# Formation of group 12 [Zn, Cd] mixed-chalcogen nanoparticles from the reagent Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub><sup>1</sup>

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**Abstract:** Mixed-chalcogen metal chalcogenide nanoparticles ( $MSe_xS_{1-x}$ ; M = Zn, Cd) have been synthesized using  $Me_3Si$ -SeS-SiMe<sub>3</sub> as a delivery source of  $Se^{2-}$  and  $S^{2-}$  to the metal core. This method demonstrates the ease with which mixed-chalcogen particles can be fabricated at low temperature using colloidal techniques. Reaction with  $Me_3Si$ -SeS-SiMe<sub>3</sub> occurs via a redox pathway resulting in Se–S bond cleavage and ultimately contributing to the non-equivalent Se:S ratio observed in the isolated particles. Subsequent thermolysis of  $ZnSe_{0.57}S_{0.43}$  and  $CdSe_{0.28}S_{0.72}$  in hexadecylamine gives rise to controlled particle growth while maintaining the observed stoichiometry. Particles are characterized by EDX, TEM, and powder X-ray diffraction analysis in conjunction with UV–vis absorption and photoluminescence (PL) spectroscopy.

Key words: nanoparticles, semiconductors, mixed-chalcogen, quantum confinement, Group 12.

**Résumé :** On a effectué la synthèse de nanoparticules mixtes comportant un chalcogène et un chalcogénure métallique (MeSe<sub>x</sub>S<sub>*l*-x</sub>; M = Zn, Cd) en utilisant le Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> comme source pouvant livrer les groupes Se<sup>2-</sup> et S<sup>2-</sup> au métal central. On a fait une démonstration de cette méthode par la facilité avec laquelle des particules de chalcogènes mixtes peuvent être fabriqués à basse température en faisant appel à des techniques colloïdales. La réaction avec le Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> se produit par une voie réactionnelle redox qui provoque un clivage de la liaison Se-S et qui contribue éventuellement au rapport non équivalent de Se:S qui est observé dans les particules qui ont été isolées. Une thermolyse subséquente du ZnSe<sub>0.57</sub>S<sub>0.43</sub> et du CdSe<sub>0.28</sub>S<sub>0.72</sub> dans l'hexadécylamine conduit à une croissance contrôlée des particules tout en maintenant la stoechiométrie observée. On a caractérisé les particules par le biais de la diffraction des rayons X par des poudres et les techniques « EDX » et « TEM » en relation avec les spectres d'absorption UV–vis et la spectroscopie de photoluminescence (PL).

Mots-clés : nanoparticules, semiconducteurs, chalcogènes mixtes, confinement quantique, groupe 12.

[Traduit par la Rédaction]

## Introduction

Metal-chalcogenides (ME; M = Zn, Cd, Hg; E = S, Se, Te; or  $M_2E$ ; M = Cu, Ag) have been of tremendous interest over the past several decades (1). In particular, an extensive amount of research has surrounded both the synthesis (2) and characterization (3) of group 12–16 nanomaterials. Upon constricting the dimensions of a given material to the nanometer-size regime, quantum confinement effects predominate such that electronic, physical, and optical properties become size specific (4). Ultimately, for semiconductors, these phenomena give rise to an increase in band gap energy from that of the bulk material, where the

Received 17 May 2007. Accepted 21 June 2007. Published on the NRC Research Press Web site at canjchem.nrc.ca on 3 August 2007.

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<sup>1</sup>This article is part of a Special Issue dedicated to Professor G. Michael Bancroft.

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band gap becomes tunable to a desired particle size. As a result, group 12–16 nanomaterials have found potential applications in the fabrication of new devices such as LEDs, photovoltaic, and photoelectrochemical devices (5). The control of particle size and the efficient delivery of chalcogen ( $E^{2-}$ ) to the metal core, however, are two challenging aspects of nanomaterial synthesis. One means of managing these two synthetic obstacles is through the use of trimethylsilyl-chalcogenide reagents as an easily handled chalcogen source in conjunction with passivating the metal core with long alkyl chain amine (phosphine) ligands, thereby preventing possible aggregation (6).

One of the pioneering methods in controlling particle size is what is commonly referred to as the controlled arrested precipitation method from colloidal solutions where dilute aqueous mixtures of  $M^{2+}$  and  $E^{2-}$  species are combined together (7). This method was further extended into what is considered to be one of the most notable advances in the formation of discrete nanoparticles, the TOP or TOPO (trioctylphosphine or trioctylphosphine oxide) pyrolysis method. The rapid injection of sources of both  $M^{2+}$  and  $E^{2-}$ species into a hot coordinating solvent facilitates the development of nanoparticles (8). An extension of this method has been to inject metal clusters, where the metal-chalcogen bond is already prepositioned, into a hot hexadecylamine (HDA) solution (9). By increasing the reaction temperature, particles are found to grow via Ostwald ripening (10) where the more soluble smaller particles grow in an effort to form larger particles (11). The large surface area to volume ratio of the smaller particles promotes the number of energetically less stable surface molecules, and larger particles having a greater volume to surface area ratio are of a lower energy state and thus preferentially form at the expense of smaller particles (12).

