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# Comparative study of the effect of the incorporation of cobalt and nickel oxides on the density and optical properties of copper tellurite glasses

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Two series of ternary semiconducting glasses with composition 65 $TeO_2$–(35 − $x$)CuO–$x$MO in mole percent ($x$ = 0, 0.5, 1, 2, 3, 4 and M stands for Co or Ni) were prepared by a melt quenching technique. The densities of annealed and unannealed disc-shaped samples and the optical energy gap of thin blown films of both series of glasses were measured, and the comparative effect of each transition metal (TM) oxide was estimated. It was found that for $x$ = 0.5 to 1 mol% and $x$ = 2 to 4 mol%, the optical energy gap ($E_{opt}$) was somewhat greater in $TeO_2$–CuO–NiO than in $TeO_2$–CuO–CoO glasses. This increase in $E_{opt}$ is interpreted in terms of the decreasing number of non-bridging oxygen ions with the increase of each TM oxide. NiO was found to be more effective in increasing the density than CoO in annealed copper tellurite glasses.

## 1. Introduction

There have been many recent investigations of oxide glasses containing two different transition metal (TM) oxides for the purpose of understanding the structure of glasses containing ions of the first transition series and on the role of the more metallic p-elements and their effects on the optical properties. The two TM ions in different valency states in the glassy network constitute a complex system and the important consequences of two TM ions include

(i) reduction–oxidation (or redox) interactions between the two TM ions in the melts, and

(ii) a change in the activation energies due to the distortions of lattice site positions and phase separation.

Transition metal ion glasses consist of inorganic oxides containing significant amounts of TM ions which may enter the glassy structure in at least two different valency states. In such glasses, an incident photon with a defined energy is absorbed by TM ions by two different processes:

1. The absorption may be due to an internal transition between d-shell electrons.
2. The absorption may be due to the transfer of an electron from a neighbouring atom to a TM ion and vice versa.

The study of optical absorption, particularly the absorption edge, is a technique for investigating the optically induced transitions and provides us with information about the band structure and energy gap of both crystalline and non-crystalline materials. In crystalline non-metallic materials, for example semiconductors, there are two main types of optical transitions that can occur at the fundamental absorption edge, namely a direct transition in which momentum is conserved and an indirect transition in which the required change in momentum $\hbar k$ (where $k$ is the wave vector) needs co-operation from a phonon.

In many crystalline and non-crystalline semiconductors, the absorption coefficient, particularly at the lower level of absorption, depends exponentially on photon energy. The exponential dependence known as the Urbach [1] rule may be expressed as

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/E_e) \qquad (1)$$

where $\alpha(\omega)$ is the absorption coefficient at an angular frequency of $\omega = 2\pi\nu$, $\alpha_0$ is a constant and $E_e$ is the energy which indicates the width of the tails of the localized states in the band gap which are associated with the amorphous nature of the materials. The origins of this exponential dependence is still not clearly established and several predictions have been made about it. Tauc and Zanini [2] have suggested that it arises from the electronic transitions between localized states in band edge tails, the density of which falls off exponentially with energy. According to Mott and Davis [3] this explanation for all disordered materials is not valid because the slopes of observed exponential absorption edges are very much the same for many crystalline and non-crystalline materials. Dow and Redfield [4] suggested that the band tails may arise from the random fluctuations of internal fields associated with the structural disorder in many amorphous materials. For higher absorption values ($\alpha > 10^4\,\mathrm{cm}^{-1}$), a relation proposed by Tauc *et al.* [5] and deduced in more general form by Davis and Mott [6],

$$\alpha(\omega) = B(\hbar\omega - E_{opt})^n/\hbar\omega \qquad (2)$$

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TABLE I Relative density of unannealed copper tellurite glasses containing NiO and CoO

| Number | $TeO_2$-CuO-NiO | | | $TeO_2$-CuO-CoO | | | Relative increase in density (%) $(N - C)$ |
|---|---|---|---|---|---|---|---|
| | NiO content (mol %) | Relative density | Increase (%) $(N)$ | CoO content (mol %) | Relative density | Increase % $(C)$ | |
| 1 | 0 ($TeO_2$-CuO) | 5.24 | – | 0 ($TeO_2$-CuO) | 5.24 | – | – |
| 2 | 0.5 | 5.28 | 0.9 | 0.5 | 5.27 | 0.7 | 0.2 |
| 3 | 1 | 5.35 | 2.1 | 1 | 5.325 | 1.6 | 0.5 |
| 4 | 2 | 5.475 | 4.5 | 2 | 5.425 | 3.5 | 0.95 |
| 5 | 3 | 5.525 | 5.4 | 3 | 5.475 | 4.5 | 0.95 |
| 6 | 4 | 5.675 | 8.3 | 4 | 5.625 | 7.3 | 0.95 |

is found to describe the experimental data and to give the value of energy gap $E_{opt}$. $B$ is constant, $\omega$ is the angular frequency and $n$ is an index having values 2, 3, $\frac{1}{2}$, $\frac{3}{2}$ depending on the nature of the electronic transitions. For many glasses [6, 7] and amorphous materials, the value $n = 2$ gives the best fit to the experimental results and this applies to the indirect transitions in such materials when the electron wavevector $k$ is not well defined. For our materials $n = 2$ and we therefore plot our results for the absorption edge region as $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$.

