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Research Article

OPTICAL PROPERTIES OF NbS_xSe_{2-x} SINGLE CRYSTALS

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ABSTRACT
The optical properties of as grown crystals have been obtained by optical absorption. The optical spectra of NbS_xSe_{2-x} (x = 0, 0.5, 1, 1.5 and 2) single crystals have been measured at room temperature near the fundamental absorption edge. Results have been analyzed on the basis of three-dimensional models. Both direct as well as indirect transitions are involved in the absorption process. The indirect transition was found to be allowed with two phonons involved in the process. The three-dimensional model can be used to describe the optical optical properties of NbS_xSe_{2-x} single crystals. They direct and indirect energy gap and phonon energies for all the crystals have been estimated and described in detailed.

Key Words: *Transition Metal Dichalcogenides, Optical Parameters, Band Gap*

INTRODUCTION
The transition metal dichalcogenides NbS_2 and $NbSe_2$ are layer compounds consisting of sandwiches with strong covalent/ionic intralayer bonds and weak Van der Waals interlayer interactions. These MX_2 (M = Nb, Ta and X = S, Se) are of interest for many technological applications. They are suitable for use as high-temperature lubricants, hydrogenation catalysts, and batteries due to weak van der Waals interactions between adjacent layers in the MX_2 lattice (Lewkebandara and Winter, 1994; Whittingham, 1978; Cheon *et al.,* 1997; Nazri *et al.,* 1989). The single crystal of $NbSe_2$ and NbS_2 were grown by chemical vapour transport technique. The structural properties of NbS_2 single crystals have been studied (Vaidya *et al.,* 2005, Dave *et al.,* 2012). The band structure of 2H-MX_2 (M= Nb, Ta, X = S, Se) crystallize in the structure in which M atoms are sandwiched by X sheets of trigonal prismatically arranged chalcogen atoms. The superconducting properties of the transition-metal dichalcogenides TaS_2, $TaSe_2$, NbS_2 and $NbSe_2$ have been studied as a function of structural disorder induced by heavy-ion bombardment and by deintercalation at temperatures between 300 K and 800 K (Tsang *et al.,* 1975). The band structure of 2H-NbS_2 the S 3s states dominate the four bands with lowest energy. These bands are separated by a gap of 5.3 eV from the highest valence bands, which consists mainly of S 3p orbitals (Fang *et al.,* 1995). The peak positions correspond quite closely to those seen in 3R-NbS_2, and are in basic agreement with band structure calculations for group Va sulphur compounds (Mattheiss 1973). The resulting electronic structure was described in terms of the rigid band model, i.e. the band structure is not affected by any changes except for a shift of the Fermi level to higher energies. Structure elucidation of the hexagonal platelets yielded crystal structures in the space group $P6_3/mmc$ with NbS_2 layers, separated by intercalated alkali metals. The alkali metal niobium disulphides exhibit many interesting properties such as ionic/electronic conductivity (Harper, 1977) and superconductivity (McEwen and Sienko, 1982; Gareh *et al.,* 1995). The optical and electrical properties of the transition metal dichalcogenides have been investigated by many authors (Frind *et al.,* 1963; Evans *et al.,* 1965, 1967).
The structural properties of $NbSe_2$ single crystal was observed by
However, looking at the importance of optical band gap in these materials and because of the fact that no such information available for these single crystals, the authors have carried out a detailed study on the determination of optical band gap in these materials by optical absorption. The results thus obtained have been described in this paper.

Research Article

Experimental

Niobium sulphoselenide single crystals have been grown by a chemical vapour transport technique using iodine as transporting agent. The chemical composition of the as grown samples has been well confirmed by carrying out EDAX analysis. The structural properties of crystals have been measured with the help of X-ray diffraction analysis. The optical band gap of as grown crystals has been measured with the help of UV-VIS-NIR photo spectrometer (Make: Perkin Elmer, Model: Lambda –19). For obtaining the absorption spectra from single crystal specimens, thin flakes of as grown crystals are used. These flakes are pasted on a thick black paper with a cut exposing the crystal flake to the incident light. The reference used is a replica of the black paper, having the cut at exactly the same position as the crystal flake. This arrangement is necessary because the crystal size is smaller than that of the sample compartment. Blank glass slides can also use as replica. The optimum conditions for the growth of niobium sulphoselenide single crystals are shown in Table1. For reflectance measurement standard aluminum coated mirror can be used as reference. The absorption spectra of as grown crystals are shown in Figure 1.