Manipulating particle size is one means of dictating their physical properties. An additional degree of freedom can be gained by substituting some metal (or chalcogen) atoms with another metal (or chalcogen), thus forming ternary MM'E (or MME';  $M \neq M'$  and  $E \neq E'$ ) materials. These materials exhibit physical properties whose energies are intermediate between those of ME and M'E (or ME'). Recent studies have focused on the synthesis and characterization of group 12– 12'-16 nanoclusters and nanoparticles through the use of trimethylsilyl-chalcogenide reagents (13). The formation of 12–16–16' nanomaterials, however, remains relatively unexplored (vide infra).

Only a few known examples exist where discrete quantum dots, rather than thin films, of mixed-chalcogen cadmium materials have been synthesized. Quantum dots and tetrapod nanocrystals of  $CdSe_{x}Te_{l-x}$  (14) have been synthesized from cadmium salts and stock solutions of selenium and tellurium using either TOP, TOPO, or stearic acid as surface stabilizing ligands. Homogeneously alloyed zinc-blende  $CdSe_xS_{1-x}$ (15) nanocrystals have also been prepared from cadmium oxide, oleic acid, and stock solutions of elemental sulfur and selenium, added in varying proportions. Discrete particles were observed using transmission electron microscopy (TEM) and chemical homogeneity was demonstrated by powder X-ray diffraction (PXRD). By changing the ratio S:Se, the photophysical properties could be altered such that an increasing selenium content leads to a shift to lower energy of the excitonic transition, as observed in the absorption spectra. The majority of reports on mixed-chalcogen ternary alloys, however, involve the preparation of  $CdSe_xS_{1-x}$  thin films typically on glass, quartz, GaAs, and silicon. A typical procedure involves the mixture of CdS and CdSe powders combined in a desired ratio (16). Other methods employ CdCl<sub>2</sub>, thiourea and sodium selenosulfate as precursors (17), while the elemental forms of cadmium, sulfur, and selenium can also be combined with a desired stoichiometry in a glass melt (18). An extension to this synthesis involves the use of elemental sulfur and selenium with cadmium salts (19), while other procedures use a combination of metal salts with various chalcogen precursors (i.e.,  $H_2E$  and  $CS(NH_2)_2$ ) (20). Regardless of the choice of reagents, the methods involve specialized techniques such as chemical bath deposition, molecular beam epitaxy, or pulsed laser ablation, all of which require extremely high temperatures. The deposited materials typically have nanometer dimensions, where examples of nanowires and nanoribbons have been formed on a Si[111] substrate (21).

Herein we report the synthesis of  $MSe_xS_{1-x}$  (M = Zn, Cd) nanoparticles formed from the reagent  $Me_3Si$ -SeS-SiMe<sub>3</sub>. The highly reactive nature of this reagent allows for the facile low temperature delivery of both sulfur and selenium to the corresponding metal acetate. The resulting nanoparticles are easily formed in solution at room temperature (RT). Subsequent thermolysis of the zinc and cadmium mixedchalcogen nanoparticles in hot hexadecylamine is found to provide controlled particle growth. The resulting nanoparticles are analyzed by UV–vis absorption and PL spectroscopy, in addition to TEM, powder X-ray diffraction, and EDX analysis.

## **Experimental**

#### **Materials**

All synthetic procedures and manipulations were performed under an inert nitrogen atmosphere using standard Schlenk techniques and gloveboxes, unless otherwise noted. Toluene, pentane, and hexanes (all from Caledon) were dried and collected using an MBraun MB-SPS solvent purification system with tandem activated alumina - activated copper redox catalyst (22). Dichloromethane (EMD) was dried and distilled over P2O5. Anhydrous methanol was purchased from Caledon. Cadmium acetate dihydrate (98%), anhydrous zinc acetate (99.99%), N,N,N',N'-tetramethylethylenediamine (TMEDA), n-butyl lithium in hexanes (1.6 mol/L), tri(nbutyl)phosphine, and hexadecylamine (HDA) were purchased from Sigma-Aldrich. Sulfur (99%) was purchased from EM Science. Cadmium acetate dihydrate was dried under vacuum ( $10^{-3}$  torr; 1 torr = 133.322 4 Pa) at 130 °C and stored under inert conditions. TMEDA was dried and distilled over a lump of sodium and stored under inert conditions. The reagent Se(SiMe<sub>3</sub>)<sub>2</sub> was prepared according to literature procedures (13c, 23).

