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$K_2Cd_2S_3$ vs CdS: Can the Properties Of Quantum-Sized CdQ Semiconductors Be Emulated by Bulk Alkali Metal Ternary A/Cd/Q Phases (Q = Chalcogen)?

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During the last decade a new direction in the study of CdS and other II–VI materials has been the size dependent electronic properties caused by quantization in diminishing dimensions.[1,2] Often called "quantum dots", small nanometer-sized CdS clusters have been studied extensively, and their behavior has been rationalized by their being considered as pieces formed by slicing the three-dimensional (3-D) diamond-like lattice. It is intriguing to conceive that, in some cases, size quantization in CdS and other materials could be emulated by ternary compounds of the formula $(A_2S)_n(CdS)_m$ (A = alkali metal). In this class of compounds, the dense 3-D binary sulfide lattice would be dimensionally reduced/dismantled to either "porous" three-dimensional, layered, or one-dimensional, by adjusting the n:m ratio.[3] The resulting $(Cd_xS_y)^{n-}$ frameworks in such compounds may possess nanometer-sized dimensions along certain lattice directions. While nanometer-sized CdS particles are quantized in three dimensions, bulk $(Cd_xS_y)^{n-}$ frameworks may only be quantized in one or two. Such systems may possess electronic properties, mimicking those of "quantum dot" CdS in certain crystallographic directions. In the $(A_2S)_n(CdS)_m$ system we discovered a novel, strongly luminescent, ternary cadmium sulfide, $K_2Cd_2S_3$, with a "hollow" 3-D Cd/S framework. This compound exhibits bulk spectral properties reminiscent of those of quantum-confined CdS. Ternary A/M/Q compounds (M = Zn, Cd) are very few and include A_6CdQ_4,[4] A_2CdQ_2,[5] $ALiZnS_2$,[6] $A_2Zn_3S_4$,[7] and $Na_4Cd_3Se_5$.[8]

The structure of $K_2Cd_2S_3$[9] contains a unique 3-D Cd/S framework, with tetrahedral Cd atoms. One-third of the S atoms have V-shaped coordination, and two-thirds have trigonal pyramidal coordination. The 3-D $(Cd_2S_3)_n^{2n-}$ framework features three types of K^+-filled tunnels running parallel to the crystallographic c axis, as seen in Figure 1A. This structure can be thought of as a 3-D array of interconnected $Cd_4S_6^{4-}$ cluster building blocks. These clusters (see Figure 1B) consist of eclipsed Cd_2S_2 rhombi joined at the Cd atoms by bridging S^{2-} ligands. The $Cd_4S_6^{4-}$ clusters form K^+-filled hexagonal tunnels. The distorted octagonal tunnels consist of CdS tubes filled with K^+ ions, Figure 1C. The 12 sided cruciform tunnels consist of four Cd_2S_2 rhombi joined together by sulfide ions. Four equivalent sites exist for K^+ in this tube, near each of the connecting S^{2-} ligands. The Cd–S bond lengths are in the range 2.507(2)–2.631(2) Å. S–Cd–S angles in $K_2Cd_2S_3$ range from 107.35(6)° to 118.49(6)°.