RESULTS AND DISCUSSION

The interpretations of experimental results, viz the dependence of absorption coefficient 'α' in the term of the direct and indirect transitions is most often performed with the help of formula derived for three dimensional (3D) crystal their simplest form is as follows (Pankow, 1965).

for direct band gap $$\alpha h\upsilon = A(h\upsilon - E_g)^r \quad (1)$$

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

Here α is absorption coefficient, hν is the energy of the incident photon, Eg the energy for the direct transition, Eg' the energy for the indirect transition and E_{pj} the energy of the phonons assisting at indirect transition. A and B are parameters depending in the more complicated way on temperature, photon energy and phonon energies Ep.

Table 1: The optical parameter for NbS_XSe_{2-X} (x = 0, 0.5, 1, 1.5, 2) single crystals

Parameter	**$NbSe_2$**	**$NbS_{0.5}Se_{1.5}$**	**NbSSe**	**$NbS_{1.5}Se_{0.5}$**	**NbS_2**
E_1	1.38	1.41	1.44	1.46	1.40
E_2	1.41	1.44	1.46	1.47	1.46
E_3	1.43	1.47	1.48	1.48	1.52
E_4	1.46	1.49	1.50	1.49	1.58
$E_g^{'}$	1.43	1.45	1.47	1.48	1.49
$E_g^{'}$ (c)	1.42	1.45	1.47	1.48	1.49
Direct band gap E_g	1.46	1.46	1.48	1.51	1.56
E_p^1	0.039	0.043	0.030	0.019	0.09
E_p^2	0.014	0.14	0.010	0.006	0.03
θ_1	458.34	501.49	348.26	220.56	1044.78
θ_2	156.71	171.80	116.08	69.65	348.26

