

OPTICAL AND RELATED PROPERTIES OF THE SYNTHETIC QUASI-TWO-DIMENSIONAL SEMICONDUCTORS $K_2Cd_3S_4$, $Rb_2Cd_3S_4$ AND $Cs_2Cd_3S_4$

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During the last few years, a large number of low-dimensional (LD) semiconducting systems based on inorganic units, i.e., quantum wells (2D), quantum wires (1D), and quantum dots (0D) have been prepared and studied (for a review see [1]). It has been found that, when the dimensionality of the inorganic-units network decreases, the peak position of excitons is shifted to higher energy with increased excitonic binding energy and oscillator strength. In the case of PbI_6 -based perovskites, for example, the excitonic peak positions exhibit shifts of 778, 264, and 638 meV for the “transitions” 3D→2D, 2D→1D, and 1D→0D, respectively. Similar effects have been observed for the PbX_6 based materials ($X=I, Br$) with fractional dimensionality (see [1-3]).

In this paper the optical and related properties of $K_2Cd_3S_4$ and similar synthetic quasi-two-dimensional (q-2D) semiconductors ($Rb_2Cd_3S_4$, and $Cs_2Cd_3S_4$) are described. The results are compared to those of the corresponding 3D system (i.e. CdS).

The preparation and crystal structure determination of $K_2Cd_3S_4$ and other CdS-based compounds are described in [4]. These compounds have been obtained in single crystal form (plates). Optical absorption (OA) spectra of thin deposits [5] were recorded on a Varian model 2390 spectrophotometer. Photoluminescence (PL) and resonance Raman (RR) spectra were recorded on a Jobin-Yvon model HG2S Raman spectrophotometer using Argon and Krypton Lasers. Resonant Raman excitation (RRE) spectra were observed from rotating single-crystal mosaics on a KBr compressed pellet containing an internal standard. The out-of-resonance Raman spectra were recorded on a Bruker model RFS 100 spectrophotometer using a Nd-YAG Laser. Far-IR spectra were recorded on a Bruker model IFS 113v spectrophotometer. Photoconductivity (PC) spectra were recorded as in [6]. All measurements were performed at room temperature.

Fig. 1 shows the crystal structures of $K_2Cd_3S_4$ and $Cs_2Cd_3S_4$ as well as the structure of CdS (hexagonal) for comparison. $Rb_2Cd_3S_4$ is isostructural with $K_2Cd_3S_4$. One can see that the compounds form $(Cd_3S_4)_n^{2n-}$ layers interspersed with K^+ (or Rb^+ or Cs^+) cations [4].

The in-plane (layers) dc-conductivity at room temperature is *ca* 10^{-4} S/cm, while the out-of-plane conductivity is almost 100 times smaller. The compounds

characterised as quasi-2D semiconductors, in which the $(\text{Cd}_3\text{S}_4)_n^{2n-}$ layers are the active part of the system and A^+ ($\text{A}=\text{K}, \text{Cs}, \text{Rb}$) or A_2S play the role of barrier.

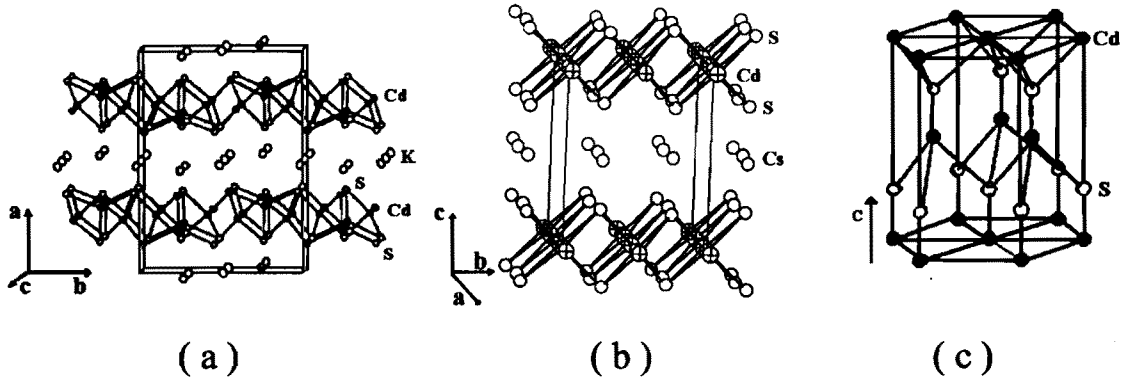


Figure 1. Crystal structures of $\text{K}_2\text{Cd}_3\text{S}_4$ (a), $\text{Cs}_2\text{Cd}_3\text{S}_4$ (b) and CdS (c).

