

First examples of sulfides in the quaternary A/Cd/Sn/S (A = Li, Na) systems: molten flux synthesis and single crystal X-ray structures of $\text{Li}_2\text{CdSnS}_4$, $\text{Na}_2\text{CdSnS}_4$ and $\text{Na}_6\text{CdSn}_4\text{S}_{12}$

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Received 9th November 2001, Accepted 19th February 2002
 First published as an Advance Article on the web 3rd April 2002

Three new sulfides $\text{Li}_2\text{CdSnS}_4$ (**1**), $\text{Na}_2\text{CdSnS}_4$ (**2**) and $\text{Na}_6\text{CdSn}_4\text{S}_{12}$ (**3**), have been synthesized using a molten flux of alkali-metal polysulfides and structurally characterized by single crystal X-ray diffraction studies. Both the layered compound **1** and the three-dimensional compound **2** have tetrahedral anionic frameworks of $(\text{CdSnS}_4)^{2-}$ and, for charge compensation, alkali-metal cations. The two-dimensional compound **3** has Na^+ ions interleaved between anionic $(\text{CdSn}_4\text{S}_{12})^{6-}$ layers with an octahedral framework. Compounds **1**, **2** and **3** are structurally related to $\text{Cu}_2\text{CdGeS}_4$, LiAlSe_2 and Na_2SnS_3 respectively. Compound **2**, as determined from its diffuse reflectance spectrum, is a semiconductor with a band gap of 1.52 eV.

Introduction

In the past fifteen years, the reactive molten flux method¹ employing alkali-metal polysulfides, has become a powerful technique for synthesising, at relatively low temperatures, a number of novel phases, mostly in the form of single crystals that enable unambiguous characterization by single crystal X-ray diffraction. The new phases,^{2,3} generally metastable in nature, are the intended mixed-metal polysulfides and, to a smaller extent, simple ternary and quaternary sulfides. Similar reactive molten flux methods⁴ have been developed for the synthesis of selenides and tellurides. The simple sulfides can be broadly categorized into three types, namely, metal-rich compounds such as $\text{Rb}_2\text{Au}_2\text{Cu}_2\text{S}_4$,⁵ sulfur-rich ones such as $\text{RbPbBi}_3\text{S}_6$ ⁶ and those, like the recently reported⁷ $\text{K}_3\text{Bi}_5\text{Cu}_2\text{S}_{10}$, having a 1 : 1 ratio of metal to sulfur. A large number of sulfides of the third type have been reported^{8,9} to be synthesized by the molten flux method; mainly in the quaternary A/M/M'/S system, where A is an alkali-metal and M and M' represent transition, post-transition and main group metals in the oxidation states I, II, IV and VI. Some of these compounds of general formula $\text{A}_2\text{MM}'\text{S}_4$ ^{2,9,10} are A_2AgTaS_4 (A = K, Rb, Cs), A_2AgNbS_4 (A = K, Rb, Cs), A_2AgVS_4 (A = K, Rb, Cs), A_2CuNbS_4 (A = K, Rb), A_2CuVS_4 (A = K, Rb), K_2MnSnS_4 and the solvothermally synthesized A_2AgSbS_4 (A = K, Rb). They possess diverse types of structures ranging from linear to three-dimensional.

We have become interested in the investigation of the quaternary A/Cd/Sn/S systems because they are, to our knowledge, unexplored and also the new phases in this systems could be expected to possess novel structures with both the Cd and Sn atoms in tetrahedral and octahedral coordination sites. It is during these exploratory synthetic attempts that we have isolated three new compounds, $\text{Li}_2\text{CdSnS}_4$ (**1**), $\text{Na}_2\text{CdSnS}_4$ (**2**) and $\text{Na}_6\text{CdSn}_4\text{S}_{12}$ (**3**) that represent the first examples of sulfides in these quaternary systems. In this paper, we report the synthesis and characterization, by single crystal X-ray diffraction and diffuse reflectance spectroscopy, of these three new sulfides, having layered and three-dimensional structures.

