

Synthesis and Characterization of the $Zn_xCd_{1-x}In_2S_4$ Pseudoternary Solid Solution

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We have synthesized several compounds of the $Zn_xCd_{1-x}In_2S_4$ family by solid phase reactions and chemical transport reactions using iodine. The reaction products have been characterized as to composition, structure, and lattice dynamics. Here we discuss and compare the different results obtained by the two synthesis methods. © 1987 Academic Press, Inc.

Introduction

Recently defective ternary compounds of $A^{II}B^{III}_2X^{VI}_4$ stoichiometry (where $A = Zn, Cd$; $B = Ga, In$; $X = S, Se$) have received renewed attention due to their fundamental and applied interest (1-5). These compounds show generally high nonlinear optical susceptibilities as well as electrooptical coefficients: because of their figures of merit, these compounds are of interest for possible applications in the field of optical communications (6).

As to their fundamental interest, all defective ternary compounds are characterized by a tridimensional (defect chalcopyrites) or bidimensional (layered compounds) ordered array of vacancies. In these structures the presence of two cation and one vacancy sublattices raises many questions about their structural stability, the ordering within each sublattice, and related order-disorder phase transitions (7).

From a structural viewpoint the layered structures which are found among ternary compounds like $ZnIn_2S_4$ or $MnAl_2S_4$ and among some quaternary compositions like $CdGaInS_4$ (8), $CdIn_2S_2Se_2$ (9), $CoGaInS_4$ (10), and $HgGaInS_4$ (11) are particularly intriguing. In these layered systems two cations have tetrahedral coordination and the third an octahedral one: this situation is intermediate between that found in spinels (like $CdIn_2S_4$) and that of defect chalcopyrites (like $CdGa_2S_4$). It has been shown, moreover, that some ternary layered or defect chalcopyrite compounds may transform under pressure to spinel structure and spinels to sodium chloride structure (12-15). This situation is mirrored by the fact that the structural coordinates built from hard core pseudopotentials (16-18) show a continuous trend from tetrahedral to spinel structures.

These fundamental points, together with specific applicative interest for electro-optical memories (19-23), stimulated the

study of the $Zn_xCd_{1-x}In_2S_4$ system whose ternary end members have rhombohedral layered ($ZnIn_2S_4$) or cubic spinel ($CdIn_2S_4$) structures (24, 25), and are affected by a variable degree of static disorder as antisites and nonstoichiometry (26, 27). Here we report the main results on polycrystalline and single crystal preparations of several $Zn_xCd_{1-x}In_2S_4$ compounds and their compositional, structural, and dynamical characterization.

Results

Synthesis and Characterization

Polycrystalline samples of $Zn_xCd_{1-x}In_2S_4$ were prepared at 900°C by heating under vacuum stoichiometric amounts of the corresponding sulphides (Koch-Light, 5 N pure) in a sealed quartz tube. After about one week the ampoules were quenched to room temperature. The reaction products were monitored by X-ray diffraction: for each synthesis several grindings and thermal treatments were necessary before definite phases were obtained. Crystalline samples were prepared by the closed tube chemical transport reaction (CTR), which is usually employed for the synthesis of compounds which melt incongruently or at high temperatures. Quartz ampoules (12 cm length, 2 cm internal diameter) were loaded with 2–5 g charges of the elements (5 N pure, K&K or Koch-Light) in a ratio corresponding to the expected stoichiometric composition of the final solid solution. Suitable amounts of iodine (3 mg/cm^3) were then distilled into the ampoule evacuated to 10^{-4} Torr. After iodine distillation the ampoules were sealed and placed in a temperature gradient within a two zone horizontal furnace.

