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Varied pore organization in mesostructured semiconductors based on the [SnSe₄]^{4–} anion

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Open framework metal chalcogenide solids, with pore sizes in the nano- and mesoscale, are of potentially broad technological and fundamental interest in research areas ranging from optoelectronics to the physics of quantum confinement^{1,2}. Although there have been significant advances in the design and synthesis of mesostructured silicas^{3,4}, the construction of their non-oxidic analogues still remains a challenge. Here we describe a synthetic strategy that allows the preparation of a large class of mesoporous materials based on supramolecular assembly of tetrahedral Zintl anions [SnSe₄]⁴⁻ with transition metals in the presence of cetylpyridinium (CP) surfactant molecules. These mesostructured semiconducting selenide materials are of the general formulae $(CP)_{4-2x}M_xSnSe_4$ (where 1.0 < x < 1.3; M = Mn, Fe, Co, Zn, Cd, Hg). The resulting materials are open framework chalcogenides and form mesophases with uniform pore size (with spacings between 35 and 40 Å). The pore arrangement depends on the synthetic conditions and metal used, and include disordered wormhole, hexagonal and even cubic phases. All compounds are medium bandgap semiconductors (varying between 1.4 and 2.5 eV). We expect that such semiconducting porous networks

could be used for optoelectronic, photosynthetic and photocatalytic applications.

The discovery of a general synthetic pathway to ordered mesoporous silicates by the Mobil group^{3,4} led to new hybrid mesoporous solids and has captured the imagination of many materials scientists. During the past decade, assembling inorganic molecular species in the presence of long-chain organic liquid-crystal templates has been used extensively to construct mesoporous oxides. In general, the synthetic approaches involve the organized polymerization of the basic tetrahedral $[SiO_4]^{4-}$ anion in the presence of various surfactants⁵⁻⁷. Non-oxide porous solids, however, are also important^{8,9}, because they may impart electronic properties to the framework, and thus make mesoporous solids into nano-electronic materials^{7,10}. Nevertheless, rational synthetic routes to such systems remain a challenge. A promising pathway for the construction of non-oxide mesoporous solids such as sulphides, selenides or tellurides is the supramolecular assembly of suitable chalcogenide anion species in the presence of metals. Recently, the synthesis of mesostructured solids based on the adamantane $[Ge_4Q_{10}]^{4-}$ (where Q = S, Se) clusters and metal ions (such as Zn²⁺, Co²⁺, Ni²⁺, Cu²⁺) has been described. Depending on preparation conditions, these materials possess either a disordered three-dimensional framework structure or a regular hexagonal symmetry^{11–14}. The energy bandgaps of these solids however are still too high for electronic applications.

We describe the design and synthesis of mesostructured materials based on the elementary tetrahedral Zintl anion [SnSe₄]⁴⁻. This anion is a chemical and structural analogue of the SiO₄ unit and we expect it to yield topologically similar structures. It is also smaller and heavier than the [Ge₄S₁₀] cluster and more likely to yield narrow-gap semiconductors. Spatially controlled assembly of [SnSe₄]⁴⁻ anions¹⁵ in formamide with various divalent metals in the presence of cetylpyridinium molecules as the surfactant template resulted in the formation of new mesophases. These materials, indicated as $(CP)_{4-2x}M_xSnSe_4$ (where 1.0 < x < 1.3; $M = Mn^{2+}$, Fe²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Hg²⁺), show uniform pore size and large diversity in pore organization, depending on the metal, and ranging from wormhole to hexagonal to cubic. The elemental composition (CP)_{4-2x}M_xSnSe₄ was determined by energy-dispersive microprobe analysis (EDS), elemental C, H, N and thermogravimetric analysis (TGA). In all samples the ratio of Sn:Se was very close to 1:4, in agreement with the expected ratio for the tetrahedral [SnSe₄]⁴⁻ anions. Infrared spectroscopy confirmed the presence of cetylpyridinium ions in the mesostructured $(CP)_{4-}$ _{2x}M_xSnSe₄ solids. A summary of the analytical and other data is shown in Table 1.

