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ARTICLE

Zinc Selenide Nano- and Microspheres via Microwave-Assisted Ionothermal Synthesis

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Zinc selenide nanospheres were prepared from a diphenyl diselenide precursor and a range of chloro- and bromozincate(II) ionic liquids via a microwave-assisted ionothermal route; this is the first report on the use of microwave irradiation in combination with ionic liquids to prepare this material. The method is time-efficient and a facile one-pot reaction to produce zinc(II) selenide nanomaterials. The product formation in the ionic liquids has been monitored using Raman spectroscopy. The products have been characterised using PXRD, SEM, EDX, Photoluminescence and UV-VIS spectroscopy. Advantages of this new route, such as ease of solubilisation of all reactants into one phase at high concentration, the negligible vapour pressure irrespective of the reaction temperature, very fast reaction times, ease of potential scale-up and reproducibility are discussed.

Introduction

Zinc Selenide (ZnSe), is a light yellow solid compound. It is an intrinsic semiconductor with a band gap energy of 2.67 eV and a large exciton binding energy (21 meV) at room temperature. The types of ZnSe that can be produced are the hexagonal (wurtzite) and cubic (zincblende) structure.¹

ZnSe has numerous potential applications such as in electroluminescent devices, field effect transistors, sensors, light emitting diodes, photo detectors, room temperature excitonic devices and solar cells.^{2,3} Due to its excellent optoelectronic properties, this material has attracted much attention with its capability to be implemented into blue laser diodes, photo detectors, gas sensors, photonic crystal devices, short wavelength optoelectronics, to name a few.⁴

Most of the literature has previously focused on the preparation of cadmium-based materials of selenide or telluride as they exhibit a band gap that results in an emission spectrum in the visible region.⁵ Due to the toxicity of cadmium compounds, the investigation into other metal chalcogenides, including zinc selenides has increased. In the preparation of these materials, especially at room temperature, introduces toxic solvents and precursors such as H₂Se or high temperatures to be implemented in order to use elemental precursors or zinc and selenium.⁵

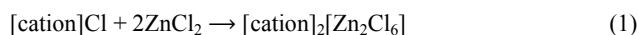
The methods generally employed for the synthesis of ZnSe, include the hydrothermal approach,^{2,6} which uses elemental zinc and selenium in a NaOH (aq) solution and reacting for 24 hours at 150 °C. A solvothermal approach has also been reported,^{3,7,8} which requires a reaction temperature of 60 °C, for 4 hours, but also needs the precursors to be calcined at 500 °C, before they are suitable to use, as well as using ethylenediamine

as a solvent and hydrazine hydrate as the reducing agent. This type of synthesis is termed as an amine-assisted solvothermal method, since the amine is used as a templating agent, and it has been reported that this is a crucial parameter for controlling the morphology of the resulting metal chalcogenide nanoparticles. Finding novel ways to produce these materials using a range of amines is becoming increasingly popular with monoamine, diamine, and tertiary amines already implemented.⁸ A wet chemical method^{9,10} can also be employed as it is simple and inexpensive, which uses non-hazardous starting materials. Thiols, phosphines and amines have been reported, used as capping agents, with continuous stirring for 36 hours, with subsequent drying for 8-10 hours at 120 °C. A direct thermal route can also be used, through heating the elemental precursors in ammonia under an ammonia atmosphere, at 500 °C for several hours.¹¹ The microwave reactor has also been implemented in the formation of zinc selenide nanomaterials, which has numerous advantages over traditional thermal methods, including, fast and homogeneous heating of the reaction mixture, high speed of interaction, an inverse temperature gradient and the possibility of fast selection of chemical reaction conditions.¹² Microwave irradiation is different from other techniques in that it does not rely on black body radiation to heat the reaction mixture, which allows for greater advantages for colloidal nanostructured materials to be formed. The synthesis is efficient, with a uniform nucleation and growth process, without suffering sharp thermal gradient effects. The intermediate compounds and transition states are considerably different than those formed from traditional solvothermal reactions.¹³ The use of alkylamines as the ligating solvent, reacted in the microwave at 140 °C for 1 minute has

been reported¹³, with an inverse correlation between the size of the nanoparticles and the length of the amine used. These findings are contradicted by Sofronov *et al.*, who employ reaction temperatures of 240 °C as it is claimed that the interaction between zinc and selenium only occurs at temperatures above 218 °C.¹² Employing a temperature of 240 °C, is still considerably low, but with this, fast heating of the particles at 500-600 °C, is still necessary with subsequent injection of alkaline metal halogenides.