Three different temperature vs time profiles were employed, namely the Stationary Temperature Profile (STP), the Linear Time Varying Temperature Profile

(LTVTP), and the Oscillating Temperature Profile (OTP) (28–31). The STP procedure was employed to determine the best growth temperature for each nominal composition. The transport kinetics observed in STP for $x = 0.6$ is reported in Fig. 1 as a function of iodine concentration. For this composition we have observed phase separation. The LTVTP method, which is suitable for growth of a reduced number of larger crystals in comparison to the STP method, was employed for the crystal growth. In this method the deposition temperature T_D is kept constant while the source temperature T_S is increased linearly with time. In the present case the temperatures were varied from $T_S - T_D \approx -10^\circ\text{C}$ to $T_S - T_D \approx 80^\circ\text{C}$. With T variations of about 0.3°C/hr we obtained $20 \times 10 \times 1 \text{ mm}^3$ $ZnIn_2S_4$ crystals and $10 \times 10 \times 5 \text{ mm}^3$ $CdIn_2S_4$ crystals. Smaller size crystals were obtained in the coexistence region of the quaternary compounds, namely $10 \times 5 \times 2 \text{ mm}^3$ and 5×5

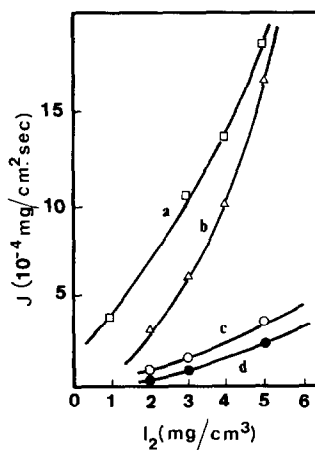


FIG. 1. Mass transport coefficient J for layered ($ZnIn_2S_4$ -like) and cubic ($CdIn_2S_4$ -like) phases as a function of iodine concentration. Stationary temperature profile: $T_S \approx 830^\circ\text{C}$ $T_D \approx 780^\circ\text{C}$. (a) Layered phase, 2-cm-internal-diameter ampoules; (b) spinel phase, 2-cm-internal-diameter ampoules; (c) layered phase, 1-cm-internal-diameter ampoules; (d) spinel phase, 1-cm-internal-diameter ampoules.

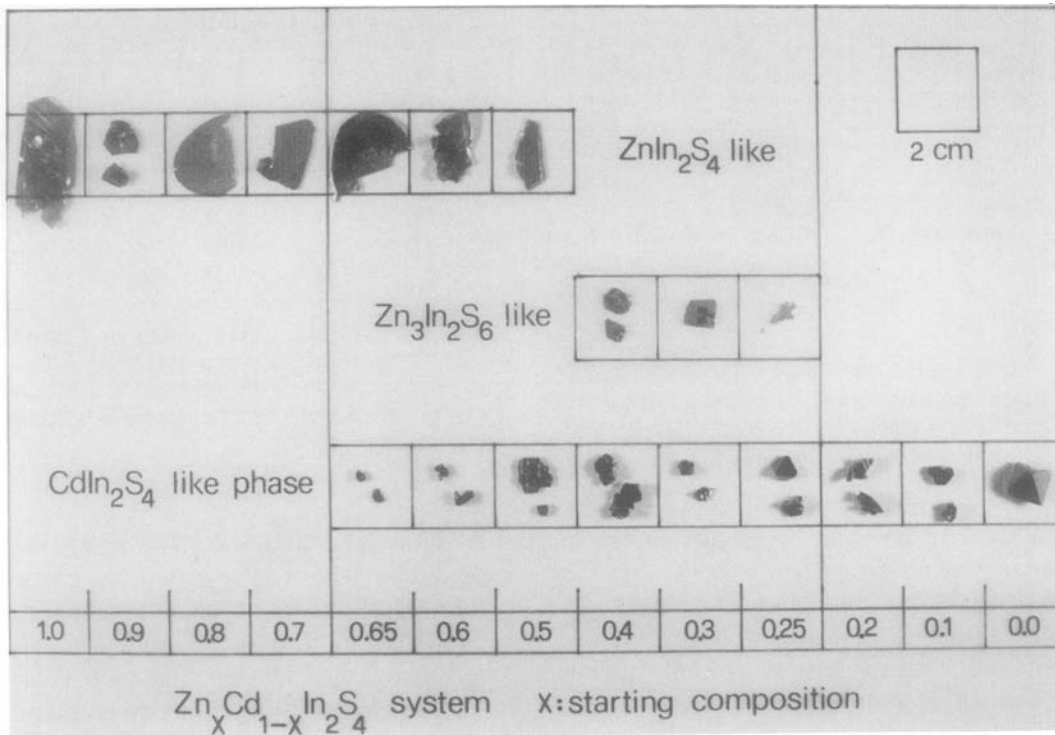


FIG. 2. The CTR crystalline reaction products as a function of starting composition x .