Experimental

Synthesis

A mixture of CdS (0.039 g; 0.027 mmol), SnS (0.041 g; 0.027 mmol), Li_2S (0.1 g; 0.218 mmol) and S (0.349 g; 1.088 mmol), taken in an evacuated, sealed quartz tube of 13 cm length and 1.3 cm diameter, was heated at 560 °C for four days and then cooled to room temperature over a period of four days. The entire product-content of the reaction tube was washed thoroughly with water to isolate the water-insoluble, homogeneous phase of $\text{Li}_2\text{CdSnS}_4$ (**1**), in the form of orange, needle crystals (0.0543 g; 53.5% yield, based on SnS).

A similar synthetic attempt involving a reactant mixture of CdS (0.032 g; 0.022 mmol), SnS (0.037 g; 0.0244 mmol) and Na_2S_5 (0.2 g; 0.097 mmol) at 780 °C, resulted in a biphasic mixture of products, a large amount of chunky brownish yellow crystals (0.04 g; 58.8% yield, based on SnS) of $\text{Na}_6\text{CdSn}_4\text{S}_{12}$ (**3**) and a very few, block shaped, bright yellow crystals of $\text{Na}_2\text{CdSnS}_4$ (**2**). These two compounds were separated manually.

X-Ray diffraction and crystal structure

The powder X-ray diffraction (XRD) patterns of the compounds **1** and **3** were recorded on a Shimadzu XD-D1 powder diffractometer, using Cu-K α ($\lambda = 1.5405 \text{ \AA}$) radiation. The monophasic nature of these two compounds was ascertained by comparing their powder XRD patterns with those simulated, using the LAZY-PULVERIX program,¹¹ on the basis of their single crystal X-ray structures.

Single crystals of the compounds **1**, **2**, and **3**, suitable for X-ray diffraction, were selected and mounted on thin glass fibers with epoxy glue. Data sets were gathered from the crystals at 25 °C, using Mo-K α radiation ($\lambda = 0.7103 \text{ \AA}$), on an Enraf-Nonius CAD4 automated four-circle diffractometer, by standard procedures involving ω - 2θ scan techniques. These data sets were reduced by routine computational procedures. The structure solution and refinements were done by the programs SHELXS 86 and SHELXL 93, respectively^{12,13} and the graphic

Table 1 Crystal data and data collection parameters for compounds **1**, **2** and **3**

Formula	Li ₂ CdSnS ₄ 1	Na ₂ CdSnS ₄ 2	Na ₆ CdSn ₄ S ₁₂ 3
<i>M</i>	373.18	405.36	1109.98
Crystal system	Orthorhombic	Monoclinic	Monoclinic
<i>a</i> /Å	7.965(2)	9.282(1)	6.622(4)
<i>b</i> /Å	6.492(2)	9.421(3)	11.489(8)
<i>c</i> /Å	6.9685(12)	6.593(9)	6.999(2)
β /°		134.83(9)	108.56(4)
<i>V</i> /Å ³	360.33(12)	408.9(7)	504.8(5)
Space group (no.)	<i>Pmmm</i> (59)	<i>C2</i> (5)	<i>C2/m</i> (12)
<i>Z</i>	2	2	1
μ (Mo-K α)/mm ⁻¹	7.258	6.499	3.651
Total reflections	750	789	970
Independent reflections (<i>R</i> _{int})	378 (2.16)	728 (3.18)	470 (3.07)
<i>R</i> ^a	4.95	5.88	2.43
<i>R</i> _w ^b	14.76	14.37	7.73

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)]^{1/2}.$$

programs ATOMS¹⁴ and ORTEP¹⁵ were used to draw the structures.

For compound **1**, the two possible space groups, *Pmmn*₂₁ and *Pmmm*, determined from the systematic absences of the measured data, were tried. *Pmmm* was preferred, as it led to the structure solution and refinement with better *R* values. For the compounds **2** and **3**, every one of the three possible space groups *C2*, *C2/m* and *Cm* was tried and structure refinements were successful in the space groups *C2* and *C2/m* respectively.

