JOURNAL OF MATERIALS SCIENCE 33 (1998) 4333–4339

Chemical synthesis of the high-pressure cubic-spinel phase of $ZnIn_2S_4$

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Chemical reactions conducted in solution are known to generate solid precursors containing molecular units that help in the formation of high-temperature phases. The structural units are created by controlling the molecular environments in solution, and as a result, phases that normally form and are stable at high temperatures can be synthesized at low or moderately elevated temperatures. However, the application of chemical approaches for synthesizing phases that normally form at high pressure are relatively unknown. In this work, a simple room-temperature aqueous chemical precipitation route has been used to synthesize the high-pressure cubic spinel modification of $ZnIn_2S_4$. A solution coordination model (SCM) has been proposed to explain the formation of the high-pressure phase. The crystallinity, phase purity and phase transformation characteristics of the cubic phase have been studied using X-ray diffraction (XRD) including Rietveld refinement, transmission electron microscopy (TEM), and Auger electron microscopy (AEM). Results of these studies are discussed in the light of a proposed solution coordination model (SCM).

1. Introduction

Zinc indium sulphide is a ternary chalcogenide which belongs to the AB_2X_4 (A = Zn, Cd, Hg, B = Al, Ga, In, X = S, Se, Te) class of compound semiconductors [1]. These ternary chalcogenide semiconductors, despite their varying lattice structures, have localized centres not attributed to impurities but to "intrinsic disorder", which is a result of disorder in the cationic sublattice [1–3]. The high density of such centres contributes to some interesting physical properties. Single crystals of hexagonal zinc indium sulphide grown by chemical vapour deposition (CVD) have been reported to exhibit photoluminescence [4, 5] and photoconductivity [6–8]. These properties could make the material particularly useful for various electronic and optical device applications. Bilenkii *et al.* [9] have also reported that all of the valuable properties observed in single-crystal zinc indium sulphide could be reproduced in thin layers (which are required in many device applications) if stoichiometric layers could be synthesized with minimum defects.

$ZnIn_2S_4$ exhibits two distinct polymorphs based on hexagonal and cubic lattices. The hexagonal polymorph of $ZnIn_2S_4$ also exhibits several different polytypes. The structure of these polytypes is essentially based on a stacking of packets of S–Zn–S–In–S–In–S layers. Each packet could have an ABCA stacking of sulphur atoms or an ABAB stacking of sulphur atoms [10]. In each packet containing zinc, indium and sulphur, the zinc atoms are tetrahedrally coordinated by sulphur atoms, the indium atoms of one layers are tetrahedrally coordinated and those of the other layer are octahedrally coordinated by sulphur atoms. The stacking of these packets also generates a layer of vacancies between two weakly bonded sulphur layers. Therefore, several polytypes exist from a single packet per unit cell (1H polytype, $a = 0.385$ nm, $c = 1.234$ nm [10]) and three packets per unit cell (3R polytype, $a = 0.385$ nm, $c = 3.70$ nm [11]) to 24 packets per unit cell (24R polytype, $a = 0.385$ nm, $c = 29.62$ nm [10]). Lappe *et al.* [11] first synthesized the 3R polytype of $ZnIn_2S_4$ from a solid-state reaction of precipitated ZnS and In_2S_3 powders encapsulated in an evacuated quartz ampoule.

The cubic spinel phase of $ZnIn_2S_4$ (exhibiting a normal spinel structure) has been synthesized by Range *et al.* [12] by transforming the 3R polytype at 400 °C with the application of a pressure of 4Mpa for 2h. They have observed that this cubic spinel phase is stable at room temperature and atmospheric pressure and that no transformation to the hexagonal phase occurred even after a period of 1 y. However, when the cubic phase was heated above 500 °C under vacuum or under ambient pressure, it transformed back to the hexagonal phase. The structure of this phase has been reinvestigated recently by the same group [13] using the Rietveld refinement of X-ray diffraction patterns. The normal spinel structure can be described by an ABC stacking of sulphur atoms with zinc atoms occupying tetrahedral interstices and indium occupying only octahedral interstices in the structure. While the hexagonal phase has been studied for its electronic and optical properties, very little is known regarding similar properties of the high-pressure cubic-spinel phase of $ZnIn_2S_4$. Unger *et al.* [14], for example, have compared Raman and photoluminescence spectra of the spinel phases of $CdIn_2S_4$ and $ZnIn_2S_4$.