$\times 3 \text{ mm}^3$ for the largest layered and spinel crystals, respectively (Fig. 2).

Another synthesis method, namely LTVTP + OTP, which is more effective the slower the growth kinetics of the crystals, was employed in those cases in which very small amounts of one of the two phases were obtained. The LTVTP + OTP procedure is based on an initial LTVTP stage by which a few initial seed crystals are grown, followed by T_D oscillations. Large frequencies and small amplitudes of the change in T_D , once properly chosen, can control the growth of the best seeds, while reducing and even eliminating a faulty growth. Our purpose was to increase the sample size and to modify the mL and mS (layer to spinel phase mass) ratio toward more favorable values. The temperature profile used was: $T_S = 780^\circ\text{C}$ (fixed); T_D (sawtooth) linear increase from 770 to 830°C in $20\text{--}80$

min, linear decrease back to 770°C in $20\text{--}80$ min, hold in for 10 min. at 770°C . Figure 3 shows how it is possible to change the layer

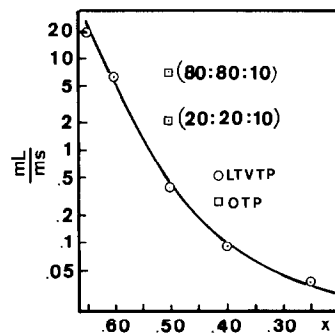


FIG. 3. Ratio of the layered (mL) to spinel (mS) phases as a function of the starting composition x obtained by LTVTP (solid line). For $x = 0.5$ some OTP results are shown. The numbers in parentheses indicate the time profiles used. OTP favors the spinel phase.

TABLE I

Starting composition x	Found ratio (Zn + Cd)/In	Found ratio Zn/Cd
1.0	1.10/2	—
0.8	1.00/2	0.82/0.18
0.7	1.06/2	0.77/0.22
0.6	1.00/2	0.76/0.21
0.5	1.18/2	0.81/0.19
0.4	2.15/2	0.86/0.13
0.3	3.10/2	0.77/0.22

Note. Compositional analysis results obtained by atomic absorption spectroscopy from layered phase crystals as a function of the starting composition x . Notice the discontinuity beyond $x = 0.5$.

to spinel mass ratio by modifying the frequency of the temperature oscillations. The masses of the two phases obtained were measured by directly weighing the red (spinel) and yellow (layered) crystals obtained from the reaction and selected manually under a metallographic microscope. The compositions of the crystals obtained by LTVTP were determined by atomic absorption spectroscopy after dissolution of the samples in $\text{H}_2\text{O}:\text{HCl}:\text{HNO}_3$ (100 : 100 : 1) medium at 40–50°C. In this way it was possible to determine only

TABLE II

Starting composition x	$x(\text{Zn})$	$x(\text{Cd})$	Found composition
1.0	0.98	0.00	$\text{Zn}_{0.98}\text{In}_2\text{S}_4$
0.9	0.84	0.11	$\text{Zn}_{0.84}\text{Cd}_{0.11}\text{In}_2\text{S}_4$
0.8	0.76	0.21	$\text{Zn}_{0.76}\text{Cd}_{0.21}\text{In}_2\text{S}_4$
0.7	0.72	0.26	$\text{Zn}_{0.72}\text{Cd}_{0.26}\text{In}_2\text{S}_4$
0.6	0.72	0.27	$\text{Zn}_{0.72}\text{Cd}_{0.27}\text{In}_2\text{S}_4$

Note. Microprobe analysis results for cations, obtained from some CTR grown layered crystals as a function of the starting composition. As in Table I the limit of substitution of Zn by Cd appears to be around 0.3.

the cation concentrations. The results are reported in Table I. These data have been confirmed, for some of the solid solutions, by microprobe analysis (Table II). The structure of the samples was then determined by X-ray diffraction using photographic and diffractometric methods. The cell parameters were refined by a least-squares fitting procedure and the results obtained are shown in Table III.