The positions of the tin and cadmium atoms in all the three compounds were located by direct methods. Refinement of these positions and subsequent Fourier difference maps led to the location of the remaining atoms, namely, alkali-metal and sulfur atoms of the asymmetric units. Isotropic refinement of all the atoms for compound **2** proceeded smoothly. For compound **1**, however, the equivalent isotropic displacement parameters (*U*_{eq}) of the sulfur atoms were found to be very large, in the range 0.055 to 0.066 Å², and indicated the possibility of partial site occupancies. The variation of these site occupancies in the subsequent refinement proceeded smoothly and led to a marked decrease of *U*_{eq} values with a concomitant 50% decrease in their site occupancy factors. The site occupancy factors of S(1), S(2) and S(3) were respectively fixed at 0.25, 0.25 and 0.5 in the latter cycles of refinement and the *R* values improved quite significantly. Similarly, for compound **3**, the site occupancy factor of cadmium was refined in view of its large thermal parameter and then fixed at 0.125 in the final cycles of refinement. The isotropic thermal parameter of lithium in compound **1** was fixed at a value of 0.02 in the final cycles of refinement. All other atoms of compound **1** and all the atoms of compounds **2** and **3** were refined anisotropically and the final difference Fourier maps did not show any chemically significant features. The chemical compositions, Li₂CdSnS₄ and Na₆CdSn₄S₁₂, as determined from X-ray crystallography, were ascertained to be correct by conventional quantitative chemical analysis of sulfur and cadmium by the standard procedures.¹⁶ Pertinent crystallographic data and bond lengths of the three compounds, **1**, **2** and **3** are given in Tables 1 and 2, respectively.

CCDC reference numbers 173898–173900.

See <http://www.rsc.org/suppdata/dt/b1/b110254k/> for crystallographic data in CIF or other electronic format.

Spectroscopic data

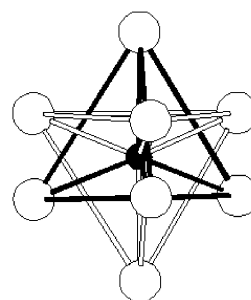
Optical diffuse reflectance measurements were made at room temperature, to measure the band gap, with a CARY [5E] UV–VIS–NIR spectrophotometer. BaSO₄ powder was used as reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka–Munk¹⁷ function: $a/S = (1 - R)^2/2R$, where *R* is the reflectance at a given wavelength, *a* is the absorption coefficient and *S* is the scattering coefficient. The scattering coefficient is known to be practically wavelength-

independent for particles larger than 5 μm, which is smaller than the particle size of the sample used here.

Results and discussion

The three new, air-stable sulfides, **1**, **2** and **3** could be prepared from a molten alkali-metal polysulfide flux only and not by conventional high-temperature, solid state reaction from a stoichiometric mixture of reactants. Our attempts to prepare compound **2** or **3** as a single phase have always resulted in a mixture of both of them. Several synthetic trials have been made by varying the temperature of the reaction and the ratio of alkali-metal polysulfide flux to metal sulfides and the optimized synthetic conditions are given in the Experimental section. Lower temperature and lower quantities of alkali-metal polysulfide flux have been found to decrease the yield of the desired products.

Li₂CdSnS₄ (**1**) is a two-dimensional compound, consisting of Li⁺ ions interleaved between (CdSnS₄)²⁻ anionic layers, which are built from the corner-connection of two types of tetrahedra, SnS₄ and CdS₄. A tetrahedron of one type is corner-connected to four tetrahedra of the other type. Lithium, also, has tetrahedral coordination. All the metal atoms, Sn, Cd and Li, lie on crystallographic mirror planes with their coordination polyhedra, namely, MS₄ tetrahedra, disordered over two orientations, which are mirror images, as shown below schematically.

