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# OPTICAL PROPERTIES OF CO-EVAPORATED THIN FILMS OF BINARY $Bi_2O_3$-$Te O_2$ AND $Bi_2O_3$-$V_2O_5$ SYSTEMS

A. A. Hosseini[1] and C.A. Hogarth[2]

[1]*Physics Department, Faculty of Science, University of Mazandaran, Babolsar, Islamic Republic of Iran*
[2]*Physics Department, Brunel University, Uxbridge, Middx, UB8 3PH, UK*

**Abstract**

Thin films of binary $Bi_2O_3$-$TeO_2$ and $Bi_2O_3$-$V_2O_5$ systems were prepared by the thermal co-evaporation technique in a vacuum at room temperature. The optical absorption edge of these systems are studied in the wavelength of 200-800 nm using a PERKIN-ELMER uv/vis spectrophotometer. It is found that the value of n=3/2 in the Davis-Mott equation is best fitted for the fundamental absorption edge for these materials. It is also found that the optical energy gap ($E_{opt}$) for the $Bi_2O_3$-$V_2O_5$ system lies between 0.65 and 3.5 eV. and for the $Bi_2O_3$-$TeO_2$ system between 0.95 and 3.25 eV. depending on the film composition. The exponential behaviour of the absorption coefficient with photon energy for the systems under invesgiation are verified as suggested by Urbach.

## Introduction

The analysis of optical spectra over a wide range of photon energy has been one of the most productive tools for understanding and developing the theory of electronic structure in crystalline and amorphous solids. For the amorphous materials in the high absorption region, which is associated with interband transition, Tauc [1] and Davis-Mott [2] independently derived an expression relating the absorption coefficient $\alpha(\omega)$ to the photon energy ($\hbar\omega$) as,

$$a(\omega)= A \frac{(\hbar\omega - E_{opt})^n}{\hbar\omega} \qquad (1)$$

where $E_{opt}$ is the optical energy gap and n is a number which characterizes the optical absorption processes. Its values for different kinds of transitions are as follows:

n= 1/2: direct-allowed transition [3]
n= 1: non-metalic materials [4]
n= 3/2: direct-forbidden transition [5,6,7]
n= 2: indirect-allowed transition [8]
n= 3: indirect-forbidden transition [3]

A in Equation (1) is a constant and is given by,

$$A= \frac{4\pi G_0}{ncE_{e\,l}} \qquad (2)$$

where c is the speed of light, n is the refractive index of the material, G is the extrapolated dc. conductivity at T= 0 K and $E_{el}$ is the extent of the band tailing.

The absorption edge in many disordered materials

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follows the Urbach rule [9] given by:

$$a_{(\omega)} \propto Exp\ (\frac{\hbar\omega}{\Delta E}) \qquad (3)$$

where ($\hbar\omega$) is the photon energy and $\Delta E$ is the width of the tail of the localized states in the band gap.

## Experimental Procedure

### Sample Preparation

Thin films of $Bi_2O_3$-$TeO_2$ and $Bi_2O_3$-$V_2O_5$ binary systems with different composition were coated on cleaned Corning 7059 glass substrate using thermally co-evaporation technique at room temperature under a pressure of $p \cong 4\times10^{-6}$ torr.

Samples specification and the condition of preparation are given in Tables 1 and 2. Tungsten boats were found to be most suitable for the evaporation since boats made of other materials react with the evaporants, as was confirmed by XPS. The film thickness and rate of deposition were monitored using a quarts crystal monitor unit (Intellometrics model IL-150).

The absorption coefficient for the samples listed in Tables 1 and 2 was calculated from the following equation,

$$\alpha_{(\omega)} = \frac{1}{d} \ln \frac{I_0}{I_t} \qquad (4)$$

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

### Optical Data Measurement

We have investigated Bismuth oxide in thin film form to determine,

a) the position and shape of absorption edge.

b) the value of n, in Equation (1) and therefore the kind of transition in these materials.

c) the optical energy gap, $E_{opt}$, and

d) the effects of increasing the concentration of Vnadium oxide and Tellerrium oxide on absorption edge and the value of $E_{opt}$.