As to spinel phases, the crystalline and polycrystalline samples gave the same results for all the starting compositions. On

TABLE III

x	Layered phase				
	Cubic phase a	Polycrystalline		Crystalline	
		a	c	a	c
1.0	—	3.856(3)	36.98(6)	3.859(2)	36.99(1)
0.8	10.720(4)	3.859(3)	36.99(7)	3.861(3)	36.98(9)
0.6	10.730(5)	3.864(5)	37.00(8)	3.863(9)	37.01(2)
0.5	10.726(4)	3.863(4)	37.00(8)	3.863(7)	37.05(1)
0.4	10.742(6)	3.870(5)	37.01(8)	3.869(7)	18.58(7)
0.3	10.754(5)	3.871(5)	37.02(9)	3.889(2)	6.359(4)
0.2	10.758(4)	—	—	—	—
0.0	10.810(5)	—	—	—	—

Note. Least-squares fitting results of X-ray diffraction data: lattice parameters a and c (in Å) of the reaction products as a function of nominal composition and growth procedure.

the other hand, the polycrystalline and single crystal layered phases showed the same cell parameters only in the $1 \leq x \leq 0.5$ range whereas for $x = 0.4$ and $x = 0.3$ different results were obtained, in agreement with the AAS measurements.

From the extinction conditions, Bunn's chart, lattice parameters, and comparison with standard structures (32) we propose the space groups reported in Table IV.

Raman Spectrum of Zn_xCd_{1-x}In₂S₄

Raman scattering has proven to be a sensitive, fast, and nondestructive tool for characterizing and distinguishing the crystalline phases even in the case of very small amounts of reaction products. Raman spectra were taken at room temperature, in backscattering geometry, using 6471 Å (Kr laser) or 5145 Å (Ar laser) exciting wavelengths. Scattered radiation was generally not polarization analyzed. The spectra were recorded through a SPEX 1401 double monochromator and a RCA 31034A cooled photomultiplier, by the photon counting technique. The comparison between the Raman spectra of the ternary end members

TABLE IV

Samples	Space group	Structures
Polycrystalline layered $1 \geq x \geq 0.3$	<i>R3m</i>	ZnIn ₂ S ₄ P (III)
Crystalline layered $1 \geq x \geq 0.5$	<i>R3m</i>	ZnIn ₂ S ₄ P (III)
$x = 0.4$	<i>P3m1</i>	Zn ₃ In ₂ S ₈
$x = 0.3$	<i>P6mc</i>	Disordered wurtzite
Polycrystalline and crystalline spinels $0.8 \geq x \geq 0$	<i>Fd3m</i>	CdIn ₂ S ₄

Note. Summary of the proposed space groups and parent structures in Zn_xCd_{1-x}In₂S₄ as a function of composition and growth procedures.

(26, 33–36) and those of the samples under investigation gives information on their actual composition and structure. In Fig. 4 we show the results obtained at 6471 Å, as a function of composition, on the spinel CdIn₂S₄-like phase. Our results on CdIn₂S₄ agree with those of the literature (33) except for the strong intensity of the 92-cm⁻¹ peak. Symmetry and character are not univocally assigned, especially in the high energy part of the spectra (33, 34). This region (molecular mode region) seems to be affected by disorder connected to partial inversion of Cd and In on tetrahedral and octahedral sites (27), hence the apparent broadening of the peaks.

As to the solid solution, the partial substitution of Cd by Zn has little effect on these peaks. Even if the smaller ionic

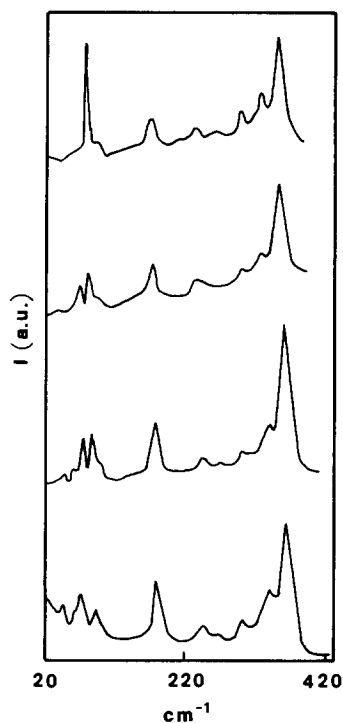


FIG. 4. The Raman spectra of the spinel phases. Top to bottom: CdIn₂S₄, Zn_{0.2}Cd_{0.8}In₂S₄, Zn_{0.4}Cd_{0.6}In₂S₄, Zn_{0.6}Cd_{0.4}In₂S₄ starting compositions. The first two are obtained as a single phase while the latter two are in coexistence with layered phases.