## Synthesis of TMEDA Li<sup>+</sup> -SeSiMe<sub>3</sub>

In a Schlenk tube with no stir bar,  $(SiMe_3)_2Se (0.15 \text{ mL}, 0.7 \text{ mmol})$  and TMEDA (0.1 mL, 0.7 mmol) were added to tetrahydrofuran (10 mL) and cooled to 0 °C, producing a light brown solution. *n*-Butyl lithium (0.44 mL, 0.7 mmol) was added to the reaction, upon which the solution immediately became colourless, and the reaction was kept at 0 °C for 30 min with periodic mixing via agitation. A stir bar was then added to the solution and the reaction was warmed to RT with stirring. The solvent was removed under vacuum  $(10^{-3} \text{ torr for one hour})$  producing a colourless oil. The anion was used immediately in the subsequent chalcogen insertion as the product has limited stability at RT. <sup>1</sup>H NMR  $(C_7D_8, 203K) \delta$ : 0.72 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 1.64 (br s, CH<sub>2</sub>), 2.11 (s, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} (C<sub>7</sub>D<sub>8</sub>, 203 K)  $\delta$ : 8.41 (Si(CH<sub>3</sub>)<sub>3</sub>), 47.08 (CH<sub>2</sub>), 56.11 (CH<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>7</sub>D<sub>8</sub>, 203 K)  $\delta$ : 1.1. <sup>77</sup>Se NMR (C<sub>7</sub>D<sub>8</sub>, 203 K)  $\delta$ : -520.

## Synthesis of TMEDA Li<sup>+</sup> -SSeSiMe<sub>3</sub>

In a Schlenk tube, sulfur (0.023 g, 0.7 mmol) was suspended in pentane (10 mL) and cooled to -78 °C. Toluene (5 mL) was added to the lithio trimethylsilyl selenolate anion (0.7 mmol) and the solution was cooled to -78 °C. The anion solution was rapidly added to the sulfur suspension at -78 °C upon which a slightly yellow solution developed. The reaction was removed from the cold bath until a bright yellow cloudy solution resulted. The solution was then immediately cooled again to -78 °C and allowed to stir for an additional 20 min. The product was used in situ as removal of the solvent leads to product decomposition; in addition, the lithio trimethylsilyl selenothiolate anion must be used

immediately as it quite reactive to both air and elevated temperatures. <sup>1</sup>H NMR ( $C_7D_8$ , 203 K) & 0.31 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 1.58 (br s, CH<sub>2</sub>), 2.12 (s, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} ( $C_7D_8$ , 203 K) & 1.22 (Si(CH<sub>3</sub>)<sub>3</sub>), 48.55 (CH<sub>2</sub>), 56.00 (CH<sub>3</sub>). <sup>29</sup>Si NMR ( $C_7D_8$ , 203K) & 15.3. <sup>77</sup>Se NMR ( $C_7D_8$ , 203 K) & -96.

## Synthesis of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub>

An excess of chlorotrimethylsilane (0.2 mL, 1.4 mmol) was added to lithio trimethylsilyl selenothiolate anion (0.7 mmol) at -78 °C. The reaction was allowed to gradually warm to RT upon which the cloudy solution went through a clear bright yellow stage followed by the development of a cloudy yellow suspension. Upon achieving this stage the reaction was immediately cooled to -78 °C and kept cold until further use. The product cannot be isolated as removal of the solvent leads to rapid decomposition. Furthermore, the generated lithium chloride must be added to subsequent reactions as filtration of the solution also leads to decomposition. The product is exceptionally reactive to air and has only short-term stability at RT. <sup>1</sup>H NMR ( $C_7D_8$ ,  $C_5D_{12}$ , 218 K)  $\delta$ : 0.26 (SSi(CH<sub>3</sub>)<sub>3</sub>), 0.34 (SeSi(CH<sub>3</sub>)<sub>3</sub>).  $^{13}C{^{1}H}$  NMR (C<sub>7</sub>D<sub>8</sub>, C<sub>5</sub>D<sub>12</sub>, 218 K) δ: 1.27 (SeSi(CH<sub>3</sub>)<sub>3</sub>), 3.86 (Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>7</sub>D<sub>8</sub>, C<sub>5</sub>D<sub>12</sub>, 218 K)  $\delta$ : 15.9 (SeSi(CH<sub>3</sub>)<sub>3</sub>), 16.4 (SSi(CH<sub>3</sub>)<sub>3</sub>). <sup>77</sup>Se NMR (C<sub>7</sub>D<sub>8</sub>, C<sub>5</sub>D<sub>12</sub>, 218 K)  $\delta$ : -100.

## Synthesis of CdSe<sub>x</sub>S<sub>1-x</sub> nanoparticles

Anhydrous cadmium acetate (0.320 g, 1.4 mol) was solubilized with 2.2 equiv. of tri(*n*-butyl)phosphine (0.76 mL, 3.05 mol) in toluene (30 mL), producing a turbid solution. After stirring at RT for 1 h, a solution of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> (1.4 mol) was added and the reaction was stirred at RT overnight, resulting in the precipitation of a pale yellow solid. The solid was isolated via removal of the mother liquor, followed by washing (3 × 10 mL methanol), sonication for 15 min at 45 °C, and centrifugation. The resulting solid was dried under vacuum ( $10^{-3}$  torr) for 1 h.

