

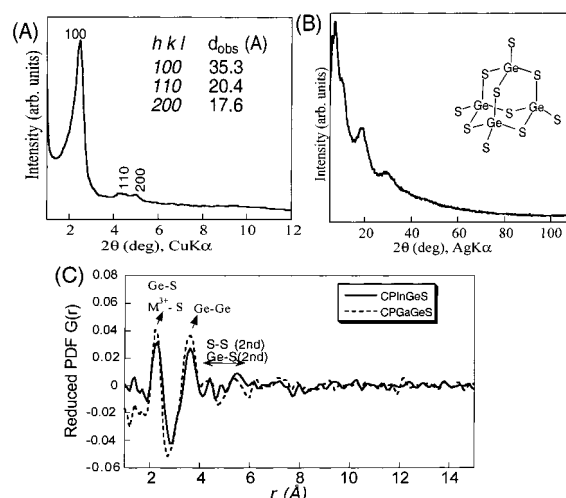
# Light-Emitting Meso-Structured Sulfides with Hexagonal Symmetry: Supramolecular Assembly of $[\text{Ge}_4\text{S}_{10}]^{4-}$ Clusters with Trivalent Metal Ions and Cetylpyridinium Surfactant

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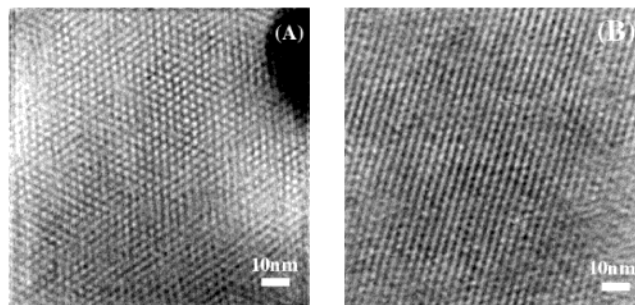
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Mesoporous materials have attracted considerable attention in the past decade because of their immense technological potential as catalysts, adsorbents, and hosts for large molecules.<sup>1</sup> The mesoporous silicates of the MCM-n family with ordered pore structure, reported by the Mobil group using long chain organic molecules as “structure directing” agents, have spawned a new era in open framework materials.<sup>2</sup> Stucky et al. and others extended the supramolecular templating approach to produce a variety of mesostructured oxide materials.<sup>3</sup> Porous low band-gap non-oxidic systems, such as chalcogenides, are also of great interest because new applications could be foreseen by combining the porous nature with their semiconducting and optoelectronic properties in fields of photocatalysis, nanotechnology, etc. Several new materials based on metal chalcogenide clusters in the microporous regime have been reported,<sup>4</sup> including those based on the adamantane  $\text{Ge}_4\text{S}_{10}^{4-}$  anionic clusters<sup>5</sup> and the super-tetrahedral  $\text{In}_{10}\text{S}_{20}^{10-}$  clusters.<sup>6</sup> Reports on the syntheses of chalcogenide-based mesostructured materials have started to appear recently. Stupp et al. reported hexagonal ordered CdS templated with the amphiphilic oligoethylene-oxide oleyl ether.<sup>7</sup> Mesostructured ZnS with disordered pore structure was reported by Li et al.<sup>8</sup> Recently, the synthesis of metal germanium sulfide mesophases  $[\text{CTA}]_2\text{M}_2\text{Ge}_4\text{S}_{10}$  (CTA = cetyl trimethylammonium,  $\text{M} = \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}$ ) in formamide (FM) was described by Ozin et al.<sup>9</sup> In addition,  $[\text{C}_{14}\text{H}_{29}\text{NMe}_3]_2\text{MnGe}_4\text{S}_{10}$  with hexagonally ordered structure and  $[\text{C}_n\text{H}_{2n+1}\text{N}(\text{CH}_3)_3]_2\text{M}^{\text{II}}\text{Ge}_4\text{Q}_{10}$  ( $\text{M}^{\text{II}} = \text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}$  and  $\text{Q} = \text{S}, \text{Se}$ ) with worm-



**Figure 1.** (A) Typical X-ray diffraction pattern of CPGaGeS. (B) Wide-angle X-ray diffraction pattern of CPInGeS showing diffuse scattering. The considerable structure in the diffuse scattering pattern comes from the adamantane  $\text{Ge}_4\text{S}_{10}$  unit, shown in the inset. (C) Reduced atomic pair distribution function  $G(r)$  for CPGaGeS and CPInGeS plotted against distance  $r$ . The major interatomic pair correlations are shown.



**Figure 2.** Representative TEM images of the indium germanium sulfide framework (CPInGeS): (A) parallel to the pore tunnels and (B) perpendicular to the pore tunnels. TEM images were acquired with a JEOL 120CX instrument with a  $\text{CeB}_6$  filament operating at 120 kV.