On the basis of our earlier experiments related to the other binary systems containing $V_2O_5$ and $CeO_2$ we found that as the concentration of $V_2O_5$ in the $V_2O_5$-$CeO_2$ system decreases the absorption edge becomes sharper

**Table 1.** Optical absorption data for $Bi_2O_3$-$V_2O_5$ system with different composition

| Sample No. | Composition $Bi_2O_3$-Te-$O_2$ | Thickness nm. | $E_{opt.}$ eV. | Pressure Torr | Temperature K |
|---|---|---|---|---|---|
| 2010 | 88%-12% | 360 | 3.5 | $2.10^{-6}$ | 305 |
| 2011 | 63%-37% | 320 | 3.15 | $4.10^{-6}$ | 302 |
| 2012 | 56%-44% | 345 | 2.55 | $2.10^{-6}$ | 300 |
| 2013 | 42%-58% | 340 | 1.72 | $2.5.10^{-6}$ | 304 |
| 2014 | 28%-72% | 330 | 1.23 | $3.10^{-6}$ | 306 |
| 2015 | 15%-85% | 355 | 0.65 | $1.10^{-6}$ | 308 |
| 100.a | 100%-00% | 560 | 3.60 | $5.10^{-6}$ | 312 |

**Table 2.** Optical absorption data for $Bi_2O_3$-$V_2O_5$ system with different composition

| Sample No. | Composition $Bi_2O_3$-Te-$O_2$ | Thickness nm. | $E_{opt.}$ eV. | Pressure Torr | Temperature K |
|---|---|---|---|---|---|
| 1050 | 23%-77% | 440 | 0.98 | $2\ .10^{-6}$ | 304 |
| 1006 | 39%-61% | 410 | 1.2 | $2.5\ .10^{-6}$ | 305 |
| 1007 | 56%-44% | 480 | 1.35 | $2\ .10^{-6}$ | 302 |
| 1008 | 72%-28% | 475 | 1.75 | $3\ .10^{-6}$ | 299 |
| 1009 | 86%-14% | 450 | 3.25 | $4.5\ .10^{-6}$ | 300 |

and the optical energy gap increases from 2.1 eV. for pure $V_2O_5$ to 3.2 eV. for the system containing 17% $V_2O_5$-83% $CeO_2$ [8].

In this work we wish to find out the effect of $V_2O_5$ and $TeO_2$ concentration on the optical properties of a binary system containing $Bi_2O_3$. The recorded absorption spectra for all the samples listed in Tables 1 and 2 are shown in Figure 1 for the $Bi_2O_3$-$V_2O_5$ and in Figure 2 for the $Bi_2O_3$-$TeO_2$ system. The absorption spectra for pure $Bi_2O_3$ is shown in Figure 3. To determine the value of *n*, in Equation (1) for the systems under investigation, the variations of $(\alpha\hbar\omega)^{1/n}$ vs. photon energy were plotted for different values of *n*. It was found that n= 3/2 gives the best linear dependence in the high absorption region for both systems, indicating that the kind of transition in these systems is a direct-forbidden transition as it was reported for other systems containing transition metal oxides [5].

Sample specifications and optical absorption data for the systems under investigation are given in Tables 1 and 2. Figures 4 and 5 represent the variation of $(\alpha\hbar\omega)^{2/3}$ with photon energy for these systems with different composition. The extrapolation of the linear part of these curves to the energy axis at the value of $(\alpha\hbar\omega)^{2/3}= 0$ gives the values of $E_{opt}$. The variation of $E_{opt}$ with $Bi_2O_3$ content for both $Bi_2O_3$-$V_2O_5$ and $Bi_2O_3$-$TeO_2$ systems are shown in Figure 6 and 7, respectively. From these figures one can see that for both systems the effect of increasing the $Bi_2O_3$ content is an increase in the optical energy gap which could arise as a result of a reduction in the higher valency state of transition metal ion in the system. To achieve a more reliable conclusion the electron spin resonance (E.S.R) experiment is recommended to evaluate the concentration of different valency states of Vanadium [13]. ($V^{+5}$, $V^{+4}$, $V^{+3}$), as well as, the concentration of the non-bridging oxygen ions in the

