the annealed glasses were measured at room temperature by using the general Archimedes displacement method with toluene as an immersion liquid and application of the formula

$$\varrho_g = W_a \varrho_L / (W_a - W_L)$$

where $W_a$, $W_L$ are the weights of glass sample in the air and liquid, respectively, and $\varrho_L$ is the relative density of toluene (0.805 at 20° C). The molar volume $V$ (i.e. the volume occupied by one gram molecule of any composition) of the annealed glasses was calculated by the following expression

$$V = (XM_a + YM_b + ZM_c)/\varrho_g$$

where the glass composition is represented by $X_a + Y_b + Z_c$, $X + Y + Z = 100\%$ and $M_a$, $M_b$, $M_c$ are the molecular weights of materials a, b and c, respectively forming the glassy network. The values of density and molar volume of all the glasses are listed in Table I.

### 2.3. Electrical measurements

The electrical measurements were made using a simple circuit similar to that described by Hogarth and Khan [17]. The circulating currents were measured by means of Keithley 610 electrometer and a stabilized power supply (Keithley 240 A) was used as a constant voltage source. The temperature of the sample was monitored using a chromel–alumel thermocouple in contact with it. All measurements were made under a vacuum of $10^{-5}$ torr to avoid atmospheric effects.

## 3. Results and discussion

### 3.1. Density

The variation of density and molar volume for all glass samples as a function of $CuCl_2$ content are plotted in Figs 1 and 2 and show that, with the addition of $CuCl_2$ in the glassy network, the density increases and the molar volume decreases depending upon the

TABLE I Composition and some measured parameters of copper tellurite glasses containing cupric chloride

| Glass No | Composition (mol %) | | | Electrical conductivity $(\Omega cm)^{-1}$ | Activation energy (eV) | Relative density of annealed samples | Molar volume ($cm^3$) | $C = \frac{[Cu^+]}{[Cu_{total}]}$ |
|---|---|---|---|---|---|---|---|---|
| | $TeO_2$ | CuO | $CuCl_2$ | | | | | |
| 1-a | 65 | 35 | 0 | $9 \times 10^{-8}$ | 0.69 | 5.47 | 24.06 | 0.28 |
| 2-b | 65 | 34 | 1 | $1.5 \times 10^{-7}$ | 0.76 | 5.50 | 24.02 | 0.93 |
| 3-c | 65 | 33 | 2 | $2.1 \times 10^{-7}$ | 0.70 | 5.57 | 24.82 | 0.96 |
| 4-d | 65 | 32 | 3 | $1.1 \times 10^{-7}$ | 0.79 | 5.56 | 24.95 | 0.99 |
| 5-e | 65 | 31 | 4 | $7.8 \times 10^{-8}$ | 0.76 | 5.62 | 24.81 | – |
| 6-f | 65 | 30 | 5 | $5.5 \times 10^{-8}$ | 0.73 | 5.68 | 24.65 | – |

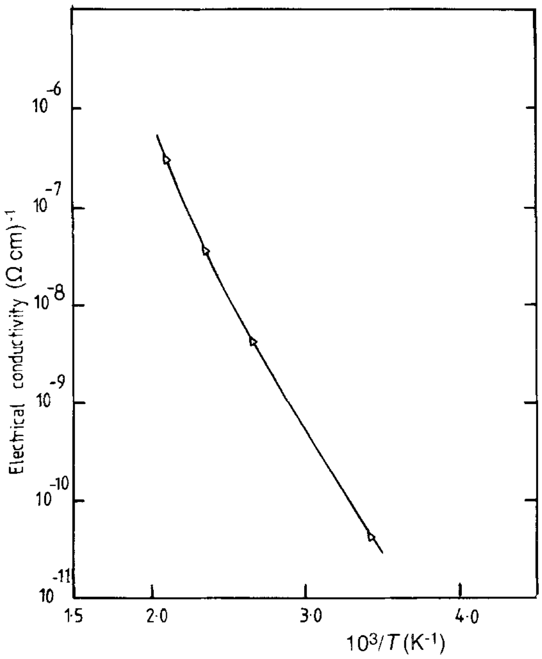


*Figure 3* Conductivity as a function of inverse temperature for binary $TeO_2$–CuO glass.

composition. This increase in density or the decrease in molar volume may be due to the change in the structure caused by the decrease of interatomic spacing which may further be attributed to an increase in the stretching force constant of the bonds inside the glassy network resulting in a more compact and dense glass. The results without $CuCl_2$ agree closely with the binary $TeO_2$–CuO results reported by Hassan and Hogarth [21] but show an opposite effect when compared with the density results of the $(100 - x)TeO_2$–$xWO_3$ system of glasses reported by El-Zaidia [22] where the density decreases with the increase of $ZnCl_2$ content causing a weakening of the structure.