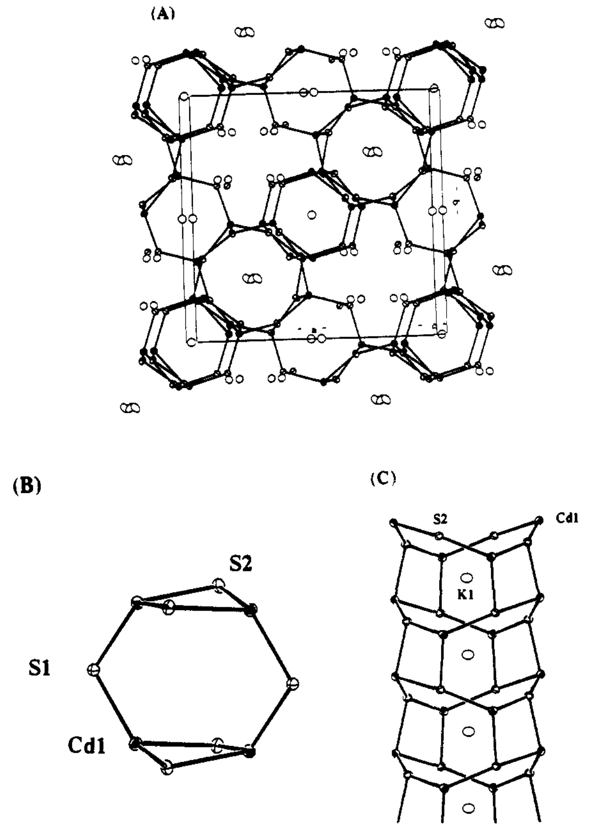

Figure 1. (A) ORTEP view of the structure of $K_2Cd_2S_3$ parallel to the crystallographic c axis, displaying the connectivity of the compound's three different channels. (Octant-shaded ellipsoids represent Cd, crossed ellipsoids represent S, and plain ellipsoids represent K.) (B) View of the $Cd_4S_6^{4-}$ unit of $K_2Cd_2S_3$ parallel to the crystallographic c axis. (C) View of the octagonal tunnel perpendicular to the crystallographic c axis.

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(9) (a) $K_2Cd_2S_3$ was prepared by the reaction of 0.331 g (3.0 mmol) of K_2S, 0.056 g (0.50 mmol) of Cd metal, and 0.096 g (3.0 mmol) of S in an evacuated ($\sim 1.0 \times 10^{-3}$ Torr), carbon-coated quartz tube at 600 °C for $6^1/_2$ days, followed by slow cooling at a rate of −5 °C/h to 450 °C and quenching to room temperature. This reaction afforded light yellow rods of $K_2Cd_2S_3$ in 72% yield, based on Cd. The product was isolated with distilled water, followed by rinses with methanol and diethyl ether, under a N_2 atmosphere. This compound is stable in air and water and is insoluble in common organic solvents. Purity was assured by comparison of experimental powder patterns to one calculated from the appropriate structural parameters.[9d] Crystal data for $K_2Cd_2S_3$: $a = 14.517(2)$ Å, $c = 6.912(1)$ Å, $V = 1456.5(4)$ Å^3, $Z = 8$; space group, $P4_2/ncm$ (No. 138), $D_{calc} = 3.36$ g/cm^3; μ(Mo Kα) = 76.85 cm^{-1}; $2\theta_{max} = 60°$; total data collected on a Rigaku AFC6 diffractometer at 23 °C, 1291; number of unique data = 1291; number of reflections with $F_o^2 > 3\sigma(F_o^2)$ = 812. Complete anisotropic refinement (37 variables) resulted in R = 2.8%, R_w = 3.6%. The structure was solved using the SHELXS 86[9b] direct methods program, incorporated into the TEXSAN software package. An empirical absorption correction based on ψ scans, followed by DIFABS,[9c] was applied to all data. (b) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Doddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175–189. (c) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983,** *39A,* 158. (d) Smith, D. K.; Nichols, M. C.; Zolensky, M. E. POWD 10: A Fortran IV Program for Calculating X-ray Powder Diffraction Patterns, Version 10. Pennsylvania State University, 1983.

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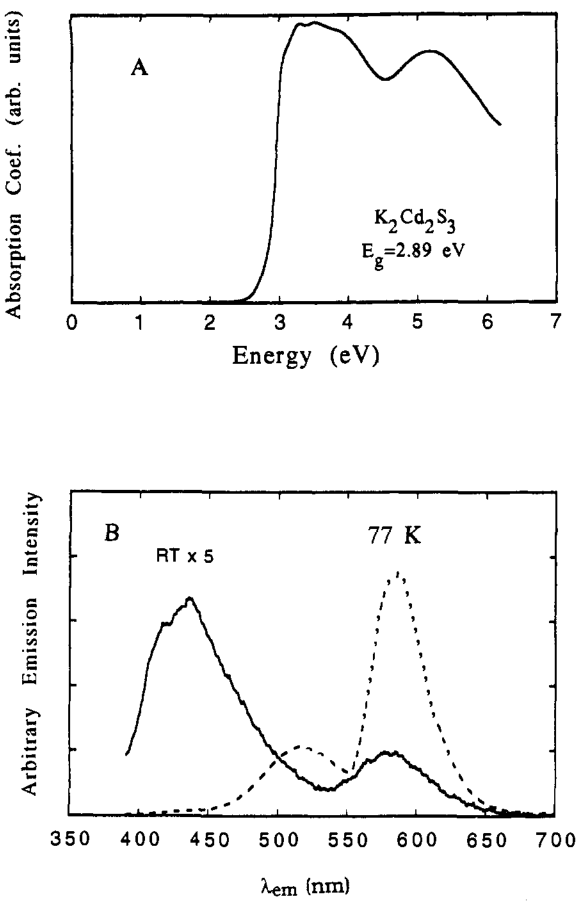