In this paper we wish to report the results of our measurements of density and optical absorption in order to study the effects of NiO and CoO on the density and the optical energy gap of copper tellurite ($TeO_2$-CuO) glasses.

## 2. Experimental technique

### 2.1. Glass preparation

Ternary glasses with composition 65 $TeO_2$-$(35 - x)$ CuO-$x$MO in mole per cent with $x = 0, 0.5, 1, 2, 3,$ 4 and M is CoO or NiO, were prepared. The chemicals were carefully weighed and their homogenized mixtures were kept for one hour in a furnace at 300° C in an alumina crucible separately for each composition. The crucible was transferred to the melting furnace with a temperature in the range of 900 to 970° C. During the two hours melting period the melt was stirred a few times with an alumina rod to improve the homogeneity. The thin blown films of glasses necessary for optical absorption measurements were prepared by blowing the molten glasses using an alumina tube with a fine bore. All these unannealed thin glass films were kept under vacuum in separated small boxes to avoid cracking and the possible absorption of moisture. The rest of the molten glasses were quenched by pouring onto a flat steel plate and covering it with another steel weight, giving samples in the form of discs. Some of these samples of each composition were annealed at 300° C immediately after quenching, while others were left unannealed.

### 2.2. Density measurement

The densities of annealed and unannealed glass samples were determined at room temperature by the general Archimedes displacement method using toluene as an immersion liquid (having relative density 0.805) by the following relation

$$\varrho = W_1 \times 0.805/(W_1 - W_2) \quad (3)$$

where $W_1$ is the weight of a sample in air and $W_2$ is its weight in liquid. The measured values of densities are listed in the Tables I and II.

### 2.3. Optical absorption measurements

The optical absorption edge measurements of these glasses were carried out at room temperature in the wavelength range 300 to 700 nm using a Perkin-Elmer 402 UV spectrophotometer and the thicknesses of these thin blown films were measured using a Sigma comparator. The general formula used to determine the optical absorption coefficient $\alpha(\omega)$ is given by

$$\alpha(\omega) = 1/d(\ln I_0/I_t) \quad (4)$$

where $\alpha(\omega)$ is the optical absorption coefficient, $I_0$ and $I_t$ are the intensities of the incident and transmitted light respectively and $d$ is the thickness of each sample.

## 3. Results and discussion

### 3.1. Density

The values of density for binary $TeO_2$-CuO and two ternary $TeO_2$-CuO-CoO and $TeO_2$-CuO-NiO glass systems are listed in Tables I and II. It was found that the density of each ternary glassy network increases with the increase of CoO and NiO content (mol %) respectively, as shown in Figs 1 and 2. It is noted that the density of annealed samples increases by more than that of the unannealed samples, indicating that

TABLE II Relative density of annealed copper tellurite glasses containing NiO and CoO

| Number | $TeO_2$-CuO-NiO | | | $TeO_2$-CuO-CoO | | | Relative increase in density (%) $(N - C)$ |
|---|---|---|---|---|---|---|---|
| | NiO content (mol %) | Relative density | Increase (%) $(N)$ | CoO content (mol %) | Relative density | Increase % $(C)$ | |
| 1 | 0 ($TeO_2$-CuO) | 5.24 | – | 0 ($TeO_2$-CuO) | 5.27 | – | – |
| 2 | 0.5 | 5.55 | 1.5 | 0.5 | 5.50 | 0.6 | 0.9 |
| 3 | 1 | 5.75 | 5.1 | 1 | 5.60 | 2.4 | 2.7 |
| 4 | 2 | 5.92 | 8.2 | 2 | 5.725 | 4.1 | 4.1 |
| 5 | 3 | 6.11 | 11.5 | 3 | 5.80 | 6.0 | 5.5 |
| 6 | 4 | 6.38 | 16.6 | 4 | 5.92 | 8.2 | 8.4 |

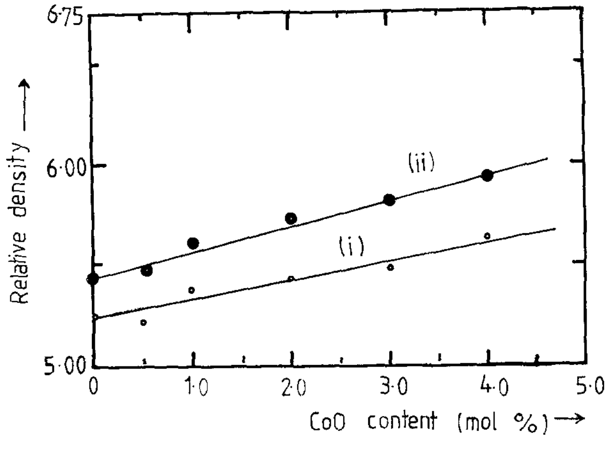

*Figure 1* Variation of relative density as a function of CoO content in $TeO_2$-CuO-CoO glasses for (i) unannealed and (ii) annealed samples.