radius of Zn should decrease the uncertainty of cation coordination (37) and increase the peak contrast, the effect of alloying results in a small broadening with respect to the end member. On the other hand, marked effects tied to Cd–Zn substitution are observed at lower frequencies, where the strong 92-cm^{-1} peak is seen to be damped and split, and some interference effects probably appear in the region from 40 to 80 cm^{-1} .

To interpret these results not only are better quality crystals needed, but also the cubic spinel form of ZnIn_2S_4 reported in the literature (33), as well as the corresponding cubic $\text{Zn}_x\text{Cd}_{1-x}\text{In}_2\text{S}_4$ alloy, in order to compare their spectra with the present ones.

In Fig. 5 we show the results obtained at 5145 \AA from single crystals (left) and poly-

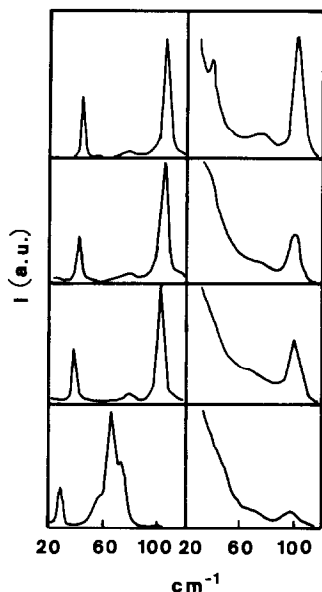


FIG. 5. Comparison of the low frequency Raman spectra obtained from the layered phases grown by CTR (left) and solid phase reaction (right), as a function of starting composition. Top to bottom: ZnIn_2S_4 , $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{In}_2\text{S}_4$, $\text{Zn}_{0.6}\text{Cd}_{0.4}\text{In}_2\text{S}_4$, $\text{Zn}_{0.4}\text{Cd}_{0.6}\text{In}_2\text{S}_4$ (left), ZnIn_2S_4 , $\text{Zn}_{0.6}\text{Cd}_{0.4}\text{In}_2\text{S}_4$, $\text{Zn}_{0.4}\text{Cd}_{0.6}\text{In}_2\text{S}_4$, $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{In}_2\text{S}_4$ (right).

crystalline samples (right) of the layered phase as a function of nominal composition. At this wavelength CdIn_2S_4 is strongly absorbing while ZnIn_2S_4 is still transparent: so the Raman spectra reported for polycrystalline materials contain contributions only from the layered ZnIn_2S_4 -like phase.

The Raman spectrum of ZnIn_2S_4 is known, but the symmetry and character assignments of the phonons are questionable (26). The high energy part of the spectral distribution seems to be affected by disorder (35, 36): in the alloy the disorder-induced broadening is larger and the spectra are quite similar to each other. Hence we report and discuss only the lower energy part of the Raman spectra. In this frequency range rigid layer (RL) modes are usually observed in layered structures (32, 38). As seen from Fig. 5 the spectra of crystalline samples are characterized, in the RL mode region, by two strong peaks whose frequency shifts to lower energies as the nominal Cd content increases. This effect is stronger for the 42-cm^{-1} peak (4 cm^{-1} ; 10%) than for the 104-cm^{-1} peak (3 cm^{-1} ; 3%). For the nominal composition $x = 0.5$, or lower, the spectral distribution changes abruptly, showing an increased number of lower energy features, thus suggesting some structural change.

The polycrystalline samples, on the other hand, show a continuous variation of the spectrum down to the existence limit of the phase ($x = 0.30$). The 42-cm^{-1} peak, due to the strong quasielastic scattering of the powder, has been tracked only for low nominal Cd content, and is smeared out in the quasielastic continuum for lower scattering intensities (higher nominal Cd content).