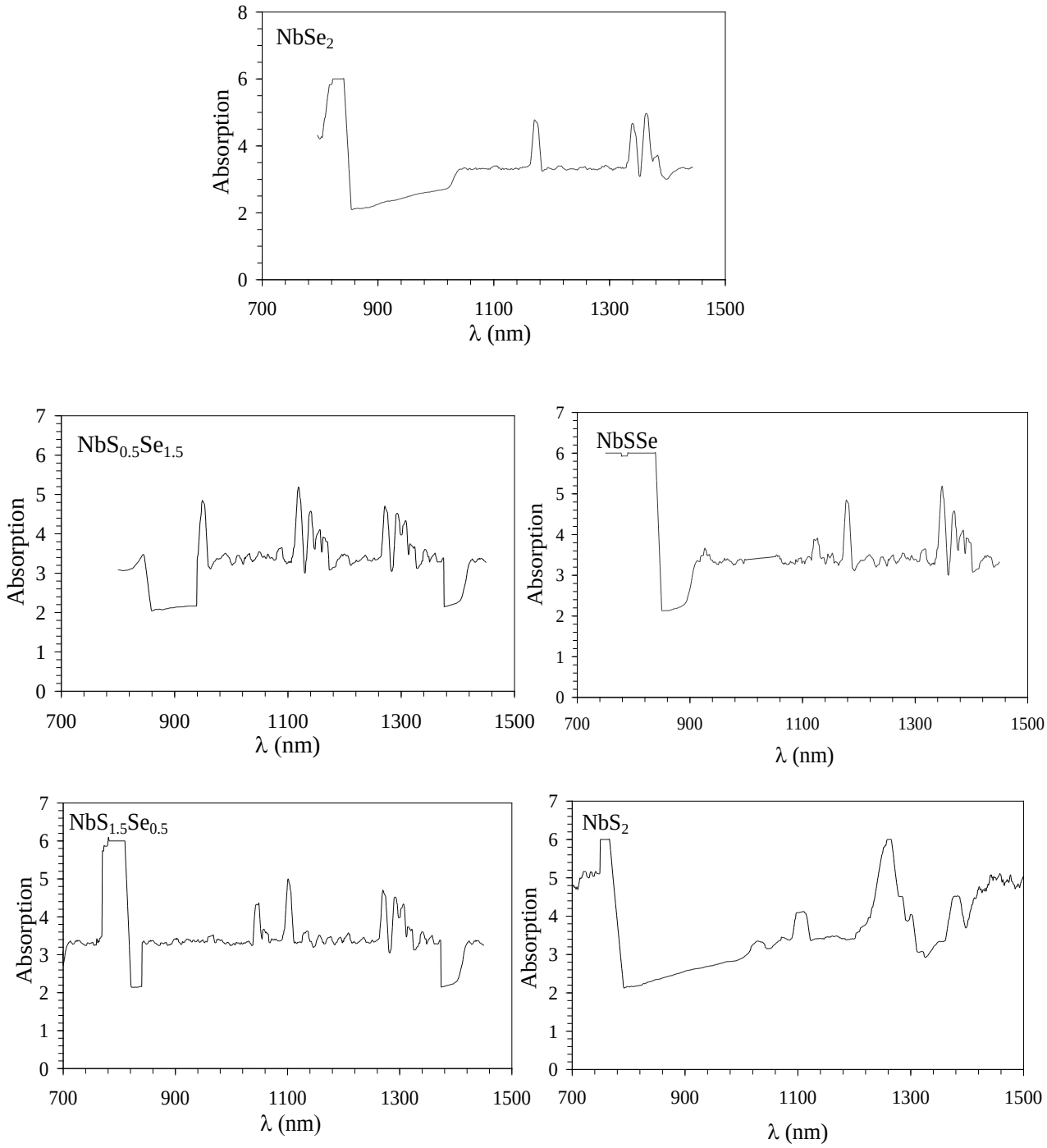

Figure 1: The graph of optical spectrum for as grown crystals of NbS_xSe_{2-x} (x = 0, 0.5, 1, 1.5 and 2) single crystals

