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Optical transitions in WSe_2 single crystals

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Optical absorption in single crystals of WSe_2 has been measured at room temperature near the fundamental absorption edge using light parallel to c – axis incident normally on the basal plane. Results have been analyzed on the basis of three dimensional (3D) and two dimensional (2D) models. Absorption near the fundamental edge was found to be due to indirect and direct allowed transitions on the basis of 3D model and indirect allowed transition on the basis of 2D model. The optical energy gaps corresponding to both transitions have also been determined.

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1. Introduction

The transition-metal dichalcogenides (TMDC) such as MX_2 (M=W or Mo and X= S, Se) show a wide variety of interesting anisotropic physical and electrical properties [1]. They display semiconducting, metallic, superconducting and magnetic behaviour [1-4]. The layered TMDCs crystallize in a lattice with strong covalent bonds within an X-M-X sandwich layer and weak van der waals (VdW) type bonding between the individual layers. Also, the strong anisotropy in the chemical bonds leads to anisotropy of the optical and electrical properties of these materials parallel and perpendicular to the layers [5]. Tungsten diselenide is a diamagnetic semiconductor and belongs to the family of transition metal dichalcogenides. It is transparent in the infrared region and thus may be used as optical windows [6]. However, the size and properties of grown crystals as well as the morphology has been found to depend on growth conditions e.g. temperature profile, heating and cooling rate, duration of growth in addition to transporters used etc. It has been reported that PEC conversion efficiency considerably depends on morphology [7].

The optical absorption is known to arise through the interaction of the excited electrons with the lattice perturbed by vibrations or imperfections. In fact, the absorption phenomenon can be considered quantum mechanically [8] as a two – step process in which the electron absorbs a photon and is excited to an intermediate state, where it interacts with the lattice vibrations or impurities and reaches a final state, the net result being the absorption of a photon. Here, the authors present the study of optical properties of WSe_2 single crystals grown by direct vapour transport technique.

2. Experimental

The room temperature absorption spectra of WSe_2 have been taken using UV- VIS-NIR spectrometer (SHMADZU-UV-365) in the wavelength range of 200 – 2000nm. For these measurements, the crystal was pasted on a thick black paper with a cut exposing the (001) plane of the crystals to the incident radiation. The reference used was a replica of the black paper having the cut in exactly the same position. This arrangement is necessary because the crystal size is smaller than that of the sample compartment. Both sample and reference were exposed to UV radiation through a chopped beam and by measuring the transmitted intensity through the sample, absorption spectrum was recorded.

All measurements were carried out at room temperature with the incident beam normal to the basal plane of as-grown crystals i.e. along c-axis of the grown crystals. Measurements along the other axes could not be performed since the specimens (too thin) were unable to be mounted along those directions.

3. Results and discussion

Fig. 1 shows the absorption spectrum taken from a WSe_2 single crystal in the form of a thin platelet over the spectral range 700 - 1400nm. A careful study of this spectrum reveals the presence of an absorption edge in the spectral range 810 - 990nm. In order to analyze the results in the vicinity of the absorption edge on the basis of three dimensional models, values of absorption coefficient 'α' were determined at step of 1nm.

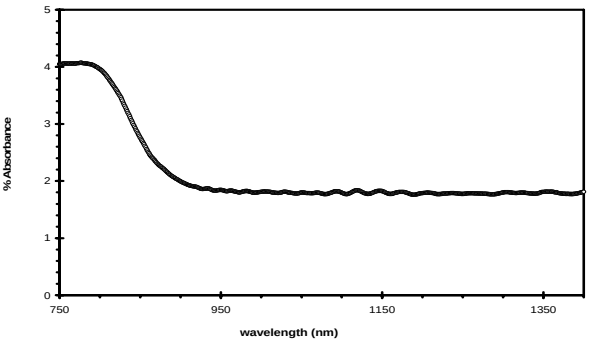

Fig. 1. Percentage of absorbance vs. wavelength for WSe_2 single crystal.

The interpretation of experimental results, in terms of the direct and indirect transitions is most often performed with the help of the following equations (1) and (2) for three dimensional (3D) model [9,10] using the values of r given in Table 1.

$$\alpha h\upsilon = A(h\upsilon - E_g)^r \quad (1)$$

for direct transitions and

$$\alpha h\upsilon = \sum_j B_j (h\upsilon - E_g' \pm E_{pj})^r \quad (2)$$

for indirect transitions

where hυis the energy of incident photon, E_g the direct band gap energy, E'g is the indirect band gap, E_{pj} the energy of absorbed (+) or emitted (-) phonon, the constants A and B assume different values for the allowed and forbidden transitions.

By plotting graphs of $(\alpha h\nu)^{1/r}$ vs. hν for various values of r given in Table 1, it is possible to determine which of the conditions given in the table dominate. Extrapolation of these plots to zero absorption will give the appropriate value of the energy gaps of WSe_2 single crystal.