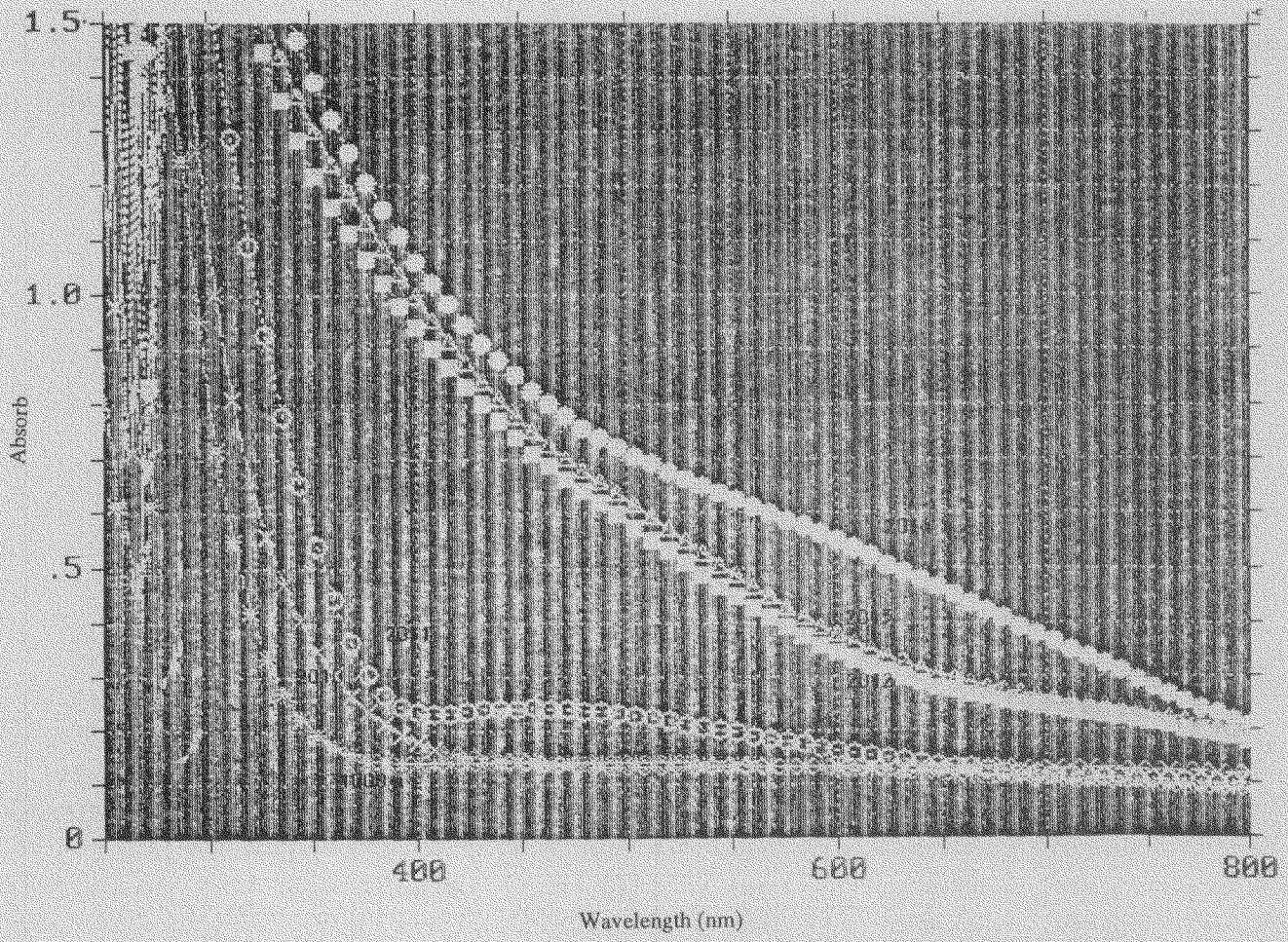


**Figure 1.** UV. Spectra of $Bi_2O_3$-$TeO_2$ system as listed in Table 1.

samples under study.

It is well established that in many crystalline and amorphous semiconductors the absorption coefficient $\alpha(\omega)$ depends exponentially on photon energy $\alpha(\omega)$. This behaviour was suggested by Urbuch [9] for the first time in the form of Equation 2. The origin of this kind of dependence is not clearly known.