the average interatomic spacing in any particular glass decreases and the structure of the glass becomes more compact compared with that of unannealed samples. It is observed from these figures (1 and 2) that the addition of NiO in copper tellurite glasses makes the glass more dense than an equivalent content of CoO. Quantitatively the effect of CoO and NiO on the $TeO_2$-CuO glassy network can be estimated by determining the relative increase in density of each glass compared with the binary system and this was determined for both annealed and unannealed samples (see Tables I and II) and relative increase in density was plotted against NiO content (Fig. 3) which has been more effective in increasing the density of copper tellurite glasses. From the comparative study of the data (Tables I and II, Fig. 3) it can be concluded that

1. The density of $TeO_2$-CuO-NiO for both annealed and unannealed glasses is more than $TeO_2$-CuO-CoO, and
2. The relative increase in density of $TeO_2$-CuO-NiO glasses for annealed samples increases linearly with NiO content, while for the unannealed samples it increases with NiO addition in the range 0.5 to 1 mol % NiO and after that it tends to a constant value.

## 3.2. Optical absorption

The optical absorption spectra of binary $TeO_2$-CuO and two ternary series of glasses, as a function of wavelength in the visible range, are shown in Figs 4, 5 and 6 respectively which do not show a sharp absorption edge, and this is characteristic of glassy or amorphous materials. Figs 5 and 6 indicate that the absorption edges shift slightly towards higher energies with the increase of NiO and CoO in their respective glasses.

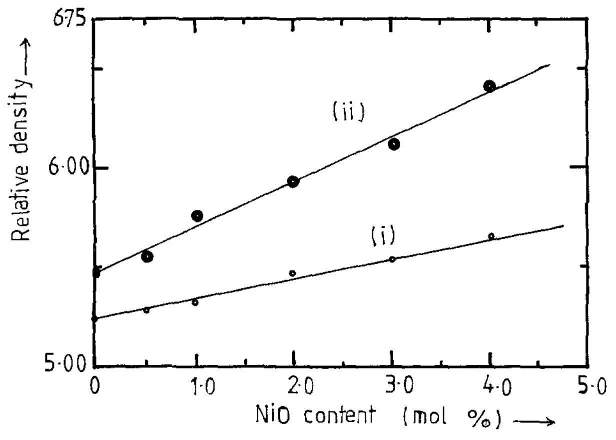

*Figure 2* Variation of relative density as a function of NiO content in $TeO_2$-CuO-CoO glasses for (i) unannealed and (ii) annealed samples.

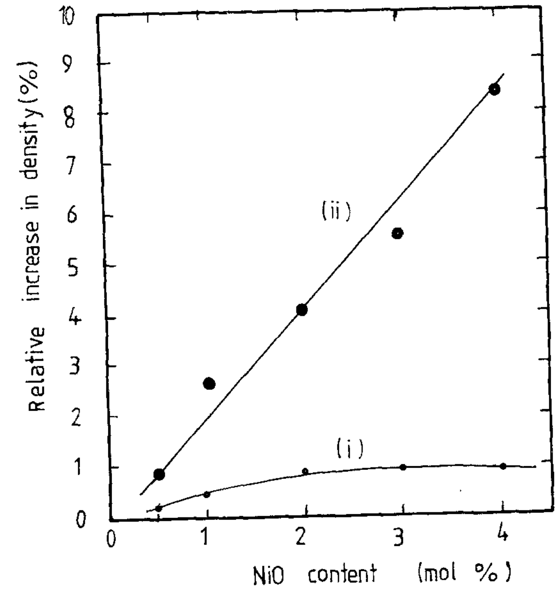

*Figure 3* Variation of relative increase in density as a function of NiO content for (i) unannealed and (ii) annealed samples.

The absorption coefficient $\alpha(\omega)$ was determined at different photon energies near the absorption edges for glasses under study and the quantity $(\alpha\hbar\omega)^{1/2}$ is plotted against photon energy ($\hbar\omega$) as shown in Figs 7 and 8. The values of the optical energy gap for each composition in these series were obtained by extrapolating the linear regions of the plots $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ in Figs 7 and 8 to $(\alpha\hbar\omega)^{1/2} = 0$ and their corresponding values are compiled in Tables III and IV. From the data it is noted that the optical energy gap ($E_{opt}$) increases with the increase of CoO and NiO content over that of binary $TeO_2$-CuO glass with $E_{opt} = 2.01$ eV which is taken as the standard glass sample. The variations of $E_{opt}$ with CoO and NiO content for these glasses are plotted in Figs 9 and 10 respectively.