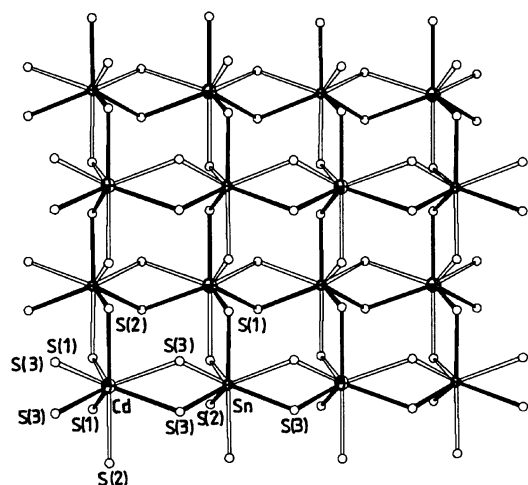


Therefore, the coordination number of each metal atom appears to be eight, with each sulfur atom having only a half occupancy. The apparent eight coordination of Sn and Cd metal atoms is seen in the ORTEP plot of the (CdSnS₄)²⁻ layer (Fig. 1), which shows the connectivity, through corners, and the disorder of the CdS₄ and SnS₄ tetrahedra. Interleaving of Li⁺ ions between these anionic layers, along the *c*-axis, is shown in the unit cell diagram (Fig. 2). Similar to the Sn and Cd atoms the lithium atoms have apparent eight coordination and show disorder in the LiS₄ tetrahedra. This compound is isostructural with Cu₂CdGeS₄.¹⁸

Na₂CdSnS₄ (**2**) is, in contrast to layered Li₂CdSnS₄ (**1**), a three-dimensional compound with the sodium, tin and cadmium

Table 2 Bond lengths (Å) in compounds **1**, **2** and **3**

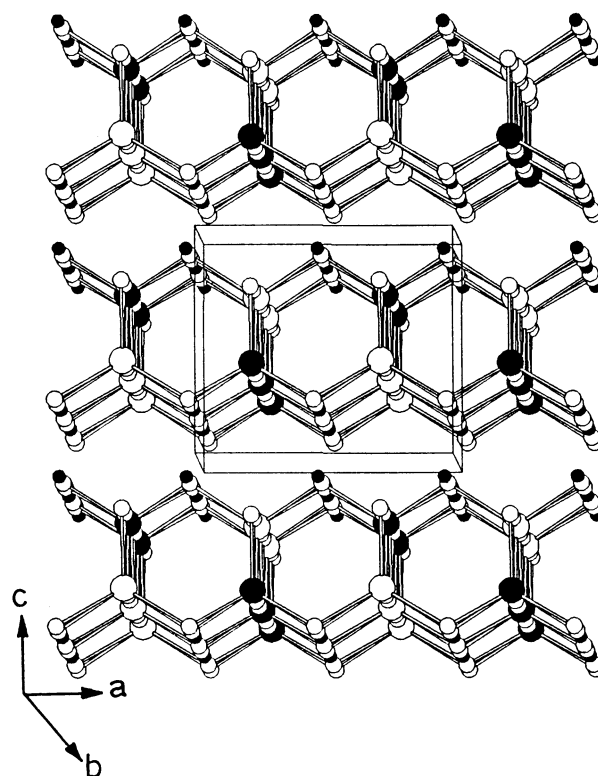
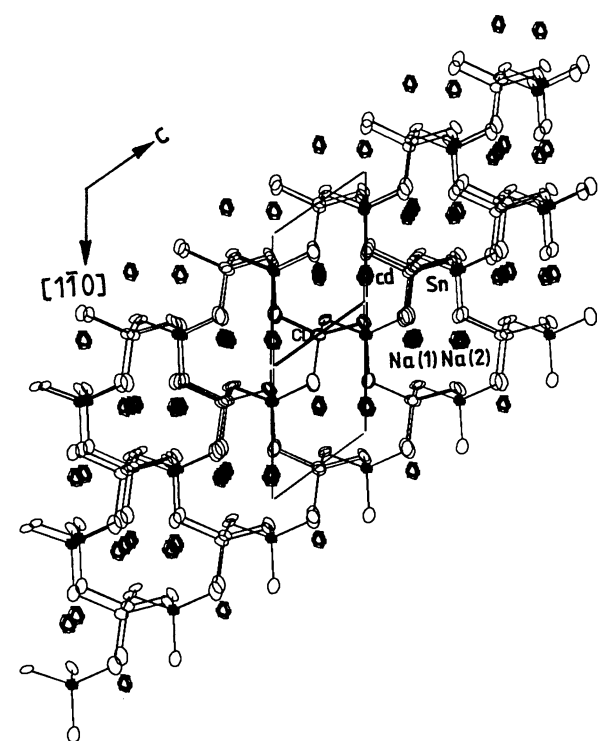
Li₂CdSnS₄			
Cd–S(1)	2.527(8)	Sn–S(1)	2.397(9)
Cd–S(2)	2.503(7)	Sn–S(2)	2.399(6)
Cd–S(3)	2.539(5) × 4	Sn–S(3)	2.406(5) × 4
Li–S(1)	2.351(20)	Li–S(2)	2.424(7)
Li–S(3)	2.445(22) × 4		
Na₂CdSnS₄			
Cd–S(1)	2.515(6) × 2	Na(1)–S(1)	2.726(8) × 2
Cd–S(2)	2.502(5) × 2	Na(1)–S(2)	3.078(13) × 2
Sn–S(1)	2.373(5) × 2	Na(2)–S(1)	2.872(13) × 2
Sn–S(2)	2.382(5) × 2	Na(2)–S(2)	2.591(8) × 2
Na₆CdSn₄S₁₂			
Cd–S(1)	2.774(2) × 2	Na(1)–S(1)	2.904(2) × 2
Cd–S(2)	2.780(2) × 4	Na(1)–S(2)	2.816(2) × 2
Sn(1)–S(1)	2.590(2) × 2	Na(1)–S(2)	2.968(2) × 2
Sn(1)–S(2)	2.577(7) × 4	Na(2)–S(1)	2.781(2) × 2
		Na(2)–S(2)	2.950(2) × 4