## Synthesis of ZnSe<sub>x</sub>S<sub>1-x</sub> nanoparticles

Anhydrous zinc acetate (0.255 g, 1.4 mol) was solubilized with 2.2 equiv. of tri(*n*-butyl)phosphine (0.76 mL, 3.05 mol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). After stirring at RT for one hour, Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> (1.4 mol) was added and the reaction was stirred at RT overnight. A resulting white solid precipitated from solution and was isolated via removal of the mother liquor and washing with hexanes (3 × 15 mL), followed by drying under vacuum (10<sup>-3</sup> torr) for 1 h.

# Thermolysis of $MSe_xS_{1-x}$ in hexadecylamine

To the obtained  $MSe_xS_{l-x}$  [M = Zn, Cd] nanoparticles, hexadecylamine (HDA; 20 g, 82.8 mmol) was added to the flask and heated to 60 °C, until all of the HDA had melted. The solution was then degassed under vacuum (10<sup>-3</sup> torr) for 20 min. The mixture was then heated to 240 °C, where at specified temperature intervals an aliquot was taken. At each temperature the reaction was annealed for 15 min, an aliquot was taken, washed with anhydrous methanol (15 mL) thus precipitating the resulting particles, centrifuged at 45 °C, and washed again with methanol. The obtained solids were dried under vacuum (10<sup>-3</sup> torr) for 15 min and stored in a glovebox.

#### Characterization

Solution <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>77</sup>Se NMR spectra were recorded on a Varian Inova 400 spectrometer with an operating frequency of 399.76, 100.53, and 76.24 MHz respectively. <sup>29</sup>Si NMR spectra were obtained indirectly as gradient heteronuclear multibond coupling (g-HMBC) experiments to proton ( $J_{Si-H} = 6$  Hz). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced internally to the respective deuterated solvent as well as externally to TMS, <sup>29</sup>Si NMR spectra were referenced to silicon grease (-20 ppm), and <sup>77</sup>Se NMR spectra were referenced externally to PhSeSiMe<sub>3</sub> (+85.6 ppm) (24). Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku diffractometer with a Co K $\alpha$  radiation source ( $\lambda = 1.799260$  Å). UV-vis absorption spectra for  $ZnSe_xS_{1-x}$  nanoparticles were recorded on an Ocean Optics SD2000 UV-vis fiber optic spectrometer equipped with a Mini-D2T light source and a UV2/OFLV-4 detector. The spectra were obtained as a mineral oil mull between two quartz plates. UV-vis absorption spectra of the  $CdSe_xS_{1-x}$  nanoparticle series were recorded on a Varian Cary 100 UV-vis absorption spectrometer. The spectra were obtained in a CH<sub>2</sub>Cl<sub>2</sub> solution. Luminescence measurements were obtained using a Photo Technology International fluorimeter equipped with an LPS 220B lamp power supply and an 814 photomultiplier detection system. Energy dispersive X-ray (EDX) analyses were carried out by Dr. Brian Hart at Surface Science Western (UWO). A Quartz Xone EDX analysis system coupled to a Leo 440 SEM equipped with a Gresham light element detector was used to obtain semiguantitative analysis of Zn, Cd, S, and Se. Analyses were carried out using a 20 kV electron beam rastered over 100  $\mu$ m × 100  $\mu$ m areas and repeated to ensure reproducibility. Samples for high-resolution transmission electron microscopy (HR-TEM) were obtained by dispersing the solid in CH<sub>2</sub>Cl<sub>2</sub> and dropping these dilute suspensions on gold-plated grids, allowing the excess solvent to evaporate. TEM investigations were performed in a Philips Tecnai F20 ST operated at 200 kV. The TEM was equipped with an EDAX Energy-Dispersive X-ray SiLi detector with a S-UTW (super ultra-thin window). EDX analyses were carried out in the STEM mode with a HAADF (high angle annular dark field) detector using a nanometer-sized probe (1 nm spot size for the presented measurements). Use of an analytic double tilt holder (Philips) was made. High-resolution micrographs were taken with a  $1K \times 1K$  CCD camera and analyzed with the software package Digital Micrographs (Version 3.7.4, Gatan Company) to perform fast Fourier Transformations (FFT).