Fig.2 shows the OA spectra of $\text{K}_2\text{Cd}_3\text{S}_4$ (two samples), $\text{Rb}_2\text{Cd}_3\text{S}_4$ and $\text{Cs}_2\text{Cd}_3\text{S}_4$ as well as the OA spectrum of CdS , for comparison. One can see that the OA spectra of q-2D compounds exhibit broad bands at ca 474 nm, while that of CdS at 496nm. These bands are attributed to excitons. Fig.3a and Fig. 3b show the PL and RR spectra observed from the surface of freshly cleaved single crystals of $\text{K}_2\text{Cd}_3\text{S}_4$ and CdS , respectively. The broad bands at 484 nm and 505 nm are the excitonic bands, while the sharp lines with shifts of ca 303, 607, 911 etc cm^{-1} are the lattice vibrational lines, i.e., the fundamental longitudinal optical mode (LO) and its overtones (2LO, 3LO, etc), arising from the exciton-phonon interaction (see also [3,7]). Figure 3a' shows the PL and RR spectra of $\text{K}_2\text{Cd}_3\text{S}_4$ after ageing. The aged samples exhibit the RR lines. They do not exhibit the excitonic PL band but a broader band (not shown in Fig. 3a') in the region 550-660 nm, which varies from crystal to crystal (see also [4,7]). The effects are similar to those obtained from other CdS -based systems (bulk, thin films and small particles or clusters) [4,8-11].

Fig. 4 and Fig. 5 show the corresponding RRE and PC spectra of $\text{K}_2\text{Cd}_3\text{S}_4$ and CdS single crystals. As in the cases of the OA and PL spectra, the RRE and PC excitonic bands of $\text{K}_2\text{Cd}_3\text{S}_4$ are blue-shifted in comparison to those of CdS . This is due to the confinement of excitons, as in the case of other synthetic LD semiconductors or the LD artificial systems based on conventional semiconductors (see for example [1]).

The spectra of freshly cleaved crystals covered with a polymer do not show ageing effects, i.e., the crystals remain stable for long time.

The PL, RR, RRE, and PC spectra of $\text{Rb}_2\text{Cd}_3\text{S}_4$ and $\text{Cs}_2\text{Cd}_3\text{S}_4$ are the same as the corresponding spectra of $\text{K}_2\text{Cd}_3\text{S}_4$ in accordance with the OA spectra (Fig. 2). However, the out-of-resonance Raman and far-IR spectra of $\text{Rb}_2\text{Cd}_3\text{S}_4$ are the same as $\text{K}_2\text{Cd}_3\text{S}_4$, but different from those of $\text{Cs}_2\text{Cd}_3\text{S}_4$ (and CdS), due to the different symmetry (Fig. 1). Fig. 6 shows the out-of-resonance Raman spectra of $\text{K}_2\text{Cd}_3\text{S}_4$, $\text{Rb}_2\text{Cd}_3\text{S}_4$, $\text{Cs}_2\text{Cd}_3\text{S}_4$ and CdS , single crystals. Fig. 7 shows the far-IR reflectance spectra of $\text{K}_2\text{Cd}_3\text{S}_4$, $\text{Cs}_2\text{Cd}_3\text{S}_4$, $\text{Cs}_2\text{Cd}_3\text{S}_4$, and CdS single-crystal mosaics.

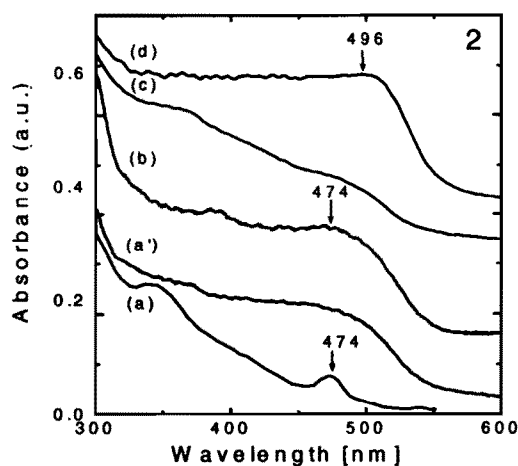


Figure 2. OA spectra of $K_2Cd_3S_4$ (a, a'), $Rb_2Cd_3S_4$ (b), $Cs_2Cd_3S_4$ (c) and CdS (d).

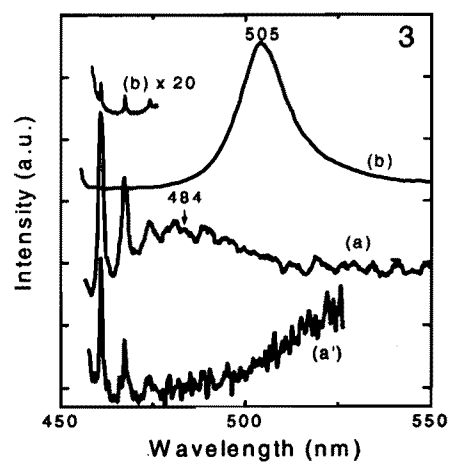


Figure 3. PL and RR spectra of $K_2Cd_3S_4$ (a,a') and CdS (b) freshly cleaved single crystals (a,b) and after ageing (a') (excitation line 454.5 nm).