Tauc [10] suggested that the exponential behaviour arises from the electron transition between localized states where the density of localized states is exponentially dependent on photon energy (Band tais). Another suggestion is based on the presence of a strong internal electric field due to structural disorder [11]. Mott and Davis have rejected the Tauc suggestion because the slope of the exponential absorption edge is much the same in a variety of materials.

Variation of $Ln(-a)$ with photon energy ($\hbar\omega$) for both systems are shown in Figure 8 and 9. These figures show that the absorption coefficient, in terms of photon energy for both $Bi_2O_3$-$TeO_2$ and $Bi_2O_3$-$V_2O_5$ systems follows the Urbach exponential rule.

1. If the films behave as quasiintrinsic semiçonductors, the Fermi energy will be located in the middle of the band gap and the electrical energy gap $E_{el}$ would be twice the activation energy and equal to the optical gap ($E_{el} = E_{opt}$). But if the values of the electrical activation energy is much less than the optical energy gap it would be clear that the electrical activation process is certainly not across a band gap but rather between bands and trapping centres.

## Conclusion

The results of optical absorption measurements for the systems under study is summerized as follows;

The absorption spectra obseryed in amorphous $Bi_2O_3$-$V_2O_5$ and $Bi_2O_3$-$TeO_2$ thin films in the wavelength region