## **Results and discussion**

## Synthesis of mixed-chalcogen nanoparticles

Trimethylsilyl-chalcogen reagents (RESiMe<sub>3</sub>, E(SiMe<sub>3</sub>)<sub>2</sub>; R = alkyl, aryl, ferrocenyl) are valuable in the formation of structurally characterized nanoclusters (25) and nanoparticles (26). The reactive pendant trimethylsilyl moiety allows for the facile and homogeneous delivery of either chalcogenolate (RE<sup>-</sup>) or chalcogenide (E<sup>2-</sup>) bonding interactions to a metal salt via the generation and elimination of the corresponding trimethylsilane (27). Although the synthesis of binary and ternary mercury chalcogenides has been a synthetically challenging area (28), one recent example involves the formation of  $HgSe_xS_{1-x}$  particles from both  $S(SiMe_3)_2$ and  $Se(SiMe_3)_2$  and mercury acetate, using TOP in a phase separation method, to control particle growth (29). Particles varying in size from 2 to 3 nm were formed.

Traditional trimethylsilyl-chalcogenide reagents (i.e.,  $E(SiMe_3)_{2;} E = S$ , Se, Te) are well-known and extensively used in synthesis, however, there is recent interest in synthesizing silylated-chalcogen reagents containing two chalcogen elements, whereby both  $E^{2-}$  and  $E'^{2-}$  are supplied to the metal core. Recently we have communicated the synthesis and characterization of the first mixed-chalcogen silylated reagent Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> and demonstrated its use in the formation of a  $[Cu_{84}Se_{15}S_{27}(PEt_2Ph)_{24}]$  cluster (30).

Bis(trimethylsilyl)selenosulfide [Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub>] is a highly reactive reagent, for which both exposure to atmosphere and elevated temperatures leads to rapid decomposition. In addition, the reagent cannot be isolated and can only be synthesized in dilute solutions. Lithium chloride generated in the formation of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> cannot be removed via filtration and must be carried forward in subsequent syntheses. Although Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> is not a storable precursor, its low temperature stability is ideal for the generation of MSe<sub>x</sub>S<sub>1-x</sub> (M = Zn, Cd) nanoparticles at RT vs. the typically explored high temperature methods.

## CdSe<sub>x</sub>S<sub>1-x</sub> nanoparticles

Given the sensitivity of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub>, cadmium acetate  $[Cd(OAc)_2]$  can only be introduced in a select number of solvents. The addition of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> at RT to a toluene solution of  $(P^nBu_3)_2Cd(OAc)_2$  results in the immediate consumption of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub>, as noted by the disappearance of the yellow colour associated with the in conjunction selenosulfide, with the complete solubilization of Cd(OAc)<sub>2</sub>. This reactivity is then followed by the precipitation of a colourless solid from solution, which gradually develops into a pale yellow colour after stirring overnight. The resulting solid is easily isolated where washing with anhydrous methanol effectively removes any LiCl. Isolated particles were characterized by HR-TEM, however, given their poor solubility a UV-vis absorption spectrum could not be obtained.

To investigate the growth of the resulting  $CdSe_xS_{I-x}$  nanoparticles in a coordinating solvent, the solid was added to a hot (60 °C) solution of hexadecylamine (HDA) and heated to 240 °C. Upon increasing the temperature, the sample colour changes from pale yellow to an intense red (Supplementary data, Fig. S1).<sup>4</sup> At specified temperature intervals the sample is annealed (where upon there is no corresponding change in colour) and an aliquot is taken. The resulting nanoparticles are isolated by precipitating from solution using anhydrous methanol.

Lyothermal growth of the nanoparticles results in an increase in particle size without altering the chemical composition (i.e., the ratio between Cd:Se:S). EDX (energy dispersive X-ray) analysis was performed on three separate areas of each sample, where the overall ratio was determined by calculating the average based on the atomic percentages for the corresponding elements. Table 1 clearly demonstrates the nondeviating stoichiometry beginning with the assynthesized particles and those obtained through thermolysis in HDA. The ratio between Se and S in the isolated particles is not 1:1 although a stoichiometrically precise reagent is used in the synthesis. The reactivity of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> however, is expected to occur with Se–S bond cleavage as has previously been established with the synthesis of a  $[Cu_{84}Se_{27}S_{15}(PEt_2Ph)_{24}]$  cluster (30). It is necessary to note that the stoichiometry is reproducible and is a reflection of the isolated particles.

The growth in particle size is surveyed using HR-TEM microscopy. Shown in Fig. 1 are the HR-TEM images for assynthesized, 180 °C, 210 °C, and 240 °C lyothermally grown particles. At 180 °C the particles are found to be ~3.5 nm in diameter, while an increase in thermolysis temperature to 240 °C leads to particles of ~9 nm in diameter. The *d* spacing, as determined by TEM (3.54 Å), is relatively consistent with the *d* spacing associated with the (1 1 1) reflection in the powder X-ray diffraction pattern (3.40 Å).

properties of the The photophysical obtained nanoparticles were analyzed using UV-vis absorption and photoluminescence (PL) spectroscopy. The UV-vis absorption spectra of the thermolysed samples (Fig. 2) distinctly display a red shift in absorption maximum upon increasing thermolysis temperature. At a thermolysis temperature of 160 °C, the absorption maximum is observed at 445 nm (2.79 eV) and shifts by over 100 nm to lower energy upon increasing the thermolysis temperature to 240 °C (560 nm; 2.21 eV). This shift in absorption maximum is consistent with an increase in particle size upon increasing thermolysis temperature. The observed absorption maxima are consistent with what has previously been reported for  $CdSe_{r}S_{l,r}$  having a similar stoichiometry and particle size (15).