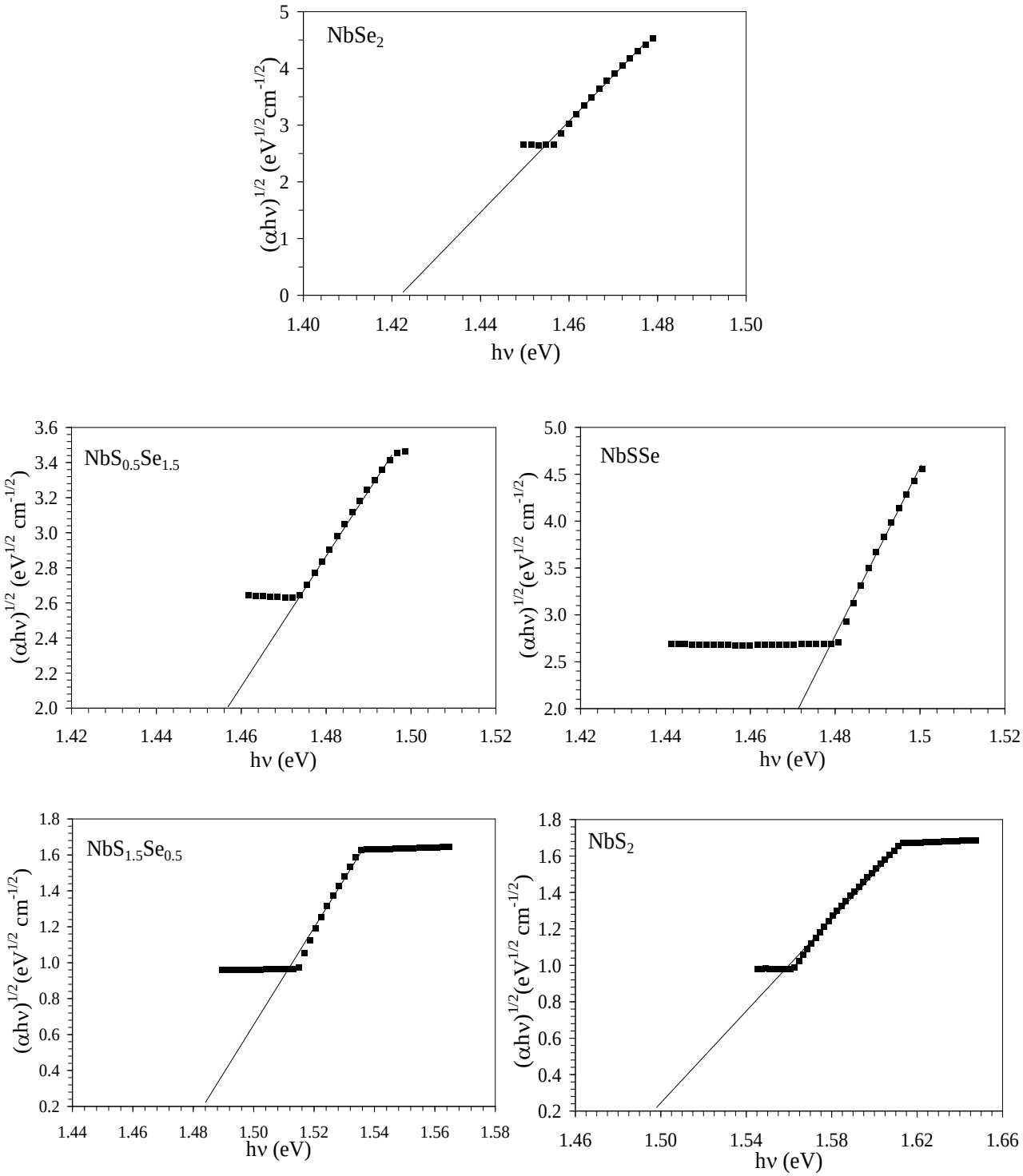

Figure 2: The graph of $(\alpha h\nu)^{1/2}$ versus hν for as grown crystals of NbS_xSe_{2-x} (x = 0, 0.5, 1, 1.5 and 2) single crystals