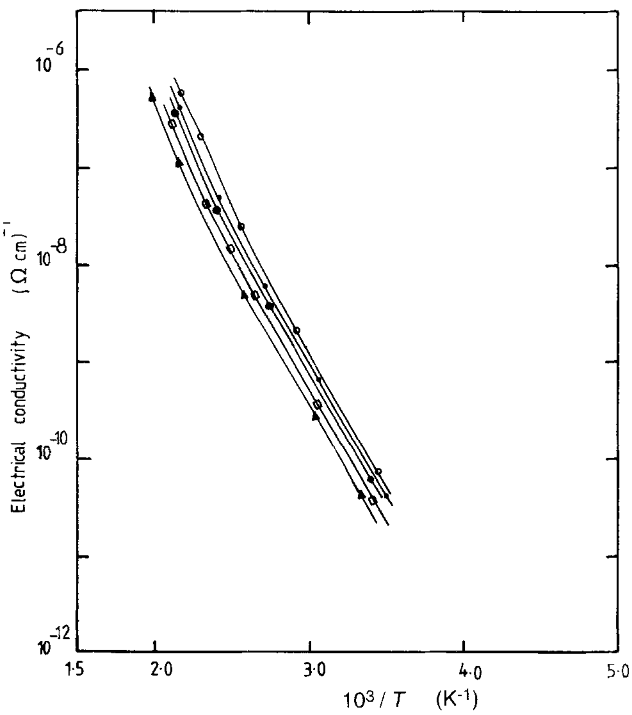


*Figure 4* Conductivity as a function of inverse temperature for five samples of $TeO_2$–CuO–$CuCl_2$ glasses. (○ 1 % $CuCl_2$, □ 2 % $CuCl_2$, ● 3 % $CuCl_2$, × 4 % $CuCl_2$, ▲ 5 % $CuCl_2$).

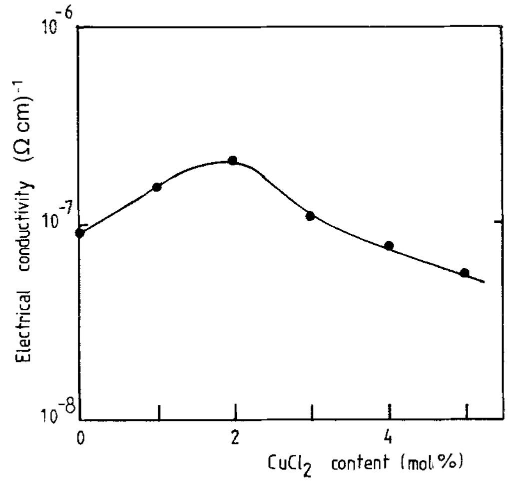


*Figure 5* Conductivity as a function of $CuCl_2$ content of $TeO_2$–CuO–$CuCl_2$ glasses.

## 3.2. Electrical conductivity

The results of temperature variation of conductivity show that log $\sigma$ is nearly a linear function of $1/T$ for both binary and ternary glasses as shown in Figs 3 and 4, respectively. The values of activation energies were calculated by measuring the slopes of these curves at the relatively high temperature of 444 K. The value of activation energies for $55P_2O_5$–$(45 - x)CuO$–$xCuCl_2$ (mol %) glasses as reported by Hogarth and Popov [12] lie in the range 1.25 to 1.28 eV. They reported that up to 3.5 mol % of $CuCl_2$, the electrical conductivity decreases and after this limit with the greater admixture of chlorine, the conductivity increases again. Kutub *et al.* [13] have also reported the change in the electrical conductivity with the admixture of chlorine in the $GeO_2$–$V_2O_5$–$VCl_3$ glasses where the activation energies lie in the range 0.29 to 0.40 eV. For our present glassy system, the values of electrical conductivities along with activation energies of all glasses measured at 444 K are compiled in Table I. The values of the activation energies lie in the range 0.69 to 0.79 eV which is approximately in the intermediate range of the values of activation energies reported by previous workers [12, 13]. The values for the glass containing no chlorine agreed closely with the results of similar glasses reported earlier by Hassan and Hogarth [18]. The variation of electrical conductivity with $CuCl_2$ content is shown in Fig. 5 which indicates that the conductivity rises up to 2 mol % of $CuCl_2$ while the further admixture of chlorine up to 5 mol % of $CuCl_2$ causes a systematic decrease in the conductivity. The fact that the electrical conductivity is very sensitive to the reduced valency ratio $C = [Cu^+]/[Cu_{total}]$ has also been studied in the present glasses. From our electron spin resonance (ESR) experiments on these glasses [19], it is clear that copper exists in the glass in more than one valency state and also at 4 to 5 mol % of $CuCl_2$ in the glass, ESR signals were completely relaxed because of spin diffusion, thus making the estimation of the concentration of $Cu^{2+}$ ions in the glass impossible. The electrical conductivity as a function of reduced valency ratio $C$ has been plotted in Fig. 6 and indicates that the maximum in the conductivity is obtained at $C = 0.96$ for 2 mol % $CuCl_2$ and with any further rise in the value of $C$, the conductivity

