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Ionothermal Syntheses of Nano- and Microstructured Ternary Copper–Indium–Chalcogenides

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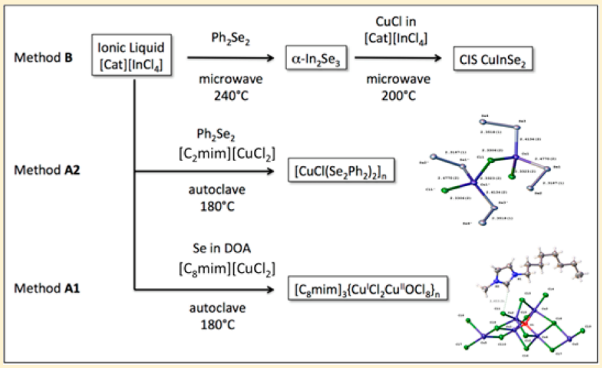
Supporting Information



ABSTRACT: Ternary compounds of copper indium selenide nano- and microsized materials were prepared through colloidal synthesis using an indium(III) selenide precursor and copper(I) chloride via a microwave-assisted ionothermal route. The indium(III) selenide precursor used in the reaction was formed in situ from a diphenyl diselenide precursor and chloroindate(III) ionic liquids (ILs), also via a microwave-assisted ionothermal route. The crystal structures of three intermediates, namely, $CuCl_2(OMe)_2(H_2O))\{Cu(PhSeO_2)_2\}_n$, $[CuCl(Se_2Ph_2)_2]_n$, and $[C_8mim]_3\{Cu^ICl_2Cu^{II}OCl_8\}_n$, were determined after formation through a ionothermal procedure utilizing metal-containing imidazolium ILs and a selenium precursor with conventional heating. Herein, we compare the use of microwave irradiation over conventional heating with different ILs on the stoichiometry of the resulting products. The influence of the reaction temperature, reaction time, order of addition of reagents, and variation of ILs, which were characterized using PXRD, SEM, and EDX, on the final products was investigated.

■ INTRODUCTION

Copper indium selenide, abbreviated as CIS, is a I–II–VI$_2$ chalcopyrite p-type semiconductor material often employed in thin film solar cells as an efficient light absorber with a bandgap of 1.04 eV. This material can be deposited on substrates producing lightweight, highly flexible solar cells[1] with a defect tolerance and a solar energy conversion of up to 20%, which has already been achieved in thin films.[2] It is considered a nontoxic alternative to cadmium-based semiconductors and offers a band gap suitable for tuning.[3] CIS is reported as a good candidate for photovoltaic applications due to its high absorption coefficient, good radiation stability, low toxicity, and high photovoltaic efficiency.[4] Bulk CIS crystals can be found in two polymorphs: chalcopyrite (tetragonal unit cell), often produced via low-temperature syntheses, and a sphalerite phase (cubic unit cell) formed at higher temperatures.[5] One of the first reports on the production of CIS quantum dots was in 1999 using a hot-injection technique with trioctylphosphine selenide (TOPSe) as the selenium precursor along with trioctylphosphine oxide (TOPO).[6] Other reports on the synthesis of CIS using trioctylphosphine (TOP) and/or dioctylphosphine oxide (DOPO) as nonpolar solvents have also been published,[7,8] with amines also extensively utilized.[5,9−13] These additives have been implemented as structure-directing agents, capping agents, and solvents in the preparation of CuInSe$_2$.[14] High-temperature methods have been reported such as a sintering method,[15,16] sputtering selenization,[17,18] and hydrothermal selenization in the formation of CIS. Furthermore, the high costs and scale-up difficulties associated with vacuum-based fabrication have led research into solution-phase processes of chalcopyrite nanocrystal inks for implementation in solar cells.[19−21]

One of the challenges in the synthetic chemistry of I–III–VI$_2$ semiconductor nanocrystals is the control of their composition and crystal structure. In bulk materials chalcopyrite semiconductors tolerate a large range of nonstoichiometry; CIS is an important example of this family of compounds. Its phase diagram shows a number of off-stoichiometric ordered structures, such as $CuIn_5Se_8$, $CuIn_3Se_5$, $Cu_2In_4Se_7$, and $Cu_3In_5Se_9$.[22] However, in contrast to many binary semiconductors, this off-stoichiometry does not lead to the formation of deep trap states, which would compromise the use of these materials in optoelectronics. In general, both p- and n-type doping can be obtained depending on the stoichiometry, which has been used for the production of CuInS$_2$ or CuInSe$_2$ homojunction solar cells.[3]

Other structures, including $Cu_{0.9}InSe_{1.95}$, $Cu_{0.82}InSe_{1.91}$, and $Cu_2In_3Se_{5.5}$ have been reported with a nominally four-coordinated InSe$_4$ structure as interpreted from extended X-ray absorption fine structure, with compounds such as $CuIn_3Se_5$ and $CuIn_5Se_8$ possessing two different InSe$_4$ structures. $Cu_{12.32}In_{18.04}Se_{32}$ nanopowders have also been reported using the codeposition method.[23] Many studies have been done on

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these materials through density functional theory, X-ray absorption fine structure, X-ray photoelectron spectroscopy, and simulations to interpret their ability to act as semiconductors in comparison with $CuInSe_2$.

The preparation of advanced functional materials using ionic liquids (ILs), in particular, ionothermal synthesis, has proven to be very promising.[24−27] However, these syntheses are still at an early stage with regard to chalcogenides, and those compounds that have been prepared in ILs thus far are nanomaterials of known binary compounds.[28−30] Nanoparticles (NPs) of metal sulfides ZnS,[31] CdS,[32] Bi_2S_3,[33] Sb_2S_3, CuS,[34] MoS_2[35] have been successfully synthesized using the IL 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]). Jiang et al.[29] have prepared uniform flowers of Bi_2S_3 at low temperature and ambient pressure also using a tetrafluoroborate IL. The same group has reported the production of M_2S_3 (where M = Bi or Sb) nanorods in IL systems using microwave irradiation.[36] Other ILs, as outlined previously, have been used to synthesize chalcogenide binary systems including [Bmim][PF_6] in the preparation of PbS nanocubes[37] and [Emim][$EtSO_4$] in an Ultrasonic-assisted Aqueous Room-Temperature Ionic Liquid (UARTIL) synthesis of monodispersed nanocrystalline ZnS.[38] A range of transition metal systems, including PbS, CdS, ZnS, CoS, and Cu_2S, has been synthesized through a facile hydrothermal route, using [Bmim][SCN] as both the sulfur source and the capping ligand.[39]