**Fig. 1** A segment of the $(\text{CdSnS}_4)^{2-}$ layer in $\text{Li}_2\text{CdSnS}_4$.

metals having tetrahedral coordination. SnS_4 and CdS_4 tetrahedra constitute the three dimensional $(\text{CdSnS}_4)^{2-}$ anionic framework, in which the tetrahedron of one metal is corner connected to four tetrahedra of the other metal. Sodium ions, as shown in Fig. 3, occupy the tetrahedral holes, in the channels parallel to the $[110]$ direction, of the $(\text{CdSnS}_4)^{2-}$ anionic framework. This structure is similar to that of LiAlSe_2 ,¹⁹ in that the aluminium sites are occupied, in an orderly fashion, by Sn and Cd in compound **2**. Its larger unit cell, compared to that of LiAlSe_2 , is due to the ordering of Sn and Cd.

The two compounds, **1** and **2**, containing a tetrahedral anionic framework are the first examples of $\text{A}_2\text{MM}'\text{S}_4$ containing lithium and sodium and are structurally different from other $\text{A}_2\text{MM}'\text{S}_4$ compounds reported⁹ so far. These corner connected, tetrahedral CdSnS_4^{2-} frameworks of compounds **1** and **2** are distinctly different from the layered CdSnS_4^{2-} frameworks of BaCdSnS_4 , wherein CdS_4 and SnS_4 tetrahedra are connected through both corners and edges.²⁰ In these two compounds, Sn–S and Cd–S bond lengths (Table 2) are in the ranges, 2.373(5)–2.406(5) Å and 2.502(5)–2.539(5) Å, respectively and the bond angles are close to the ideal value of 109.4°. The bond length variations are more apparent in **1** than in **2**.