As the main difference between crystalline and polycrystalline samples is the synthesis procedure, we argue that CTR is more critical, as to reaction products, than solid phase reaction. This is confirmed by the results obtained from different synthe-

sis runs at $x = 0.5$ (Fig. 6) and $x = 0.3$ (Fig. 7). In Fig. 6 we compare two 0.5 runs (unstable) to a 0.4 run (stable): we see that in one case we obtain the ZnIn₂S₄-like spectrum, in the other a singular spectrum, which could be seen as a convolution of the spectra of the two different structures. In Fig. 7 we compare the $x = 0.4$ spectrum to those of three different $x = 0.3$ synthesis runs: the general features are similar to each other, but the 0.3 samples show marked frequency differences from run to run. In this case it is the higher energy part of the spectrum to be affected in stronger way. The $x = 0.3$ nominal composition, which is the existence limit of the layered phase, is another example of CTR instability.

Raman scattering has not only been able to finely discriminate between different synthesis runs, but also to give definite evidence of the nature of the 0.4 compound. The composition analysis results (Table I) suggested that higher polytypes of

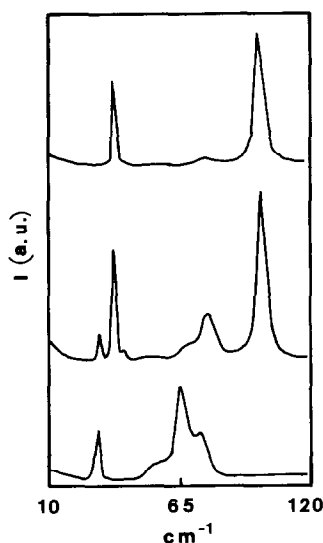


FIG. 6. Comparison of the low frequency Raman spectra of the layered phases obtained in three different CTR runs for $x = 0.5$. The instability of CTR for this starting composition is immediately evident.

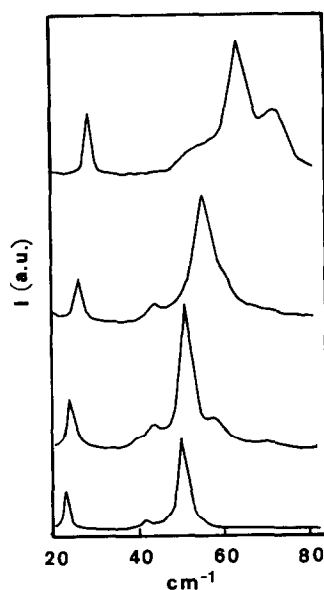


FIG. 7. The low frequency Raman spectra of the CTR layered phases obtained at $x = 0.4$ (top) and three different runs at $x = 0.3$. The instability of CTR for this composition is again immediately evident.

ZnIn₂S₄ (i.e., Zn₂In₂S₅ or Zn₃In₂S₆) could have been obtained (32, 38–46). To check this possibility we synthesized by LTVTP Zn₃In₂S₆ and Zn_{2.4}Cd_{0.6}In₂S₆. Their Raman spectra, together with that of $x = 0.4$ layered alloy phase, are reported in Fig. 8. We notice the similarities of the Raman spectra of Zn₃In₂S₆ and Zn_{2.4}Cd_{0.6}In₂S₆ (starting composition): apart from a knee around 50 cm⁻¹, the spectra are almost indistinguishable. On the other hand, this knee transforms into a shoulder in the spectrum of Zn_{0.4}Cd_{0.6}In₂S₄. Hence the knee at 50 cm⁻¹ may be clearly attributed to Cd. So we conclude that the layered crystals obtained for $x = 0.4$ have a Zn₃In₂S₆-like structure (32), in accordance with the results of X-ray and composition analysis.

