OPTICAL AND RELATED PROPERTIES OF SOME SYNTHETIC LOW-DIMENSIONAL SEMICONDUCTORS BASED ON METAL SULFIDE UNITS

G. C. Papavassiliou, G. A. Mousdis, I. B. Koutselas, M. G. Kanatzidis*, E. A. Axtell III*, and M.-H. Whangbo**

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
48, Vassileos Constantinou Ave., Athens 116/35, Greece
*Department of Chemistry, Michigan State University, East Lancing,
MI 48824 – 1322, USA
**Department of Chemistry, North Carolina State University,
Raleigh, N.C.2 7695-8204, USA

The room temperature optical and related properties of $K_2Cd_3S_4$ and similar low-dimensional semiconductors with metal sulfide units are described. The near-band-edge optical absorption and photoluminescence bands dominated by excitonic transitions exhibit blue shifts and the corresponding binding energy values are larger, in comparison to those of the corresponding three-dimensional systems. The results are similar to those obtained from low-dimensional semiconductors based on metal halide units and similar to those of artificial systems based on conventional semiconductors.

INTRODUCTION

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 (D) of 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 from 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 low-dimensional semiconductors with metal sulfide units are described. The results are compared to those of the corresponding three dimensional systems (i.e., CdS etc.).

EXPERIMENTAL

The preparation and crystal structure determination of $K_2Cd_3S_4$ and other CdS based compounds are described in [4]. The preparation and structures of $Na_8In_4S_{10}$, $(Me_4N)_xIn_yS_z$ and $(Me_4N)_2Sn_3S_7$ are described in [5], [6] and [7], respectively. The

compounds based on CdS have been obtained in single crystal form (plates), while compounds $Na_8In_4S_{10}$, $(Me_4N)_xIn_yS_z$ and $(Me_4N)_2Sn_3S_7$ in microcrystalline form. Before the optical measurements, the crystal structures of these materials were identified with a $P2_1$ Nicolet difractometer using Mo $K\alpha$ radiation at room temperature. Optical absorption spectra were recorded on a Varian model 2390 spectrophotometer. Photoluminescence and (resonance) Raman spectra were recorded on a Jobin-Yvon model HG25 Raman spectrophotometer using argon and Krypton Lasers. All the measurements were performed at room temperature.

RESULTS AND DISCUSSION

Fig. 1 shows the crystal structure of $K_2Cd_3S_4$. One can see that the compound forms as $(Cd_3S_4)_n^{2n-}$ layers interspersed with K^+ cations. The layers are composed of $Cd_3S_4^{2-}$ units shaped as truncated cubes. Employing the extended Hückel tight binding method [8,9] using atomic parameters (for the parameter definition see [9]), the valence and conduction bands of a single $Cd_3S_4^{2-}$ layer were calculated. Fig. 2a shows the dispersion relations of the valence and conduction bands and Fig. 2b the total density of states (DOS), while Figs. 2c,d show the projected DOS of Cd^{2+} and S^{2-} in $K_2Cd_3S_4$, respectively. It was found that the highest filled levels are related to the 3p-orbitals of S^{2-} and the lowest unfilled levels to the 5s-orbitals of Cd^{2+}. This means that the lowest intrinsic electronic transitions of $K_2Cd_3S_4$ should be approximately given by the energy difference between the 5s-orbitals of Cd^{2+} and the 3p-orbitals of S^{2-}. This is similar to the case of CdS (bulk and small particles) [10,11]. The in-plane dc-conductivity at room temperature is ca 10^{-4} S/cm, while the out-of-plane conductivity is almost 100 times smaller. The compound is characterized as a quasi-2D semiconductor, in which the $(Cd_3S_4)_n^{2n-}$ layers is the active part of the system and K^+(or K_2S) plays the role of barrier.

Fig.3 shows the optical absorption and photoluminescence (excitation 406.7 nm) spectra of thin deposits of $K_2Cd_3S_4$ on quartz plates. The peaks are attributed to excitons. The peak positions of the spectra occur at higher energies (shorter wavelengths) than
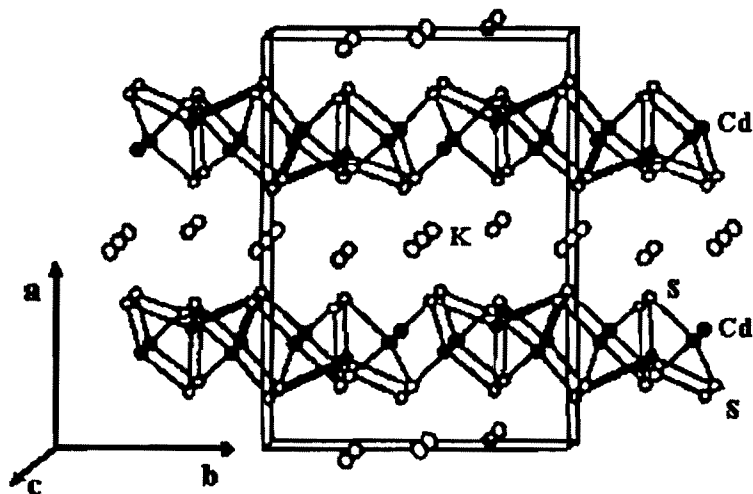