An example of the synthesis of a ternary metal chalcogenide system using ILs has been reported by Li et al.,[40] who formed $ZnIn_2S_4$ in [Bmim][BF_4]−water binary emulsions. The size and morphology of the synthesized products were strongly affected by the aid of the [Bmim][BF_4] IL and by selectively controlling the reaction conditions $ZnIn_2S_4$ spherical nanospheres, microspheres, or three-dimensional (3D) flowerlike structures could be selectively prepared.[36]

The conventional methods reported to synthesize nanostructured $CuInSe_2$ (CIS) often involve the use of long-chained alkylamines.[41,42] These additives and solvents dissolve elemental selenium and facilitate the formation of nanocrystal seeds. The balance between retardation and activation is important for successful control of the nucleation and growth processes, with the capping agents playing a particularly important role for the shape of the products. Furthermore, trioctyl phosphine and trioctyl phosphine oxide, TOP and TOPO, are commonly implemented as capping agents in the chalcogenide CIS formation.[43]

Ionic liquids, as alternative media for the preparation of these ternary compounds, can actively participate in the capping and structuring during nanoparticle growth, and they can also withstand sufficiently high temperatures without degradation. Furthermore, a good solubility of the chalcogens sulfur, selenium, and tellurium has been demonstrated in ILs, such as [C_8mim][NTf_2], [P(Bu^i_3)CH_3][OTs], and [C_6mim][OTs].[44] The authors have stated that the influence of the IL anions is stronger than that of the IL cations and that the nucleophilicity of the anion is an important factor in determining the solubility. The ease of solubility, along with the thermal and oxidation stability of the IL systems, makes them suitable media for the production of nanocrystalline ternary chalcogenide materials.

Some progress has been made with the synthesis of CIS nanomaterials, but there are still many holes in the understanding of the chemistry and reaction process that is taking place. This paper addresses the reaction process and gives an insight into the chemistry taking place during the production of CIS NPs via a purely ionothermal synthesis. This is the first report on the synthesis of CIS using chlorometallate ILs as precursors and reaction medium.[45]

■ EXPERIMENTAL SECTION

Instrumentation. The microwave reactions were performed using an Anton Parr Monowave 300. The scanning electron microscopy (SEM) studies were performed using JEOL 6500F Field Emission and Quanta FEG 250 Scanning Electron Microscopes. The energy dispersive X-ray analysis (EDX) was performed using Oxford Instruments INCA systems. X-ray diffraction (XRD) data were collected using a Siemens D5000 powder diffractometer with Cu K• radiation (• = 1.542 Å). Data were recorded from between 10° and 60° in steps of 0.0167.

The single-crystal X-ray structure determination was performed at 100 K by using an Oxford Diffraction Gemini diffractometer. The images were interpreted and integrated with CrysAlisPro. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using OLEX2[46] and the SHELX structure solution program package.[47,48] Non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). Additional crystallographic information is available in the Supporting Information.

Materials. Indium(III) chloride, 99%, anhydrous, diphenyl diselenide, copper(I) chloride, 99%, anhydrous, and indium(III) selenide, 99%, anhydrous, were purchased from Sigma-Aldrich. Ionic liquids [C_8mim]Cl and [C_2mim]Cl were synthesized as reported in literature,[49] and [$P_{6\,6\,6\,14}$]Cl was obtained from Cytec; synthesis as described elsewhere.[50] Syntheses of the metal-containing ILs were performed in a glovebox under nitrogen atmosphere.

Synthesis of [C_8mim][$CuCl_2$] and [C_2mim][$CuCl_2$]. [C_8mim]Cl (1.0452g, 4.5443 mmol) was added to CuCl (0.4417 g, 4.4616 mmol) in a 1:1 ratio to produce [C_8mim][$CuCl_2$]. [C_2mim]Cl (1.1935 g, 8.1468 mmol) was added to CuCl (0.8065 g, 8.1465 mmol) in a 1:1 ratio to produce [C_2mim][$CuCl_2$]. The reagents were placed in a round-bottomed flask equipped with a stirring bar. The flasks were closed with a stopper and placed in a heating bath, and the mixture was stirred vigorously (80 °C, overnight). Brown liquids were formed in both cases. Characterized through C, H, N analysis; [C_8mim][$CuCl_2$] C 43.5% (43.7% calc), H 7.3% (7.0% calc), N 8.4% (8.5% calc), and [C_2mim][$CuCl_2$] C 28.21% (29.3% calc), H 4.76% (4.5% calc), N 11.0% (11.4% calc).

Synthesis of [C_8mim][$InCl_4$] and [C_2mim][$InCl_4$]. [C_8mim]Cl (2.3873 g, 10.3796 mmol) was added to $InCl_3$ (2.2533 g, 10.1811 mmol) in a 1:1 ratio to produce [C_8mim][$InCl_4$]. [C_2mim]Cl (1.1943 g, 8.1522 mmol) was added to $InCl_3$ (1.8057 g, 8.1588 mmol) in a 1:1 ratio to produce [C_2mim][$InCl_4$]. The reagents were placed in a round-bottomed flask equipped with a stirring bar. The flasks were closed with a stopper and placed in a heating bath, and the mixture was stirred vigorously (80 °C, overnight). Brown liquids were formed in both cases. Characterized through C, H, N analysis; [C_8mim][$InCl_4$] C 32.1% (31.6% calc), H 5.3% (5.1% calc), N 6.2% (6.2% calc), and [C_2mim][$InCl_4$] C 19.1% (19.6% calc), H 2.8% (3.0% calc), N 7.1% (7.6% calc).

Synthesis of Chalcogenide Materials via Conventional Heating. In a typical process, Ph_2Se_2 or elemental selenium with a cosolvent, was added to a chloroindate(III) IL and a chlorocuprate IL/Cu(I)Cl as the copper precursor. The reagents were added in a 1:1:1 ratio with Ph_2Se_2 and 2:1:1 ratio with elemental selenium and were heated together in a round bottomed flask for 24 h at 180 °C. The final product formed was either crystalline needles or suspensions of a fine powder in an IL, which were subsequently washed with methanol to separate the particles from the IL.