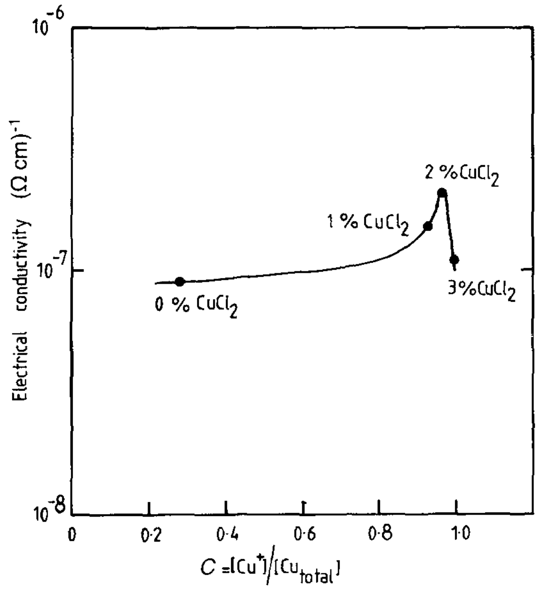


*Figure 6* The electrical conductivity as a function of $C = [Cu^+]/[Cu_{total}]$ for four samples of glasses.

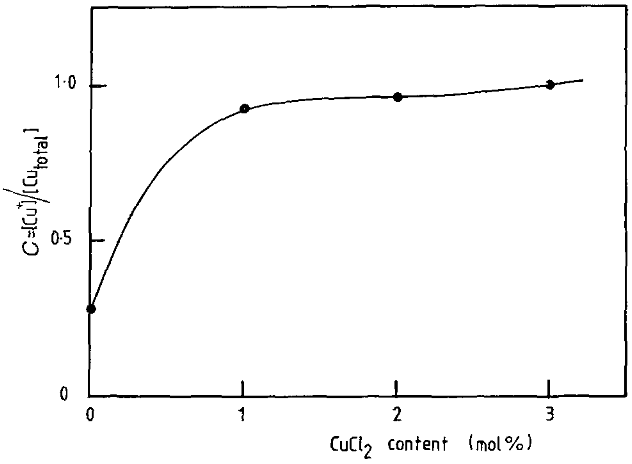


*Figure 7* Variation of $C = [Cu^+]/[Cu_{total}]$ with $CuCl_2$ content for four samples of glasses.

drops rapidly contradicting the general concept of the theories of hopping conduction in mixed valency semiconductors where a maximum in the conductivity is obtained when there are roughly equal numbers of occupied and unoccupied sites i.e. when $C = 0.5$. This discrepancy between theory and experiment has also been observed by other workers [6, 23, 24]. The conductivity dependence on the ratio $C$ has been well discussed in a review by Murawski *et al.* [9]. In the present study, the value of $C$ increases rapidly by adding 1 mol % of $CuCl_2$ to the glass but after that the increase in the value of $C$ is observed to be very minute as is obvious from Fig. 7 and $C$ tends to a value of unity. The increase in the value of $C$ indicates that the concentration of paramagnetic $Cu^{2+}$ ions has decreased corresponding to an increase in the density of the low valency state $Cu^+$ ions (diamagnetic) but despite this fact the conductivity was found to increase. The results for five glass samples show a systematic variation of conductivity with chlorine addition although the value of copper tellurite glass containing no chlorine is out of sequence with the other four curves of Fig. 4. The five curves in Fig. 4 are close together but not coincident. Thus we note that the conductivity $\sigma$ is more complex in its origin than simply being proportional to $[Cu^{2+}]$ ions.