In this contribution, we propose an innovative route to nanosize and microcrystalline zinc(II) selenide, taking advantage of possibilities offered by ionic liquid-based synthesis in the microwave reactor. Ionic liquids are salts, typically based on organic cations, with melting points below 100 °C, and often much lower than ambient temperature.^{14,15} These salts have a range of advantages over traditional solvent systems, with their wide liquid range which allows for the dissolution of a large variety of materials and negligible vapour pressure, making them an attractive and safer choice for use in microwave synthesis, with no sudden pressure surges. Thermal and hydrolytic stability, with a tunable viscosity and a large electrochemical window are also some of the benefits that ionic liquids can display.^{16,17,18,19,20} Due to this, ionic liquids have been used as both a reagent involved in the reaction process and as the solvent, known as a 'ionothermal' procedure.²¹

Chlorometallate ionic liquids are a class of ionic liquids based on a bulky organic cation and chlorometallate anion, which have very interesting and useful properties.²² They are prepared by the reaction of an organic chloride salt with a metal chloride; various ratios of reactants may be used, which leads to different anionic speciation, with the specific reaction ratio used outlined below.^{23,24}



*Cation = [phosphonium] or [imidazolium]

Chlorometallate ionic liquids are excellent media for the synthesis of inorganic materials, as they contribute added benefits, including, acting as a metal source, availability in very high concentrations and with a tuneable coordination.²⁵

Microwave-assisted synthesis may in many cases, dramatically reduce the reaction time, and has been successfully implemented in the preparation of a variety of inorganic materials.^{26,27} Ionic liquids readily absorb microwave irradiation and do not increase vapour pressure upon rapid heating, hence are particularly suitable for fast-paced microwave-assisted synthesis.²⁸

To our knowledge, ionic liquids and the ionothermal approach, in conjunction with microwave-based synthesis, have not been adopted to prepare zinc(II) selenide, to date. In this work, advantages of chlorometallate ionic liquids and microwave-assisted synthesis were combined to produce both nano and microcrystalline zinc(II) selenide in a fast, safe and elegant synthetic pathway.

Experimental

Materials

Zinc (II) chloride, zinc (II) bromide, 99% anhydrous, diphenyl diselenide, 99%, and zinc (II) selenide were purchased from Sigma-Aldrich. The ionic liquids; [P_{6 6 6 14}]Cl [P_{8 8 8 4}]Cl, and [P_{5 5 5 10}]Cl, as well as [P_{6 6 6 2}]Br, [P_{6 6 6 4}]Br, [P_{6 6 6 5}]Br were prepared as described elsewhere.²⁹

Synthesis

HALOZINCATE IONIC LIQUIDS. Appropriate amounts of zinc(II) chloride with a phosphonium chloride ionic liquid, were placed in a glass reaction vessel, equipped with a stirring bar. Appropriate amounts of zinc(II) bromide with a phosphonium bromide ionic liquid, were also placed in a glass reaction vessel, equipped with a stirring bar. Each flask was closed with a stopper, placed in a heating block, and the mixtures were stirred vigorously (120 °C) overnight. Yellow chlorozincate ionic liquids were formed, with colourless solids being formed for the bromozincates. ESI-MS after the reaction shows no signs of degradation of the ionic liquid, which indicates recyclability.

ZINC(II) SELENIDE. In a typical process, Ph₂Se₂ was added to either a chlorozincate(II) or bromozincate(II) ionic liquid, in a 1:1 ratio, before being placed in the microwave reactor, Anton Parr Monowave 300, for 1 min. Reaction temperatures were varied between 180 and 240 °C. The product formed was a suspension of a fine powder in an ionic liquid, and was subsequently washed with methanol and centrifuged to separate the particles from the ionic liquid. The fine powder was produced in a variety of colours, including orange, red, bright yellow and black, which depended on the ionic liquid used, as well as the size and mass of material that was formed.

Characterisation

Raman spectra were recorded using a PerkinElmer RamanStation 400F spectrometer, with a 785 nm focussed laser beam. All studied samples were placed in quartz cuvettes and analysed neat; ten scans of 5 s each were recorded.