In recent years, there has been considerable interest in processing materials based on solution chemistry techniques. Various modifications of chemical reactions have been incorporated for synthesizing a number of oxide and non-oxide materials for electronic, optical, electro-optical, and magnetic applications. This surge of interest has arisen with the advent of the sol–gel technique and its demonstrated flexibility in synthesizing stoichiometric, high-purity single and multicomponent oxide materials in amorphous and crystalline forms [15–18]. The technique has also been exploited to synthesize nanocrystalline materials in thin film and particulate forms. In addition, its applicability to synthesize non-oxide sulphide and nitride ceramics has also been demonstrated [19–21]. The excellent potential and flexibility demonstrated by various solution chemical methods has initiated considerable research, mainly directed at understanding the influence and role of precursor chemistry on the formation and stability of phases, particularly in oxide systems. It is now well known that the reactions occurring in solution strongly influence the formation of molecular units in the precursor whose short-range structures resemble the near-neighbour cationic coordinations present in the desired high-temperature phases. These units therefore play an important role in enhancing the kinetics of formation of the desired high-temperature phases at low or moderately low temperatures, and in short reaction times. In this context, the nature of the starting materials, the extent of mixing at the molecular level, the resultant chemical homogeneity in solution, and their combined effects on the evolution of phases, have been demonstrated in certain systems, such as cordierite [22]. In the last few years, the advantages of techniques based on solution chemistry for processing ceramic materials have become particularly distinct and a considerable amount of research has been conducted in this area. However, while chemical techniques have been routinely used to synthesize high-temperature phases, their application to synthesize directly high-pressure phases is relatively unknown apart from few reports in the literature [23, 24] on indirectly synthesizing these phases by application of high pressures to the chemically derived precursors.

Most chemical approaches involve the use of inorganic salts which are dissolved in aqueous (highly polar) or non-aqueous (polar or non-polar) solvents. These salts undergo chemical modifications in solutions. Salts of most electropositive elements exhibiting complete ionic bonding (Na^+, Li^+, etc.) are entirely dissociated in aqueous solutions with a spherical coordination of water molecules around the metal ions. However, less electropositive metals possessing more covalent bonding are not completely dissociated, and tend to form specific coordinated complexes with the solvent molecules. The coordinated complex which has a net charge, is known to play a significant role in the formation of novel molecular clusters. It is possible that these molecularly coordinated species in solution also play an important role in the formation of solid precursors possessing similar structures. These coordinated clusters in solution could undergo a reaction, causing replacement of the coordinated solvent species leading to the formation of a solid wherein the cations retain the same coordinated states seen in solution. As a result, solid precursors can be generated from solution, exhibiting metastable cation environments that normally would have to be stabilized under conditions of high pressure and/or temperature. In this paper, we describe a simple aqueous chemical approach to synthesize the high-pressure modification (cubic spinel structure) of $ZnIn_2S_4$. The Rietveld technique was used to refine the XRD pattern of the cubic spinel phase in order to determine the lattice parameter and cation distributions. The experimental results can be explained by correlating the molecular environment of cations in solution to the coordination of cations seen in the resulting precipitated solid.

2. Experimental procedure

Stock solutions of zinc chloride (Alfa, 99.99% metals basis) and indium chloride (Alfa, 99.999%) corresponding to a 1 : 2 molar ratio were prepared separately. Owing to their hygroscopic nature, the salts were weighed in an atmosphere-controlled glove box (Vacuum Atmospheres, CA) in order to prevent any absorption of moisture. The molarity of the zinc and indium chloride solutions were 0.01223 M and 0.02446 M, respectively. Equal volume amounts of each of the two solutions were mixed and sulphidized using H_2S gas (commercial purity, 99.5%). Passage of H_2S gas resulted in a voluminous precipitate which was collected using a high-power centrifuge. The powder collected after centrifugation was washed several times using both deionized water and 200 proof ethanol, and then dried in air for 5d to obtain several pieces of hard agglomerates. The dried precipitate was ground and analysed using X-ray diffraction (Rigaku θ/θ diffractometer, Tokyo, Japan, equipped with a diffracted beam graphite monochromator; the radiation used contained $CuK_{\alpha1}$and $CuK_{\alpha2}$ components). The precipitate was also analysed for its crystallite size and chemical composition using high-resolution transmission electron microscopy (HRTEM, Jeol 4000EX).