$\text{Na}_6\text{CdSn}_4\text{S}_{12}$ (**3**) is a new two-dimensional compound, having $(\text{CdSn}_4\text{S}_{12})^{6-}$ anionic layers interleaved with Na^+ ions. This compound is structurally related to Na_2SnS_3 ,²¹ Tin, cadmium and sodium atoms, in compound **3**, could be conceived as occupying, in an orderly fashion, the octahedral sites in a hexagonal close packed array of sulfur atoms. As shown in Fig. 4, the structure has one layer of octahedral sites between every

**Fig. 2** Unit cell diagram of $\text{Li}_2\text{CdSnS}_4$ viewed along the b -axis. [● Cadmium. ○ Tin. ◦ Sulfur. • Lithium.]**Fig. 3** Unit cell diagram of $\text{Na}_2\text{CdSnS}_4$ viewed along the $[110]$ direction. For the sake of clarity, the sulfur atoms are not labelled.

two $(00l)$ planes of hexagonally close packed sulfur atoms. Every alternate layer of octahedral sites is exclusively occupied by sodium atoms. In every other layer, 2/3 of the octahedral sites, occupied by tin, and the remaining 1/3 sites, statistically half-occupied by cadmium, are ordered. That these 1/3 sites in Na_2SnS_3 are fully occupied by monovalent sodium is the only structural difference between Na_2SnS_3 and compound **3**. The structural correlation between Na_2SnS_3 and compound **3** can be

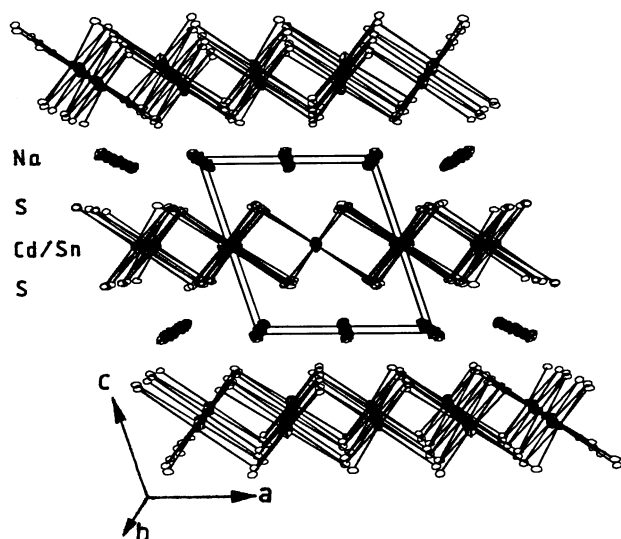


Fig. 4 Unit cell diagram of $\text{Na}_6\text{CdSn}_4\text{S}_{12}$ viewed along the b -axis.

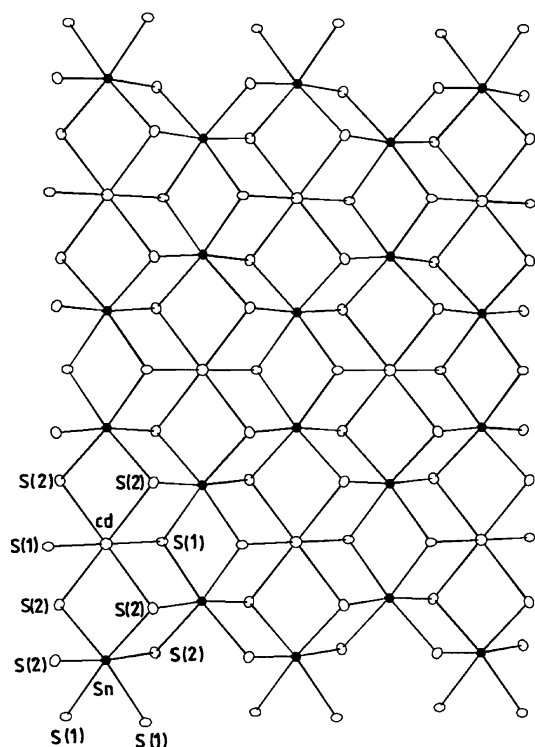


Fig. 5 A segment of the $(\text{CdSn}_4\text{S}_{12})^{6-}$ layer in $\text{Na}_6\text{CdSn}_4\text{S}_{12}$.

recognized from their alternative formulations, $\text{NaSn}_{2/3}\text{Na}_{1/3}\text{S}_2$ and $\text{NaSn}_{2/3}\text{Cd}_{1/6}\square_{1/6}\text{S}_2$ (\square = vacancy), respectively.