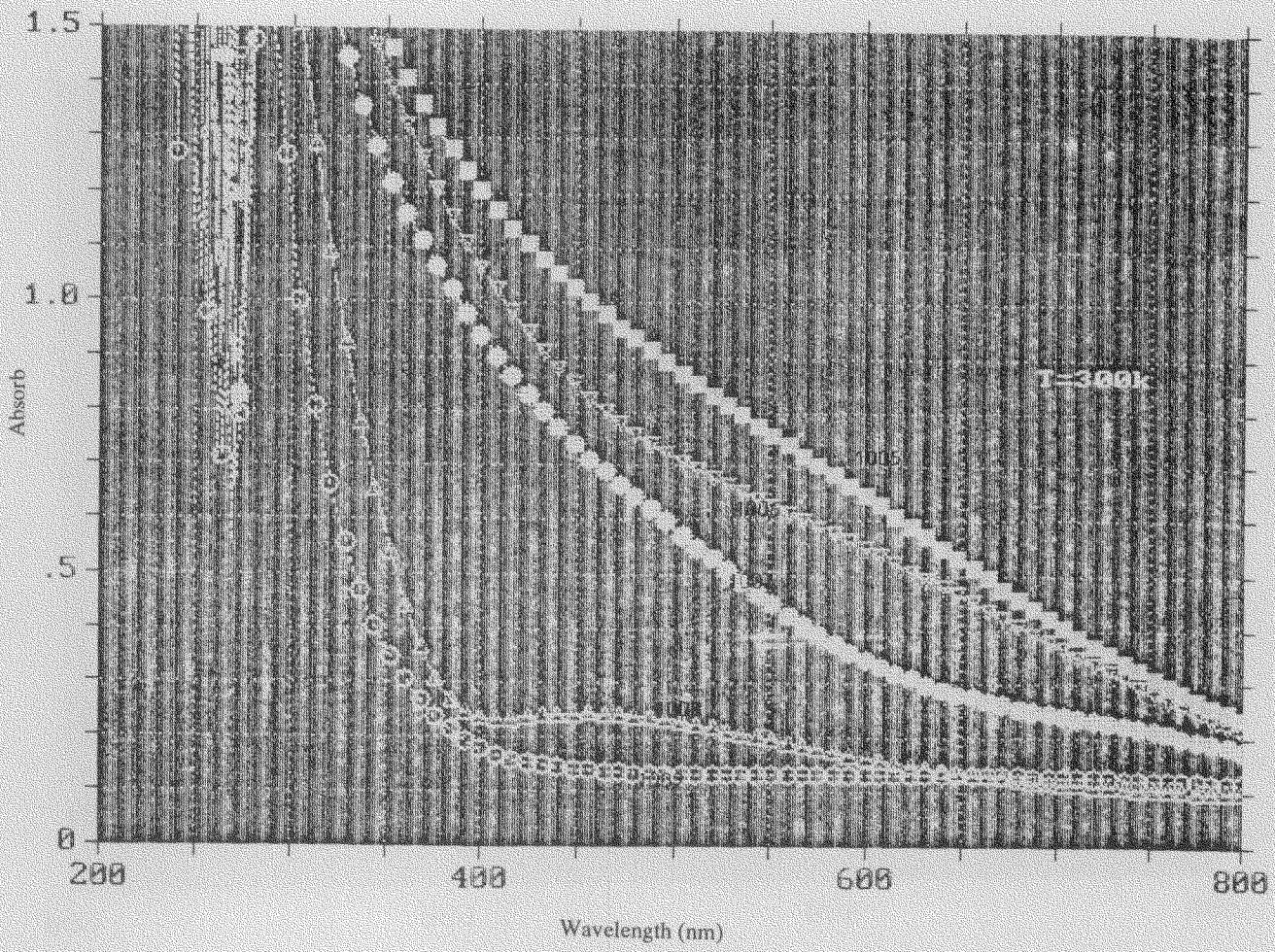


**Figure 2.** UV. Spectra of $BiO_3V_2O_5$ $Bi_2O_3$-$V_2O_5$ system as listed in Table 1.

of 200-800 nm have similar structures as in many binary oxide systems.

The fitted value of n= 3/2 indicates that the transition in these materials is a K-conserving transition (direct-forbidden transition, without phonon envolvement) which shows that the electron wave function in the valence band near K= 0 is not much different from those in crystal.

For both systems the optical absorption edge becomes sharper as the content of $Bi_2O_3$ increases and for a film with a high concentration of $Bi_2O_3$ the absorption edge is similar to that of crystalline structure.

The optical energy gap for the $Bi_2O_3$-$V_2O_5$ system ranges from 0.65 to 3.5 eV. depending on composition and increases with $Bi_2O_3$ concentration. For the $Bi_2O_3$-$TeO_2$ system the optical energy gap varies between 0.95 and 3.25 eV. and increases with the content of $Bi_2O_3$ in the system.

Absorption coefficients in both systems follows the Urbach exponential dependent on the photon energy indicating the existence of localized states at the band tails arising from the lack of long range order in these systems.

To give a more qualitative description of the transition mechanism and extent of the band tailing an E.S.R measurement is recommended to evaluate the concentration of different valency states in these systems.

Electrical measurements such as a.c and d.c conductivity could be useful in evaluating the extent of band tailing and the concentration of localized states in the tailes region, as well as, trapping centres.

To evaluate the strength of the bonding, specially the concentration of non-bridging V-O and Te-O bonding and the strength of the possible Bi-Te bonding, IR and X-ray spectroscopy measurements are also recommended.

