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The optical energy gap in $Mo_{0.5}W_{0.5}Se_2$ single crystals grown by a direct vapour transport technique

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Abstract : Optical absorption in single crystals of $Mo_{0.5}W_{0.5}Se_2$ has been measured at room temperature near the fundamental absorption edge. The incident light was kept normal to the basal plane *i.e.* along the *c*-axis of the grown flakes. Results have been analyzed on the basis of two dimensional and three dimensional models. Both direct and indirect transitions are involved in the absorption process. The indirect transition was found to be allowed with two phonons involved in the process. The direct and indirect energy gaps and phonon energies were found to be 1.56 eV, 1 02 eV and 10 MeV, 40 MeV respectively. The three dimensional model and not the two dimensional model could be used to describe the optical properties of $Mo_{0.5}W_{0.5}Se_2$ single crystals.

Keywords : Optical properties, energy gap, $Mo_{0.5}W_{0.5}Se_2$, single crystals

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1. Introduction

Since the pioneering work of Tributsch [11], the behaviour of covalent semiconducting layer-type group VI transition metal dichalcogenides, and in particular of WSe_2 [2,3] and $MoSe_2$ [4,5] as electrodes in Photoelectrochemical (PEC) solar cells for conversion of solar into electrical energy has been extensively studied. Such detailed studies [6] have however not been made on mixed crystals of tungsten and molybdenum diselenides. In order to study their photoconversion behaviour with Photoelectrochemical solar cells fabricated with them, it is highly desirable to determine their band gaps from an analysis of their absorption spectra. Authors have therefore carried out a detailed study of the absorption spectra of $Mo_{0.5}W_{0.5}Se_2$ (with equal amounts of molybdenum and tungsten) and the results of these investigations are described in this paper.

$Mo_{0.5}W_{0.5}Se_2$ belongs to the system $Mo_xW_{1-x}Se_2$ with $x = 0.5$. It possesses MoS_2 structure (C_7 type). The metal atoms are in trigonal prismatic coordination between two superimposiable sheets of hexagonally packed chalcogen atoms. No strong bond exists between the layers, however, only long range van der Waals forces hold atomic sandwiches together. This gives the crystals their characteristic platy habit, with extended growth and pronounced cleavage perpendicular to c-axis. The stacking sequence is ABA, BAB with the space group D_{6h}^4 ($P6_3/mmc$). The lattice constant of $Mo_{0.5}W_{0.5}Se_2$ is : $a = 3.288 \pm 0.002$ and $c = 12.95 \pm 0.01$ [7].

2. Experimental

The single crystals of $Mo_{0.5}W_{0.5}Se_2$ used in the present study are grown by Direct Vapour Transport technique. A stoichiometric mixture of Mo (99.95% purity), W (99.95% purity) and Se (99.999% purity) was loaded in a high quality fused quartz ampoule and the ampoule containing the mixture was sealed at a pressure of 10^{-5} torr. The sealed ampoule was then introduced into a two zone horizontal furnace at a constant reaction temperature to obtain the charge of $Mo_{0.5}W_{0.5}Se_2$. The charge so prepared was rigorously shaken to ensure proper mixing of the constituents and kept in the furnace under appropriate condition to obtain single crystals of $Mo_{0.5}W_{0.5}Se_2$. The growth condition used for the synthesis are given in Table 1. Room temperature Hall measurements on as-grown crystals revealed that

Table 1. Growth parameters used to synthesize single crystals of $Mo_{0.5}W_{0.5}Se_2$.

Reaction temperature	973
Growth temperature	1103 K
Growth time	144 hrs.
Crystal size (maximum)	17 mm × 14 mm × 0.2 mm
Appearance	Black opaque

they exhibit p-type conductivity with hole concentration of about 10^{16} cm^{-3}. Thin samples for absorption measurements were as-grown single crystals which grew in the growth ampoule in the form of thin flakes. The absorption spectrum was obtained by means of a UV-VIS-NIR Schimadzu Spectrophotometer in the range 700 nm to 1450 nm. All measurements were performed at room temperature with the incident beam normal to the basal plane *i.e.* along the c-axis of the as-grown flakes. Measurements along the c-axis could not be performed since the specimens were too thin to be mounted along this direction.

