

Optical constants of $\text{Mo}_x\text{W}_{1-x}\text{Se}_2$ single crystal solid solutions

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Abstract. Single crystal solid solutions in the series $\text{Mo}_x\text{W}_{1-x}\text{Se}_2$ ($0 \leq x \leq 1$) have been studied by reflectivity measurements at oblique angles of incidence. The optical constants at a few wavelengths have been determined.

Keywords. Optical constants; optical energy gap; single crystal solid solutions.

1. Introduction

The dichalcogenides of Mo and W have been extensively studied for their interesting optical properties. These crystals exhibit very strong excitonic absorption in the visible region of the spectrum (Wilson and Yoffe 1969; Beal *et al* 1972). From transmission studies Beal *et al* (1972) considered the excitonic absorption peaks due to direct interband transitions. Photoemission measurements by Shepherd and Williams (1974) indicated that the band gap in these materials may be larger than that proposed by Wilson and Yoffe (1969). Goldberg *et al* (1975) proposed a modified band scheme and have suggested that the strong absorption above 1.8 eV in 2H-MoSe₂ and 2H-MoS₂ are due to direct allowed transitions. In the present study an attempt has been made to determine the optical constants at a few wavelengths in the visible region, of the single crystal solid solutions $\text{Mo}_x\text{W}_{1-x}\text{Se}_2$.

2. Experimental

The R_p/R_s method of reflectivity measurements has been employed (Goswami and Rao 1974). The optical constants have been determined from the R_p/R_s values by a graphical method due to Avery (1952). The details of the instrumentation and experiment have been published earlier (Agarwal *et al* 1980).

The crystals used in the present study have been grown in this laboratory by a direct vapour transport technique (Agarwal and Wani 1979). Stoichiometrically mixed powders of molybdenum (99.95 % pure), tungsten (99.95 % pure) and

selenium (99.999 % pure) were placed in etched and vacuum-backed quartz ampoules of 0.02 m diameter and 0.21 m length. The ampoules were evacuated to 10^{-5} torr and sealed. A charge was prepared after 40 hr of heating in a two zone furnace having a linear temperature gradient around 800°C. The temperature was controlled to within $\pm 1^\circ\text{C}$ by Eurotherm controllers. The resulting free flowing compound was vigorously mixed and again placed in the furnace for crystal growth for 150 to 240 hr. Growth temperatures were from 900 to 1060°C.

The crystals grown were analysed by electron microprobe analysis for their composition and the lattice parameters were determined by x-ray powder method. The crystals were found to have their nominal composition; and a linear variation of the lattice parameters with composition was obtained. The crystals used have either 2H or mixed 2H/3R polytypes. The as-grown faces of the crystals perfectly shine and easily lend themselves for reflectivity studies. Wherever the surfaces were not clean, a fresh cleavage was used.

Five wavelengths, obtained from a mercury vapour lamp with appropriate filters (5461 Å, 4360 Å, 4050 Å), a sodium vapour lamp (5893 Å) and a helium neon laser (6328 Å) were used for the study. The absorption coefficients have been derived from the experimentally determined extinction coefficients k using the relation $\alpha = 4\pi k/\lambda$.

3. Results and discussion

Table 1 represents the values of n , k and α for these crystals. For MoSe_2 and WSe_2 the absorption coefficients obtained are almost half of those values obtained for 2H- MoSe_2 and 2H- WSe_2 by Wilson and Yoffe (1969) from transmission measurements; and by Beal *et al* (1976) and Beal and Hughes (1979) from normal incidence reflectivity measurements. Antoci *et al* (1972) have determined the refractive index and the extinction coefficients of 2H- WSe_2 , at room temperature, by ellipsometric measurements. Their results agree fairly well with those obtained in the present study (see table 1). Here it must be mentioned that there will be difference, quantitatively and qualitatively, in the absorption for the $E \perp c$ and $E \parallel c$ cases (Liang 1973). And, in the R_P/R_S method of reflectivity at oblique angles of incidence only average values (with respect to the two polarizations) of the absorption coefficients can be obtained. And hence the better agreement with the results of Antoci *et al* (1972). It has also been suggested by Liang (1973) that as the crystals have high refractive indices ($n \sim 4$) the reflectivity at oblique angles of incidence will be preferable only when: (i) the light is incident on the crystal surface from a dielectric of high refractive index or (ii) at higher energies when the refractive indices are comparatively smaller. This limitation of the method chosen also may have caused a deviation of the parameters determined here from those determined by transmission or normal incidence reflectivity measurements. Further, as the crystals grow at high temperatures there is always a possibility of slight deviations from stoichiometry. Such impurities will play an important role in the absorption process (Liang and Yoffe 1967).