The low- and high-energy PL spectra for this series is shown in Fig. 3, where the spectra were obtained by irradiating samples at 468 nm. As is illustrated in Fig. 3a, the emission maximum shifts from 488 nm (2.54 eV) to 590 nm (2.10 eV) upon increasing thermolysis temperature and is associated with band-edge emission. At lower energy, two types of emission are observed (Fig. 3b) that, although normalized in the figure, are found to increase in intensity (relative to the high energy emission) as the thermolysis temperature is raised. The emission observed at lower energy is much broader in comparison to the sharp band-edge emission and results from deep-trap emission coinciding with nanoparticle defects. The appearance of both band-edge and deep-trap emission is not uncommon for  $CdSe_xS_{1-x}$  systems, although several reported examples have developed techniques thereby eliminating deep-trap emission (16-21). One method is to prolong the thermal annealing time, thus forcing defects within the nanoparticle to move to the surface creating a defect-free nanoparticle core. This was investigated for the sample prepared at 230 °C, where, rather than annealing for 15 min, the thermolysis temperature was held for 4 h. Based on the PL spectrum (not shown) after 4 h,

<sup>&</sup>lt;sup>4</sup> Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5193. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/irm/unpub\_e.shtml

**Table 1.** Cd:Se:S ratios as determined by EDX analysis. Ratios were calculated using atomic percentages.

	Ratio as determined by EDX analysis		
	Cadmium	Selenium	Sulfur
As-synthesized	1	0.31	0.57
160 °C	1	0.34	0.57
180 °C	1	0.32	0.57
200 °C	1	0.31	0.56
210 °C	1	0.30	0.56
220 °C	1	0.31	0.56
230 °C	1	0.31	0.56
240 °C	1	0.30	0.54

**Fig. 1.** HR-TEM images of (*a*) as-synthesized CdSe<sub>x</sub>S<sub>1-x</sub> and HDA capped particles thermolysed at (*b*) 180 °C, (*c*) 210 °C, and (*d*) 240 °C. Box outlines individual particles.



prolonged annealing times minimized the low energy emission but did not all together eliminate it.

Spectroscopically, the two types of deep-trap emission behave differently. The higher energy emission maximum is red-shifted upon increasing thermolysis temperature from 620 nm (2.00 eV) at 160 °C to 770 nm (1.61 eV) at 240 °C. The lower energy emission however only begins to appear at 200 °C and remains relatively unaltered in peak position upon increasing thermolysis temperature (~790 nm; 1.57 eV). Conversely, the intensity of this low energy emission greatly increases upon raising the thermolysis temperature, where at 240 °C this is the predominant emission observed. Photoluminescence excitation (PLE) measurements confirm the single species nature of the observed emission (Fig. S2).<sup>4</sup> Previous work with CdS and CdSe nanocrystals have described a similar spectroscopic behaviour where the higher energy emission is associated with shallow traps, while the lower energy emission results from deep traps (7c, 31).

The powder X-ray diffraction (PXRD) patterns for  $CdSe_xS_{I-x}$  (Fig. 4) thermolysed at 200 °C, 220 °C, and 240 °C display two important features. First, the relative

**Fig. 2.** UV–vis absorption spectra of thermolysed  $CdSe_xS_{I-x}$  nanoparticle series. The spectra have been normalized for clarity.



**Fig. 3.** Photoluminescence spectra of the  $CdSe_xS_{I-x}$  thermolysis series at (*a*) high energy and (*b*) low energy. Excitation at 468 nm. The spectra have been normalized for clarity.



peak positions remain unchanged with increasing thermolysis temperature, which is consistent with the chemical composition remaining unaltered. Second, the diffraction peaks become sharper as the thermolysis temperature is raised, consistent with the observed particle growth. The observed PXRD pattern is characteristic of the cubic phases of CdS and CdSe (32). Thus using the  $(1 \ 1 \ 1)$  reflection, the lattice parameter *a* can be calculated using eq. [1]. From

**Fig. 4.** Powder X-ray diffraction patterns of  $CdSe_xS_{1-x}$  samples thermolysed at (*a*) 200 °C, (*b*) 220 °C, and (*c*) 240 °C. Asterisk (\*) Denotes (1 1 1) reflection.



each PXRD pattern the *d* spacing of  $(1\ 1\ 1)$  is found to be 3.40 Å and *a* is calculated to be 5.89 Å, where the corresponding lattice parameters for CdS and CdSe are 5.818 and 6.077 Å, respectively (33).