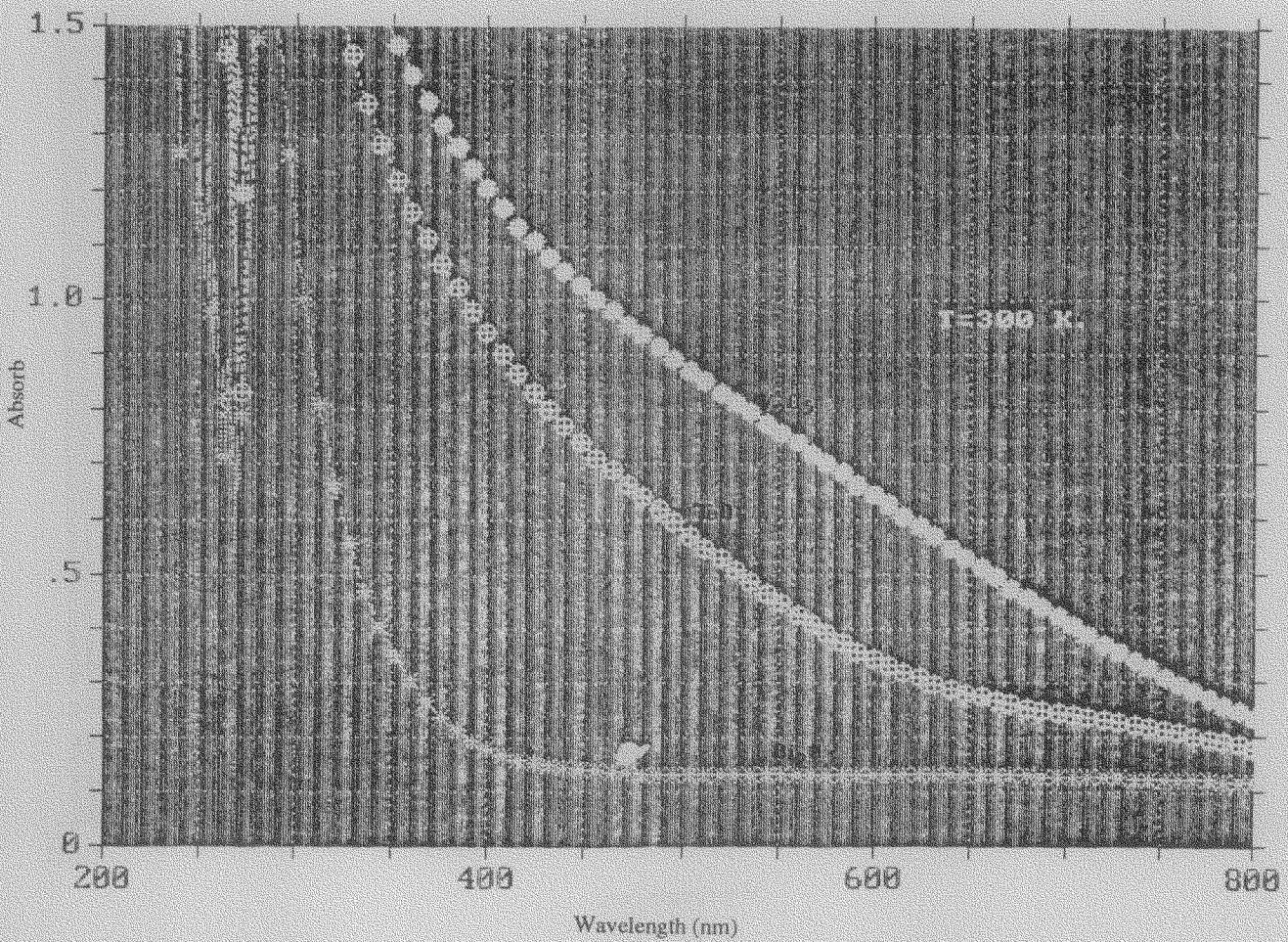


**Figure 3.** UV. Spectra of pure $TeO_2$, $V_2O_5$, and $Bi_2O_3$ samples

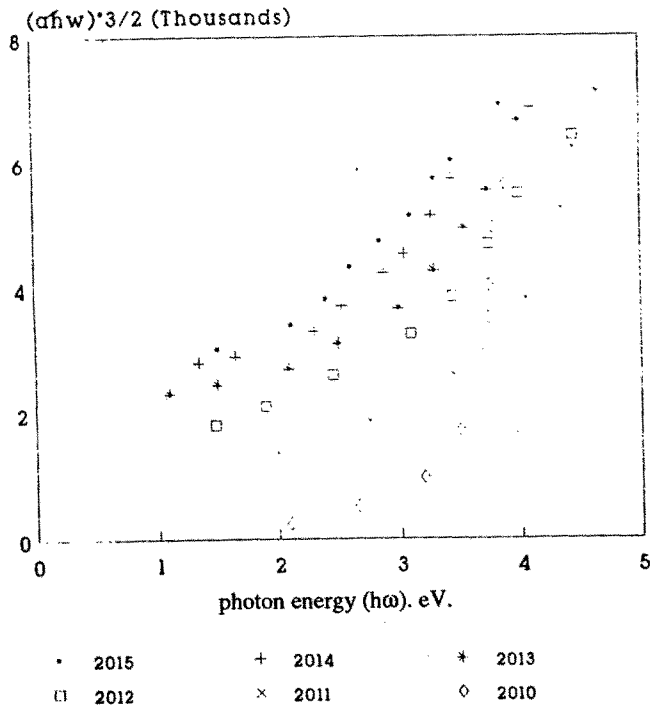


**Figure 4.** Variation of $(\alpha h\omega)^{*3/2}$ vs. $(\hbar\omega)$ for $Bi_2O_3$-$V_2O_5$ system

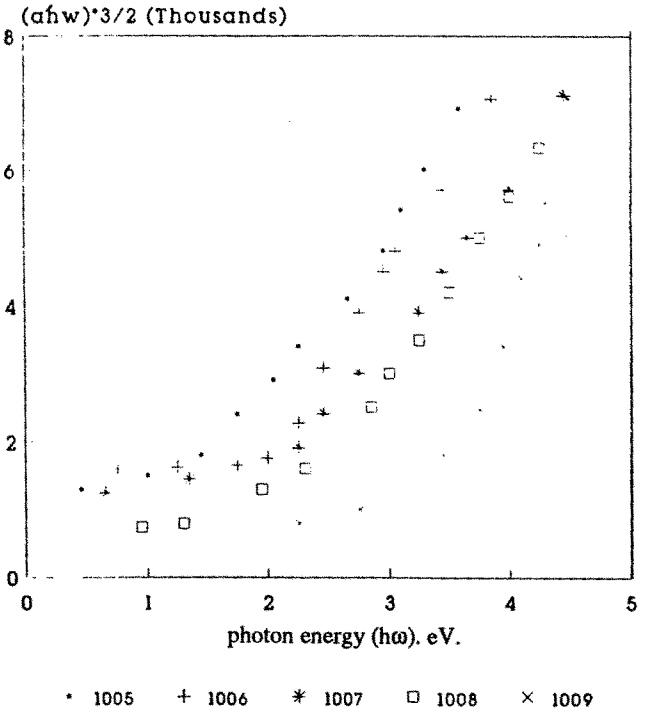