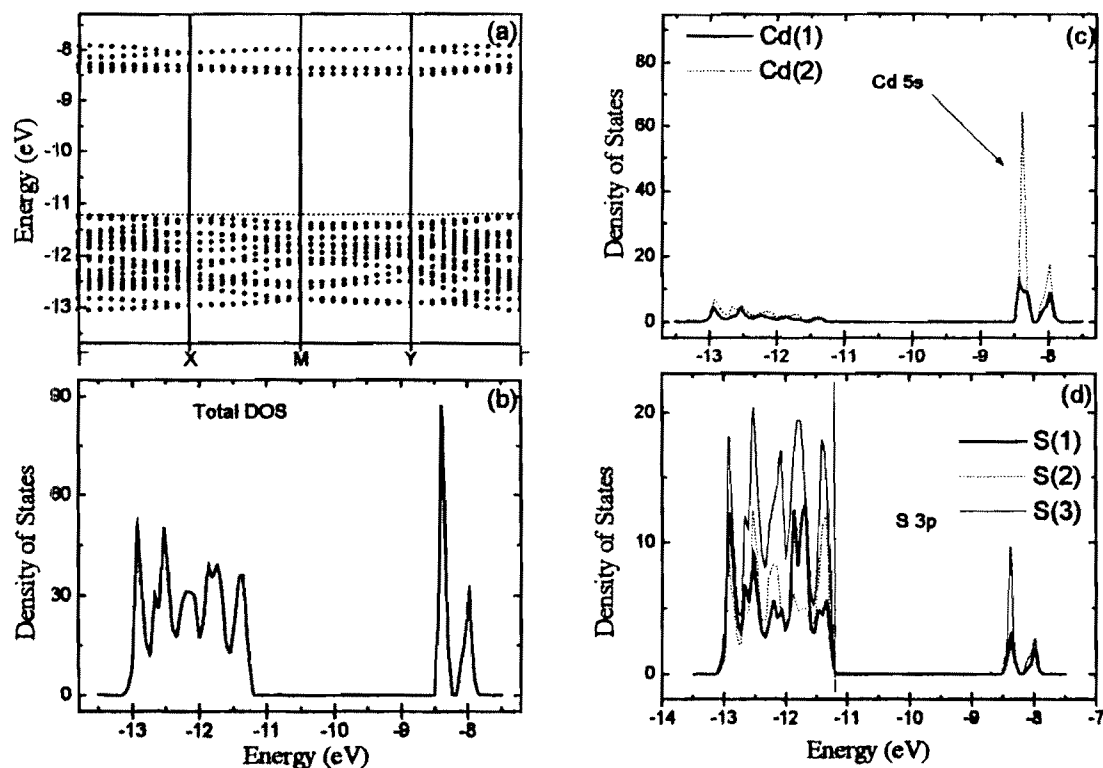Fig. 1. The crystal structure of $K_2Cd_3S_4$ looking down the crystallographic c-axis.

Fig. 2. Calculated electronic band structure (a), total density of states (b), projected density of states for Cd^{2+} (c) and S^{2-} (d) in $K_2Cd_3S_4$

those of CdS continuous films, but almost at the same positions as those found for CdS-particles of *ca* 100 Å in diameter [12]. From the optical absorption spectrum (Fig.3a), it was estimated that the excitonic binding energy of $K_2Cd_3S_4$ is 109 meV at room temperature, namely, almost four times the binding energy of the corresponding 3D system, CdS (this is 28 meV at 4.2 K [10]).