3. Results and discussion

The absorption spectrum was taken for $Mo_{0.5}W_{0.5}Se_2$ single crystals over the spectral range 700 nm to 1450 nm. The results from this spectrum were analysed on the basis of three as well as two dimensional models. For this purpose, values of absorption coefficient α were determined at every step of 10 nm from 700 nm to 1450 nm from the spectrum.

The interpretation of the results in terms of the direct and indirect transitions can be performed with the help of formulae derived for three dimensional (3D) crystals. According to Bardeen *et al* [8], these formulae can be written as follows :

$(\alpha h\nu) \propto (h\nu - E_o)^{1/2}$ for direct allowed and

$(\alpha h\nu) \propto (h\nu - E_g)^{3/2}$ for direct forbidden transitions,

$(\alpha h\nu) \propto (h\nu - E_g' \pm E_p)^2$ for indirect allowed and

$(\alpha h\nu) \propto (h\nu - E_g' \pm E_p)^3$ for indirect forbidden transitions.

where E_g is the energy gap corresponding to direct transition and E_g' the energy gap corresponding to indirect transition and E_p is the energy of the phonon absorbed or emitted.

Figures 1 and 2 show the spectral variation of the quantities $(\alpha h\nu)^{1/3}$ and $(\alpha h\nu)^{1/2}$ *vs* $h\nu$ respectively. Since both the curves indicated discontinuous straight lines it is quite plausible that they represent indirect interband transitions involving the emission or absorption of phonons. However from Figure 1, it is seen that it is not possible to fit all the

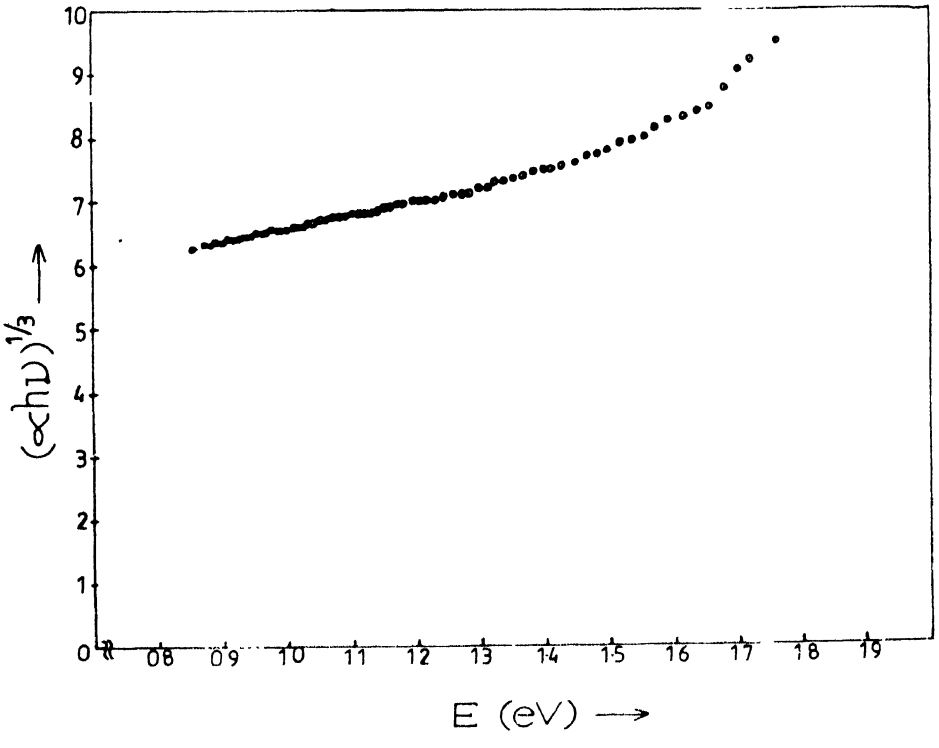

Figure 1. The spectral variation of $(\alpha h\nu)^{1/3}$ *vs* $h\nu$ for $Mo_{0.5}W_{0.5}Se_2$ crystal.

experimenal points on this curve. It is therefore conjectured that the indirect transitions represented by the absorption curve is an indirect allowed. In order to make an accurate

determination of the point of discontinuties in Figure 2 we have followed the method adopted by Koshkin *et al* [9] and Elkorashy [10].