The precipitated $ZnIn_2S_4$ powders were heat treated in an evacuated quartz tube according to the following temperature schedule: ramp rate of $5\,^\circ C\,min^{-1}$ from room temperature to 400 °C, dwell time = 2h, followed by a heating rate of $5\,^\circ C\,min^{-1}$

from 400–500 °C with a dwell time of 1h. The heat-treatment conditions led to the growth of the cubic phase without permitting significant transformation to the hexagonal phase. X-ray diffraction was conducted on the powder using the same instrument, and following identical conditions employed in the analysis of the precipitated powder. In order to perform Rietveld refinements to determine structural parameters of the heat-treated powder, an XRD pattern was again obtained in the range from $2\theta = 10^\circ - 145^\circ$ using a Sintag PAD(V) instrument. A side-loading sample holder was used to minimize the effects due to preferred orientation. The sample was continuously scanned using a scan rate of $0.2^\circ\ \mathrm{min}^{-1}$ and a step chop of $2\theta = 0.02^\circ$. A copper target was used and the radiation obtained contained both Cu$K_{\alpha1}$ and Cu$K_{\alpha2}$ components. These conditions were necessary to obtain peaks with high signal to noise ratios required to obtain a good fit between the experimental results and the calculated patterns. Rietveld refinement of this pattern was performed using a refinement software name "RIETAN" [25, 26].

In addition, because an aqueous route was used to synthesize the powder, Auger electron spectroscopy (AES) was used to map the oxygen content of the heat-treated powder as a function of depth from the surface of the sample. Samples for AES were prepared by pressing the powder on an indium foil. The spectra were collected using a gun voltage of 3kV and a gun current of $\sim 0.23\ \mu$A. Samples were sputtered using Ar^+ ions at a pressure of 10mPa using a 1 mm × 1 mm raster. The sputtering conditions were calibrated to erode the surface at the rate of $\sim 10\ \mathrm{nm\,min}^{-1}$.

3. Results and discussion

The as-precipitated powder collected after drying was ground and subjected to X-ray analysis. A typical XRD trace of the as-precipitated powder is shown in Fig. 1a. The three broad X-ray peaks (located at $2\theta \approx 27^\circ$, 30° and 47°) shown in the XRD trace reveal two characteristics of the precipitated powders: (i) the phase present in the as-precipitated product is the cubic-spinel phase of $ZnIn_2S_4$ that has been reported to form at high pressures [12], and (ii) that the precipitated powders are nanocrystalline. A high-resolution transmission electron micrograph of the precipitate is shown in Fig. 2 indicating the nanocrystalline nature of the powder. From these micrographs, the particle size of the powders was estimated to be about 5 nm. In addition, energy-dispersive X-ray analysis (EDAX) performed on several regions of the powder indicated an In/Zn ratio of 2, confirming the chemical homogeneity of the precipitate at that scale.

Heat treatment of the precipitated powders at 500 °C resulted in the growth of the high-pressure cubic-spinel phase of $ZnIn_2S_4$. An XRD pattern collected on this powder clearly sows the resolved intensities (see Fig. 1b) of the original broad peaks centred at about $2\theta = 27.5^\circ$ as shown in Fig. 1a. All the peaks visible in the scale shown in Fig. 1b have been indexed to the cubic spinel phase; however, a small amount of hexagonal $ZnIn_2S_4$ was also present, which had formed due to transformation of the cubic phase during heat treatment. The presence of the hexagonal phase was accounted for in the Rietveld analysis (explained in the next section). This shows that primarily the cubic spinel phase of $ZnIn_2S_4$ can be synthesized under ambient temperature and pressure conditions without the application of high pressures at elevated temperatures.