**Figure 5.** Variation of $(\alpha h\omega)^{*3/2}$ vs. $(\hbar\omega)$ for $Bi_2O_3$-$TeO_2$ system

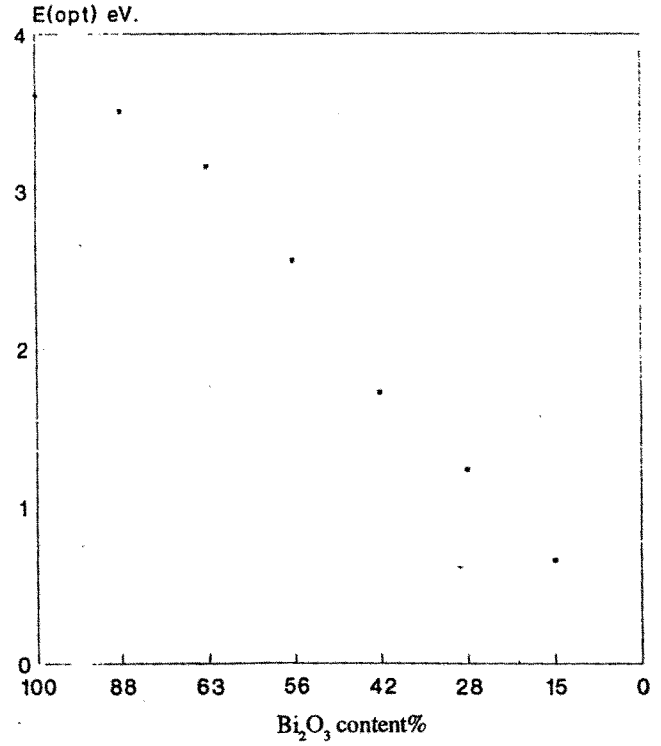


**Figure 6.** Variation of *E(opt)* vs. $Bi_2O_3$ content for $Bi_2O_3$-$V_2O_5$ system

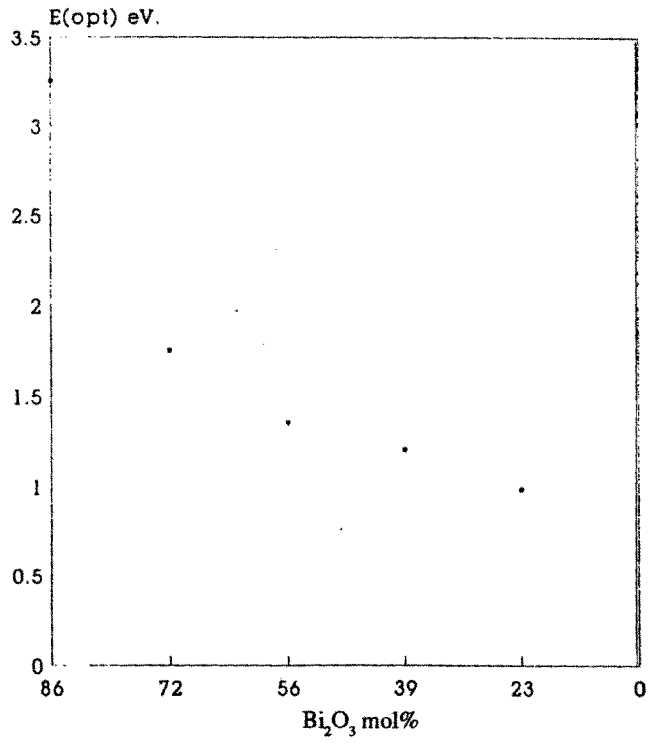


**Figure 7.** Variation of E(opt) vs. $Bi_2O_3$ content for $Bi_2O_3$-$TeO_2$ binary