The values of the absorption coefficients, estimated by using Equation 3 for the binary and two series of ternary glasses, are plotted against photon energy as shown in Figs 11 and 12. The value of $E_e$ in Equation 1 can be calculated from the slopes of the linear parts

TABLE III Some characteristic energy parameters of six copper tellurite glasses containing CoO

| Number | Glass sample | Composition (mol %) | | | $E_{opt}$ (eV) | Effect of CoO on $E_{opt}$ (%) | $E_e$ (eV) |
|---|---|---|---|---|---|---|---|
| | | $TeO_2$ | CuO | CoO | | | |
| 1 | a | 65 | 35 | 0 | 2.01 | – | 0.5 |
| 2 | g | 65 | 34.5 | 0.5 | 2.04 | 1.5 | 0.86 |
| 3 | h | 65 | 34 | 1 | 2.07 | 2.2 | 0.76 |
| 4 | i | 65 | 33 | 2 | 2.12 | 5.5 | 0.75 |
| 5 | j | 65 | 32 | 3 | 2.17 | 8.0 | 0.59 |
| 6 | k | 65 | 31 | 4 | 2.21 | 9.9 | 0.57 |

TABLE IV Some characteristic energy parameters of six copper tellurite glasses containing NiO

| Number | Glass sample | Composition (mol %) | | | $E_{\text{opt}}$ (eV) | Effect of NiO on $E_{\text{opt}}$ (%) | $E_{\text{e}}$ (eV) | Excessive effect of NiO (%) |
|---|---|---|---|---|---|---|---|---|
| | | $TeO_2$ | CuO | NiO | | | | |
| 1 | a | 65 | 35 | 0 | 2.01 | – | 0.5 | – |
| 2 | b | 65 | 34.5 | 0.5 | 2.05 | 2.0 | 0.44 | 0.5 |
| 3 | c | 65 | 34 | 1 | 2.08 | 3.5 | 0.33 | 0.5 |
| 4 | d | 65 | 33 | 2 | 2.20 | 9.5 | 0.37 | 3.98 |
| 5 | e | 65 | 32 | 3 | 2.25 | 12.0 | 0.40 | 3.98 |
| 6 | f | 65 | 31 | 4 | 2.29 | 13.9 | 0.40 | 3.98 |

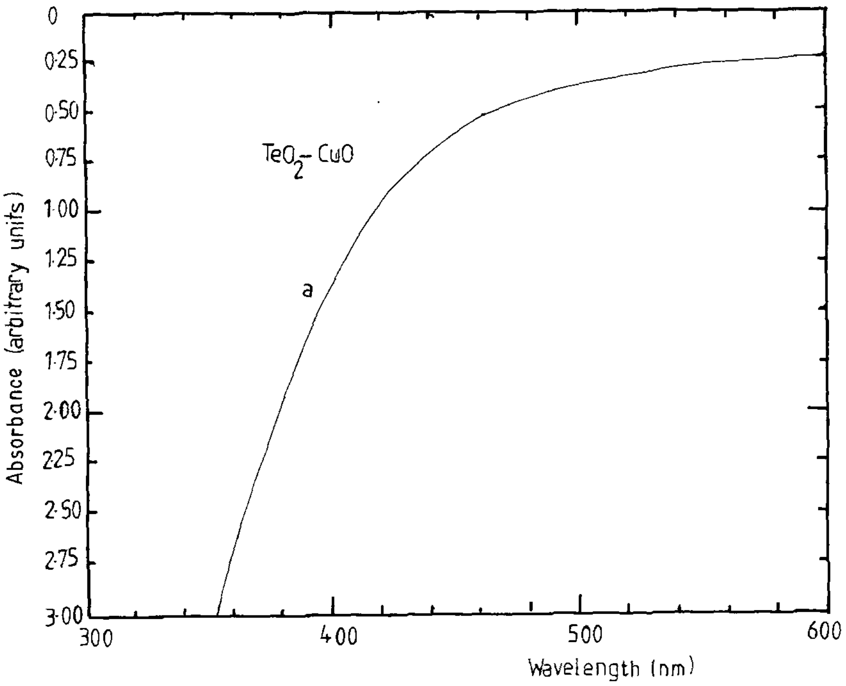

*Figure 4* Variation of optical absorption with wavelength for a 65 $TeO_2$–35 CuO glass film (sample a in Table IV).

