Purification, crystal growth and characterization of CdSe single crystals

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CdSe single crystals have been grown from the stoichiometric melt and from Se rich solutions. Here we report the first mid and far infrared spectra of CdSe crystals free of any known impurity bands. Previous studies of the lattice vibrational properties of CdSe crystals have shown the presence of two bands at 538 and 270 cm^{-1}. Modifications in the purification and crystal growth conditions lead us to assign these two bands to a sulfur impurity. Low temperature photoluminescence spectra are also presented and discussed.

1. Introduction

Wide-band-gap II–VI compounds, which include CdSe crystals, are important candidates for many electronic and optoelectronic devices. For example, the advantages of semi-insulating CdSe as a novel material for spectrometer-grade nuclear radiation detection application were recently reported [1]. Although the lattice vibrational properties of CdSe [2] and the localized modes in doped CdSe : S [3] and in mixed CdS_xSe_{1-x} single crystals [4–6] have been investigated in the past, some difficulties remain to be explained. First, a study of undoped CdSe [2] showed a sharp absorption band around 540 cm^{-1}, which was attributed to an unidentified impurity. This band was also present in all other mid IR (400–4000 cm^{-1}) spectra of CdSe reported in the scientific literature [7]. In the far IR region (70–500 cm^{-1}), the same study [2] reported a band observed around 270 cm^{-1} and assigned it to LO + TA and TO + LA phonon combinations. Second, in all far IR studies of S-doped CdSe or mixed CdS_xSe_{1-x}, the authors do not provide spectra of undoped CdSe [3,4], or report [6] the presence of the weak mode near 270 cm^{-1}, even for the "pure" CdSe crystals. Attempts to fit far infrared reflectivity data with a the classical dispersion formula [2,6], did not prove succesful. The crystals have been found [6] to contain 1–2% S impurity which causes a fine structure on top of the CdSe reststrahlen band.

The present study was triggered by the above problems and the need for high purity, stoichiometric CdSe single crystals to fabricate room temperature gamma-ray detectors. We demonstrate the use of infrared spectroscopy as a sensitive tool in the characterization of CdSe material and report the first mid and far IR spectra of CdSe single crystals free of any impurity bands. Our interpretation of the origin of the 270 and 538 cm^{-1} bands is discussed.

2. Experimental

2.1. Purification, synthesis and crystal growth

CdSe commercial reagents (Alfa, 99.999% purity on a metal basis, and General Electric, electronic grade) were subjected to repeated vacuum sublimations (VS) at 700 and 1000°C. Unlike Cd, Se is not commercially available in high purity. We used Se of 99.999% purity (Johnson Matthey) and purified it in a laboratory-built zone refiner [8]. Up to 40 g of raw material composed of Cd having 99.9999% purity (Cominco) and a stoichiometric amount of zone refined Se were loaded in a quartz reaction ampoule. The ampoule was vacuum sealed at 10^{-5} Torr, mounted in a rocking furnace, and the temperature was increased to 900°C at a rate of 100°C/day. After two weeks the reaction was completed and the charge, to-

gether with 10% additional Se, was used as starting material (SY) for growing crystals by the traveling solution method (TSM) [9]. The crystal growth ampoule had an internal diameter of 1 cm and was about 30 cm long. The crystal growth system included a three-zone furnace mounted on a vertical translational stage. The middle zone was narrow (approximately 3 cm) and its temperature was increased to 1160°C, while the upper and lower zones were kept at 970°C. The ampoule was static and the furnace was moved upwards at 0.5 to 2 cm/day. On growth experiment was performed without additional Se in a 7 mm ID quartz tube. The technique is equivalent to one pass of slow zone refining (ZR1). In this case the temperature of the middle zone was 1260°C, slightly above the melting point of CdSe ($M_p = 1248°C$).

2.1. Characterization

The samples were prepared by cleaving the crystal along the (10$\bar{1}$0) or (0001) planes, followed by grinding and polishing to the desired thickness. Lapping and etching were performed with solutions containing 10% bromine in methanol. Electric contacts were applied by vacuum evaporation of In and Au. The Fourier transform infrared spectra were recorded in the 240–4000 cm^{-1} range using a Bomem DA.3 FT-IR spectrometer at a resolution of 5 cm^{-1}.