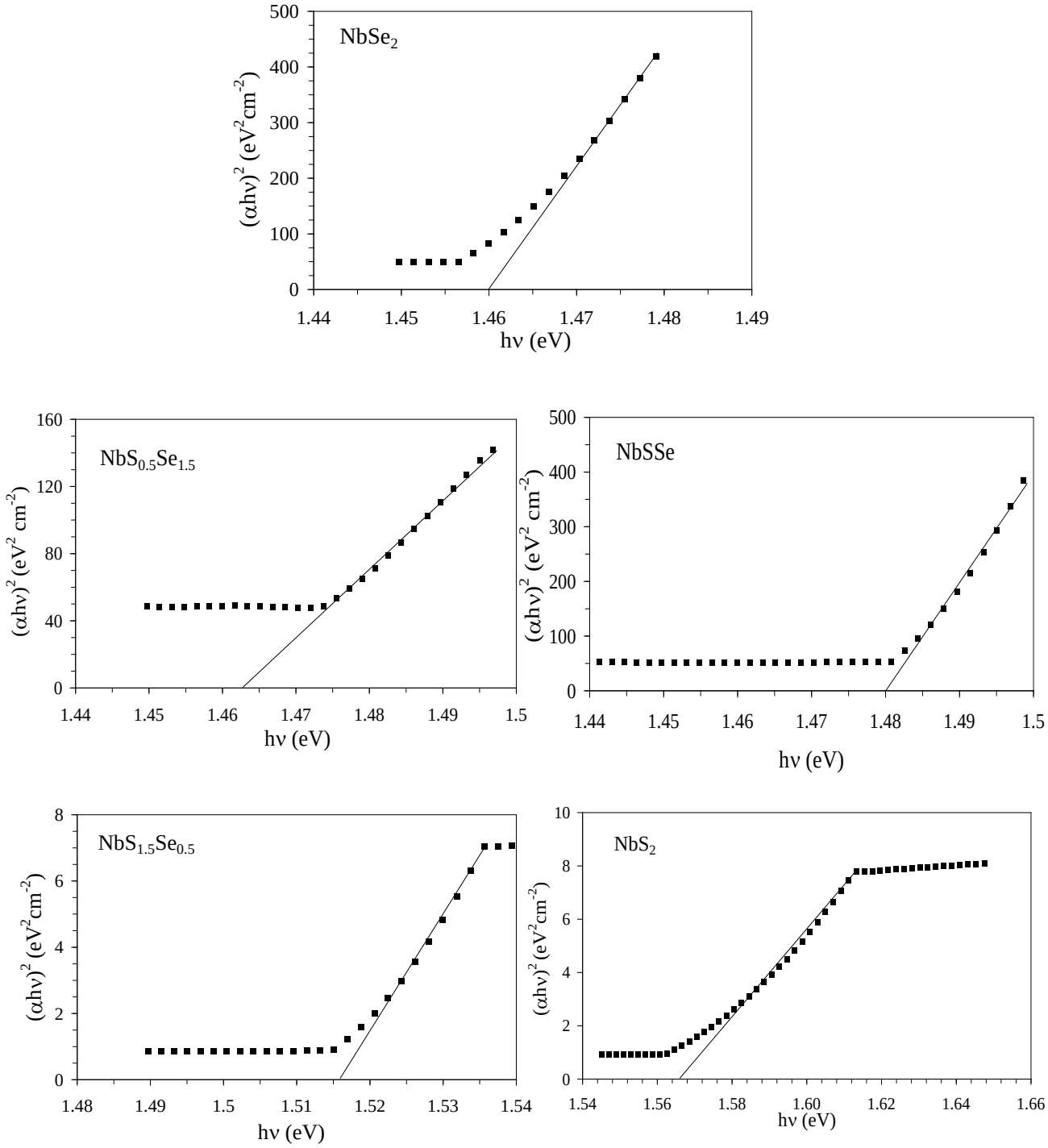

Figure 3: The graph of $(\alpha h\nu)^2$ versus hν for as grown crystals of NbS_xSe_{2-x} (x = 0, 0.5, 1, 1.5 and 2) single crystals