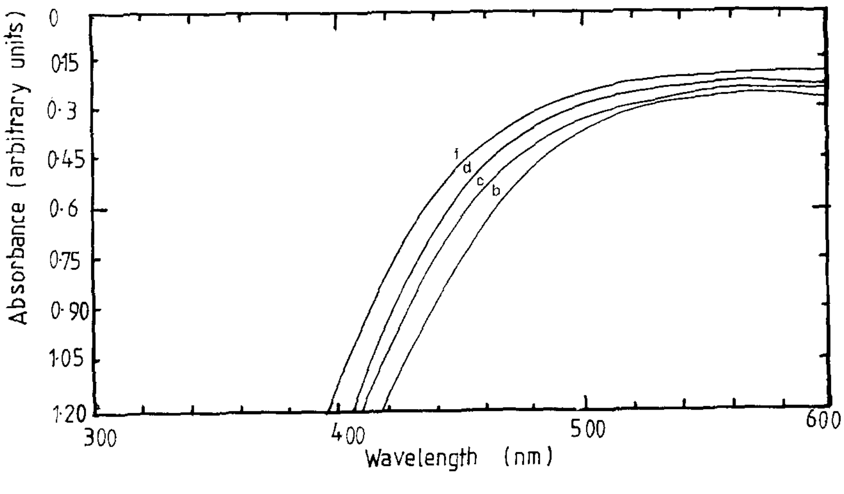

*Figure 5* The optical absorption spectra as a function of wavelength of $TeO_2$–CuO–NiO glasses for different compositions b, c, d, f (see Table IV).

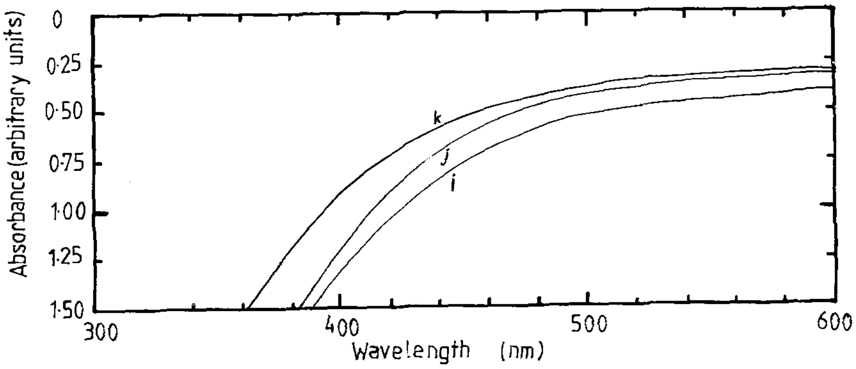

*Figure 6* The optical absorption spectra as a function of wavelength of $TeO_2$–CuO–CoO glasses for different compositions, i, j, k (see Table III).

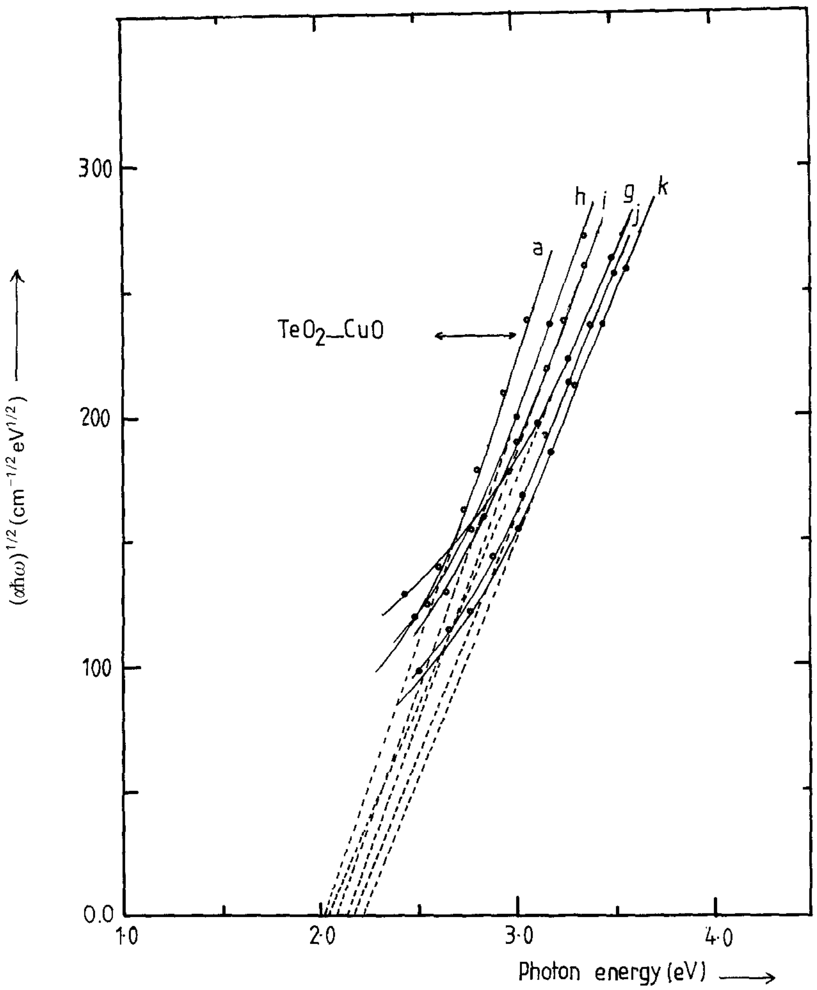

*Figure 7* $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy ($\hbar\omega$) for $TeO_2$–CuO–CoO glasses.