Low temperature (20 K) photoluminescence (PL) measurements were performed on CdSe single crystals, TSM-SY and TSM-VS, and on a CdS crystal. Excitation was via the focused 488 nm line of an argon-ion laser with a power of 12 mW. The luminescence was focused into a detection system composed of a Spex model 1403 0.85 m double spectrometer and a photomultiplier. The spectra were measured in the range of 670 to 750 nm, with a resolution of about 0.1 nm,

3. Results and discussion

The diffuse reflectance infrared Fourier transform (DRIFT) spectra of CdSe powder purchased from two different vendors showed the presence of impurity peaks, as shown in fig. 1. Since the
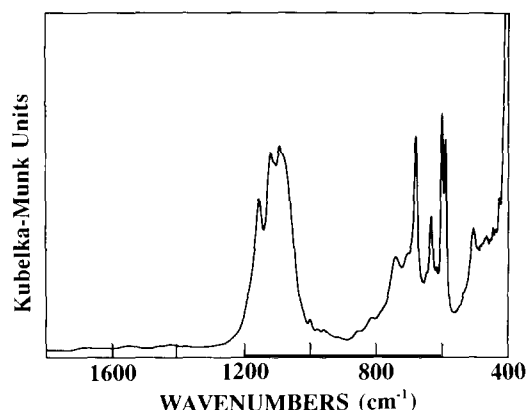

Fig. 1. The DRIFT spectra of the commercial CdSe powder showing the presence of the SO_4^{-2} group bands.

reaction of $CdSO_4$ with H_2Se is one common way to synthesize CdSe, the presence of an unreacted residue of $CdSO_4$ is one possibility for this major impurity. In order to confirm this possibility a DRIFT spectrum of $CdSO_4$ (not shown) was obtained and proved to have similar features. $CdSO_4$ is highly soluble in water, while CdSe is practically insoluble. As a first attempt, we tried to use a differential solubility method that would have separated the $CdSO_4$ impurity, if present as a second phase. Since no changes were observed in the DRIFT spectra following this treatment, we concluded that the $CdSO_4$ impurity forms a solid-solution with the major compound, CdSe. The DRIFT spectra of vacuum sublimed powders showed that the SO_4^{-2} bands disappeared, due probably to thermal decomposition. Apparently, the sublimation was not sufficiently efficient in removing the sulfur impurity, as was determined by the following measurements.

The CdSe crystals grown from the melt, ZR1, resulted in lower as-grown resistivities, of about $10^3–10^4$ Ω cm when compared with the medium resistivities obtained for the TSM crystals, which were in the $10^6–10^7$ Ω cm range. The IR measurements performed on ZR1 crystals showed a broad band in the 500 to 1200 cm^{-1} spectral region; fig. 2 shows a log-log plot of its absorbance versus wavelength at room temperature. A power law with a slope of 2.09 was obtained, which is characteristic of infrared absorption by free carriers
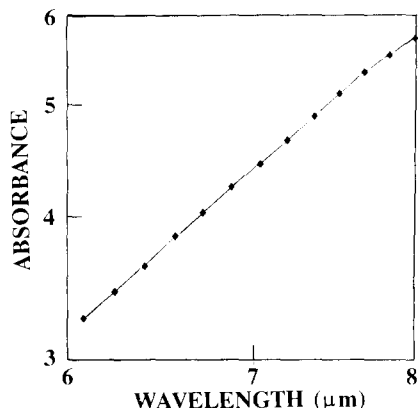
Fig. 2. Log-log plot of IR absorbance versus wavelength at room temperature. The power law with a slope of 2.09 is characteristic of infrared absorption by free carriers.

[10]. Free-carrier infrared absorption in CdSe was previously reported [11,12] in melt grown crystals and attributed to absorption due to free electrons, arising from a mixed contribution of optical mode and ionized impurity scatterings.

The IR spectra of CdSe crystals grown by TSM using starting material purified by vacuum sublimation, TSM-VS, showed an additional band at 538 cm^{-1} (not present in the DRIFT spectrum of the raw material), as shown in fig. 3a. In the far infrared region, presented in fig. 3b, a band around

270 cm^{-1} was present. Both he 538 and 270 cm^{-1} bands and the general features of the spectra were similar to the ones reported by Geick et al. [2].

To check the possibility of formation of a complex defect, the TSM-VS and the ZR1 CdSe as-grown crystals were further annealed in vacuum or in a Se atmosphere (4 days at 800°C). The infrared spectra, taken after the heat treatments, showed no significant effect on the TSM crystal, while in the ZR1 crystal the broad band feature disappeared after the heat treatment (HT) in Se atmosphere, leaving only the 538 cm^{-1} peak.

The most important results of this study were obtained for the crystals obtained from elemental Cd and Se as starting materials for the TSM experiments. Figs. 4a and 4b show the infrared absorbance spectra measured for a 0.5 mm thick sample; the absence of any major bands at 538 and 270 cm^{-1} is obvious. The facts that the 538 cm^{-1} band has almost twice the frequency of the 270 cm^{-1} band and that these two bands appear and disappear together, depending on the purification method, leads to the conclusion that both can be attributed to the same defect, and that the 538 cm^{-1} band is the second harmonic of the 270 cm^{-1} band. The absence of a band at 270 cm^{-1} indicates that its previous assignment [2] to LO + TA and TO + LA phonon combinations cannot
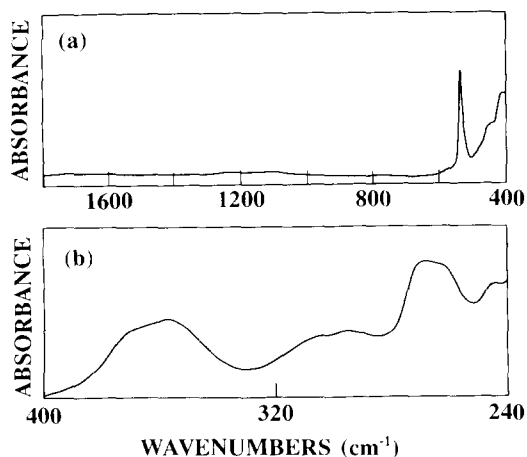