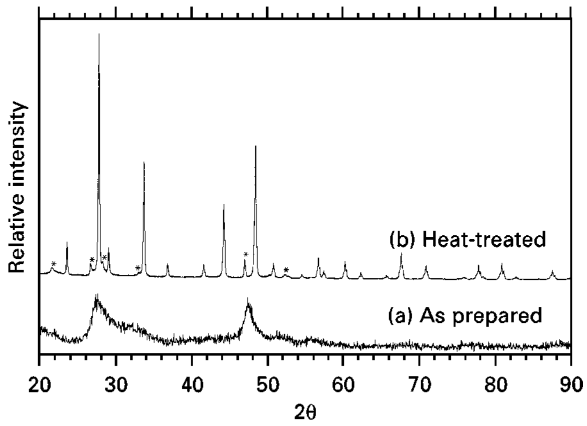

Figure 1 XRD patterns of (a) the as-prepared precipitate, and (b) heat-treated powders. The as-prepared precipitate shows broad peaks characteristic of nanocrystalline cubic-spinel particles. The heat-treated powder shows peaks corresponding to the high-pressure cubic-spinel phase of $ZnIn_2S$ along with some low-intensity peaks corresponding to the hexagonal phase (*).

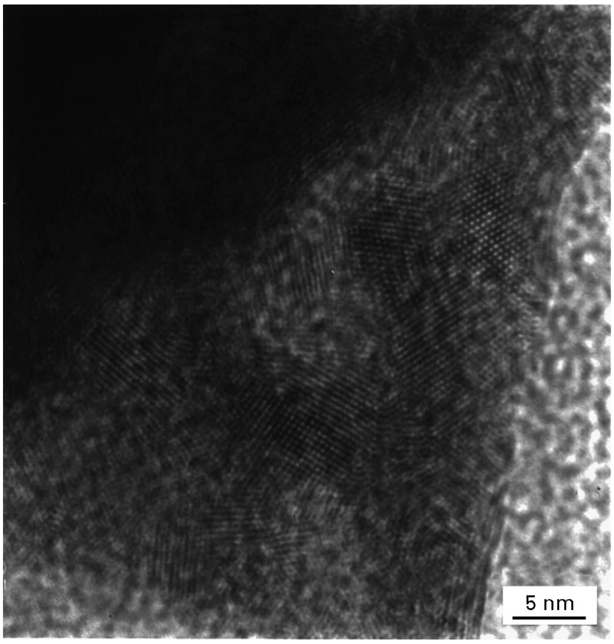

Figure 2 A high-resolution electron micrograph of the as-prepared precipitate. The particle size, estimated from boundaries of fringes, is in the range of 5–10 nm.

It is also well known that aqueous routes can result in the incorporation of significant amounts of oxygen in the precipitate. During aqueous precipitation of indium sulphide (In_2S_3) for example, it has been reported [27] that 15 at % oxygen is incorporated in the precipitate. Auger electron spectroscopy (AES) was therefore used to estimate the oxygen content of the heat-treated powder. The Auger spectrum collected showed the expected amounts of zinc, indium and

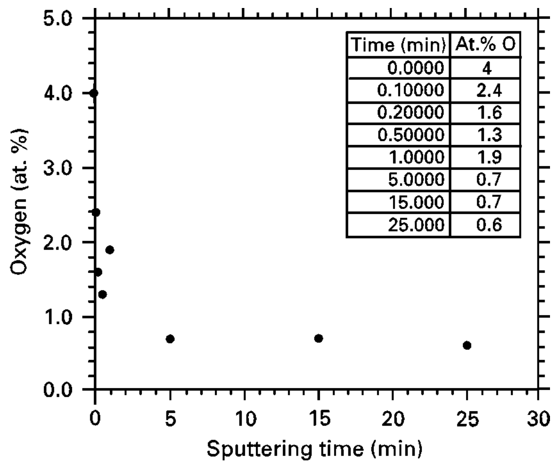

Figure 3 The oxygen depth profile of the heat-treated sample measured using Auger electron spectroscopy shows a drop in the oxygen content from 4 at% at the surface of the particles to 0.6 at% in the bulk.