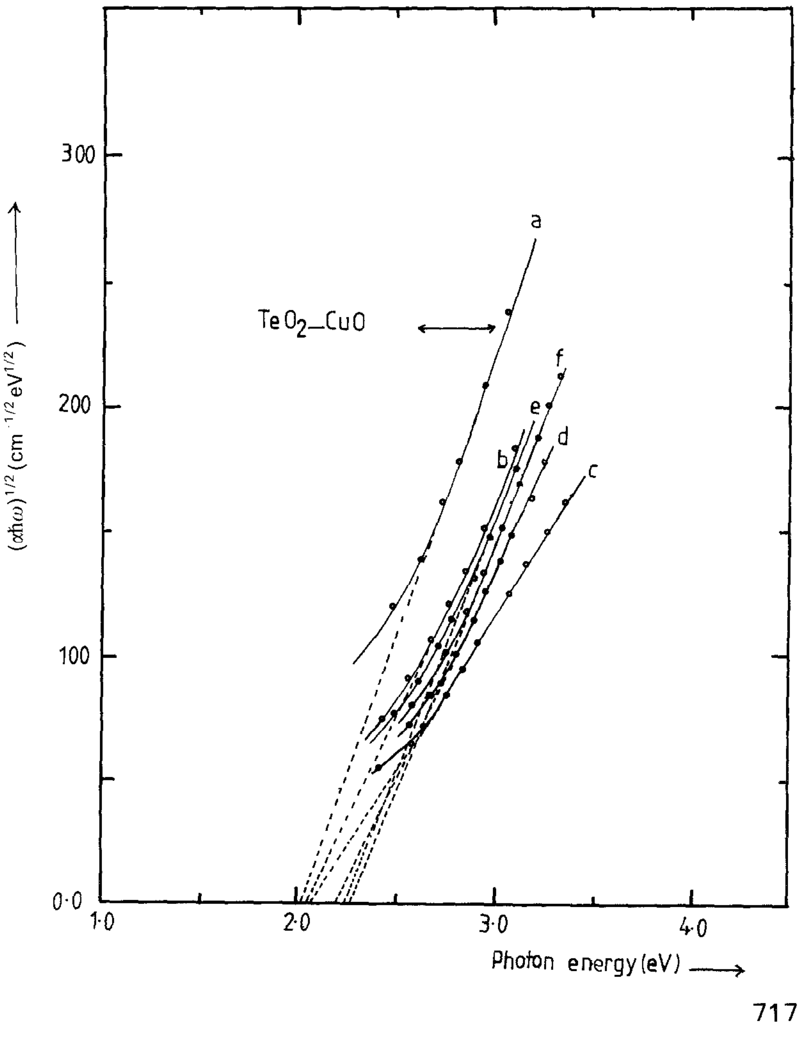

*Figure 8* $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy ($\hbar\omega$) for $TeO_2$–CuO–NiO glasses.

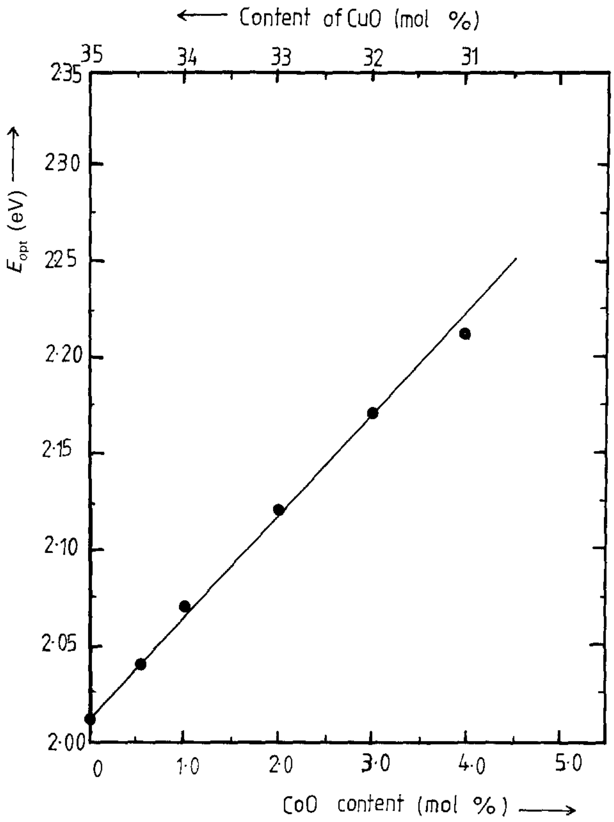

*Figure 9* Variation of optical energy gap with CoO content $TeO_2$–CuO–CoO glasses.