Synthesis of Copper Indium Selenide via Microwave Heating. In a typical process, Ph_2Se_2 was added to a chloroindate(III) IL, in a 3:4 ratio, before being placed in the microwave reactor, for 1 min at 240 °C. The product was left as a suspension in the IL, with the addition of

Table 1. Method A, Ionothermal Autoclave Reactions

no.	reagents	reaction conditions	reagent ratios Cu/Se/In	appearance of product	elemental composition of product
1a	$[C_8mim]_3[CuCl_4]$: Se: $[C_8mim][InCl_4]$ solvent: dioctylamine	180 °C autoclave 24 h	1:2:1	black suspension formed	100% selenium
1b	$[C_2mim][CuCl_2]$: Se: $[C_2mim][InCl_4]$ solvent: dioctylamine	180 °C autoclave 24 h	1:2:1	black suspension formed	100% selenium
2a	CuCl: Se: $[C_8mim][InCl_4]$ solvent: dioctylamine	180 °C autoclave 24 h	1:2:1	blue/green crystalline solid	$[C_8mim]_3\{Cu^ICl_2Cu^{II}OCl_8\}_n$
3a	$[C_8mim]_3[CuCl_4]$: Ph_2Se_2: $[C_8mim][InCl_4]$	180 °C autoclave 24 h	1:2:1	orange/brown gel	Ph_2Se_2
3b	$[C_2mim][CuCl_2]$: Ph_2Se_2: $[C_2mim][InCl_4]$	180 °C autoclave 24 h	1:2:1	orange/brown gel	$[CuCl(Se_2Ph_2)_2]_n$
4	CuCl +Ph_2Se_2 solvent: MeOH	heated at 180 °C for 1 h	2:1	dark blue crystals	$(CuCl_2(OMe)_2(H_2O))\{Cu(PhSeO_2)_2\}_n$

Table 2. Crystal Data and Structure Refinement

empirical formula	$C_{12}H_{23}Cl_{3.33}Cu_{1.67}N_2O_{0.33}$	$C_{24}H_{20}CuClSe_4$	$C_{14}Cl_2Cu_2O_7Se_2H_{20}$
formula weight	424.72	723.23	656.20
temperature/K	293(2)	100.15	373.3
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$	$P2_1/c$
a/Å	19.8719(14)	13.5566(10)	22.2186(16)
b/Å	9.0935(5)	5.7532(4)	5.3982(4)
c/Å	29.202(2)	14.7074(10)	16.8604(12)
α/deg	90.00	90.00	90.00
β/deg	91.777(2)	91.859(7)	93.530(2)
γ/deg	90.00	90.00	90.00
volume/Å^3	5274.4(6)	1146.48(14)	2018.4(3)
Z	12	2	4
ρ_{calc} g/cm^3	1.605	2.095	2.159
μ/mm^{-1}	2.524	7.429	6.012
F(000)	2600.0	692.0	1280.0
crystal size/mm^3	0.20 × 0.08 × 0.01	0.07 × 0.01 × 0.01	0.24 × 0.05 × 0.01
radiation	Mo Kα (λ = 0.710 75)	Mo Kα (λ = 0.710 75)	Mo Kα (λ = 0.710 75)
2Θ range for data collection/deg	5.04 to 54.96	6.02 to 54.96	5.08 to 54.98
index ranges	$-25 \leq h \leq 25, -11 \leq k \leq 11, -37 \leq l \leq 37$	$-17 \leq h \leq 17, -7 \leq k \leq 6, -18 \leq l \leq 19$	$-28 \leq h \leq 28, -6 \leq k \leq 7, -21 \leq l \leq 21$
reflections collected	36 327	15 312	21 173
independent reflections	12 051 [R_{int} = 0.1301, R_{sigma} = 0.1329]	4953 [R_{int} = 0.0926, R_{sigma} = 0.1083]	4558 [R_{int} = 0.0641, R_{sigma} = 0.0426]
data/restraints/parameters	12 051/0/529	4953/1/271	4558/6/290
flack parameter		0.000	
goodness-of-fit on F^2	1.050	1.028	1.028
final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0966, wR_2 = 0.2494	R_1 = 0.0548, wR_2 = 0.1134	R_1 = 0.0651, wR_2 = 0.1591
final R indexes [all data]	R_1 = 0.1485, wR_2 = 0.2787	R_1 = 0.0785, wR_2 = 0.1264	R_1 = 0.0754, wR_2 = 0.1670
largest diff. peak/hole/e Å^{-3}	2.07/−1.17	0.93/−1.02	7.15/−0.88

copper(I) chloride before reacting once again in the microwave for 1 min, between 180 and 240 °C. Masses of reagents are given in the Supporting Information.

■ RESULTS AND DISCUSSION

We pioneered and successfully demonstrated an approach for the formation of binary compounds such as In_2Se_3 and ZnSe using a ionothermal approach combined with microwave heating.[51,52] The same approach has been further applied in a recent study on nano- and microparticle semiconductor syntheses in phosphonium ILs.[53] However, the formation of nanosized ternary compounds requires additional parameters to be taken into account. The production of ternary compounds from ILs has been reported to a lesser extent than binary analogues. Zhang and co-workers have reported on the production of a ternary nanocrystalline compound from ILs, $ZnInS_4$ in $[Bmim][BF_4]$.[36]

Ionothermal Reactions for the Formation of $CuInSe_2$. The purpose of this study was to find an alternative pathway to nanosized CIS using an IL-based approach. In method (**A**) for the synthesis of nanocrystalline $CuInSe_2$ using ILs, approach (**A1**) elemental selenium in the presence of an amine reducing agent was used, whereas approach (**A2**) starts from diphenyl diselenide as the selenium precursor. This method was employed using $[C_8mim]_3[CuCl_4]$ with $[C_8mim][InCl_4]$ or $[C_2mim][CuCl_2]$ with $[C_2mim][InCl_4]$, while heating to 180–200 °C in an autoclave for 24 h (Table 1 entries 1–4).

The second method (**B**) was a purely ionothermal one-pot synthetic procedure implementing the use of a microwave reactor, using the indium-containing ILs $[C_8mim][InCl_4]$ and $[P_{6\,6\,6\,14}][InCl_4]$ along with Ph_2Se_2 heated between 200 and 240 °C for 1 min (Table 2, entries 1–3). An overview of the reactions performed in both method **A** and method **B** can be seen in Figure 1.