In every $(\text{CdSn}_4\text{S}_{12})^{6-}$ layer (Fig. 5), as a result of the ordering of tin and half-occupied cadmium atoms, each CdS_6 octahedron shares six edges with six SnS_6 octahedra and each SnS_6 octahedron shares an edge each, with three SnS_6 octahedra and one and half CdS_6 octahedra. All the sodium, tin and cadmium metal atoms are each octahedrally coordinated to two S(1) and four S(2) sulfur atoms. The two S(1) atoms are *cis* to each other in the octahedral coordination of Sn and Na(1) and *trans* in those of Cd and Na(2). Sn–S bond lengths in **3** are, as expected, longer than those in **1** and **2** containing tetrahedrally coordinated tin whereas the Cd–S bond lengths in all three compounds are similar (Table 2). Each sulfur atom is six-coordinated in **3** and four coordinated in **1** and **2**. The metal–sulfur bond lengths (Table 2) for the three compounds, in general, compare well with those reported in the literature.^{17,21–23} The structures of the three compounds, **1–3** could be imagined to have resulted from the different ways of ordering Li^+/Na^+ , Sn^{4+} and Cd^{2+} ions in

either the octahedral or tetrahedral sites in the arrays of sulfur atoms and this ordering is essentially due to the difference in sizes and charges of the ions.

The optical absorption spectrum (Fig. 6) of compound **2** clearly exhibits a steep absorption edge from which the band gap has been calculated to be 1.52 eV, indicating its semiconducting nature. The spectra of the other two compounds do not show any absorption edge around this semiconducting region. We have not succeeded in the synthesis of related compounds such as selenide analogues and isostructural sulfides containing other metal ions with tetrahedral coordination. Also unsuccessful were the ion-exchange reactions of layered compounds **1** and **3**, carried out by stirring/refluxing with aqueous/methanolic solutions of alkali-metal and tetramethylammonium salts.

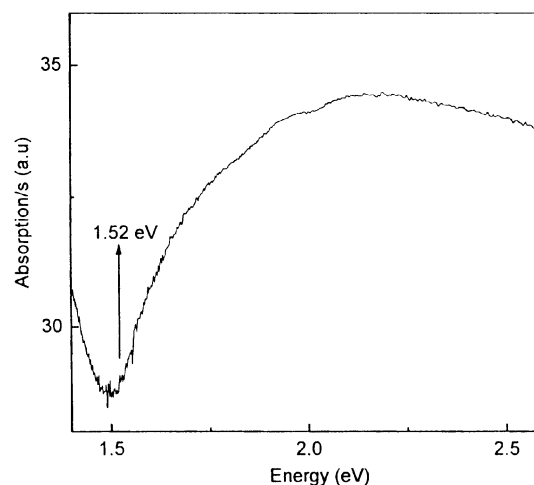


Fig. 6 Optical absorption spectrum of $\text{Na}_2\text{CdSnS}_4$.

Conclusion

Three new sulfides, layered $\text{Li}_2\text{CdSnS}_4$ (**1**), three-dimensional $\text{Na}_2\text{CdSnS}_4$ (**2**) and layered $\text{Na}_6\text{CdSn}_4\text{S}_{12}$ (**3**) have been synthesized using a molten flux of alkali-metal polysulfides. Their crystal structures have been determined by single crystal X-ray diffraction studies and shown to be related to those of $\text{Cu}_2\text{CdGeS}_4$, LiAlSe_2 and Na_2SnS_3 . These three compounds constitute the first examples of sulfides in the quaternary A/Cd/Sn/S systems.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research (CSIR), Government of India, for financial support (Project No. 01(1339)/95/EMR-II) and Regional Sophisticated Instrumentation Center of our institute for single crystal X-ray data collection.

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