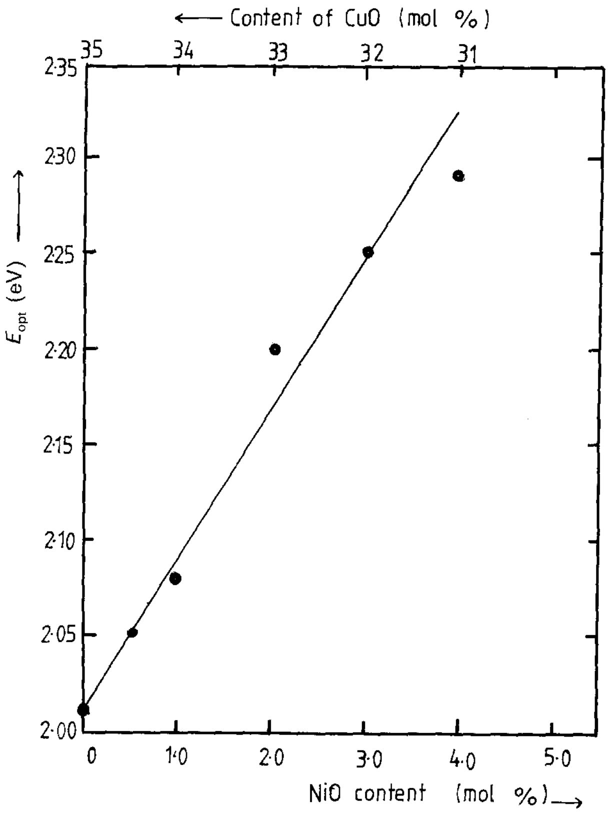

*Figure 10* Variation of optical energy gap with NiO content for $TeO_2$-CuO-NiO glasses.

of these curves and are recorded in Tables III and IV. According to Davis and Mott [3], the values of $E_e$ for a range of amorphous semiconductors lie in the range 0.045 to 0.067 eV. For binary tungsten tellurite glasses [8], the values of $E_e$ lie between 0.11 and 0.14 eV, depending upon the composition. For molybdenum phosphate glasses [9], the value of $E_e$ was as high as 0.16 eV, whereas for ternary tellurite glasses of types

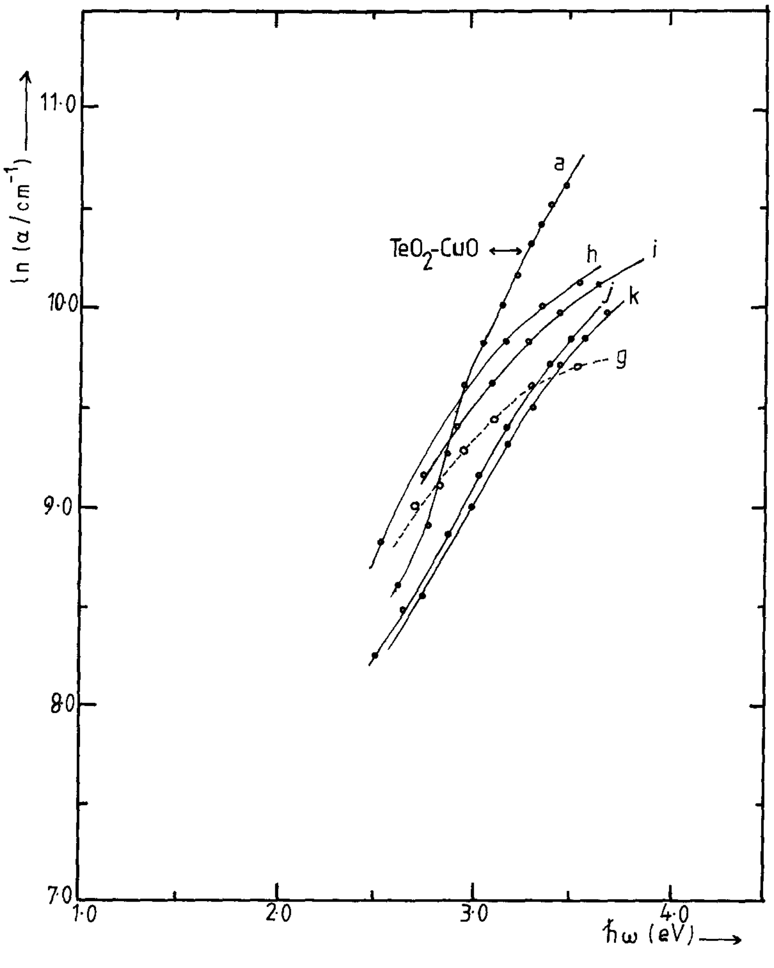

*Figure 11* Absorption coefficient $\alpha(\omega)$ as a function of photon energy for $TeO_2$-CuO-CoO glasses.