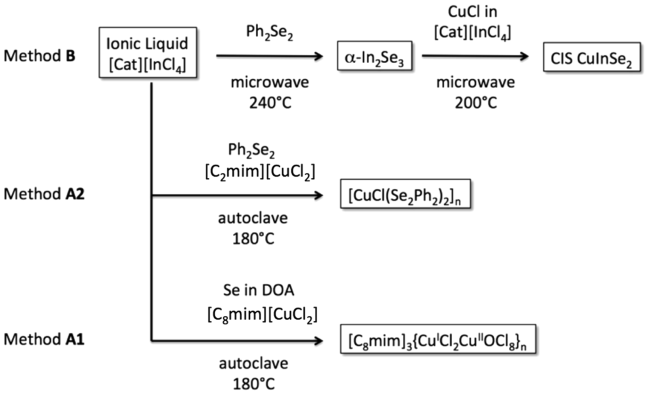

Figure 1. Overview of the reaction pathways and methods used.

Method A: Ionothermal Reactions with Conventional Heating. In the first set of experiments outlined in Table 1, entries 1a and 1b, involving the reaction of elemental selenium with an amine reducing agent in an autoclave for 24 h, resulted in purely selenium-containing products with no trace of copper or indium. However, despite not forming new products the morphologies of the resulting selenium, shown in Figures 2 and 3, were different than the morphology of the elemental selenium precursor. Neither the copper nor indium from the anions of the imidazolium ILs, $[C_n\text{mim}][CuCl_2]$ and $[C_n\text{mim}][InCl_4]$ ($n = 2, 8$), reacted with selenium, and therefore no metal chalcogenide or the copper indium selenide (CIS) product was formed.

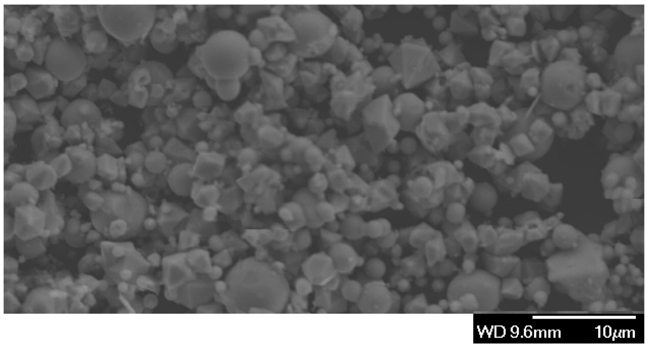

Figure 2. SEM of the crystalline selenium formed from $[C_8\text{mim}]_3[CuCl_4]$, Se, and $[C_8\text{mim}][InCl_4]$ in reaction 1a.

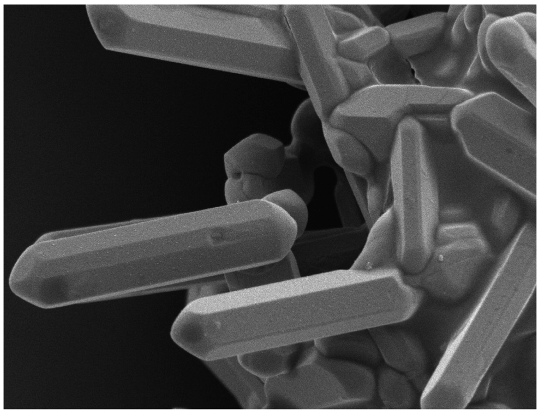

Figure 3. SEM of the crystalline selenium from $[C_2\text{mim}][CuCl_2]$, Se, and $[C_2\text{mim}][InCl_4]$ in reaction 1b.

Kar et al.[19] have studied the reaction between indium and copper chlorides with elemental selenium and have indicated that the Gibbs free energy of the overall reaction at 275 °C, is 308 kJ mol^{-1}, eq 1. This therefore indicates that this reaction is thermodynamically unfavorable and that the formation of CIS can only take place if other reactants are involved such as solvents or ligands.

$$CuCl(s) + InCl_3(s) + 2Se(l) \rightarrow CuInSe_2(s) + 2Cl_2(g) \quad (1)$$

As seen from Figures 2 and 3, the morphology of both crystallized selenium products is different and depends on the IL used. The results indicate that depending on the reaction media with the cations $[C_2\text{mim}]^+$ and $[C_8\text{mim}]^+$ of the ILs, the resulting size and morphology of the selenium products varies. Despite CIS not being formed, the results give an insight into the role that ILs can play as structure-directing agents, capping agents, and stabilizers; however, these differences may also be a result of differences in the viscosity of the ILs. As shown in Figure 2, a range of spherical and diamond-shaped products were formed with a size range of 1−2 μm when using 1-octyl-methylimidazolium (C_8mim) ILs, whereas, when using 1-ethyl-methylimidazolium (C_2mim) ILs, the shape and morphology of the resulting particles are very different, with elongated polygons being formed in the range of 5 μm, as shown in Figure 3. According to literature, CIS formation is majorly temperature-dependent, which plays a significant role in the shape and size of the resulting compounds. At high temperatures spherical CIS NPs form due to isotropic growth minimizing the surface energy (thermodynamic regime) and can only form when used in conjunction with a strong capping agent such as ethylenediamine (EDA). At low reaction temperatures (kinetic regime) the resulting NPs become elongated and build 3D multipods instead of flowerlike shapes, using solely EDA as the structure-directing agent, capping agent, and solvent.[14]

As an alternative precursor, Cu^{I}Cl was investigated instead of the copper IL analogue and was dissolved in the indium-containing $[C_8\text{mim}][InCl_4]$. The amine reducing agent was used as an additive to dissolve the elemental selenium precursor. From this reaction blue-green crystals were obtained, and the crystal structure was determined. The structure contains $[C_8\text{mim}]^+$ cations and polymeric anionic strands of $\{Cu^{I}Cl_2Cu_4^{II}OCl_8\}_n^{3-}$. These anionic strands contain copper in mixed oxidation states +1 and +2. Copper(I) is tetrahedrally coordinated by four chloride anions. These tetrahedra are edge-sharing with a cluster of four copper(II) tetrahedrally arranged around a central oxygen O^{2-}, where each of the Cu^{II} is coordinated to four chloride anions, resulting in a trigonal bipyramidal coordination environment. The $[C_8\text{mim}]^+$ cations are surrounding these linear polymeric strands and form hydrogen bonding from the acidic imidazolium C2−H to the chloride anions as shown in Figure 4, with H···Cl distances ranging from 2.653(3) to 2.817(2) Å. This structure has rather high final *R* indices, which may result from residual electron density close to the copper centers in the $\{Cu^{I}Cl_2Cu^{II}OCl_8\}_n$ strands, which could be the result of a low percentage of nonmerohedral twinning.

