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Hexagonal mesostructured chalcogenide frameworks formed by linking $[Ge_4Q_{10}]^{4-}$ (Q = S, Se) clusters with Sb^{3+} and Sn^{4+}

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The synthesis and properties of new hexagonal ordered mesostuctured phases of framework containing adamantane $[Ge_4Q_{10}]^{4-}$ (Q = S, Se) clusters linked by Sb^{3+} and Sn^{4+} ions and templated with cetylpyridinium surfactant are reported.

Mesoporous non-oxidic semiconductor materials have the potential to combine electronic and optical properties with shape selectivity.[1–3] However this potentially large class of materials remains an underdeveloped area. Chalcogenide analogs to mesostructured silicates[4,5] are still scarce because their synthesis remains a challenge although progress in this area has been reported recently.[6–8] We are exploring the use of cetylpyridinium bromide (CPBr) surfactant in the synthesis of mesostructured chalcogenido frameworks. We recently reported that hexagonally ordered metal germanium sulfides form with $[Ge_4S_{10}]^{4-}$ anions and tetrahedral cations and show intense photoluminescence.[9] In order to probe whether the stability of the phases depends on the coordination properties of the linking metal ion, we explored ions that generally do not adopt tetrahedral coordination such as Sb^{3+}, Bi^{3+}, Sn^{2+}, Pb^{2+}, or are capable of several coordination environments *e.g.* Sn^{4+}. We find that many of these in fact fail to produce hexagonal mesostructures under our synthetic conditions. Namely, Bi^{3+}, Sn^{2+} and Pb^{2+} form highly disordered phases.[10] Only Sb^{3+} and Sn^{4+} form readily hexagonal sulfido and selenido frameworks of the type $CP_2M_xGe_4Q_{10+y}$ and are described here. The Sb/Ge_4Se_{10} analog features the smallest semiconductor energy gap reported so far in this class of materials.

The $CP_2M_xGe_4Q_{10+y}$ phases (denoted as CPMGeQ where M = Sb^{3+}, Sn^{4+} and Q = S, Se) were synthesized by the addition of a formamide (FM) solution of Sb^{3+} or Sn^{4+} in to a solution of supramolecularly organized $[Ge_4Q_{10}]^{4-}$ and CP surfactants in warm FM. In a typical experiment, $K_4Ge_4Q_{10}$ (1 mmol) and 4 g cetylpyridinium bromide monohydrate ($CPBr·H_2O$) were dissolved in 20 mL of FM. On adding 1 mmol of SbI_3 or SnI_4 in 10 mL of FM to this solution precipitation occurs immediately. The mixtures were aged for 24 h at 80 °C, filtered, washed with hot FM and methanol and dried under vacuum. The sulfide phases were yellow and the selenides were brown in color. The elemental C, H, N and EDS analyses of these phases are given in Table 1. These analyses did not show potassium or halide ions in the products. Thermal gravimetric analyses (TGA) are in agreement with the C, H, N analyses results (see Table 1). The results suggest chemical formulae $CP_2Sb_{1.3}Ge_4S_{11}$, $CP_2Sn_{1.6}Ge_4S_{11.8}$, $CP_2Sb_{1.5}Ge_4Se_{11.5}$ and $CP_2Sn_{1.7}Ge_4Se_{12.3}$ for the mesophases. The compositions observed are similar to those reported for $CTA_2M_2Ge_4S_{10}$ (M = Ni^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+})[11] and $CPM^{III}GeS$ (M^{III} = Ga and In) phases.[9] The charge balance of the CP^+ and Sb^{3+}/Sn^{4+} cations in the compounds is presumably achieved by both $Ge_4Q_{10}^{4-}$ clusters and Q^{2-}

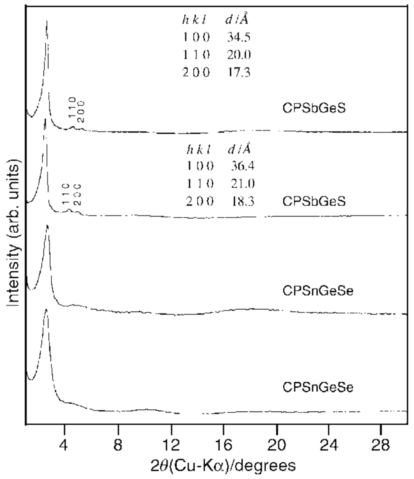

Fig. 1 X-Ray diffraction patterns of the CPMGeQ phases.