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hole pore structure were reported.<sup>11</sup> Here we report the use of trivalent metals  $\text{Ga}^{3+}$  and  $\text{In}^{3+}$  as linking agents of  $[\text{Ge}_4\text{S}_{10}]^{4-}$  clusters to form ordered mesostructured sulfidic solids with photoluminescent properties. The surfactant of choice was cetylpyridinium bromide (CPBr) used in FM solvent.<sup>12</sup> Although the materials synthesized in FM show good hexagonal order, as with most mesostructured silicates, their exact composition remains unclear. For example, the metal content is very high raising questions as to the charge balancing scheme of the given formulas. Possible reasons for this are discussed below.

The thiogermanates CPGaGeS and CPInGeS were synthesized by the addition of trivalent metal ions  $\text{Ga}^{3+}$  or  $\text{In}^{3+}$  solution in FM to a solution of  $\text{K}_4\text{Ge}_4\text{S}_{10}^{13}$  and supramolecularly organized CP surfactants in warm FM.<sup>14</sup> Elemental C, H, N analyses and EDS results together suggest a chemical formula close to

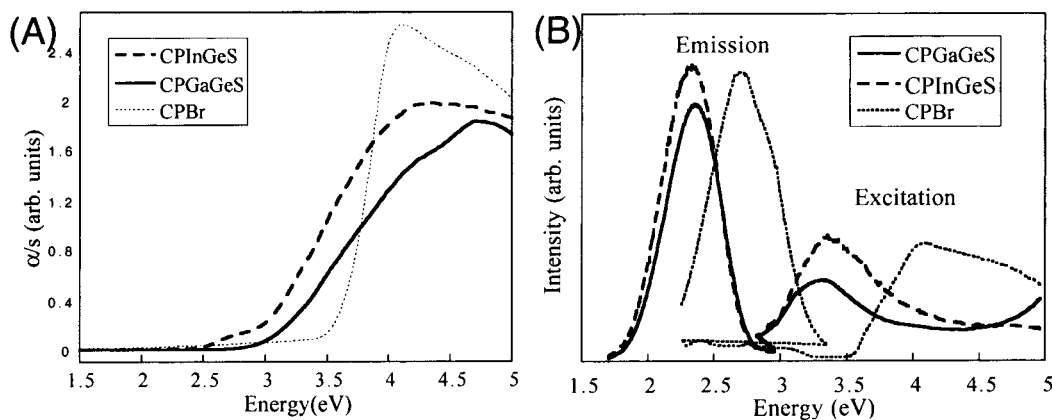
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(12)  $\text{CP}^+$  has been little exploited in the construction of mesoporous oxides<sup>3</sup> and even less for sulfidic materials.

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**Figure 3.** (A) Electronic absorption spectra. (B) Photoluminescence and excitation spectra. For comparison the spectra of CPBr are also shown.

“(CP)<sub>2</sub>M<sub>1.3</sub>Ge<sub>4</sub>S<sub>11</sub>” (M = Ga<sup>3+</sup>, In<sup>3+</sup>).<sup>15</sup> The observed composition of these new mesostructured sulfides cannot be explained based on charge compensation between CP<sup>+</sup>:M<sup>3+</sup>:Ge<sub>4</sub>S<sub>10</sub><sup>4-</sup>. The same issue exists for the metal-rich compositions (CTA)<sub>2</sub>M<sub>2</sub>Ge<sub>4</sub>S<sub>10</sub> (M = Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>).<sup>9</sup>

To explain these results we envisage that the higher M:Ge ratio could result from the presence of sulfide species. Consistent with this proposal is the persistently higher than 4:10 Ge:S ratios obtained by elemental analysis. The Ge:S ratios are closer to 4:11–12.<sup>16</sup> The lack of a characteristic signature for S<sup>2-</sup> makes it difficult to detect these species by standard techniques. However, such framework materials incorporating mixed [Ge<sub>4</sub>S<sub>10</sub>]<sup>4-</sup>/S<sup>2-</sup> species have already been observed in the crystal structure of TMA-CuGS-2.<sup>17</sup>

Powder XRD patterns of CPGaGeS (Figure 1A) and CPInGeS show a strong peak followed by two weak reflections in 2° < 2θ < 6°. The three peaks could be indexed in a hexagonal unit cell as (100), (110), and (200) reflections characteristic of a P6mm structure. The calculated lattice constants are a<sub>H</sub> = 40.8 and 41.9 Å for CPGaGeS and CPInGeS, respectively. The presence of higher order (110) and (200) reflections in the XRD patterns indicates good textural uniformity in these materials.

The hexagonal symmetry of CPGaGeS and CPInGeS was readily observed by transmission electron microscopy (TEM). Figure 2A shows a TEM image of the hexagonal uniform arrangement of pores occupied by the assembly of CP molecules. Figure 2B shows a TEM image perpendicular to the pore channel direction. The pore/pore separation is in good agreement with those obtained from the XRD patterns.