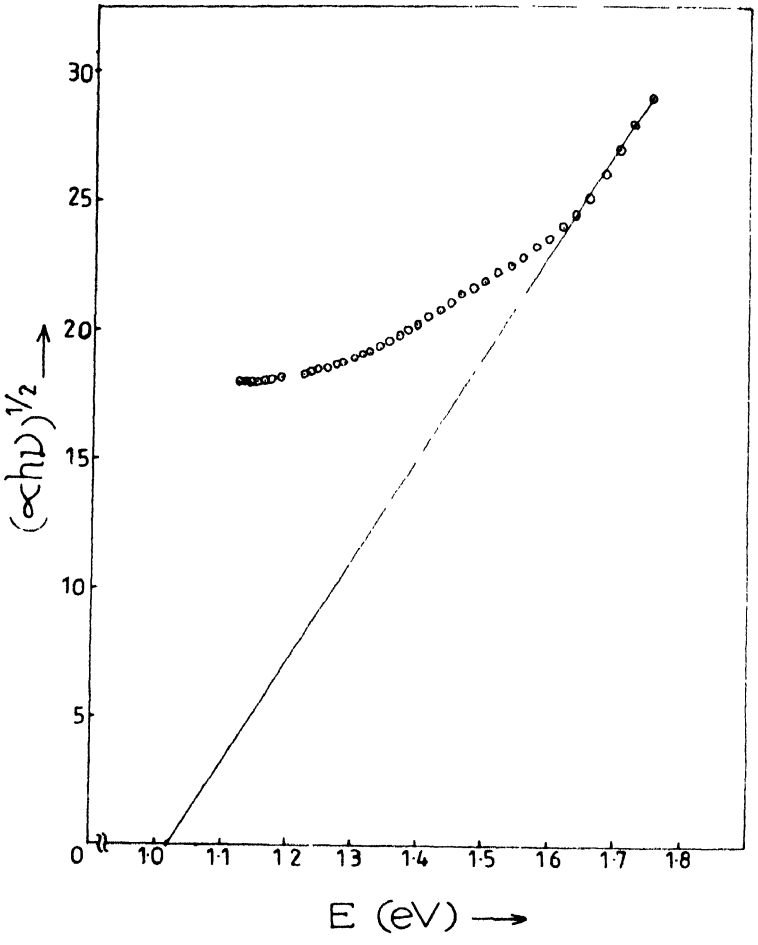

Figure 2. The spectral variation of $(\alpha h\nu)^{1/2}$ *vs* $h\nu$ for $Mo_{0.5}W_{0.5}Se_2$ crystal.

Accordingly from the graphical differentiation of the data presented in Figure 2 we have shown the dependence of the derivative $\delta(\alpha h\nu)^{1/2}/\delta E$ on $h\nu$ in Figure 3. It can be clearly seen from this figure that the derivatives are step functions of energy with four steps well defined in the range

$$E_1 < E < E_2,$$

$$E_2 < E < E_3,$$

$$E_3 < E < E_4,$$

$$E_4 < E.$$

The values of E_1, E_2, E_3 and E_4 indicate the points of discontinuities in the plot of $\delta(\alpha h\nu)^{1/2}/\delta E$ *vs* $h\nu$ in Figure 3.

The indirect energy gap obtained from these values of E_1, E_2, E_3 and E_4 are given by

$$E_g' = \frac{E_1 + E_4}{2} = \frac{E_2 + E_3}{2}$$

and the phonon energies are given by

$$E_{p1} = \frac{E_4 - E_1}{2} \quad \text{and} \quad E_{p2} = \frac{E_3 - E_2}{2}$$

The value of E_g' can also be obtained from the intersection of the linear protion of graph in Figure 2 with the energy axis. This value is in good agreement with value obtained from equations above.