Fig. 8 shows the $-\text{Im}(1/\epsilon)$ and ϵ_2 spectra of $K_2Cd_3S_4$ and CdS obtained from a Kramers-Krönig analysis of the reflectance spectra (where $\epsilon = \epsilon_1 + i\epsilon_2$). Two common features are the dip in the reflectance spectra and the corresponding peak in $-\text{Im}(1/\epsilon)$, i.e. the LO vibrational mode around 300 cm^{-1} , which is also observed in the RR spectra of CdS-based systems. The far-IR structures in the region $ca\ 50 - ca\ 200\text{ cm}^{-1}$ are attributed to A_2S -vibrations. However, details on the lattice vibrational spectra of these compounds will be published elsewhere.

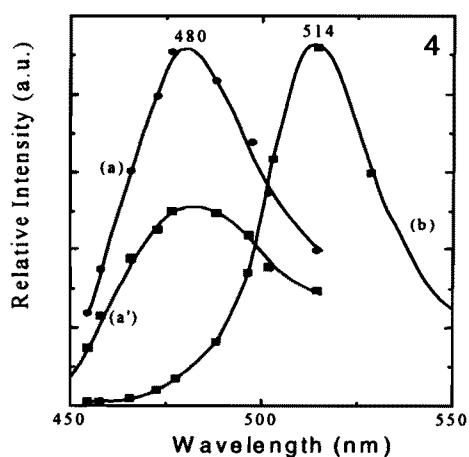


Figure 4. As in Fig. 3, but for RRE spectra of single-crystal mosaics.

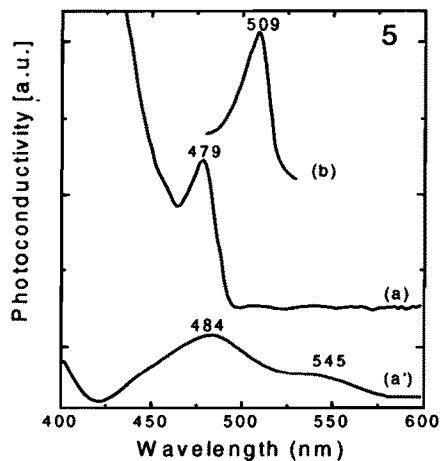


Figure 5. As in Fig. 3, but for PC spectra of single-crystals.

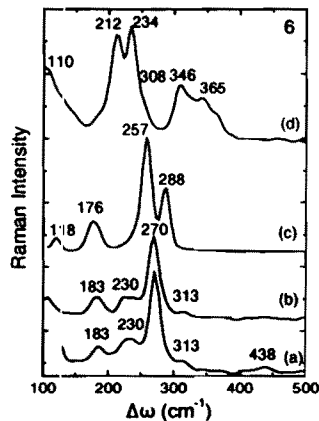


Figure 6. Out-of-resonance Raman spectra of $K_2Cd_3S_4$ (a), $Rb_2Cd_3S_4$ (b), $Cs_2Cd_3S_4$ (c) and CdS (d), single crystals (excitation line 1064 nm).

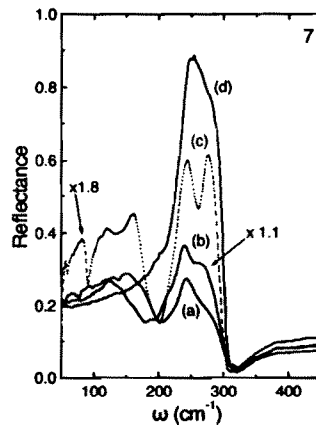


Figure 7. Far-IR reflectance spectra of $K_2Cd_3S_4$ (a), $Rb_2Cd_3S_4$ (b), $Cs_2Cd_3S_4$ (c), and CdS (d) single-crystal mosaics.

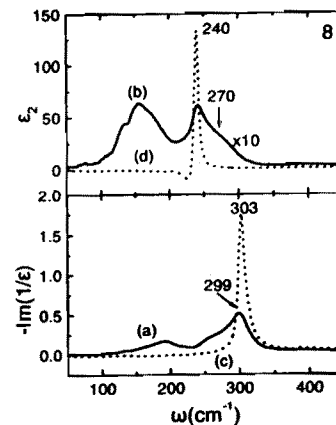


Figure 8. $-\text{Im}(1/\epsilon)$ and ϵ_2 spectra of $K_2Cd_3S_4$ (a,b) and CdS (c,d) obtained from Kramers-Krönig analysis of reflectance spectra.

In conclusion, the electronic spectra of the q-2D semiconductors $K_2Cd_3S_4$, $Rb_2Cd_3S_4$ and $Cs_2Cd_3S_4$ show excitonic bands at shorter wavelengths than those of CdS. These new systems as well as $K_2Cd_3S_{4-x}Se_x$, $K_2Cd_3S_{4-y}Mn_yS_4$, etc. [4,7] can be considered as candidates for optoelectronic applications as CdS and other similar systems based on CdSe, $CdS_{1-x}Se_x$, ZnS, $Cd_{1-y}Mn_yS$, etc. (see for example [9-12]).

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