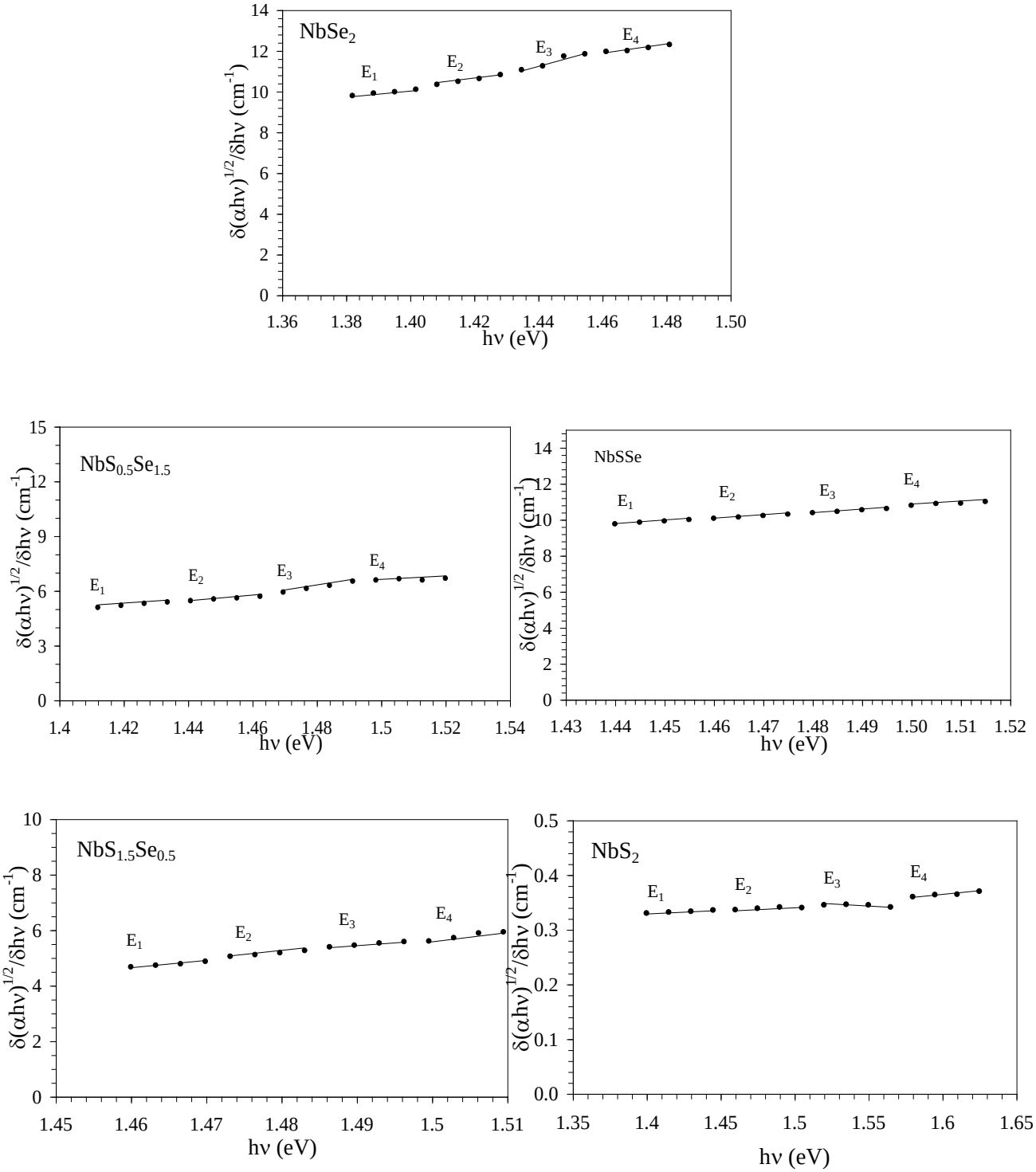

Figure 4: The spectral variation of $\delta(\alpha h\nu)^{1/2}/\delta h\nu$ versus hν for as grown crystals of NbS_xSe_{2-x} (x = 0, 0.5, 1, 1.5 and 2) single crystals

By plotting graph of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{2}$ vs hν as shown in Figures 2 & 3. It is possible to determine the indirect as well as direct band gap respectively for niobium sulphoselenide single crystals. As shown in

Figure 2 the curves indicated discontinuous straight line it is quit plausible that they are represent indirect interabands transition involving the emission or absorption of photons. The dependence of the derivation $\delta (\alpha h\nu)^{1/2}/\delta h\nu$ on $h\nu$ has been shown in Figure 4 for Niobium sulphoselenide single crystal. It can be clearly seen from the Figure 3 that the derivation are step function of energy with four steps well defined in the rang $E_1 < E < E_2$, $E_2 < E < E_3$, $E_3 < E < E_4$ and $E_4 < E$ given by

$$Eg' = \frac{E_1 + E_2}{2} = \frac{E_2 + E_3}{2} \quad (3)$$

and the phonon energies are given by

$$Ep' = \frac{E_4 - E_1}{2} \text{ and } Ep^2 = \frac{E_3 - E_2}{2} \quad (4)$$

the values of indirect band gap, direct band gap and phonon energy thus obtained are presented in Table 1.

Conclusion

This works described in this paper is an attempt to provide some explanation of the problem of dimensionality of the layered NbS_xSe_{2-x} single crystals. We conclude that, these compounds are indeed having a strong intarlayer bonding i.e. within the layer, compared to the interlayer bonding i.e. along the layers.

(1) The Niobium sulphoselenide single crystals are grown by chemical vapour transport (CVT) technique using iodine as a transporting agent.

(2) The analysis of the optical absorption in these crystals near the fundamental edge has been shown that both direct as well as indirect transition takes place in this compound.

(3) The indirect transition are involving two different phonons.

(4) The optical band gap increase with increase the sulfur proportion in the series NbS_xSe_{2-x} single crystals.

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