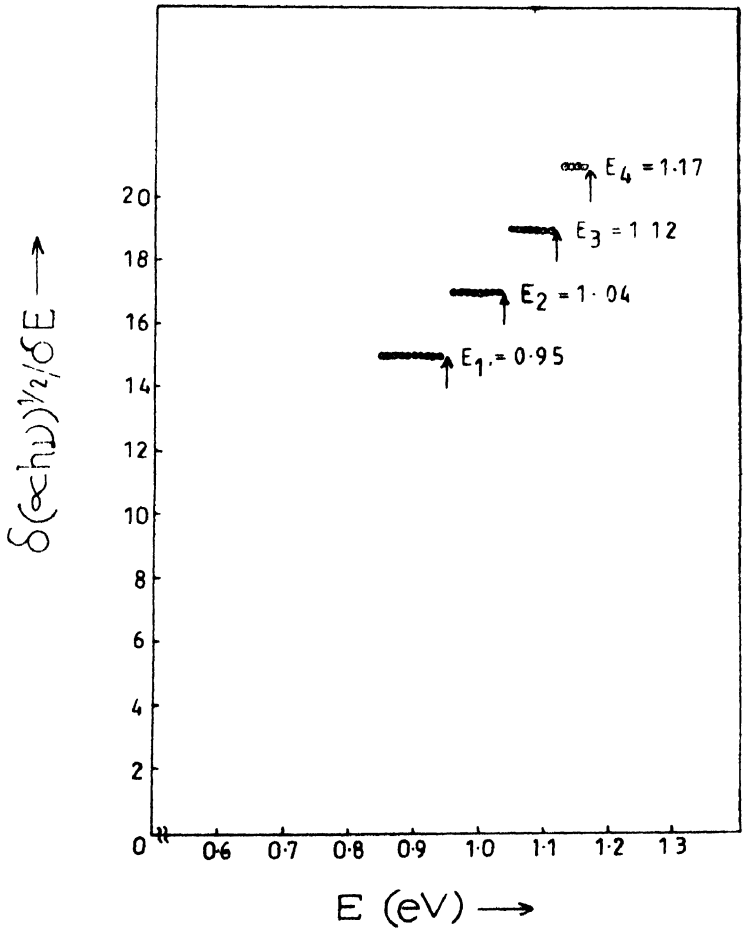

Figure 3. The dependence of $\delta(\alpha h\nu)^{1/2}/\delta E$ on $h\nu$ for $Mo_{0.5}W_{0.5}Se_2$ crystal.

In order to analyse the data from absorption spectrum on the basis of two dimensional model, we studied the variation of $\alpha^{1/2}$ *vs* $h\nu$. However it was not possible to fit the experimental results on a straight line. It was therefore conjectured that the two dimensional model does not work in the present case.

According to theory, for an indirect interband transition, the absorption coefficient can be written as

$$\alpha = \sum_{l=1}^{-} \left\{ B_{na} \frac{1}{\exp\left(E_{pl}/kT\right) - 1} \left(h\nu - E_g' + E_{pl}\right)^n \right.$$

$$\left. + B_{ne} \left[1 - \exp\left(-E_{pl}/kT\right)\right] \left(h\nu - E_g' - E_{pl}\right)^n \right\},$$

where B_{na} and B_{ne} are temperature dependent coefficients representing the processes with phonon absorption and phonon emission, E_{pl} is the energy of the phonon assisting at the transition, $n = 2$ or 3 for indirect allowed and indirect forbidden transitions. From the expression for E_{pl}, we define a phonon equivalent temperature $\theta_l = E_{pl}/KT$.

The energy values E_1, E_2, E_3, E_4 together with indirect energy gap E_g' as well as the two phonon energies E_{p1} and E_{p2} as obtained on the basis of three dimensional indirect (forbidden and allowed) models are shown in Table 2. Knowing the values of $h\nu$, E_g', E_{pl} at room temperature, the constants B_{a1}, B_{a2}, B_{e1}, B_{e2}, θ_1, θ_2 have been determined and are also given in Table 2.