Entries 3a and 3b were concerned with using an alternative selenium precursor diphenyl diselenide (Ph_2Se_2) to try and eliminate the necessity of using an amine cosolvent in the

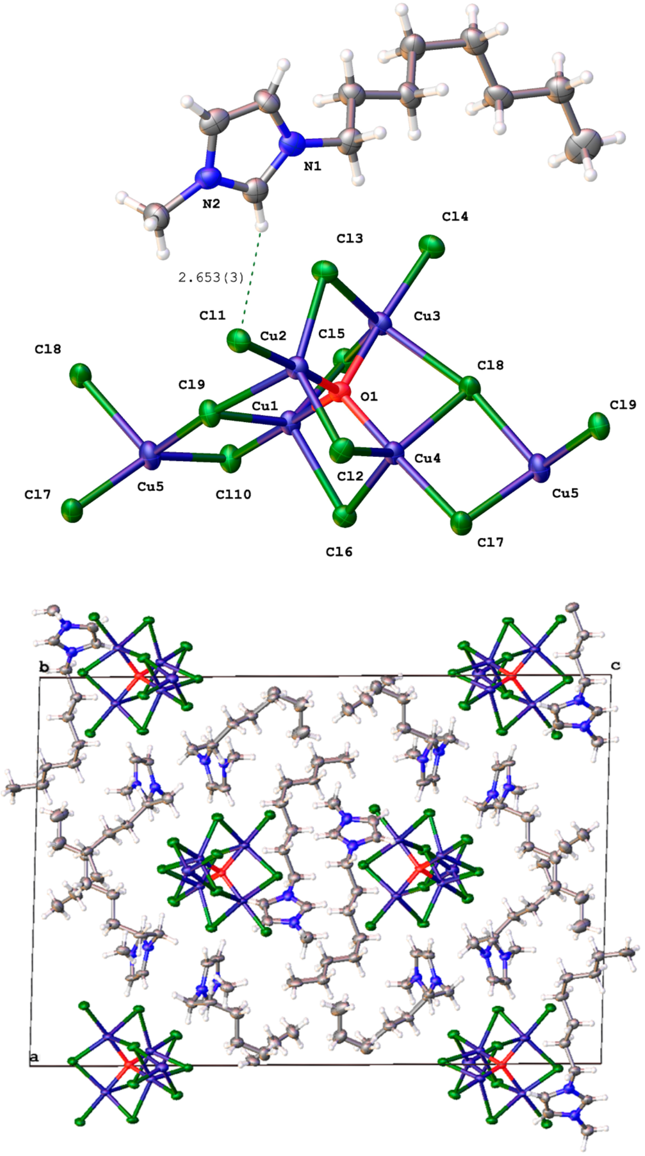

Figure 4. Part of the crystal structure of $[C_8mim]_3\{Cu^ICl_2Cu^{II}OCl_8\}_n$ (above) and packing in the structure viewed along the *b* axis (below). Ellipsoids are shown at a 50% probability level.

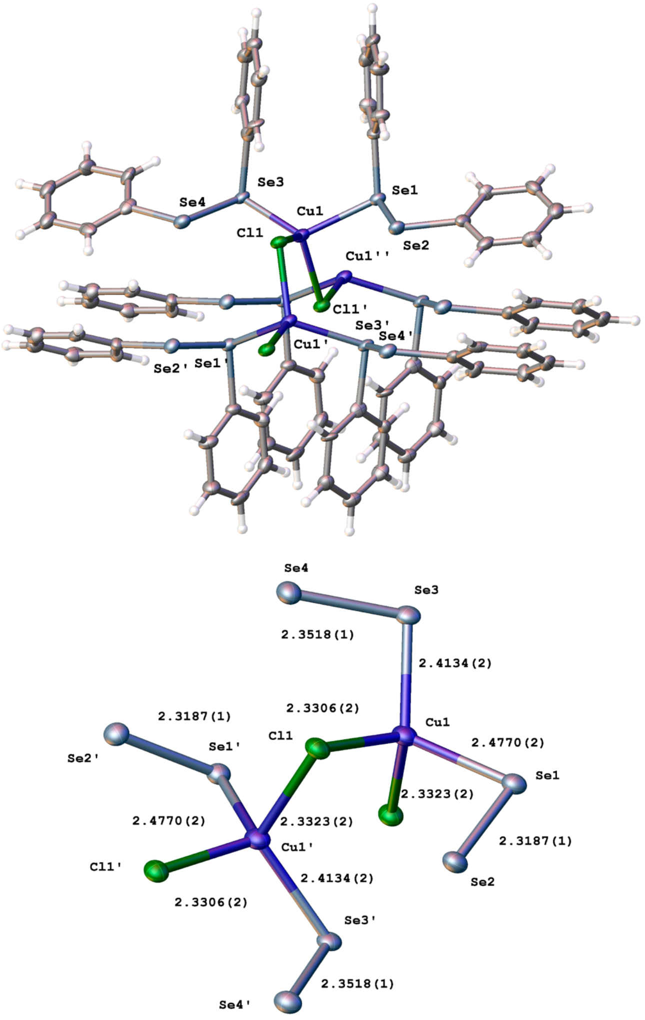

Figure 5. Part of the crystal structure of the polymeric $[CuCl(Se_2Ph_2)_2]_n$. Ellipsoids are shown at a 50% probability level.

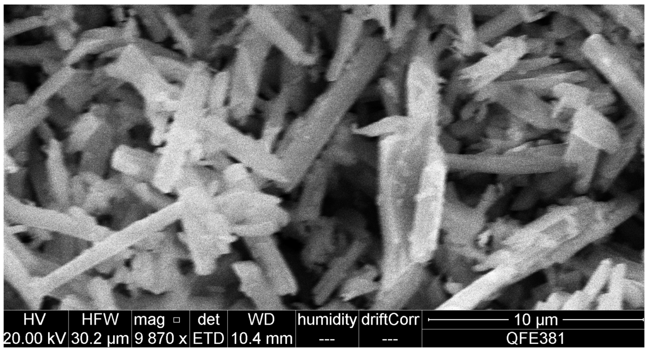

Figure 6. SEM/EDX image of the nanocrystals $[CuCl(Se_2Ph_2)_2]_n$ formed by the reaction of $[C_2mim][CuCl_2]$, Ph_2Se_2, and $[C_2mim][InCl_4]$ (3b).

reaction system. The Ph_2Se_2 was readily dissolved in both ILs, which was one of the main problems when using elemental selenium in reactions 1a and 1b with the dissolution in both imidazolium ILs being very slow and incomplete even after several hours of heating. The partial dissolution of the elemental selenium may have been the reason for the change in morphology of the selenium product instead of the formation of $CuInSe_2$. However, the reactions involving Ph_2Se_2, once again utilizing $[C_8mim]Cl$ and $[C_2mim]Cl$ ILs, readily dissolved the precursor to form a stable, orange homogeneous liquid.