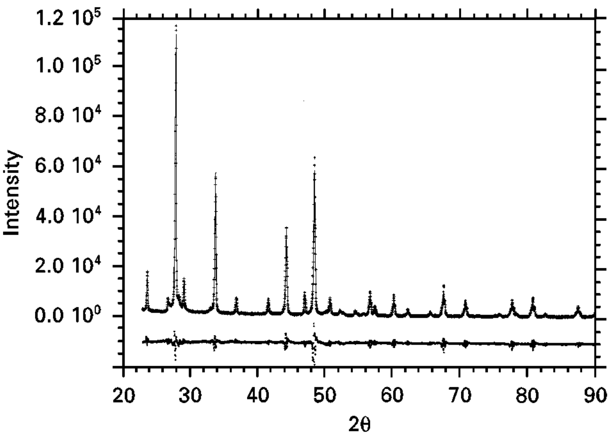

Figure 4 Results of Rietveld refinement of the XRD pattern collected on the heat-treated $ZnIn_2S_4$ powder (data points indicated). (+) y(meas), (—) y(calc). (●) The difference curve, y_i(calc) − y_i(meas), is shown to scale.

sulphur, and in addition, also showed a small amount of oxygen. However, an oxygen depth profile performed on the sample (shown in Fig. 3) indicated a considerable reduction from approximately 4 at % oxygen on the surface to 0.6 at % after the surface was sputtered for 25 min (corresponding to ~ 250 nm). These results indicate that a small amount of oxygen is present as an impurity in the bulk of the material, possibly substituted on anion sites.

3.1. Rietveld refinement of cubic zinc indium sulphide

Fig. 4 shows the XRD pattern collected for the refinement studies, together with the difference graph (y_i(obs) − y_i(calc)) obtained from the analysis. "RIETAN" was used to refine reflections between $2\theta = 23^\circ$ and 90° from both cubic and hexagonal phases. Although the pattern showed predominantly cubic reflections, a small amount of hexagonal phase had to be accounted for in the analysis using a refineable scale factor.

For the whole pattern ten background parameters, two scale factors (one for each phase), and ten profile shape parameters (five for each phase; best results were obtained using Lorentzian peak profiles) were selected for refinement. In the cubic phase, the lattice parameters, the Wyckoff parameter and occupancy for the sulphur atom, and the isotropic thermal parameters were considered for the refinement analysis. The occupancies of zinc and indium atoms were fixed at 1.0 in their respective sites. None of the structural parameters for the hexagonal phase were refined because the peak intensities were very small. The structural parameters for the hexagonal phase were obtained from the results of a previous structural analysis conducted by Lappe *et al.* [11]. Convergence was obtained in 20 cycles with the following R factors (in %): $R_{wp} = 13.06$, $R_p = 9.95$, for the cubic phase $R_i = 3.06$, $R_F = 2.03$ and for the hexagonal phase, $R_i = 3.63$, $R_F = 1.89$. (An explanation of the refinement errors has been given by Young and Prince [28], for example.) The final refined structural parameters obtained for the cubic phase are shown in Table I and compared with the data obtained by Berand and Range [13]. The refinement errors (R_{wp} and R_i) are within the acceptable levels expected using the Rietveld refinement procedure [28]. Thus, the analysis by itself and also in comparison with the data obtained by Berand and Range [13] suggests that the chemically synthesized $ZnIn_2S_4$ phase is indeed the direct cubic spinel phase (isostructural with the high-pressure phase synthesized by Range *et al.* [12, 13]) exhibiting little or no inversion in cation occupancies.