[1] 
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{3}{a^2}$$

Using Vegard's rule (34), which assumes a linear dependence of composition on lattice parameter, the stoichiometry of the obtained  $CdSe_xS_{I-x}$  nanoparticle system can be determined using eq. [2],

# $[2] \qquad a(x) = x \cdot a_{\text{CdSe}} + (1 - x)a_{\text{CdS}}$

Based on eq. [2], x is calculated to be 0.28 (i.e.,  $CdSe_{0.28}S_{0.72}$ ), which is similar to what is observed via EDX analysis.

#### $ZnSe_{x}S_{I-x}$ nanoparticles

A handful of published examples have investigated the synthesis of  $ZnSe_xS_{1-x}$  nanomaterials.  $ZnSe_xS_{1-x}$  (where x =0.05-0.08) is almost perfectly lattice-matched to GaAs and thus improves the blue-green response over the conventionally used ZnSe. Consequently,  $ZnSe_xS_{1-x}$  is well-suited for fabricating optoelectronic devices (35). Much like its cadmium counterpart,  $ZnSe_xS_{1-x}$  is formed as thin films on either glass or GaAs substrates. The synthesis typically involves the mixing of ZnS and ZnSe powders in a specified ratio (35, 36), although some procedures use dimethylzinc in the presence of gaseous  $H_2Se$  and  $H_2S$  (37) as well as  $ZnCl_2$ with thiourea and selenourea (38). A variety of specialized techniques such as spray pyrolysis, atomic layer epitaxy, and close-space evaporation are used for thin film formation and thus require high operating temperatures. Using Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub>, discrete nanoparticles of  $ZnSe_xS_{1-x}$  can be produced.

As previously reported (30), the use of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> imposes limitations with regards to solvent choice and reaction conditions that must be considered when designing a chemical reaction. Employing similar conditions used in the formation of  $CdSe_xS_{1-x}$ , zinc acetate  $[Zn(OAc)_2]$  was solubilized in toluene with 2.2 equiv. of tri(n-butyl)phosphine. Toluene, however, does not effectively solubilize  $Zn(OAc)_2$  and Pn-Bu<sub>3</sub>. As opposed to using phosphine-based ligands to coordinate to Zn(OAc)<sub>2</sub> in toluene, an amine ligand (triethylamine) was alternatively employed. Although this leads to the dissolution of Zn(OAc)<sub>2</sub>, the addition of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> results in the formation of a brightly coloured red solid after a few hours of stirring, suggesting decomposition and the possible precipitation of elemental selenium. In contrast, tri(n-butyl)phosphine oxide is able to solubilize Zn(OAc)<sub>2</sub> in toluene, however, the addition of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> leads to the immediate formation of a red solid. This reactivity suggests an additional limitation of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> in which hard bases such as amines and oxides should be avoided, while soft bases such as phosphines are less reactive toward Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub>.

An alternative solvent to toluene is to use dichloromethane to solubilize  $Zn(OAc)_2$  and Pn-Bu<sub>3</sub>. The addition of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> causes the immediate consumption of the selenosulfide. Although a precipitate does not form initially, continued stirring overnight results in the formation of a white solid. The solid, however, is quite soluble in anhydrous methanol and thus LiCl cannot be removed at this stage and must be carried through to the thermolysis.

The obtained solid is added to a hot (60 °C) HDA solution and gradually heated to 240 °C. At specified temperature intervals the sample is annealed for 15 min, an aliquot is taken, precipitated out with anhydrous methanol, and isolated via centrifugation. By washing with methanol, LiCl is effectively removed from the sample as determined by EDX analysis. The increase in thermolysis temperature does not result in an associated colour change.

To ensure that the chemical composition remains unaltered during the thermolysis, the atomic ratio between zinc, selenium, and sulfur was determined from EDX analysis (Table 2). As is shown in Table 2, the ratio between zinc, selenium, and sulfur remains relatively unaltered throughout thermolysis, however, at 240 °C the quantity of both sulfur and selenium increases, although the ratio between the two elements is similar to what is observed at the lower thermolysis temperatures. The same ratio is not observed in the as-synthesized  $ZnSe_xS_{1-x}$  largely because of the presence of chloride within the sample (from LiCl), which consequently affects the overall ratio calculated for the respective elements. Again, the ratio between selenium and sulfur is not 1:1, likely due to the expected Se-S bond cleavage and the presence of both phosphine sulfides and phosphine selenides in the reaction mixture. Phosphine sulfides and selenides are known to form from Pn-Bu<sub>3</sub> with various chalcogen sources (39). Both sulfur and selenium are however, incorporated into the nanoparticles through the use of the Se-S reagent.