Table 2. Various parameters and constants obtained from the indirect band gap measurements for $Mo_{0.5}W_{0.5}Se_2$ single crystals.

	Indirect (allowed)	Direct (allowed)
E_1 (eV)	0.95	
E_2 (eV)	1.04	
E_3 (eV)	1.12	
E_4 (eV)	1.17	
E_g' (eV) C^*	1.06 and 1.08	
E_g' (eV) E^*	1.02	
E_g (eV)	–	1.56
E_{p1} (meV)	110	
E_2 (meV)	40	
θ_1 (K)	1289.5	
θ_2 (K)	468.9	
B_{a1} (cm^{-1} eV^{-1})	32.787	
B_{e1} (cm^{-1} eV^{-1})	2202.826	
B_{a2} (cm^{-1} eV^{-1})	1697.089	
B_{e2} (cm^{-1} eV^{-1})	979.216	

C^* indicates the indirect band gap obtained from calculation and

E^* indicates the indirect band gap obtained from the extrapolation curve of $(\alpha h\nu)^{1/2}$ *vs* $h\nu$.

For the determination of the direct band gap, the best fit for all the experimental points was observed in the case of $(\alpha h\nu)^2$ *vs* $h\nu$ plot (Figure 4). The value of E_g obtained

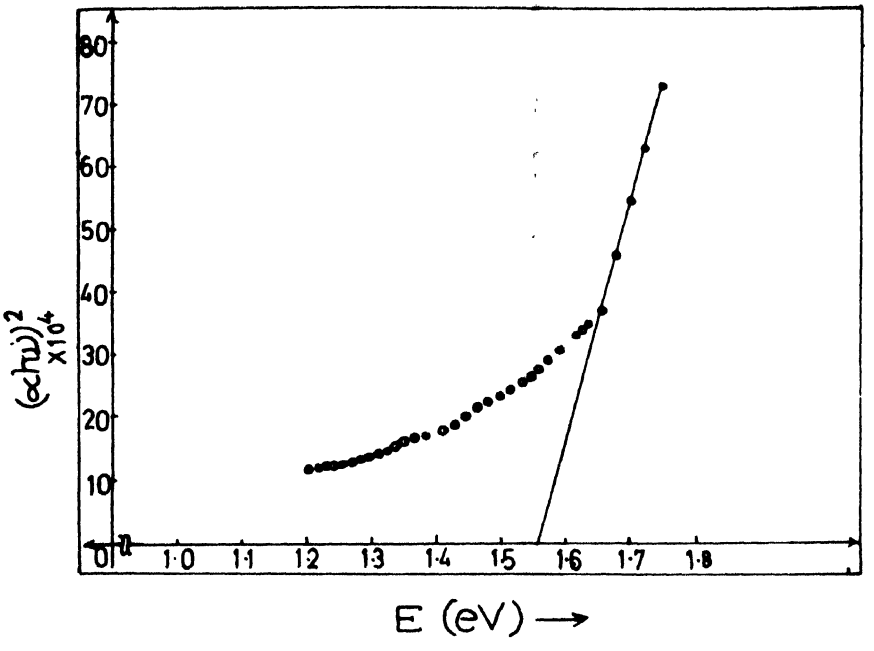

Figure 4. The plot of $(\alpha h\nu)^2$ *vs* $h\nu$ for $Mo_{0.5}W_{0.5}Se_2$ crystal

from the intercept of the straight line portion of the curve on the $h\nu$ axis is also shown in Table 2

4. Conclusions

The analysis of accurate measurements of the optical absorption in $Mo_{0.5}W_{0.5}Se_2$ crystals has shown that this material possesses both direct as well as indirect band gaps. The phonon assisted indirect transition is indirect allowed. The energies of the phonons have been determined. Further, it is concluded that the two dimensional model cannot be used satisfactorily to describe the main optical properties of $Mo_{0.5}W_{0.5}Se_2$ single crystals.

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