With regards to the $[C_8mim]^+$ system, after reacting at 180 °C for 24 h, a stable homogeneous solution was formed, which gradually crystallized over several weeks. On examination of the crystals, it was found that the Ph_2Se_2 precursor had crashed out of the reaction system in the weeks after the reaction process. In contrast, the $[C_2mim]^+$ system produced a novel crystal structure of $[CuCl(Se_2Ph_2)_2]_n$ after heating the reagents at 180 °C for 24 h (Figures 5 and 6). The crystal structure consists of strands of Cu(I) bridged by chloride anions. Both bridging chloride anions have a Cu–Cl distance of 2.3306(2) and 2.3323(2) Å, respectively. The Cu(I)–selenium distances are 2.4770(2) and 2.4134(2) Å, respectively. Two Ph_2Se_2 molecules are coordinating monodentately to the Cu(I) to complete a distorted tetrahedral coordination geometry. The adjacent Ph_2Se_2 molecules are stacked along the *b* axis and show partially π−π stacking interactions with a centroid-to-centroid distance of 3.75 Å.

A further method was employed using conventional heating with CuCl, Ph_2Se_2, and methanol as the solvent, whereby the solution was heated at 180 °C for several hours, without the use of ILs. This process was investigated to identify whether the IL played a significant role, not only on the shape, size, and morphology of the resulting materials but also on the stoichiometry of the products. Dark blue crystals were obtained, and on examination of the stoichiometry of the crystals it was confirmed that a different material had formed.

The product obtained in this reaction was a coordination complex, $(CuCl_2(OMe)_2(H_2O))\{Cu(PhSeO_2)_2\}_n$, that contains the copper(I) oxidized to copper(II) and the diphenyldiselenide precursor oxidized to benzene seleninate. The compound was isolated from the solution as dark blue crystals, and the crystal structure was determined. It contains strands of bridging benzene seleninate coordinating to each two copper(II) ions with neutral $(CuCl_2(OMe)_2(H_2O))$ molecules present. Cu1 in the $\{Cu(PhSeO_2)_2\}_n$ strands has a square planar coordination environment with Cu1−O distances ranging from 1.944(4) to 1.999(4) Å, see Figures 7 (lower) and 8. The $\{Cu(PhSeO_2)_2\}_n$ strands are separated by hydrogen-bonding $(CuCl_2(OMe)_2(H_2O))$ molecules, with Cu2 in an unusual square pyramidal coordination. The two coordinating Cl anions (distances Cu2−Cl 2.286(2) and 2.278(1) Å, respectively) are aligned on top of Cu1 in the $\{Cu(PhSeO_2)_2\}_n$ strands and complement a 4 + 2 Jahn−Teller-distorted octahedral coordination of Cu1 (Cu1···Cl1 distance is 2.7741(2) Å and Cu1···Cl2 distance is 2.8249(2) Å). Additionally, two MeOH solvent molecules and a water molecule are coordinating to Cu1. The hydrogen on the coordinating MeOH forms hydrogen bonds with the $\{Cu(PhSeO_2)_2\}_n$ strands (1.8465(1) Å), which connects these strands into a sheetlike structure.

Method B: Ionothermal Reactions with a Microwave Reactor. A variety of synthetic procedures were investigated to produce CIS using imidazolium and phosphonium-based ILs. Ph_2Se_2 was used as a precursor as it gave the most promising results from the previous autoclave experiments and avoided the use of any cosolvents.

As previously published, when using ILs with phosphonium-based cations and metal-containing anions, heating in a microwave reactor at 240 °C for 1 min can produce indium(III) selenide, without the use of very high temperatures and pressures or cosolvents. In this process the IL acts as both the solvent and reaction medium in an ionothermal procedure.[44]

In the reactions outlined in Table 2, it has been shown that when using the phosphonium-based IL $[P_{6\,6\,6\,14}][InCl_4]$ or the imidazolium-based IL $[C_8mim][InCl_4]$ with the precursors added together in a one-pot synthesis, the product that was obtained after microwave irradiation was only Cu_2Se and not a ternary selenide.

However, CIS was successfully synthesized when performing the reactions in the microwave in two stages; first, forming the In_2Se_3 precursor as microparticles suspended in the IL and second, with subsequent addition of Cu(I)Cl and further heating of the reaction mixture for 1 min $CuInSe_2$ was formed.

The products formed when using the phosphonium IL $[P_{66614}][InCl_4]$ contained indium, copper, and selenium with a weight percentage corresponding to the values calculated for $CuInSe_2$ as analyzed by EDX.