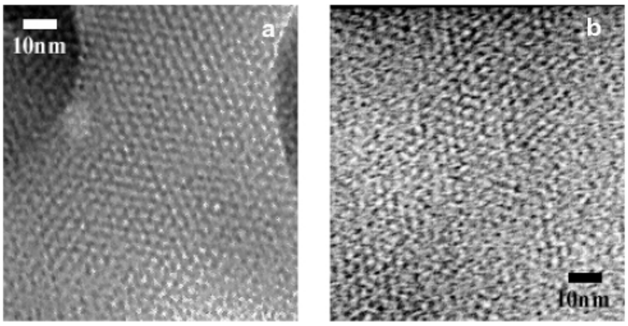

Fig. 2 TEM image of (a) CPSbGeS and (b) CPSnGeS looking down the pore channel axis. High resolution transmission electron micrographs were acquired with a JEOL 120CX instrument equipped with a CeB_6 filament and operating at 120 keV.

Table 1 Elemental analysis, powder XRD data and band gaps of CPMGeQ phases

Mesophase	Band gap/eV (colour)	C, H, N analyses (%)	Atom ratio[a] M:Ge:Q	Powder XRD data *d*/Å	$a_H{}^b$/Å	TGA wt. loss (%)
CPSbGeS	2.69 (yellow)	36.5, 5.8, 2.1	1.3:4:11.0	34.5, 20.0, 17.3	40.0(6)	44.5
CPSnGeS	2.89 (yellow)	33.0, 5.3, 2.0	1.6:4:11.8	34.2, 19.9, 17.2	39.7(6)	41.1
CPSbGeSe	1.74 (brown)	27.7, 4.5, 1.6	1.5:4:11.5	36.4, 21.0, 18.3	42.2(6)	34.8
CPSnGeSe	2.02 (brown)	21.5, 3.5, 1.4	1.7:4:12.3	35.9, 20.3	41.3(6)	31.4

[a] EDS data normalized with Ge atom ratio. [b] Maximum estimated error.

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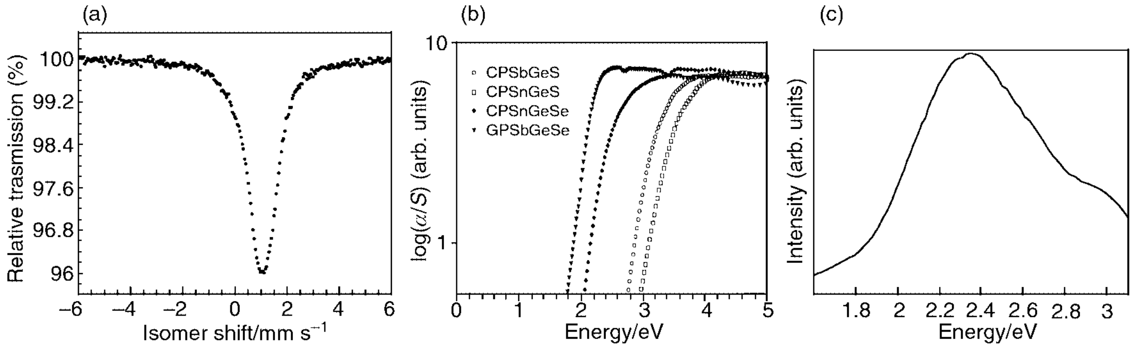

Fig. 3 (a) ^{119}Sn Mössbauer spectra (85 K) of CPSnGeS. The IS value (mm s^{-1}) is referenced to BaSnO$_3$. (b) Solid state optical absorption spectra of CPMGeQ compounds and (c) photoluminescence spectrum of CPSbGeS at 77 K.

anions.[12] Such framework materials incorporating mixed [Ge$_4$S$_{10}$]$^{4-}$/[S^{2-}] species have already been observed in the crystal structure of TMACuGS-2 (TMA = tetramethylammonium).[13]