The higher angle region (>10°) of the powder XRD patterns did not show Bragg peaks (Figure 1B) indicating that the walls do not possess a well-defined long range order. However, the diffraction pattern exhibits well-defined diffuse scattering which arises from local order existing in the material. To explore the local structure, pair distribution function (PDF) analysis was used. The powder X-ray diffraction patterns of CPMGeS were measured

(14) In a typical experiment, 0.76 g of K<sub>4</sub>Ge<sub>4</sub>S<sub>10</sub> (1 mmol) and 4 g of cetyl pyridinium bromide monohydrate were dissolved in 20 mL of formamide (FM) at 85 °C forming a clear solution. On adding 0.25 g of Ga(NO<sub>3</sub>)<sub>3</sub> (1 mmol) in 10 mL of FM to this solution a white precipitate formed immediately. The solution was stirred at 80 °C for 24 h, filtered, and washed with hot FM and hot water to remove excess surfactant. It was then washed with ether and dried in a vacuum. For CPInGeS, InCl<sub>3</sub> was used and the synthesis is similar to that of Ga phase. The products were pale yellow free flowing powders. Yield ~86% based on K<sub>4</sub>Ge<sub>4</sub>S<sub>10</sub>.

(15) Microprobe EDS analysis of these phases gives an atomic ratio of Ge:S 1:2.7 close to 1:2.5 as expected for the Ge<sub>4</sub>S<sub>10</sub> cluster. The M<sup>3+</sup>:Ge ratio is 1.30:4 for the Ga<sup>3+</sup> phase and 1.32:4 for the In<sup>3+</sup> phase. EDS analysis also confirmed the absence of bromide, chloride, and oxide ions. C, H, N analysis % gave C 39.36, H 6.24, N 2.14 and C 38.64, H 6.08, N 2.12 for CPGaGeS and CPInGeS, respectively.

(16) Excess sulfide could come from adventitious K<sub>2</sub>S present in the starting material K<sub>4</sub>Ge<sub>4</sub>S<sub>10</sub>, which is typically prepared via the reaction of K<sub>2</sub>S and GeS<sub>2</sub> or cannibalization of the [Ge<sub>4</sub>S<sub>10</sub>]<sup>4-</sup> cluster.

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using Ag Kα radiation (λ = 0.5608 Å) to collect data at higher Q values.<sup>18</sup>

The reduced atomic pair distribution functions for CPMGeS, obtained from high-angle X-ray scattering data (Figure 1B), are shown in Figure 1C. The PDFs clearly show the presence of a well-defined local structure with peaks at 2.2, 3.6, and 4.4 Å corresponding to Ge–S, Ge–Ge, and Ge–S<sub>second</sub> atomic pair vectors in the Ge<sub>4</sub>S<sub>10</sub> cluster. This indicates that the adamantane clusters are the predominant species. Moreover, atomic pair correlation peaks are not observed at distances >8 Å indicating the lack of long-range order in the sulfide framework.

Optical absorption UV–vis spectra (Figure 3A) show well-defined band gaps (E<sub>g</sub>) of 3.01 and 2.97 eV for CPGaGeS and CPInGeS, respectively, indicating that they are semiconductors with E<sub>g</sub> between those of ZnS and ZnSe.

A unique feature of both materials is the intense photoluminescence (PL) observed when excited with light above the band gap. With an excitation line of 3.35 eV (370 nm) an intense green emission at 77 K with a maximum 2.35 eV (528 nm) and 2.32 eV (535 nm) was observed for CPGaGeS and CPInGeS, respectively. The PL may originate from the pyridinium chromophore of the surfactant, although the spectra of Figure 3B show that PL is observed even with excitation energies below the π–π\* transition of pyridinium. In comparison with the surfactant CPBr (emission maximum at 2.87 eV (432 nm)), the emission energy is significantly red shifted possibly due to energy transfer from pyridinium headgroup to the chalcogenide framework of the mesophase. This is the first observation of light emission from mesostructured metal thiogermanates.<sup>19</sup> Light emission from amorphous chalcogenide frameworks is rare and underscores the potential of these systems for photonic function.

In conclusion, we have synthesized two new mesostructured metal germanium sulfides with hexagonal framework organization, incorporating [Ge<sub>4</sub>S<sub>10</sub>]<sup>4-</sup> and tetrahedral Ga<sup>3+</sup> and In<sup>3+</sup> linking cations. CP molecules act as templating agents and occupy the closest-packed cylindrical framework pores. The CPGaGeS and CPInGeS emit an intense green light when excited across the band gap and presage the potential of such systems in light-emitting and optoelectronic devices. Current work focuses on experiments aimed at surfactant removal to render the pores in these systems accessible.

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(19) In contrast, the worm-hole [C<sub>18</sub>H<sub>27</sub>N(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>M<sup>4+</sup>Ge<sub>4</sub>Q<sub>10</sub> materials are not emissive [ref 11].