X-ray diffraction (XRD) patterns of the products show a strong, sharp peak at low scattering angles corresponding to (100) reflections (Fig. 1). The d_{100} values, which represent the pore–pore separation, vary with the transition metal used, ranging between 35 Å and 40 Å (see Table 2). The XRD patterns also show a broad higher-order peak ($2\theta \approx 4-5$ degrees), corresponding to overlapping higher-order reflections (110) and (200) which can be indexed to a hexagonal lattice as observed by transmission electron

Table 1 Elemental analysis, colours and bandgaps for mesostructured metal tin selenides									
Sample	Sn:Se4*	M:Se4*	Percentage of C, H, N	M:Se ₄ †	Colour	Bandgap (eV)			
Mn	1.01	0.90	44.71, 7.10, 2.25	1.03	Orange	2.0			
Fe	0.91	1.22	38.40, 6.23, 2.05	1.28	Dark brown	1.4			
Co	0.98	0.94	48.35, 6.64, 2.36	1.19	Dark brown				
Zn (cubic)	0.99	0.86	40.28, 6.17, 2.18	1.20	Yellow-orange	2.5			
Zn (hex)	0.96	0.85	41.58, 6.44, 2.29	1.15	Yellow	2.5			
Cd	0.92	1.23	36.90, 6.01, 2.28	1.23	Yellow	2.4			
Hg	1.03	1.09	34.65, 5.52, 1.92	1.20	Dark orange	2.2			

* Based on energy-dispersive spectroscopy (EDS) results. Semiquantitative microprobe analyses (EDS) were performed on a JEOL JSM-6400 scanning electron microscope (SEM) equipped with a Noran EDS system. Data acquisition was performed several times in different areas of the samples using an accelerating voltage of 25 kV and 60-s accumulation time. Quoted values were obtained from an average of four measurements.

+ Calculated values according to the formula (CP)_{4-2x}M_xSnSe₄, based on C, H, N results. C, H, N analyses were performed with Perkin Elmer Series II CHNS/O Analyzer 2400.

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microscopy (TEM) (see below). The (110) and (200) reflections are well resolved in $(CP)_{4-2x}Hg_xSnSe_4$, owing to the higher degree of order and longer coherence lengths, as observed in typical XRD patterns of the hexagonal mesostructured silica MCM-41^{3,4}.

It is remarkable that under the same experimental conditions the structure of the Zn analogue, c-(CP)_{4-2x}Zn_xSnSe₄, is in fact cubic, as judged from its diffraction pattern in which up to five Bragg peaks can be resolved and indexed to a Ia-3d symmetry (Fig. 1g). Because of the presence of some disorder, evident in the TEM images shown below, the higher-order Bragg peaks observed for c-(CP)_{4-2x}Zn_xSnSe₄ are weak. To the best of our knowledge this is the first report of a cubic non-oxide mesostructured material. In the CP/Zn/SnSe₄ system the surfactant concentration plays a crucial role in directing the mesostructure. For example, when the concentration is reduced by 50%, the product, h-(CP)_{4-2x}Zn_xSnSe₄, has a hexagonal pore arrangement with a corresponding XRD pattern (Fig. 1d). We note here that even among the silicas the cubic version MCM-48 is considered to be more interesting and more important for practical applications than the hexagonal versions MCM-41. Cubic MCM-48 is more difficult to make.

The local mesopore organization in $(CP)_{4-2x}M_xSnSe_4$ is readily

observed by TEM. It is clear from all images that the pore sizes are in the range of 22-26 Å and are uniform throughout the particles. Figure 2a and b shows characteristic images of h-CP-Zn/SnSe₄ and CP-Hg/SnSe₄ parallel to the pore channel axis where the hexagonal mesostructure is clearly visible. Although the local hexagonal order of the pores is distinctly observed in these samples, the TEM micrographs reveal that the degree of organized domains varies over wide regions of the particles. This is similar to the mesoporous aluminophosphates UHM-X¹⁶, where the particles show local hexagonal pore packing alternating with wormhole domains. It is also consistent with the observed XRD patterns as discussed above. Figure 2c and d shows a view of CP-Hg/SnSe₄ and CP-Mn/SnSe₄ perpendicular to the pore axis (in the [110] direction). Long, straight parallel tunnels are apparent in these images and the observed interpore distances are in good agreement with those obtained from the XRD patterns, Fig. 1. In fact, the agreement between XRD and TEM for all materials is excellent. Figure 2e and f shows representative TEM images of particles of c-CP-Zn/SnSe₄ and CP-Cd/SnSe₄ in which the pore organization is different from those shown in Fig. 2a and b. These images reveal cubic-like pore packing along more disordered