Table 1. Optical constants of $\text{Mo}_x\text{W}_{1-x}\text{Se}_2$ single crystals.

λ (Å)	4050			4360			5461		
	n	k	α 10^7 m^{-1}	n	k	α 10^7 m^{-1}	n	k	α 10^7 m^{-1}
Composition X	1	2	3	4	5	6	7	8	9
0.0 (WSe_2)	4.12 (3.65) ^a	2.64 (2.55)	8.19 (4.85)	4.28 (3.92)	2.58 (2.40)	7.44 (4.11)	4.76 (4.38)	1.79 (1.77)	4.12 (1.89)
0.1	3.15	2.77	8.59	3.75	2.63	7.58	4.18	1.97	4.53
0.15	4.10	2.46	7.63	4.25	2.45	7.06	4.92	1.35	3.11
0.2	3.92	2.53	7.85	4.10	2.66	7.67	4.88	1.90	4.37
0.3	3.72	2.63	8.16	4.20	2.40	6.92	4.75	1.51	3.48
0.4	3.58	2.63	8.16	3.85	2.62	7.55	4.20	1.94	4.46
0.5	3.15	2.94	9.12	3.97	2.76	7.95	4.65	2.18	5.02
0.6	3.82	2.70	8.38	4.10	2.48	7.15	4.70	1.58	3.64
0.8	3.90	2.99	9.28	4.42	2.84	8.18	4.85	2.04	4.70
0.9	3.70	2.92	9.06	4.07	2.77	7.98	4.67	2.02	4.65
1.0 (MoSe_2)	3.00	3.32	10.30 (4.95)	3.60	2.98	8.59 (4.84)	4.42	2.49	5.73 (2.26)

λ (Å)	5893			6328		
	n	k	α 10^7 m^{-1}	n	k	α 10^7 m^{-1}
Composition X	10	11	12	13	14	15
0.0 (WSe_2)	4.68 (4.68)	1.88 (1.65)	4.01 (0.38)	4.98 (4.75)	0.64 (1.16)	1.27 (0.62)
0.1	4.45	2.17	4.63	3.70	1.81	3.59
0.15	4.75	1.55	3.31	6.75	1.20	2.38
0.2	4.55	1.73	3.69	4.48	0.97	1.93
0.3	4.72	1.75	3.73	3.92	1.46	2.90
0.4	3.45	2.37	5.05	4.40	1.40	2.78
0.5	4.60	2.08	4.44	5.00	1.30	2.58
0.6	4.55	2.40	5.12	5.05	1.93	3.83
0.8	4.72	2.02	4.31	3.65	1.63	3.24
0.9	4.80	1.54	3.50	4.55	1.42	2.82
1.0 (MoSe_2)	3.40	3.32	7.08 (1.56)	4.62	1.68	3.34 (1.10)

^a Values in parantheses from Antoci *et al* (1972) for n and k ; from Beal and Mughes (1979) for α .

The functional dependence of absorption coefficient α on photon energy in the region near an Mo type critical point is given by Lee *et al* (1969). Thus for direct-allowed transitions $\alpha^2 \approx (h\nu - E_g)$. The relation is strictly true only for parabolic energy bands in isotropic structures and here we are concerned with anisotropic material. Nevertheless, to get a rough estimate of the optical energy gap one can consider the above relation to be valid, neglecting excitonic effects (Goldberg *et al* 175).