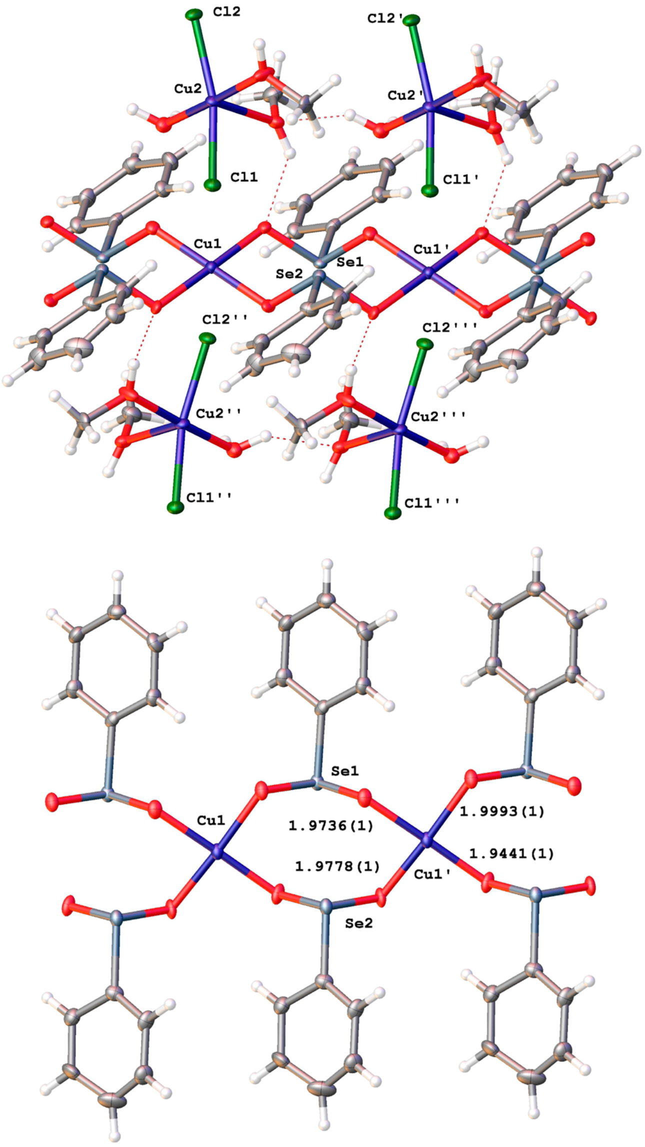

Figure 7. Crystal structure of $(CuCl_2(OMe)_2(H_2O))\{Cu(PhSeO_2)_2\}_n$. The Cu1−O bond lengths are given in angstroms. Ellipsoids are shown at a 50% probability level.

By using this two-stage approach indium(III) selenide was formed first, which was still reactive under the given conditions to form the ternary product, whereas a preformed Cu_2Se does not further react with a chloroindate(III)-containing IL to form the CIS.

A product with uniform spherical morphology was obtained as shown in the SEM image of the reaction using $[P_{66614}][InCl_4]$ with Ph_2Se_2 and Cu(I)Cl, Figure 9. The accompanying EDX analysis suggests the incorporation of solely indium, copper, and selenium in the stoichiometry of the resulting products. The SEM image also shows products in the range of 100−200 nm.

As shown in Figure 10, the SEM image shows a product with a mixed morphology of nanorods, nanoplates, and spheres. The EDX corroborates with this, with both Cu_2Se and CIS compounds found in the product formed when using $[C_8mim][InCl_4]$.

The PXRD patterns shown in Figure 11 are in agreement with the simulated data for $CuInSe_2$ in the ICSD database, with

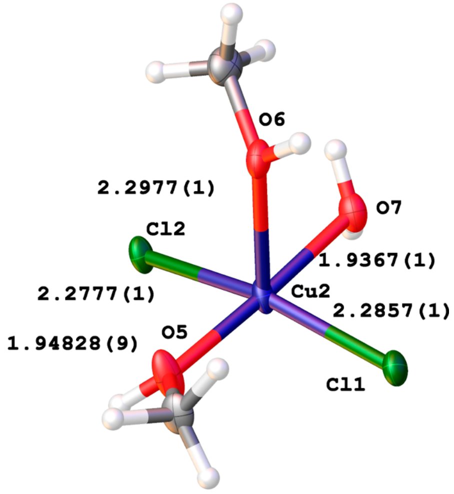

Figure 8. Coordination environment of $(CuCl_2(OMe)_2(H_2O))$ in the crystal structure of (**1**) $(CuCl_2(OMe)_2(H_2O))\{Cu(PhSeO_2)_2\}_n$. Ellipsoids are shown at a 50% probability level.

a space group of $I\bar{4}2d$.[54] These products were formed when using $[P_{66614}][InCl_4]$ with Ph_2Se_2 at 240 °C in the microwave reactor for 1 min, then with Cu(I)Cl at 200 °C for a further minute. The PXRD pattern of the products formed, using reaction temperatures of 200 or 240 °C after the addition of CuCl are identical.

The PXRD patterns shown in Figure 12, are in agreement with the simulated data for $CuInSe_2$ in the inorganic crystal structure data (ICSD) database. These products were formed when $[C_8mim][InCl_4]$ was reacted with Ph_2Se_2 at 240 °C for 1 min, then Cu(I)Cl at 200 °C 1 min and also 5 min. Both patterns are identical, indicating the formation of the same product, regardless of the reaction time in the microwave. An extra peak appears at ~22°, which does not correspond to the $CuInSe_2$ from the database, but could be attributed to the Cu_2Se found in the products.

Optimum results are found when using phosphonium ILs, with the correct stoichiometry and a uniform shape, size, and morphology produced. This is also true for the preparation of other chalcogenide semiconductor compounds including In_2Se_3[43] and ZnSe.[44]

■ CONCLUSIONS

In this study we have demonstrated the production of CIS $CuInSe_2$ using ILs in a purely ionothermal procedure in absence of any cosolvents. The chemistry and reaction process has been discussed and examined, indicating the advantages of using ILs in conjunction with microwave radiation.

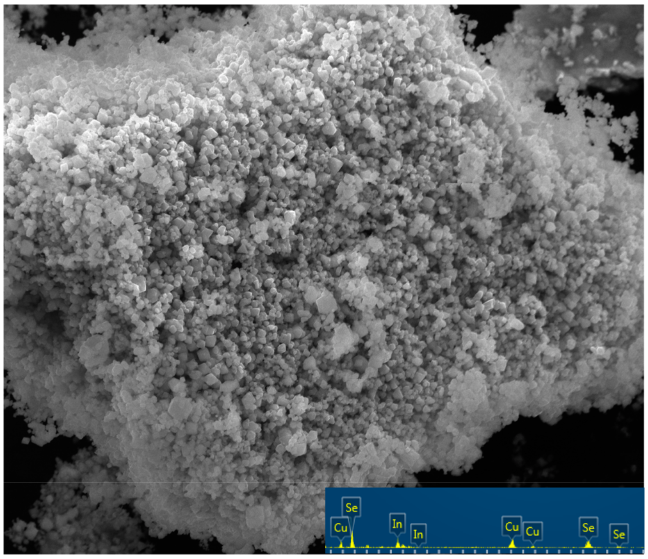

Figure 9. SEM/EDX image of product formed using $[P_{66614}][InCl_4]$ from reaction 1a, Table 3.