Figure 1 X-ray scattering of mesostructured chalcogenides. **a**, CP-Mn/SnSe₄. The second peak at 22.3 Å suggests that the pores are organized in finite but ordered domains. **b**, CP-Fe/SnSe₄. **c**, CP-Co/SnSe₄; **d**, *h*-CP-Zn/SnSe₄. **e**, CP-Cd/SnSe₄. **f**, CP-Hg/SnSe₄. The pore organization in this material into hexagonal domains is more

extensive. **g**, X-ray diffraction pattern of cubic *c*-CP-Zn/SnSe₄, with indexing. This pattern is similar to those observed in cubic silica MCM-48 systems. Powder X-ray data were collected with a Rigaku Rotaflex powder X-ray diffractometer equipped with Ni-filtered Cu K α radiation and operating at 45 kV and 100 mA.

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regions for CP-Zn/SnSe₄ and nearly wormhole-like arrangement for CP-Cd/SnSe₄.

The presence of the tetrahedral $[SnSe_4]^{4-}$ anion in these materials is supported by ¹¹⁹Sn Mössbauer spectroscopy, a powerful experimental technique for the identification and characterization of the Sn local environment and formal oxidation state. Figure 3 shows Mössbauer spectra for K₄SnSe₄, CP-Mn/SnSe₄, CP-Fe/SnSe₄, CP-Zn/SnSe₄, CP-Cd/SnSe₄ and CP-Hg/SnSe₄. The corresponding isomer shift, δ , and quadrupole splitting, ΔE_q , parameters are very similar in all compounds and characteristic of tetrahedral Sn⁴⁺ centres¹⁷ (see Fig. 3 legend). The appearance of quadrupole splitting in the spectra of the mesophases suggests that the local lattice symmetry of the Sn⁴⁺ centre is lower compared to that in K₄SnSe₄. This is attributed to binding of the metal centres which lowers the tetrahedral symmetry. The spectra also reveal two slightly different Sn environments, suggesting at least two different binding modes for SnSe₄.

The thermal stability of $(CP)_{4-2x}M_xSnSe_4$ was investigated by TGA and pyrolysis mass spectrometry (MS). (Pyrolysis MS analyses were carried out on a Hewlett Packard Series II 5890 coupled with a



Figure 2 Transmission electron microscope images of mesostructured chalcogenides. **a**, *h*-CP-Zn/SnSe₄ looking down the pore channel axis; **b**, CP-Hg/SnSe₄ looking down the pore channel axis. Inset in upper right, optical Fourier transform of image and corresponding filtered image. The straight parallel nature of the pore tunnels extends over >1,500 Å. **c**, CP-Hg/SnSe₄ perpendicular to the channel axis; **d**, CP-Mn/SnSe₄ perpendicular to the channel axis; **d**, CP-CM/SnSe₄. The cubic arrangement is shown in the boxed area. Insets in lower left and upper right, optical Fourier transform of boxed area, and corresponding filtered image. **f**, CP-Cd/SnSe₄. Disordered regions with wormhole arrangement. TEM samples were prepared by suspending the precipitate in ether, then casting on holey carbon grid. High-resolution TEMs were acquired with a JEOL 120CX instrument equipped with a CeB₆ filament and operating at 120 kV. The TEM images are typical and representative of the samples under observation.