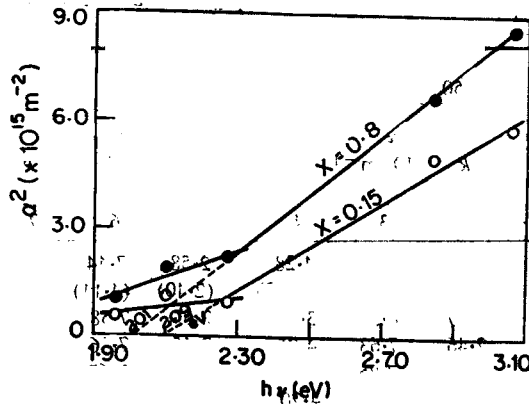
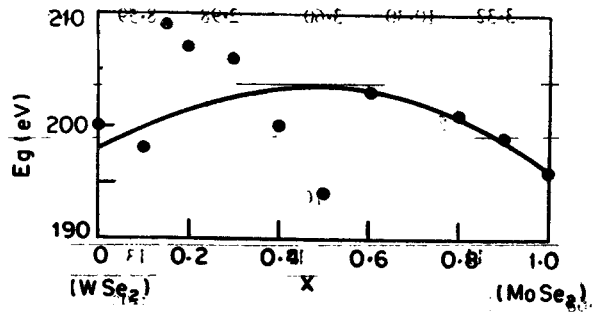
Figure 1. α^2 vs $h\nu$ plots for two crystals.

Figure 2. Variation of energy gap with composition.

Figure 1 shows typical plots of α^2 vs $h\nu$. $(E_g)_{opt}$ values have been determined from the X -intercept of the plots. Figure 2 shows the variation of $(E_g)_{opt}$ with composition x .

For $2H-MoSe_2$ considering photon energies from 1 to 1.5 eV, Goldberg *et al* (1975) obtained $E_g = 1.19 \pm 0.01$ eV at 290 K and have suggested that the fundamental absorption edge is associated with direct transitions between the d -like valence band (d_1) and d -like conduction band (d_1 , d_2 , d_3 , etc.) Further, it has been suggested that the uppermost d -like valence band overlaps the lower p -like (formed from Se $4s$ and $4p$ orbitals) band and the excitons A and B originate from transitions (p -valence band $\rightarrow d$ -conduction band).

Photoemission studies by Shepherd and Williams (1974) on $2H-MoSe_2$ and $2H-WSe_2$ give the minimum values of the $d-d$ gap to be 1.4 and 0.8 eV respectively. Evans and Hazelwood (1971) obtained the direct band gap for $2H-MoSe_2$ and Davey and Evans (1972) for $2H-WSe_2$ by transmission measurements at 77 K to be 1.67 ± 0.02 eV and 1.96 ± 0.02 eV and 1.78 ± 0.02 eV respectively. All these workers considered the excitons A and B as due to $d-d$ -transitions.

Thus, it is seen that there is no consistency in the values of the energy gap quoted in literature and the problem requires further analysis. The present study cannot settle the matter but it does give an idea as to how the band structure changes with composition in this system. It has been suggested by Wilson and Yoffe (1969) that the excitons *A* and *B* move linearly with composition in a system like (Mo/W)Se₂ or Mo(S/Se)₂. As a continuous range of wavelengths was not available for the study, such an analysis was not possible. More elaborate work on the optical properties of these crystals is required to study the variation of band structure with composition.

4. Conclusions

The optical constants of single crystals in the series Mo_xW_{1-x}Se₂ ($0 \leq x \leq 1$) determined at room temperature by reflectivity measurements at oblique angles of incidence are presented. The results for the end compounds of the system *viz.* WSe₂ and MoSe₂ are compared with the data available from literature and discussed. The optical energy gap for MoSe₂ and WSe₂ are found to be 1.96 and 2.00 eV respectively. The necessity for further work on the optical properties is stressed.

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