system

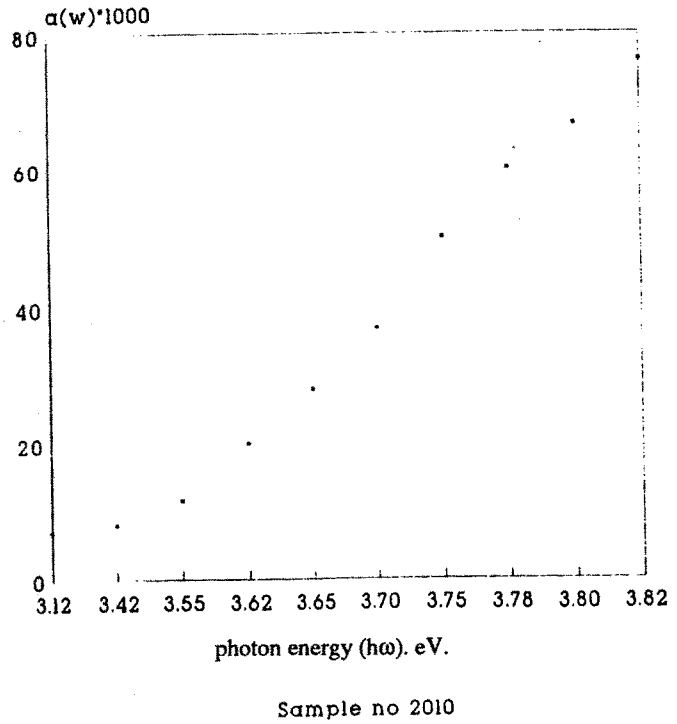


**Figure 8.** Variation of $\propto(\omega)$ vs. photon energy ($h\omega$) for the sample no 2010

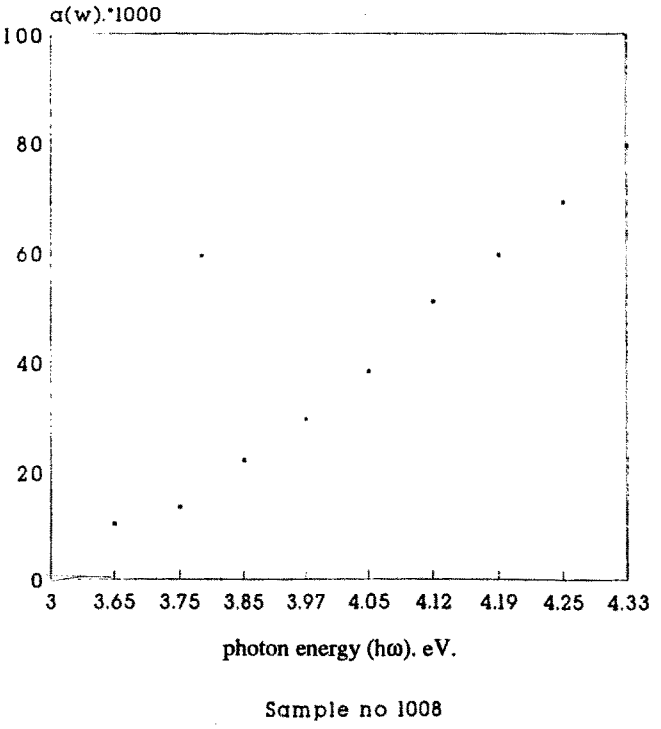


**Figure 9.** Variation of $\alpha(\omega)$ vs. photon energy for the sample no 1008

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