mass spectrometer. Samples were heated at 20 °C min⁻¹ and the volatile products were ionized by electron ionization.) See Fig. 4a for characteristic TGA curves of CP-Co/SnSe₄, CP-Zn/SnSe₄, CP-Cd/ SnSe4 and CP-Hg/SnSe4. The compounds show no appreciable weight loss up to 150 °C. Between 150 and 400 °C weight loss occurs as a result of surfactant decomposition. The XRD powder patterns of the residue correspond to a mixture of crystalline SnSe and MSe. The samples CP-Cd/SnSe₄ and CP-Hg/SnSe₄ clearly show a two-step decomposition process. The first occurs between 150 and 290 °C and the second between 290 and 400 °C, leading to a mixture of MSe and SnSe. The weight loss observed in the first step corresponds to quantitative release ($\sim 11\%$) of the pyridyl head group from the surfactant and this was verified with pyrolysis MS analysis. We note that the volatile product released between 300-400 °C was identified to be $CH_3(CH_2)_{13}CH = CHSeH$, showing that the metal chalcogenide framework is attacked during this process. Unfortunately, this form of 'calcination' is not the correct one, as the complete removal of the surfactant species results in framework collapse.

The optical absorption properties of the solids were investigated with diffuse-reflectance solid-state ultraviolet–visible/near-infrared spectroscopy. In general, chalcogenide materials have considerably narrower energy bandgaps than oxides (for example, silicates) and this property makes them attractive for optoelectronic applications. The $(CP)_{4-2x}M_xSnSe_4$ compounds possess well defined, sharp optical absorptions associated with bandgap transitions in the energy range 1.4–2.5 eV (see Table 1 and Fig. 4b). The very sharp electronic transitions in the Zn, Cd and Hg analogues suggest that their bandgaps may possibly be direct. In addition, the bandgap narrows in going from the lighter to the heavier element in the isoelectronic



Figure 3 ¹¹⁹Sn Mössbauer spectra (85 K) with derived δ/Δ*E*_q parameters. **a**, K₄SnSe₄ (standard) 1.42/0 mm s⁻¹. **b**, CP-Mn/SnSe₄, 1.54/0.86 (52%) mm s⁻¹ and 1.54/0.52 (48%) mm s⁻¹. **c**, CP-Fe/SnSe₄, 1.55/0.94 (50%) mm s⁻¹ and 1.55/0.42 (46%) mm s⁻¹. **d**, CP-Zn/SnSe₄ 1.52/0.97 (44%) mm s⁻¹ and 1.52/0.39 (56%) mm s⁻¹. **e**, CP-Cd/SnSe₄ 1.53/0.71 (50%) mm s⁻¹ and 1.53/0.33 (50%) mm s⁻¹. **f**, CP-Hg/SnSe₄ 1.54/1.13 (20%) and 1.53/0.62 (80%) mm s⁻¹. The spectra clearly show that the Sn atoms are in the +4 oxidation state. The isomer shifts are referenced to BaSnO₃ at room temperature.

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series. The Mn and Fe analogues possess the lowest energy gaps at \sim 1.4 and 2.0 eV, values similar to those of CdTe and GaP semiconductors¹⁸.

The surfactant-templated supramolecular assembly of the simple tetrahedral Zintl $[SnSe_4]^{4-}$ anion with transition metals leads to the formation of mesostructured semiconducting selenide materials of the general formulae $(CP)_{4-2x}M_xSnSe_4$ (where M = Mn, Fe, Co, Zn, Cd, Hg). The pores in these systems are uniformly sized and show local hexagonal order as observed by TEM.

The c-(CP)_{4-2x}M_xSnSe₄ represents the first example of cubic,



Figure 4 Thermogravimetric data and optical absorption spectra. **a**, TGA curves of CP-Co/ SnSe₄, CP-Zn/SnSe₄, CP-Cd/SnSe₄ and CP-Hg/SnSe₄, under nitrogen flow. Heating rate was 10° min⁻¹. Data were obtained with a Shimadzu TGA-50 thermal analyser. **b**, Optical absorption spectra of selected mesostructured chalcogenides. (Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer in the wavelength range 200–2,500 nm). Absorption (α /S) data were calculated from the reflectance data using the Kubelka–Munk function: α /S = $(1 - R)^2/2R$, where *R* is the reflectance at a given wavenumber, α is the absorption coefficient, and *S* is the scattering coefficient.