The photoluminescence spectrum from a single crystal with the same excitation line is almost the same as that of thin deposits. Fig. 4a shows the photoluminescence (and Raman) spectrum from the surface of a freshly cleared single crystal of $K_2Cd_3S_4$ (excitation 457.9 nm). The broad band at 484 nm is the excitonic band and the sharp lines with shifts of *ca* 303, 607, 911 etc cm^{-1} (from the excitation line) are the fundamental longitudinal optical vibration mode (LO) and its overtones (2LO, 3LO, etc), respectively. The broad band at *ca* 704 nm may be due to self-trapped excitons. Also, some aging effects were observed. Fig.4b,c shows the photoluminescence (and Raman) spectra of a single crystal after exposure of the crystal-surface for several days in air and light and for two-different incidence-points. In these spectra, some new bands appear, which are due to several trapped states. Similar effects have observed from a number of systems based on CdS [1,4,12-14]. Same effects were observed in the resonance Raman excitation profiles and photoconductivity spectra of $K_2Cd_3S_4$ and similar systems. Details will be published elsewhere (for instance see [3,15]).

The near-band-edge (or excitonic) peaks of some other low-dimensional crystals based on metal sulfides exhibit blue shifts and a pronounced binding energy in comparison to the
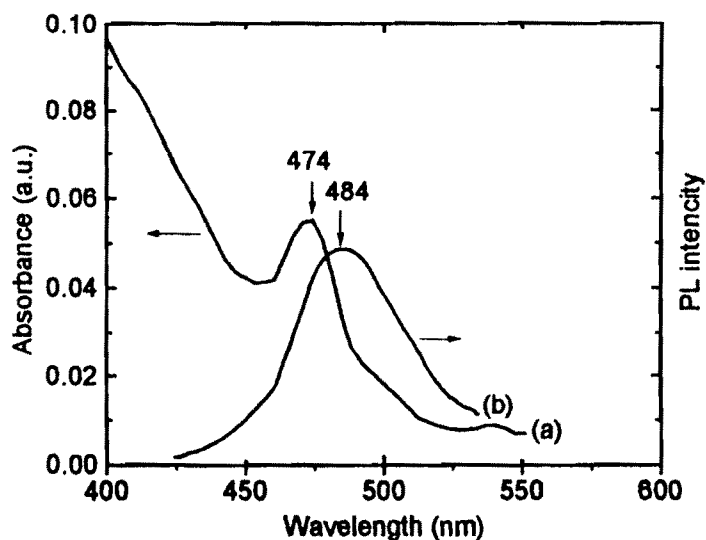
Fig. 3. Optical absorption (a) and photoluminescence (b) spectra of $K_2Cd_3S_4$ thin deposits (excitation 406.7 nm).
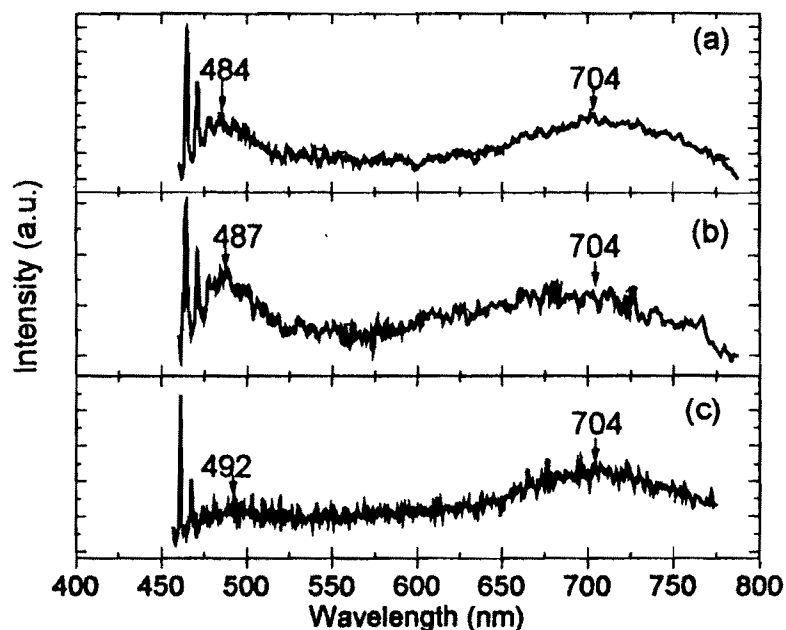

Fig. 4. Photoluminescence and resonance Raman spectra of $K_2Cd_3S_4$: (a) on the surface of a freshly cleaved crystal, (b) and (c) after exposure of the crystal in air and light for several days and at two different incidence points (excitation 457.9nm).