Discussion

We have shown that the Zn_xCd_{1-x}In₂S₄ solid solution, irrespective of the synthesis

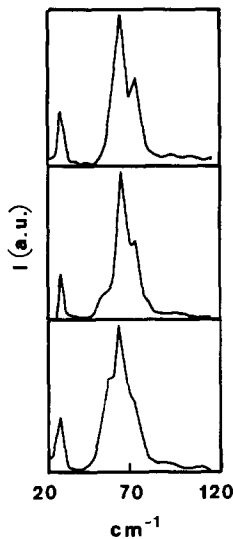


FIG. 8. The low frequency Raman spectra of (top to bottom) $\text{Zn}_3\text{In}_2\text{S}_6$, $\text{Zn}_{2.4}\text{Cd}_{0.6}\text{In}_2\text{S}_6$, and $\text{Zn}_{0.4}\text{Cd}_{0.6}\text{In}_2\text{S}_4$ layered phases, obtained by CTR. Notice the close similarity of the spectra.

procedure, is characterized by a large miscibility gap: in the immiscibility range the relative amounts of spinel and layered reaction products obtained by CTR depend on the synthesis procedure.

We have found that the $\text{Zn}_x\text{Cd}_{1-x}\text{In}_2\text{S}_4$ system exhibits (a) solid solution with layered structure in the $x \geq 0.7$ range; (b) coexistence of separate layered and spinel phases in the region $0.25 \leq x \leq 0.65$; and (c) solid solution with spinel structure in the $x \leq 0.2$ range. As to the layered phase, the low frequency part of the Raman spectra shows (Fig. 5) that the substitution of Zn by Cd causes only a shift to lower energies of the two low energy peaks. For polycrystalline samples the effect is observed down to the existence limit of the layered phase ($x = 0.25$), while for crystalline samples this is observed down to $x = 0.5$. This shows that the layered phase maintains, within the compositional limits quoted above, the structure of the ZnIn_2S_4 parent compound as suggested also by X-ray analysis (Table

III). The Raman spectra also show that spectral variations are observed for the layered phase beyond the solubility limit ($x = 0.7$): this suggests that some more Cd enters into the layered compounds even in the phase separation region.

A strong difference is observed between solid phase reaction and CTR synthesized layered phases for $0.3 < x < 0.5$. For solid phase reaction the layered phase maintains the structure of polytype III of ZnIn_2S_4 over the whole existence range. As to CTR grown samples, Table I and Fig. 5 show an abrupt structural change for $x = 0.5$. As the $(\text{Zn} + \text{Cd})/\text{In}$ ratio increases, more complex Raman spectra are obtained. At the border points $x = 0.5$ and $x = 0.3$ (Figs. 6–7) the CTR reaction appears to be unstable, as the products depend on the particular synthesis run. For $x = 0.4$, a $\text{Zn}_3\text{In}_2\text{S}_6$ -like phase is obtained, as confirmed by the synthesis of $\text{Zn}_{2.4}\text{Cd}_{0.6}\text{In}_2\text{S}_6$ (Fig. 8). For $x = 0.3$ still different results are obtained as seen from Raman spectra (Fig. 7) and X-ray analysis (Tables III–IV).

The differences observed between solid phase reaction and chemical transport reaction results may be ascribed to the effects of iodine and thermal quenching. Some of the literature results indicate in fact that ZnS-rich phases appear to be stable at high temperatures (45, 46). These two possibilities are suggested by similar results recently obtained for the systems CoGaInS_4 and HgGaInS_4 (10, 11): it is apparent that the gas phase reaction kinetics for such complex systems needs further fundamental studies before one could consider CTR a reliable synthesis technique for these compounds. Some of the uncertainties affecting the X-ray scattering results for the $0.5 < x < 0.3$ layered phases may be connected to the appearance of structural mixtures tied to this reaction instability.

From a structural point of view, the presence in all the $x = 0.3$ CTR synthesized layered phases of a phonon at 22 cm^{-1} ,

which should be indexed as an RL mode according to its frequency, is in contrast with the length of the *c* axis, determined by X-ray scattering. This length, of about 18 Å, would imply that the unit cell contains only one layer, and then no RL mode should be observed (47). This contradiction, together with the difficulty of assigning even to ZnIn₂S₄ an unambiguous space group (35, 36), would mean that these ternary layered structures have not been up to now completely understood. To further analyze this structural problem, we are presently extending the structural analysis to other ternary compounds both by means of Raman measurements as a function of temperature and pressure and by local order study using EXAFS spectroscopy.

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