Table 2 d-values for mesostructured metal tin selenides							
Sample	d ₁₀₀ values (Å)	Second-order scattering d values (Å)					
Mn	40.1	22.3					
Fe	34.3	18.2					
Co	36.2	18.5					
Zn (cubic)	$d_{211} = 35.5$	31.2 (see Fig. 1g)					
Zn (hex)	36.7	20.8					
Cd	36.1	19.7					
Hg	38.6	$d_{110} = 22.3, d_{200} = 19.6$					

non-oxide mesophase. Ten years after the discovery of mesostructured cubic silica (MCM-48), the discovery of a semiconducting chalcogenide analogue is an important milestone. The reasons for this and the advantages over previous hexagonal systems are as follows. Cubic symmetry in a porous nanostructured semiconductor provides the possibility of creating the negative image of a quantum dot crystal, that is, an array of ordered 'quantum dot' nanocrystals, also of cubic symmetry. Such a material, instead of presenting ordered semiconductor nanocrystals separated by continuous dielectric space, presents continuous semiconductor space separated by dielectric voids. It can most easily be thought of as the geometric complement or 'inside-out version' of an array of ordered 'quantum dot' nanocrystals. These types of materials have been visualized in the nanoengineering physics literature¹ and have been termed 'exosemiconductors'² or 'quantum antidots'. The relationship between these two types of nanostructures has yet to be demonstrated. This is partly because currently there are no 'quantum antidot'-type materials. c-(CP)_{4-2x} M_x SnSe₄ is a substantial step towards creating them. Cubic symmetry in this case allows for experimentation aimed at answering fundamental questions, such as: can exosemiconductors be quantized?

The present experiments establish that it is possible to construct organically templated structures with heavier SiO₄-analogues to produce semiconducting solids with well defined mesopores. Therefore they open new prospects for the design and construction of electronically active, porous chalcogenide solids and other nonoxide systems in general. These materials should help us to understand how ordered mesostructured materials form and may also enable unusual shape-selective electronically or optically driven processes. In particular, cubic nanostructured semiconductors provide an isotropic bi-continuous medium in which the pore system of the semiconductor framework can potentially be accessed by guest molecules from all directions. Three-dimensional guest diffusion in and out of the material can give rise to faster processes associated with whatever material function is being used. This, for example, could be molecule-discriminating semiconductor photocatalysis occurring in the interior of the material, rather than what is now available on the surface of the semiconductor. A hexagonal system with its unidirection pore organization does not permit pore-pore communication and could frustrate guest diffusion. We anticipate cubic nanostructured semiconductors may be tailored in several ways, through the composition of the framework, arrangement of pores, even through the electronic properties of the organic amphiphiles, for optoelectronic, photosynthetic and photocatalytic applications and membrane probes. Further work involving other chalcogenide building blocks, such as [GeSe₄]⁴⁻, [GeTe₄]⁴⁻, [SnTe₄]⁴⁻ [SbSe₃]³⁻ and [SbTe₃]³⁻ is in progress.

Methods

The starting materials were $MnCl_2 \cdot 4H_2O$, $FeSO_4 \cdot 6H_2O$, $Co(Ac)_2 \cdot 4H_2O$, $Zn(Ac)_2 \cdot 2H_2O$, $Cd(NO_3)_2$ and $Hg(Ac)_2$ (where $Ac = CH_3COO$). All reactions were carried out under N_2 atmosphere inside a glove box.

General procedure

In a typical preparation, a solution of 4.00 g (9.94 mmol) of surfactant (CPBr-H₂O) in 20 ml of formamide was heated at 75 °C for a few minutes forming a clear solution. To this solution, 0.59 g (1.00 mmol) of K₃SnSe₄ was added and the mixture was stirred for 30 min, forming a clear deep red solution. To this a solution of 1.00 mmol of the metal salt in 10 ml of formamide was added slowly, using a pipette. A precipitate formed immediately and the mixture was stirred while warm for 20 h. The products were isolated by suction filtration and washed with large amounts of warm formamide and water. The solids were dried under vacuum overnight. The yields of the orange (Mn), dark brown (Fe, Co), yellow (Zn, Cd) and dark orange (Hg) products were ~80% in all cases, based on K₄SnSe₄ as the limiting reagent. For (CP)_{4-2x}Zn_xSnSe₄ the above preparation gives a cubic phase. The hexagonal phase of this system requires 2.00 g (4.97 mmol) of surfactant.