Particle size measurements were calculated based on HR-TEM images (Fig. 5). As can be seen, the particle size increases upon increasing thermolysis temperature. At 200 °C (Fig. 5*a*), individual particles of  $ZnSe_xS_{I-x}$  are observed and

**Table 2.** Zn:Se:S ratio as determined by EDX analysis. Ratios were calculated using atomic percentages.

	Ratio as determined by EDX analysis		
	Zinc	Selenium	Sulfur
As-synthesized	1	0.47	0.36
190 °C	1	0.43	0.49
210 °C	1	0.40	0.44
220 °C	1	0.40	0.48
240 °C	1	0.52	0.59

**Fig. 5.** HR-TEM images of  $ZnSe_xS_{1-x}$  particles thermolysed at (*a*) 200 °C and (*b*) 240 °C. Box outlines individual particles.



are ~4 nm in diameter. Upon increasing the thermolysis temperature to 240 °C, the particles grow to ~8 nm in diameter, however, it appears as though homogeneity is lost at elevated temperatures.

The spectroscopic properties of the obtained nanoparticles were analyzed using UV–vis absorption and PL spectroscopy. The UV–vis absorption spectra of the thermolysis series (Fig. 6) distinctly display a red-shift in absorption maximum with increasing the thermolysis temperature. At a thermolysis temperature of 190  $^{\circ}$ C, the absorption maximum is found at 305 nm (4.07 eV) and shifts 30 nm to lower energy with increasing the thermolysis temperature to 240  $^{\circ}$ C (335 nm, 3.70 eV). This shift in absorption maximum is consistent with an increase in particle size.

The PL spectra (obtained by irradiating between 310– 320 nm) for the series  $ZnSe_xS_{I-x}$  (Fig. 7) differs significantly from the PL spectra of the  $CdSe_xS_{I-x}$  series in that one type of emission is observed, corresponding to band-edge emission. The emission maximum shifts from 342 nm (3.63 eV) at 200 °C to lower energy (362 nm, 3.42 eV) with increasing the thermolysis temperature to 240 °C. This red shift in emission maximum upon increasing thermolysis temperature confirms an increase in particle size. PLE measurements confirm the nature of the emitting species (Fig. S3).<sup>4</sup>

Much like the PXRD patterns for CdSe<sub>x</sub>S<sub>1-x</sub>, the PXRD patterns for ZnSe<sub>x</sub>S<sub>1-x</sub> thermolysed at 190 °C, 210 °C, and 220 °C (Fig. 8) indicate a sharpening of diffraction peaks with increasing thermolysis temperature, in addition to consistent peak positions. Conversely, the obtained ZnSe<sub>x</sub>S<sub>1-x</sub> nanoparticles display a characteristic hexagonal phase pattern as observed for ZnS and ZnSe (40). Thus, using the (0 0 2) reflection, the lattice parameter *c* can be calculated (double the associated *d* spacing, d = 3.2 Å). The obtained *c* parameter (6.4 Å) is found to be intermediate between the *c* parameters for ZnS (6.234 Å) and ZnSe (6.53 Å) (37), and





**Fig. 7.** PL spectra of the ZnSe<sub>x</sub>S<sub>I-x</sub> thermolysis series. Excitation between 310 and 320 nm. The spectra have been normalized for clarity.



using Vegard's rule (eq. [2], substitute a for c), x is found to be an intermediate value.

It is noteworthy to mention that the observed stoichiometry in the zinc system varies significantly from the stoichiometry of the cadmium system, thus reflecting a differing reactivity between the two elements.

## Conclusions

It has been demonstrated that  $Me_3Si-SeS-SiMe_3$  is an effective delivery agent of both sulfur and selenium. As such, the reagent has found utility in the synthesis of mixedchalcogen zinc and cadmium nanoparticles.  $Me_3Si-SeS-SiMe_3$  serves as a reagent for the distribution of both chalcogen elements at low temperature vs. the conventional methods used for the formation of  $MSe_xS_{J-x}$  materials, which typically require two chalcogen reagents and relatively high temperatures. The resulting nanoparticles display a nonstoichiometric amount of both sulfur and selenium as the ensuing chemistry with the corresponding metal acetate leads to Se–S bond cleavage. Thermolysis of both zinc and cadmium nanoparticle species in hexadecylamine leads to controlled particle growth with increasing thermolysis tem**Fig. 8.** Powder X-ray diffraction patterns of  $\text{ZnSe}_x S_{I-x}$  samples thermolysed at (*a*) 190 °C, (*b*) 210 °C and (*c*) 220 °C. \* Denotes (0 0 2) reflection.



perature, as has been noted by the red-shift in both the absorption and emission excitonic transition. An extension of this research will be to investigate the effectiveness of Me<sub>3</sub>Si-SeS-SiMe<sub>3</sub> in the synthesis of HgSe<sub>x</sub>S<sub>1-x</sub> nanoparticles.

# Acknowledgements

We gratefully acknowledge the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support of this research, equipment funding, and for a postgraduate scholarship (EAT). The Government of Ontario Premier's Research Excellence Awards (PREA) program is also acknowledged for financial support and *The* University *of* Western Ontario and the Canada Foundation for Innovation (CFI) are thanked for equipment funding.

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