Table 1. Values of the exponent r for different types of band gap transitions

Type of transition	Direct		Indirect	
	2D	3D	2D	3D
Allowed (Step function)	0	1/2	1	2
Forbidden	1	3/2	2	3

Accordingly, the inset of Fig. 2 shows the spectral variation of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ vs. hν respectively. Since both the curves indicate discontinuous straight lines it is quite possible that they represent indirect interband transitions involving the emission or absorption of phonons. However from Fig. 2, it is seen that it is not possible to fit all the experimental points on $(\alpha h\nu)^{1/3}$ curve. It is therefore conjectured that the indirect transition represented by the absorption curve is an indirect allowed type. The values of indirect energy gaps obtained from the intercepts are 1.145 eV and 0.97 eV (Fig. 2). The value of indirect allowed type transition is close to the value obtained by most of the workers [11, 12].

In order to analyse the data from the absorption curve on the basis of 2D model by considering the plot of $\alpha^{1/r}$ vs. hν for various values of r given in Table 1 using the following equation [6]

$$\alpha = A'\left(h\nu - E_g\right)^r \quad (3)$$

Fig. 3 shows the spectral variation of (α) and $(\alpha)^{1/2}$ vs. hν respectively. The best fit of all the experimental points was observed only in the case of (α) vs. hν(Fig. 3). Hence, the 2D indirect transition is the allowed type. The values of indirect band gaps in 2D model are found to be 1.288 eV and 1.10 eV respectively.

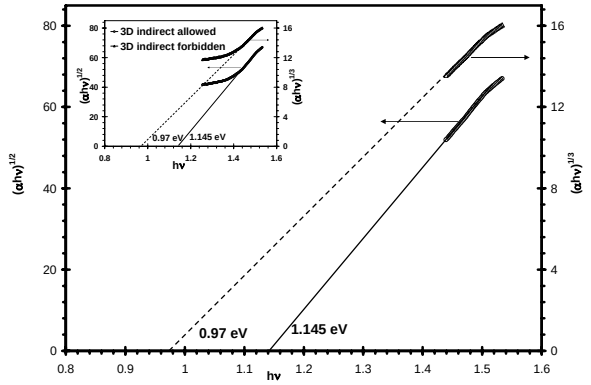

Fig. 2. The spectral variation of $(\alpha h\nu)^{1/2}$and $(\alpha h\nu)^{1/3}$ vs. $h\nu$ for WSe_2 single crystal.

For the determination of the direct band gap, the best fit of all the experimental points was observed in the case of $(\alpha\eta\nu)^2$ vs. hν (Fig. 4). The value of E_g obtained from the curve is 1.399eV, which is in good agreement with the value obtained by most of the workers [13-15].

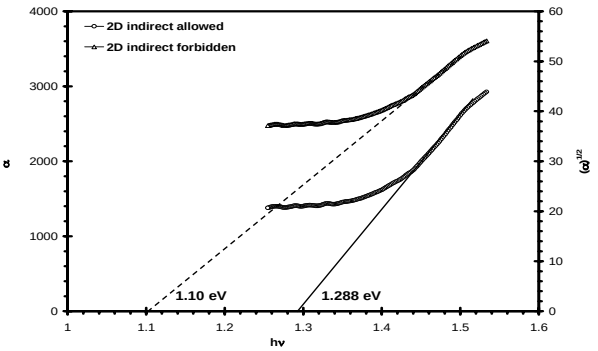

Fig. 3. The spectral variation of (α) and $(\alpha)^{1/2}$ vs. $h\nu$ for WSe_2 single crystal.

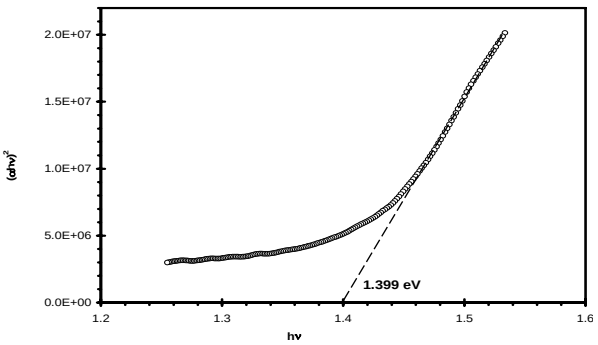

Fig. 4. The spectral variation of $(\alpha h\nu)^2$ vs. $h\nu$ for WSe_2 single crystal.

4. Conclusions

It is found that grown crystals show allowed type direct and indirect optical transitions in 3D model. The allowed indirect transition is seen even in 2D model. The values of direct and indirect energy gaps determined in the present work are in good agreement with the values obtained by most of the workers. This shows that the morphology and growth conditions do not contribute significantly to these optical absorptions, since such absorptions are likely to be dominated by bulk of the material.

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