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An alternative approach to establishing trade-offs among greenhouse gases

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The Kyoto Protocol permits countries to meet part of their emission reduction obligations by cutting back on gases other than CO_2 (ref. 1). This approach requires a definition of trade-offs among the radiatively active gases. The Intergovernmental Panel on Climate Change has suggested global warming potentials for this purpose², which use the accumulated radiative forcing of each gas by a set time horizon to establish emission equivalence. But it has been suggested that this approach has serious shortcomings: damages or abatement costs are not considered³⁻¹⁰ and the choice of time horizon for calculating cumulative radiative force is critical, but arbitrary⁵. Here we describe an alternative framework for determining emission equivalence between radiatively active

gases that addresses these weaknesses. We focus on limiting temperature change and rate of temperature change, but our framework is also applicable to other objectives. For a proposed ceiling, we calculate how much one should be willing to pay for emitting an additional unit of each gas. The relative prices then determine the trade-off between gases at each point in time, taking into account economical as well as physical considerations. Our analysis shows that the relative prices are sensitive to the lifetime of the gases, the choice of target and the proximity of the target, making short-lived gases more expensive to emit as we approach the prescribed ceiling.

Although the Kyoto Protocol encompasses a number of radiatively active gases, the assessment of compliance costs has focused almost exclusively on the costs of reducing carbon dioxide (CO₂) emissions. This is because CO₂ is, by far, the most important manmade gas². Also, until recently, few economic models have been able to conduct comprehensive multi-gas analyses¹⁰. Moreover, the quality of data pertaining to other greenhouse gases is poor (both spatially and intertemporally). Nevertheless, focusing exclusively on CO₂ will bias mitigation cost estimates and lead to policies that are unnecessarily costly.

A number of gases have now been identified as having a positive effect on radiative forcing. We consider the three that are thought to be the most important: CO_2 , methane (CH_4) and nitrous oxide (N_2O) (ref. 2).We also consider the cooling effect of sulphate aerosols, but exclude the 'second basket' of greenhouse gases included in the Kyoto Protocol. These are the hydrofluorocarbons (HFCs), the perfluorocarbons (PFCs) and sulphur hexafluoride (SF₆). We believe that these omissions do not alter the key insights of our analysis.

Table 1 shows alternative global warming potentials (GWPs) for the three gases of interest. The index is defined as the cumulative radiative forcing between the present and some time in the future caused by a unit mass of gas emitted now, expressed relative to that of CO_2 (ref. 2). Clearly, the choice of time horizon is critical. Unfortunately, as pointed out in ref. 5, there is no justification for choosing one time horizon over another. GWPs are a purely physical measure. They depend neither on damages nor mitigation costs. For a discussion of the uncertainties involved in calculating GWPs, see ref. 11.

What might then constitute a more defensible index for establishing trade-offs among gases? Ideally, the index would be the outcome of an analysis that minimizes the discounted present value of damages and mitigation costs. Unfortunately, we lack at present the necessary knowledge to specify the shapes of the damage functions and to assign values to many categories of impacts. We have therefore used an approach in which the ceiling is intended to reflect a political judgement as to what constitutes a prudent limit. These limits are based upon expectations regarding the damages associated with particular ceilings. The appropriate trade-offs among gases are then determined through a cost-effectiveness analysis.

Unlike the calculation of GWPs, the proposed approach incorporates the marginal cost of abating each greenhouse gas. This can have important implications for the trade-offs among gases. The more expensive it is to abate a particular gas, the smaller the role of that gas in a multi-gas reduction portfolio. Relying completely on

Table 1 GWPs as a function of alternative time horizons									
Species	Chemical	Lifetime (years)	Global warming potential (years)						
	Torridia		20	100	500				
Carbon dioxide	CO ₂	50-200	1	1	1				
Methane	CH ₄	12	56	21	6.5				
Nitrous oxide	N ₂ O	120	280	310	170				

Data from ref. 2.

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