corresponding 3D systems. Fig. 5 shows the optical absorption spectra of $K_2Cd_{2.4}Mn_{0.6}S_4$ and $Rb_2Cd_3S_4$ (which are isostructural with $K_2Cd_3S_4$) as well as that of CdS for comparison. Fig. 6 shows the optical absorption spectra of $Na_8In_4S_{10}$ (0D) [5], $(Me_4N)_xIn_yS_z$ [6], $TlInS_2$ (quasi-2D) (see also [16]) and In_2S_3 (3D), while Fig. 7 shows
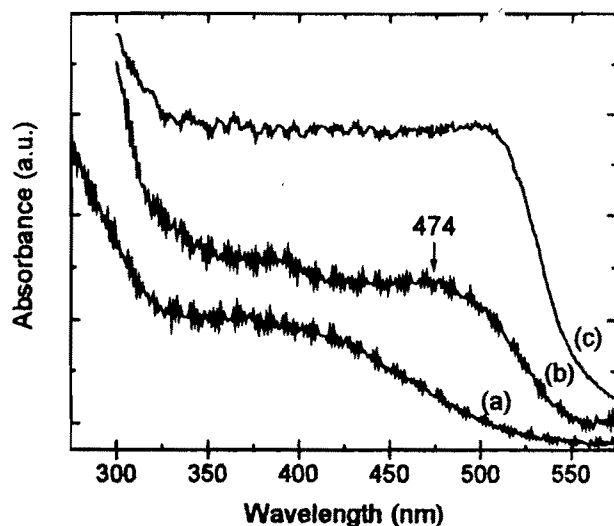
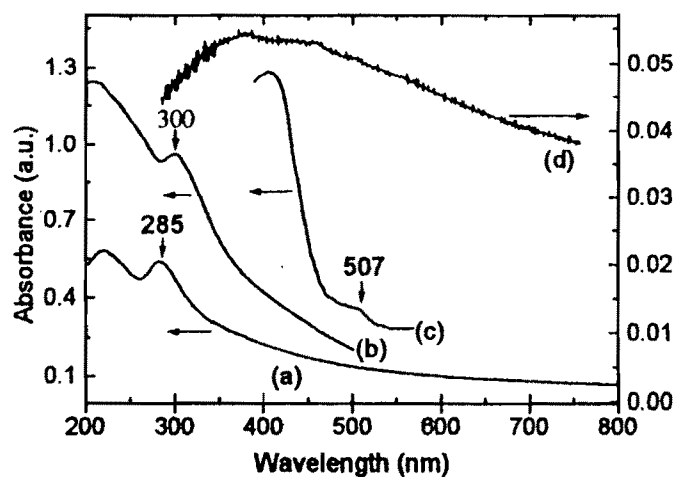Fig. 5. Optical absorption spectra of $K_2Cd_{2.4}Mn_{0.6}S_4$ (a), $Rb_2Cd_3S_4$ (b) and CdS (c) thin deposits.

Fig. 6. Optical absorption spectra of $Na_8In_4S_{10}$ (a), $(Me_4N)_xIn_yS_z$ (b), $TlInS_2$ (c), and In_2S_3 (d) thin deposits.

the spectra of $(Me_4N)_2Sn_3S_7$ (quantum antidot system) [7] and SnS_2 thin deposits on quartz plates.

In all cases, the results are qualitatively similar to those obtained from synthetic metal-halide (MX) semiconductors (where M = Pb, Sn, Ge, Bi, Sb, Cu, Ag etc; X= I, Br, Cl [1-3,6]) as well as those obtained from artificial low-dimensional systems based on conventional semiconductors (see for example [1]).

ACKNOWLEDGMENTS
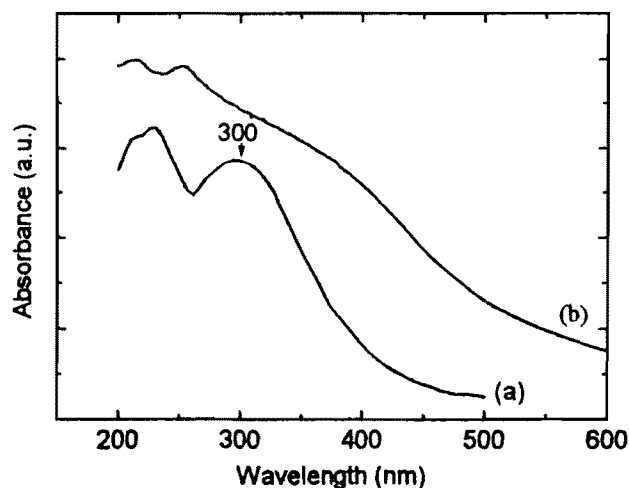
Fig. 7. Optical absorption spectra of $(Me_4N)_2Sn_3S_7$ (a) and SnS_2 (b) thin deposits.

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