Powder X-ray diffraction (XRD) patterns of the CPSbGeQ phases (Fig. 1) show a strong peak followed by two weak reflections at $2 < 2\theta < 6°$, similar to those of hexagonal mesoporous silica.[4] The three peaks could be indexed in a hexagonal unit cell as (100), (110) and (200) reflections with a_H lattice parameter of 40.0(6) and 42.2(6) Å for the sulfide and selenide phases, respectively. The presence of well defined higher order (110) and (200) reflections in the XRD patterns of CPSbGeQ indicate that the pores of the inorganic framework posses long range hexagonal order. In the CPSnGeQ phases, the first strong peak could be indexed as the (100) reflection of hexagonal lattice with a_H parameter of 39.7(6) and 41.3(6) Å for CPSnGeS and CPSnGeSe respectively. However, the higher order (110) and (200) reflections are not well resolved giving a broad peak at $3 < 2\theta < 6°$. This is attributed to the smaller coherence lengths of the hexagonal regions arising from disordered pore regions occurring in between. This is observed in the TEM images discussed below.

The pore organization of CPSbGeQ phases was readily observed by transmission electron microscopy (TEM). Fig. 2(a) shows typical TEM image of CPSbGeS with the uniform hexagonal arrangement of pores occupied by the assembly of CP molecules. The pore to pore separations are in good agreement with those obtained from the powder XRD data. Fig. 2(b) shows a characteristic TEM image of CPSnGeS down the pore channel axis. In this case (and in CPSnGeSe), the TEM image shows that the hexagonal domains are smaller (< 30 nm) and separated by disordered domains with worm-holes. This is consistent with the powder XRD patterns discussed above.

IR spectroscopy of the CPMGeQ phases shows the fingerprint pattern of the adamantane Ge$_4$Q$_{10}$ clusters. For example, CPSbGeS showed broad bands at 470, 426, 383 and 302 cm^{-1}. The band at 426 cm^{-1} corresponds to the terminal sulfur stretching modes of the adamantane Ge$_4$S$_{10}$ cluster bonded to metal cations and that at 383 cm^{-1} is due to vibrations of the inner cage Ge$_4$S$_6$.[14] These bands occur at 307 and 285 cm^{-1} in the corresponding Se phase.

The oxidation state of Sn in CPSnGeQ was probed with ^{119}Sn Mössbauer spectroscopy, a powerful tool for the characterization of tin compounds. The observed spectra show one type of Sn present in the structure with isomer shift (IS) and quadrupole splitting of 1.11, 0.45 mm s^{-1} for CPSnGeS and 1.49, 0.40 mm s^{-1} for CPSnGeSe, respectively, Fig. 3(a). These values are fully consistent with a Sn^{4+} oxidation state and confirm that no reduction of the metal has taken place.[15]

Optical absorption spectroscopy of the mesostructured chalcogenides show well defined sharp band gaps in the range 1.7–2.8 eV [Fig. 3(b), Table 1]. These energies lie in the same range as several useful semiconductors such as CdS, CdSe, GaP *etc*. Therefore, these materials may be potentially interesting, for a number of opto-electronic investigations. CPSnGeQ phases have higher band gaps than the corresponding Sb^{3+} phases. The band gaps for the selenium compounds generally occur at lower energies than those of the corresponding sulfur analogs. Accordingly, CPSbGeSe showed the lowest band gap (1.74 eV) in the CPMGeQ systems reported here.

The CPSbGeS phase shows intense photoluminescence (PL) when excited with light above the band gap. [Fig. 3(c)]. With an excitation line of 3.48 eV (356 nm) green emission was observed at 77 K, with a maximum at 2.35 eV (528 nm).[16] The PL originates most likely from the pyridinium chromophore[17] but it is believed to involve the inorganic framework as well. This is because each component alone (surfactant or framework) is not capable of producing the observed response. Typically the pyridinium chromophore alone emits at much higher energy 2.87 eV (432 nm). Further, removal of the pyridinium group at 250 °C under vacuum, resulted in the loss of PL property. Because both the organic and the inorganic components are required for green emission, the reported materials are true nanocomposites.

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