TABLE I Refined structural parameters for $ZnIn_2S_4$ cubic-spinel phase

	Present work	Berand and Range [13]
Space group	$Fd\bar{3}m$ (no. 227) [41]	$Fd\bar{3}m$ (no. 227) [41]
Setting no.	1-origin at 8a site, $\bar{4}3m$	1-origin at 8a site, $\bar{4}3m$
Sites occupied	8a (Zn), 16d (In), 32e (S)	8a (Zn), 16d (In), 32e (S)
Lattice parameter	1.06375 ± 0.00004 nm	1.0622 nm
Sulphur parameter	0.380 ± 0.001	0.378
Sulphur occupancy	0.93 ± 0.03	1.0
Refinement errors[a]: R_{wp}	13.06	4.92
R_I	3.06	5.68

[a] Defined as follows: $R_{wp} = \{[\Sigma W_i(Y_{obs} - Y_{cal})^2/(\Sigma W_i(Y_{obs})^2]\}^{1/2}$, $R_I = (\Sigma|I_{obs} - I_{cal}|)/(\Sigma I_{obs})$.

3.2. Proposed mechanisms for the formation of high-Pressure cubic spinel phase

Several arguments can be made to explain the occurrence of this thermodynamically unstable phase of $ZnIn_2S_4$. There have been a number of possible explanations suggested for the stabilization of the cubic phase that have been considered and deemed unlikely by the present authors. These possibilities are (1) nucleation of nanocrystalline particles which tend to stabilize a structure with a lower molar volume, (2) the presence of minor amounts of hydroxyl (OH^-), and oxygen (O^{2-}) within the structure, (3) surface chemistry of a hypothetically nucleated hexagonal phase which favours further growth of the cubic spinel phase. In order to provide evidence to support or invalidate these hypotheses, experiments incorporating various oxygenated and non-oxygenated solvents with different pH modifications were conducted to precipitate the powders.

The fine particle hypothesis was eliminated when the experiments were conducted using 200 proof ethanol and anhydrous acetonitrile as solvents. Broad peaks corresponding to the presence of both hexagonal and cubic phases were clearly observed in XRD pattern of the precipitate indicating the fine nature of the particles. Mixed hexagonal and cubic phases (also of very fine crystallite size) were also observed in the XRD pattern of the powders collected when the experiments were conducted in water under varying pH conditions of the solution (of the chloride salts prior to introduction of H_2S gas). The ability to synthesize the cubic spinel phase of $ZnIn_2S_4$ in anhydrous acetonitrile, a non-oxygenated organic medium, also demonstrates that hydroxyl and oxygen ions are not responsible for stabilizing the cubic spinel phase. On the other hand, it is also possible that the particles that initially nucleated in solution had a hexagonal structure, and that variations in the surface chemistry could cause growth of the cubic spinel phase on the surface. Such a situation should indeed induce alterations in the stacking sequence which should be readily resolved under a high-resolution electron microscope. High-resolution electron microscopy conducted on the as-precipitated powders did not reveal the presence of any stacking faults.

Thus the exact reasons for formation of the high-pressure cubic spinel phase are still an enigma. In order to explain the formation of this phase, a solution coordination model (SCM) has been proposed by the present authors. The model has not yet been validated, but based on the present result and reports published in the literature, it is possible to argue its application to the present work. This proposed model could also be applied to other ternary sulphides to produce their high pressure analogues without the application of high pressures at high temperatures.

Halide salts of electronegative elements such as zinc and indium exhibit more covalent behaviour and hence, in the presence of polar solvents tend to be coordinated with the solvent molecules. Zinc and indium salts, therefore, dissolve in aqueous solutions and the ions acquire different coordinations in solutions. The coordination chemistry of indium in the oxidation state 3 is quite well studied and several review papers can be found [29–31]. In^{3+} prefers to exist in six-fold coordination in aqueous solutions as $[In(H_2O)_6]^{3+}$. The existence of this coordination has been identified using ^1H and ^{115}In nuclear magnetic resonance (NMR) studies [32, 33]. Proton NMR has also been used to demonstrate the rapid exchange between coordinated water molecules and the bulk solvent phase [34]. This has been particularly studied with respect to the use of polar solvents such as dimethyl formamide (DMF), acetone and trimethyl phosphate (TMP). These polar solvent molecules being good nucleophiles can replace some of the coordinated water molecules attached to In^{3+} to form $[In(H_2O)_nL_{6-n}]^{3+}$, where L = DMF, acetone and TMP. Thus the existence of appropriate mixtures of $[In(H_2O)_6]^{3+}$, $[In_6]^{3+}$, and $[In(H_2O)_nL_{6-n}]^{3+}$ have been identified. Moreover, in the presence of nitrogen ligands, the In^{3+} can also exhibit different coordinations ranging from four to six. For example, the reaction of $InCl_3$ with sodium salts of the appropriate ligand such as maleonitriledithiolate (MNT^{2-}), the product anions show a range of In–S coordination numbers, from four $[In(MNT)_2]^{-1}$ to six $[In(MNT)_3]^{3-}$ [29]. Thus, it can be seen that, depending on the reactants and the environment of the ions in solution, In^{3+} can assume different coordination states.