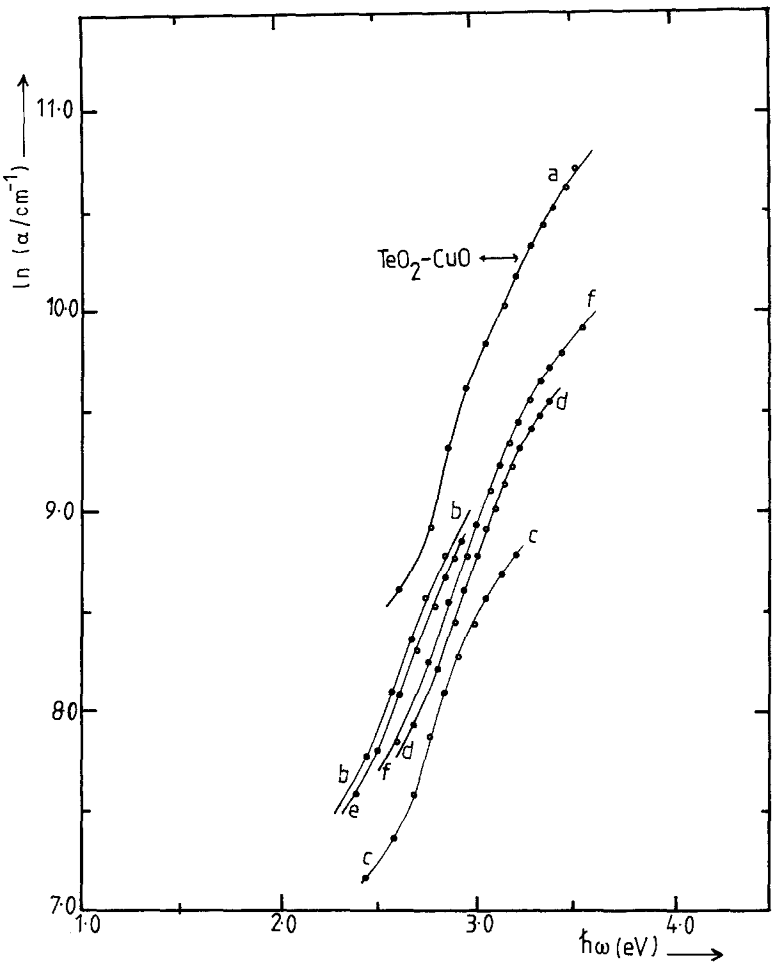

*Figure 12* Absorption coefficient $\alpha(\omega)$ as a function of photon energy for $TeO_2$-CuO-NiO glasses.

$WO_3$-CaO-$TeO_2$ [10] and $V_2O_5$-$P_2O_5$-$TeO_2$ [11], the corresponding reported values of $E_e$ lie in the range 0.12 to 0.2 eV and 0.31 to 0.68 eV, depending also on the compositions.

For the glasses studied in the present work, exponential behaviour is observed and the value of $E_e$ for $TeO_2$-CuO glass is 0.5 eV and for both ternary $TeO_2$-CuO-CoO and $TeO_2$-CuO-NiO glasses the respective values of $E_e$ lie within the ranges 0.33 to 0.44 eV and 0.57 to 0.86 eV.

The increase in $E_{opt}$ arising from the addition of CoO and NiO in the binary $TeO_2$-CuO glassy network may be ascribed to different possible oxidation states which exist due to the mixed ions and to the possible pairing of the mixed ions in the form involving oxygen bridging. So, in the binary system, Te-O-Cu bonds are formed and the addition of CoO and NiO would break some of these bonds and new bridge bonds such as Cu-O-Co, Cu-O-Ni, Ni-O-Ni, Co-O-Co and Cu-O-Te-O-Ni or Cu-O-Te-O-Co will be formed. These new bonds will not be equivalent to the previous bonds and overall the concentrations of non-bridging oxygen ions in both the ternary systems decrease, resulting in a linear rise in the $E_{opt}$ values which will clearly depend upon the composition of each glass.

From the comparative study of the data concerning the optical energy gap of two ternary copper tellurite glassy systems, it can easily be estimated which of the two TM oxides affects the value of $E_{opt}$ more when introduced into copper tellurite glasses. The analysis of the data reveals that the addition of 0.5 to 1 mol % and 2 to 4 mol % of NiO as well as CoO in copper tellurite glasses causes an increase in the value of $E_{opt}$ which is 0.5% and 3.98% respectively more in $TeO_2$-CuO-NiO than in $TeO_2$-CuO-CoO glasses under the composition range 65 $TeO_2$-(35 $-$ $x$)CuO-$x$MO in mole percent (where M is Co or Ni and $x$ = 0, 0.5, 1, 2, 3, 4). So NiO which is the extreme member of the first row of transition elements and is also a p-type oxide plays a more effective role in increasing the optical energy gap at its higher value of concentrations than CoO does.

Thus it can be predicted that the bonds of NiO and CoO in copper tellurite glasses are of somewhat different nature. When TM oxides from the first row ol transition elements in the periodic table, are introduced into copper tellurite glasses, the TM oxide of higher atomic number will be more effective in increasing the optical energy gap, as is evident in the present study.

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