OPTICAL AND RELATED PROPERTIES OF THE SYNTHETIC QUASI-TWO-DIMENSIONAL SEMICONDUCTORS K₂Cd₃S₄, Rb₂Cd₃S₄ AND Cs₂Cd₃S₄


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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 PbI₆-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 PbX₆ based materials (X=I, Br) with fractional dimensionality (see [1-3]).

In this paper the optical and related properties of K₂Cd₃S₄ and similar synthetic quasi-two-dimensional (q-2D) semiconductors (Rb₂Cd₃S₄ and Cs₂Cd₃S₄) are described. The results are compared to those of the corresponding 3D system (i.e. CdS).

The preparation and crystal structure determination of K₂Cd₃S₄ 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 K₂Cd₃S₄ and Cs₂Cd₃S₄ as well as the structure of CdS (hexagonal) for comparison. Rb₂Cd₃S₄ is isostructural with K₂Cd₃S₄. One can see that the compounds form (Cd₃S₄)₂n⁻ layers interspersed with K⁺ (or Rb⁺ or Cs⁺) cations [4].

The in-plane (layers) dc-conductivity at room temperature is ca 10⁴ S/cm, while the out-of-plane conductivity is almost 100 times smaller. The compounds

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characterised as quasi-2D semiconductors, in which the \((\text{Cd}_2\text{S}_4)_{2n-}^n\) layers are the active part of the system and \(A^+(A=\text{K, Cs, Rb})\) or \(A_2S\) play the role of barrier.

\(\text{Figure 1. Crystal structures of } K_2\text{Cd}_2\text{S}_4\) (a), \(\text{Cs}_2\text{Cd}_2\text{S}_4\) (b) and \(\text{CdS}\) (c).

Fig.2 shows the OA spectra of \(K_2\text{Cd}_2\text{S}_4\) (two samples), \(\text{Rb}_2\text{Cd}_2\text{S}_4\) and \(\text{Cs}_2\text{Cd}_2\text{S}_4\) as well as the OA spectrum of \(\text{CdS}\), for comparison. One can see that the OA spectra of q-2D compounds exhibit broad bands at ca 474 nm, while that of \(\text{CdS}\) 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 \(K_2\text{Cd}_2\text{S}_4\) and \(\text{CdS}\), 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 \(K_2\text{Cd}_2\text{S}_4\) 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 \(\text{CdS}\) -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 \(K_2\text{Cd}_2\text{S}_4\) and \(\text{CdS}\) single crystals. As in the cases of the OA and PL spectra, the RRE and PC excitonic bands of \(K_2\text{Cd}_2\text{S}_4\) are blue-shifted in comparison to those of \(\text{CdS}\). 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 \(\text{Rb}_2\text{Cd}_2\text{S}_4\) and \(\text{Cs}_2\text{Cd}_2\text{S}_4\) are the same as the corresponding spectra of \(K_2\text{Cd}_2\text{S}_4\) in accordance with the OA spectra (Fig. 2). However, the out-of-resonance Raman and far-IR spectra of \(\text{Rb}_2\text{Cd}_2\text{S}_4\) are the same as \(K_2\text{Cd}_2\text{S}_4\), but different from those of \(\text{Cs}_2\text{Cd}_2\text{S}_4\) (and \(\text{CdS}\)), due to the different symmetry (Fig. 1). Fig. 6 shows the out-of-resonance Raman spectra of \(K_2\text{Cd}_2\text{S}_4\), \(\text{Rb}_2\text{Cd}_2\text{S}_4\), \(\text{Cs}_2\text{Cd}_2\text{S}_4\) and \(\text{CdS}\), single crystals. Fig. 7 shows the far-IR reflectance spectra of \(K_2\text{Cd}_2\text{S}_4\), \(\text{Cs}_2\text{Cd}_2\text{S}_4\), \(\text{Cs}_2\text{Cd}_2\text{S}_4\), and \(\text{CdS}\) single-crystal mosaics.
Fig. 8 shows the $-\text{Im}(1/\varepsilon)$ and $\varepsilon_2$ spectra of $\text{K}_2\text{Cd}_3\text{S}_4$ and CdS obtained from a Kramers-Krönig analysis of the reflectance spectra (where $\varepsilon=\varepsilon_1+i\varepsilon_2$). Two common features are the dip in the reflectance spectra and the corresponding peak in $-\text{Im}(1/\varepsilon)$, 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 cm$^{-1}$ are attributed to $A_2S$-vibrations. However, details on the lattice vibrational spectra of these compounds will be published elsewhere.

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

Fig. 5. As in Fig. 3, but for PC spectra of single-crystals.
In conclusion, the electronic spectra of the q-2D semiconductors K₂Cd₃S₄, Rb₂Cd₃S₄ and Cs₂Cd₃S₄ show excitonic bands at shorter wavelengths than those of CdS. These new systems as well as K₂Cd₃S₄, Se₄, K₂Cd₃₋ₓMnxS₄, etc. [4,7] can be considered as candidates for optoelectronic applications as CdS and other similar systems based on CdSe, CdS₁₋ₓSex, ZnS, Cd₁₋ₓMnxS, etc. (see for example [9-12]).

References