The results of the increase in the conductivity can be interpreted since the addition of chlorine as expected replaces the oxygen and modifies the structure as well as the conduction properties of the glass by decreasing the extent of the covalency of the Cu–O bonds and effectively arranging the $Cu^+$ and $Cu^{2+}$ ions even more randomly in the network. The chlorine reacts with tellurium as shown by the following reaction,

$$Te^{4+} + 2Cl^- \rightarrow Te^{2+} + Cl_2 \text{ (gas)}$$

It is possible that some formation of $TeCl_2$ (tellurium dichloride) takes place and this material is amorphous in nature [20] possessing a lower concentration of chloride ions and making the $Cu^+ \rightarrow Cu^{2+}$ transition possible which substantially increases the electrical conductivity, but with the substitution of more than 2 mol % of $CuCl_2$, the chlorine is not evenly dispersed but forms clusters after reacting with $TeCl_2$ and hence forms $TeCl_4$ according to the following reaction

$$TeCl_2 + Cl_2 \rightarrow TeCl_4$$

which also indicates that the chloride ions take both the tetrahedral and distorted threefold coordination positions in the glass and thus prevent the conduction process from taking place. We therefore observe a sudden fall in the electrical conductivity. It is not unfair to say that only a small amount of $TeCl_2$ and $TeCl_4$ are formed at some sites in the glassy network instead of occurring in the whole volume of the sample because the quantity of chlorine from the added amount of $CuCl_2$ (mol %) is insufficient to replace the whole of the oxygen of the glassy network. Further support for the conductivity results is provided by the XPS study of these glasses. It is noted that the XPS spectra of the present glasses containing less or more than 2 mol % $CuCl_2$ are surprisingly similar [25] as shown in Fig. 8 but the twin peaks observed for the

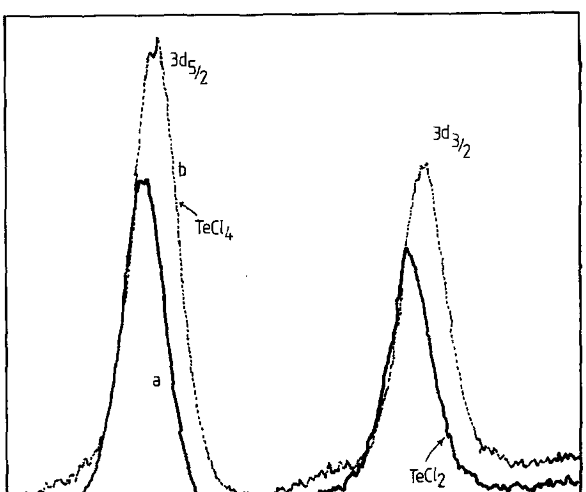


*Figure 8* XPS spectrum showing core and valence electrons of tellurium 3d in the $65TeO_2$–$(35-x)CuO$–$xCuCl_2$ glassy network for (a) $x = 1$ mol % $CuCl_2$ (b) $x = 3$ mol % $CuCl_2$.

TABLE II Some parameters derived from the XPS spectra of copper tellurite glasses containing 1 and 3 mol % of $CuCl_2$

| No | Composition (mol %) | | | Separation of peaks (eV) | Peak width of (eV) | | Binding energy of $3d_{5/2}$ (eV) |
|---|---|---|---|---|---|---|---|
| | $TeO_2$ | CuO | $CuCl_2$ | | $3d_{5/2}$ | $3d_{3/2}$ | |
| a | 65 | 34 | 1 | 10.28 | 0.76 | 0.75 | 579.7 |
| b | 65 | 32 | 3 | 10.65 | 0.98 | 0.82 | 580.0 |
| Percentage increase of the values of glass b | | | | 3.47 | 21.53 | 9.09 | 0.51 |

tellurium 3d electronic energy levels such as $3d_{3/2}$ and $3d_{5/2}$ created by the removal of an electron show a slight shift, and the electronic binding energies of the $3d_{5/2}$ level of each composition are different in the present investigations. The estimated shifts between the two peaks and the $3d_{5/2}$ binding energy are 3.47 and 0.5% greater for glasses having 3 mol % $CuCl_2$ than for the glasses containing 1 mol % $CuCl_2$ as listed in the Table II. As in solids, where the electronic energy levels form more or less broad bands, the width of the photoelectron peak reflects the bandwidth [26]. Following this criterion, it is noted that the peak width for the $3d_{5/2}$ and $3d_{3/2}$ electronic levels of glasses containing 3 mol % $CuCl_2$ are respectively 9.09 and 21.5% greater than that of glasses having 1 mol % $CuCl_2$ (see Table II). It is, thus, concluded that the addition of 3 mol % $CuCl_2$ increases the bandwidth and thus causes the conductivity to fall. The above argument also suggests that the clustering of the chlorine and the widening of the band gap decreass the conductivity if there is more than 2 mol % $CuCl_2$ in the glasses.

Thus it can be concluded that chlorine is not evenly and thinly dispersed and becomes less effective in acting as an oxidizing agent above 2 mol % due to the formation of clusters. These generally inhibit the hopping transitions and thus keep the conductivity in a relatively uncontrolled condition.

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