Figure 2. (A) The absorption spectrum of $K_2Cd_2S_3$. (B) The room temperature (solid line) and 77 K (dotted line) emission spectra of $K_2Cd_2S_3$ (λ_{exc} = 313 nm).

$K_2Cd_2S_3$ is semiconductor with a most likely direct gap of 2.89(2) eV,[10] Figure 2A. The opening of the CdS structure by K_2S has caused a concomitant blue shift of the band gap from 2.53 eV[10c] to 2.89 eV, due to the decreased Cd/S connections (compared to CdS). As a result, the narrow bandwidths and larger energy gaps which develop are similar in magnitude to those achieved by size quantization in nanometer-sized CdS.

The existence of a direct gap in $K_2Cd_2S_3$ prompted us to examine the light-emitting properties of $K_2Cd_2S_3$.[11] At room temperature, $K_2Cd_2S_3$ emits at two different wavelengths, 430 nm (2.88 eV, blue) and 580 nm (2.14 eV, green), when excited at 313 nm (3.96 eV). The former is remarkably close to the band gap value of 2.89 eV. By comparison, almost no emission is observed from bulk CdS.[12] However, multilevel emission at similar wavelengths has been observed from CdS clusters in zeolites and colloidal suspensions of CdS.[13] At 77 K, the emission band at 580 nm becomes more intense while the one at 430 nm disappears and a new emission band at 520 nm (2.38 eV) is observed; see Figure 2B. The emissive states are only accessible by band gap excitation, as the excitation spectra monitoring the 580-, 520-, and 430-nm emission lines all show profiles similar to the absorption spectrum. Further studies are needed to determine the origin of the emitting species which, in addition to near band gap emission, probably arise from at least two midgap electronic levels introduced by charge-transfer states, structural defects, and/or doping impurities. Colloidal suspensions of nanometer-sized CdS clusters also show luminescence, thought to arise from structural defect states on the surface.[14]

The similar optical absorption/emission behavior between $K_2Cd_2S_3$ and quantum-confined CdS may be accidental, but it stimulates one to ponder whether the effects of quantum confinement may be achieved in certain directions in bulk materials by "breakup" structures of the binary solids.[15] This points to a new conceptual framework with which to view certain ternary compounds and should lead to further development of these materials.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and calculated and observed powder patterns for $K_2Cd_2S_3$ (5 pages); listing of observed and calculated structure factors for $K_2Cd_2S_3$ (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) (a) Absorption spectra were obtained according to a procedure described in the literature: McCarthy, T. J.; Ngeyi, S.-P.; Liao, J.-H.; DeGroot, D. C.; Schindler, J.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331–340. (b) We have obtained a value of 2.89 eV for the band gap by extrapolating the linear region of the $(\alpha/S)^2$ versus energy plot to $(\alpha/S)^2 = 0$.[10c] (c) Pankove, J. I. In *Optical Processes in Semiconductors*; Dover Publications: New York, 1975.

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(15) A referee correctly pointed out the differences between the structure of CdS and that of $K_2Cd_2S_3$. While the coordination of Cd is similar in the two compounds, that of S is different, being four in CdS and two or three in $K_2Cd_2S_3$. However, in small (<45 Å) CdS clusters, with which the conceptual analogy is made, a considerable fraction of S atoms are located on the surface with a coordination environment of less than four.