There are several factors that affect the coordination of the indium ions. The ionic radius of In^{3+} in six fold coordination has been reported to be 0.008 nm for In^{3+} in eight-fold coordination to be 0.092 nm, while the covalent radius of indium has been estimated to be 1.050 nm. It has been well established that six-fold coordination of indium is a feature that is exhibited most commonly by In^{3+}. However, in the presence of less electronegative species attached to In^{3+}, more negative charges can be transferred to In^{3+}. As a result, the electron affinity of In^{3+} could be satisfied with fewer donor ligands thus producing a lower coordination number for In^{3+} such as in the tetrahedral coordination [29]. Thus, although the preferred coordination for In^{3+} is six, other coordination states for the ion are also possible, depending on the electronegativity of the attached species.

In the case of Zn^{2+}, the predominant species in aqueous solution has been identified to be $[Zn(OH)_4]^{2-}$. The tetrahedral coordination seems to be preferred, although, in the case of aqueous $Zn(NO_3)_2$ a coordination of six almost independent of concentration has also been reported [35–37]. Similarly, in the presence of ammonia and in an ammoniacal solution containing zinc chloride, the tetrahedrally coordinated species, $[Zn(NH_3)_4]^{2+}$ has been identified [38]. Therefore, it can be seen that both the ions exhibit a strong variation in their coordinations depending on the molecular environment of the ions. This factor could be very important in the nucleation of a particular phase during precipitation in solution. The existence of a particular coordination in the solution phase can lead to the stabilization of the same coordination in the solid state. Hence, different polymorphic phases can be produced once the solubility product is exceeded using the appropriate contributing anions such as sulphur in the present case [39].

The covalent nature of the bonding that is exhibited by electronegative elements such as those from group IIIA and group IVA and the coordinated states in which they exist in solutions, indicate a possible close relationship between the coordination exhibited by the ion in solution and the coordination of the ion seen in the solid. As discussed above, In^{3+} primarily exhibits six-fold coordination with water. During sulphidization, therefore, the stability of the six-fold coordination could result in the formation of octahedrally coordinated $In–S_6$ species. On the other hand, tetrahedrally coordinated Zn^{2+} in an aqueous solution primarily results in the formation of tetrahedrally coordinated $Zn–S_4$ species on sulphidization (Fig. 5). Thus, the solid precipitate that is generated contains both In^{3+} and Zn^{2+} in octahedral and tetrahedral coordination, respectively, with sulphur, which is the basis of the formation of the high-pressure cubic spinel phase. It is also possible that the presence of a few tetrahedrally coordinated In^{3+} in solution could result in the formation of $In–S_4$ species in the solid with the majority of In^{3+} exhibiting six-fold coordination and existing as $In–S_6$ species. The presence of both these species therefore leads to the formation of the mixed hexagonal and cubic spinel phases if significant amounts are present (which has been seen by changing the pH of the aqueous solution). Dynamic spectroscopic characterization of the sulphidization reaction could provide evidence of the conversion of $[In(H_2O)_6]^{3+}$ in solution to form $In–S_6$ species (and of $[Zn(H_2O)_4]^{2+}$ to $Zn–S_4$ species) prior to precipitation of the solid. Such a study could actually verify the validity of the proposed model. In the present case, the existence of the hexagonal phase could be due to a combination of the following: (a) the precipitated powder contains some InS_4 species which results in the formation of the hexagonal phase on heat treatment, and (b) at 500 °C the cubic phase transforms to the more stable hexagonal phase. At the same time, a slight cationic disorder within the cubic spinel structure could lead to a situation whereby some indium may be found in tetrahedral sites of the spinel phase. This interchange of cations between the octahedral and tetrahedral sites is known to be common in cubic spinel structures. Unger *et al.* [14] have observed additional peaks in the photoluminescence spectra of cubic $ZnIn_2S_4$ which they attribute to cationic disorder (indium in tetrahedral sites). However, the Rietveld refinement studies conducted on the sulphide synthesized in the present work indicate no detectable cationic disorder.