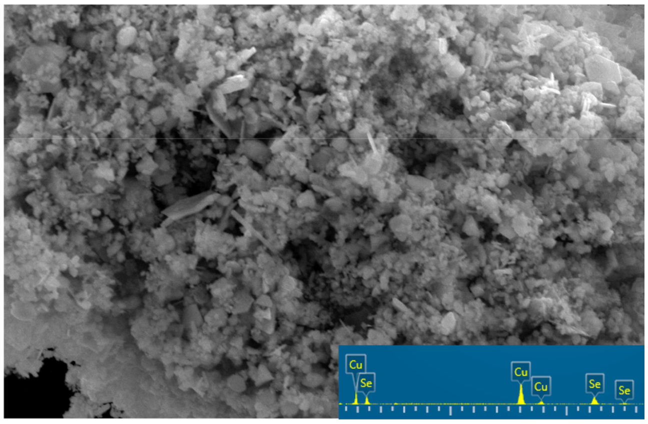

Figure 10. SEM/EDX image indicating both CIS and Cu_2Se products formed when using $[C_8mim][InCl_4]$ from reaction 2b, Table 3.

Two approaches were investigated; conventional heating, using an oil bath or furnace and autoclave, as well as using microwave irradiation. It has been demonstrated that the autoclave reactions did not go to completion; however, intermediates crystallized from these solutions, and three novel crystal structures have been determined. The intermediates formed could be used as precursors to the production of CIS. The second approach investigated was the use of microwave irradiation as the heat source. This method was successful in forming CIS with the correct stoichiometry and is

Table 3. Method B Using a Microwave Reactor

no.	IL	reaction conditions/order of reagents		elemental composition (by EDX)
1	$[P_{6\,6\,6\,14}][InCl_4]$	(a) IL + Ph_2Se_2 + CuCl	All together and reacted at 240 °C.	$Cu_2Se/CuSe$
		(b) In_2Se_3 formed + CuCl	In_2Se_3 formed at 240 °C. Cu^ICl added and heated to 240 °C. Cu^ICl added and heated to 200 °C.	$CuInSe_2$
2	$[C_8mim][InCl_4]$	(a) IL + Ph_2Se_2 + CuCl	All together and reacted at 240 °C.	$Cu_2Se/CuSe$
		(b) In_2Se_3 formed + CuCl	In_2Se_3 formed at 240 °C, Cu^ICl added and heated at 200 °C.	$CuInSe_2$ and Cu_2Se

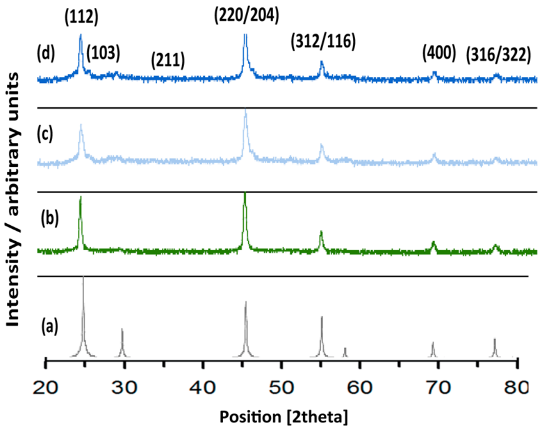

Figure 11. PXRD patterns of the products formed in reaction 1b, using $[P_{66614}][InCl_4]$ reacted with Ph_2Se_2 at 240 °C/1 min, then Cu(I)Cl at 240 °C/1 min (d), $[P_{66614}][InCl_4]$ reacted with Ph_2Se_2 at 240 °C/1 min, then Cu(I)Cl at 200 °C/1 min (c), repeated for reproducibility at 200 °C/1 min (b), $CuInSe_2$ from crystal structure database (a).

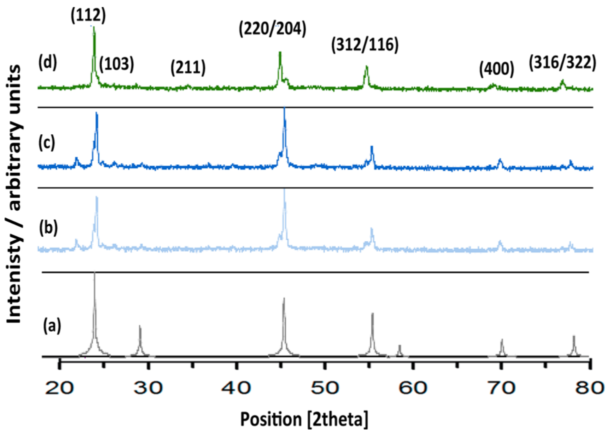

Figure 12. PXRD patterns of the products formed in reaction 2b, using $[C_8mim][InCl_4]$ reacted with Ph_2Se_2 at 240 °C/1 min, then Cu(I)Cl at 200 °C/1 min (d), repeated for reproducibility at 200 °C/1 min (c), $[C_8mim][InCl_4]$ reacted with Ph_2Se_2 at 240 °C/1 min, then Cu(I)Cl at 200 °C/5 min (b), $CuInSe_2$ from crystal structure database (a).

the first report on the production of CIS nanomaterials combining microwave heating and metal-containing ILs in a facile two-step, one-pot synthesis. This method was very efficient and has been optimized through stepwise tuning of the reaction temperature, with an initial temperature of 240 °C used to produce the In_2Se_3, and subsequent addition of Cu(I)Cl and reaction at the second stage for 1 min at 200 °C was implemented. SEM, EDX, and PXRD were used to identify the CIS products formed.

It has been demonstrated that ILs play a significant role in the shape and morphology of the resulting products, as seen from the selenium compounds formed in the autoclave and the different morphologies of CIS formed when using imidazolium and phosphonium cations. The main advantage of this process is the efficient interaction of microwaves with ILs, which yielded optimum results with a very short reaction time. The production of pure, nanosized particles of CIS has been achieved.

Nevertheless, there have been challenges and limitations associated with the use of ILs, such as the complete removal of the IL after the reaction procedure, which required several washes, sonication, and centrifugation with methanol. The production of the IL precursors is relatively straightforward and not very time-consuming, but their availability and cost in comparison to commercial solvents that are easy to source and purchase is not beneficial. However, the uniform temperature profile endorsed by the use of the microwave reactor encouraged the production of reproducible compounds of CIS allowing for stringent control over the composition and defect concentration of the resulting compounds. This was exclusively permitted due to the interaction with the IL and the microwaves, which was not afforded through autoclave experiments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Specific amounts of materials used in conventional heating methods and in microwave-assisted syntheses; C, H, N analysis results. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 1048314, 1048315, and 1048316 contains the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: +44−1223−336033; or deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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