Fig. 3. The mid (a) and far (b) infrared spectra of CdSe crystals grown by TSM using commercial starting material purified by vacuum sublimation (TSM-VS) showing the 538 and 270 cm^{-2} bands.
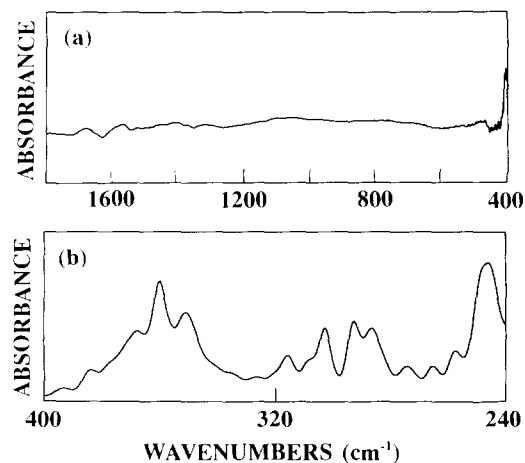

Fig. 4. The mid (a) and far (b) infrared spectra of CdSe crystals grown by TSM using high purity Cd and Se as starting materials (TSM-SY) showing the absence of the 538 and 270 cm^{-1} bands.

be supported. We attribute the origin of these two bands to a S impurity, because the 270 cm^{-1} mode is observed in S doped CdSe [3–6] and because these bands show only in crystals grown from commercial powders which contain the SO_4^{-2} impurity. It follows, therefore, that during the purification by vacuum sublimation and the high temperature crystal growth process, the SO_4^{-2} group becomes reduced to S^{-1}. Table 1 summarizes the infrared properties obtained for the different CdSe crystals investigated here.

Additional information, from photoluminescence (PL) spectra taken at 20 K for the TSM-VS and TSM-SY crystals, is presented in fig. 5. An additional spectrum (not shown) was obtained for a CdS crystal. In the TSM-SY crystal spectrum, the peak at 680 nm results from the recombination of a free exciton, referred to as X_A [13], and is clearly resolved from the peak centered around 68 nm, which is produced by a bound exciton. The dependence of the two PL spectra on the purification method used is another indication of the presence of defects due to extrinsic chemical impurities, rather than to native defects. Previous PL studies of CdS_xSe_{1-x} single crystals [14,15] reported a linear dependence of the bound exciton emission band, λ_{max}, on x, which provides an independent determination of the composition in these crystals. We have used the CdS and CdSe TSM-SY crystals as endmembers, assumed that the observed shift is due solely to the presence of the sulfur impurity (which qualitatively was determined by our IR measurements) and calculated a concentration of 0.7% of sulfur in the CdSe TSM-VS crystal.

In conclusion, it was shown that crystals of improved quality can be grown using the traveling solution method with synthesized CdSe as starting
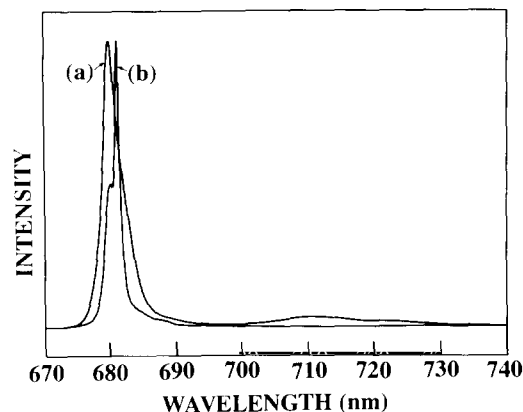

Fig. 5. Low-temperature photoluminescence spectra of the TSM-VS (a) and TSM-SY (b) samples.

material. In addition, IR spectroscopy of CdSe has elucidated the origin of the 538 and 270 cm^{-1} bands and facilitated the reassignment of the phonon combination bands in the multiphonon region of the spectrum of the sulfur free crystals.

Table 1
Summary of the infrared properties obtained in this study

Crystal growth	Purification	Infrared peaks (cm^{-1})
ZR1-VS	Vacuum sublimation	50–1200
ZR1-VS-HT	Vacuum sublimation	270, 538
TSM-VS	Vacuum sublimation	270, 538
TSM-SY	Synthesis, Cd + Se	No impurity peaks

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