Thus, the proposed solution coordination model correlates the coordination seen in solution with that in the solid. The coordination of the ions in solution thus serves as a template for retaining the same coordination in the solid. This situation could very well be compared to a template mechanism responsible for formation of diamond films from the vapour phase, wherein activation of carbon into the sp^3 hybridized state in the vapour and its retention in the solid leads to the formation of diamond [40]. The model may only be applicable to covalent and partially covalent sulphide systems that exhibit solid phases with distinct differences in cation coordination. The model could also be applied to systems whose inorganic salts being covalent exhibit variations in coordination in solution. It may not be applicable to those systems which are strongly ionic such as NaCl in water, which is completely dissociated and does not have any preferred coordination.

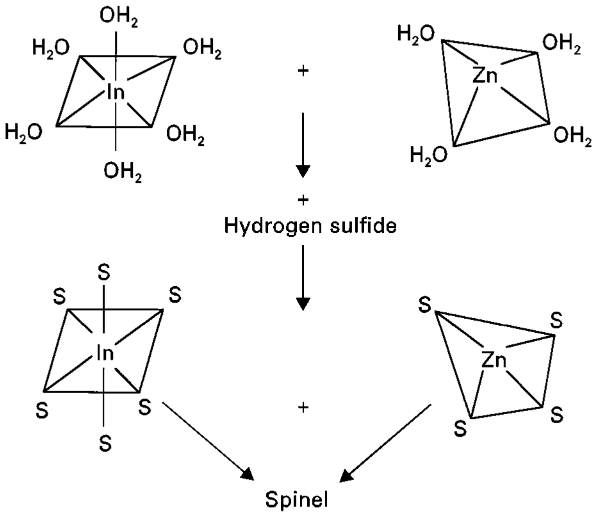

Figure 5 Schematic illustration showing the formation of the high-pressure cubic spinel modification of zinc indium sulphide using the solution coordination model (SCM).

4. Conclusion

The present work has shown that the high-pressure cubic spinel phase of zinc indium sulphide can be synthesized at ambient pressures and temperatures with relative ease using a precipitation route. The reaction of $ZnCl_2$ and $InCl_3$ (dissolved in water) with H_2S results in a precipitate. The precipitated powder can be heat treated at 500 °C in an evaluated quartz ampoule to yield the high-pressure cubic-spinel phase of zinc indium sulphide. The existence of the high-pressure phase has been verified by Rietveld refinement of the X-ray diffraction pattern. Auger electron spectroscopy shows that the oxygen content within the bulk of the heat-treated powder is less than 0.6 at %. Finally, a solution coordination model has been proposed based on results reported in the literature to explain the formation of the novel high-pressure phase.

Acknowledgements

P. N. K., A. W., M. A. S. and P. H. M. acknowledge the donors of the Petroleum Research Fund, (Grant PRF 25507-G3), Carnegie Mellon University's Student Undergraduate Research Grant program (SURG), CMU Faculty Development Fund for providing funds to support the work. The authors are grateful to Bill Pingitore for his assistance in Auger electron microscopy. P. N. K., A. W., M. A. S. and P. H. M. also acknowledge the partial support of the National Science Foundation (Grants DMR-9301014, CTS-9309073 and CTS-9700343). S. M. and X. L. W. thank the US Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory User Program under contract DE-AC05-84OR21400, managed by Lockheed Martin Energy Systems, Inc., for sponsoring the XRD work and for granting an appointment to ORNL post-doctoral research associates program administered jointly by ORNL and ORISE.

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Received 28 January
and accepted 15 May 1998