The scanning electron microscopy (SEM) studies were carried out using a JEOL 6500F Field Emission and a Quanta FEG 250 Scanning Electron Microscopes. The energy dispersive X-Ray analysis (EDX) was carried out using Oxford Instruments INCA systems.

X-Ray diffraction (XRD) data were collected using a Siemens D5000 powder diffractometer with Cu K α radiation (λ = 1.542 Å). Data were recorded from between 10° and 60° in steps of 0.0167.

Photoluminescence measurements were carried out on a Perkin Elmer LS 55 Luminescence spectrometer.

Results and Discussion

Methodology

According to literature, dispersible ZnSe hollow microspheres with an average diameter of 1.0 μm have been prepared using an ionic liquid solvothermal method, with $[\text{C}_4\text{mim}]\text{Br}$. This ionic liquid was specifically chosen due to its high conductivity and low surface tension, which allowed for the reactions to be carried out under relatively mild conditions. Hydrazine hydrate was used along with a range of other solvents and was maintained at 140 $^\circ\text{C}$ for 16 hours.³⁰

In the approach presented here, diphenyl diselenide was dissolved in a chlorozincate(II) ionic liquid and exposed to microwave radiation to result directly in both micro and nanocrystalline zinc(II) selenide. The metal-functionalised ionic liquid acts as both a non-volatile solvent and reactant in a ionothermal process.

At ambient conditions diphenyl diselenide, Ph_2Se_2 , was suspended in a phosphonium ionic liquid, with dissolution upon heating between 50-60 $^\circ\text{C}$, to form homogenous, orange/yellow solutions. Upon further heating to 240 $^\circ\text{C}$, a fine suspension in a variety of colours was formed.

For all solutions it was found that the reaction was completed after just 1 min in a microwave reactor. In various sets of experiments, the influence of the ionic liquid on the composition and morphology of zinc(II) selenide microcrystals were studied.

The Raman spectra of a solution of Ph_2Se_2 in a phosphonium ionic liquid and the solid that crystallises out upon cooling, has been compared to spectra of the neat ionic liquid and pure Ph_2Se_2 (**Figure 1**). For the spectrum of the sample of Ph_2Se_2 dissolved in the phosphonium ionic liquid (**Figure 1**), peaks are evident for both the ionic liquid and the selenium precursor, and it appears that the Ph_2Se_2 simply dissolves in the ionic liquid, without coordination to the zinc centre. When the mixture is allowed to cool, the Ph_2Se_2 precipitates out of the ionic liquid and forms two phases again. The bromozincates gave the same spectra, with the Ph_2Se_2

dissolving in the ionic liquid at 55-65 $^\circ\text{C}$, and the Ph_2Se_2 separating out of the mixture again after cooling.

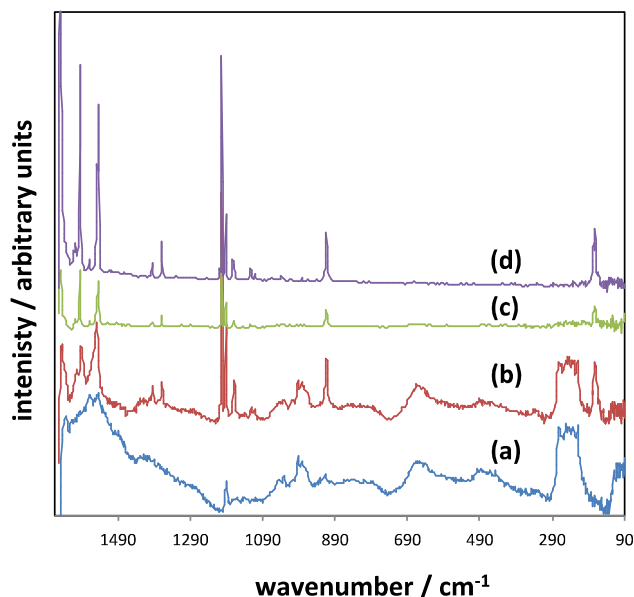


Figure 1. Raman spectra of neat ionic liquid $[\text{P}_{66614}][\text{ZnCl}_2]$ (a) Ph_2Se_2 in $[\text{P}_{66614}][\text{ZnCl}_2]$ liquid state (b), Ph_2Se_2 in $[\text{P}_{66614}][\text{ZnCl}_2]$ solid state (c) and diphenyl diselenide (d).

Morphologies of the nano and microcrystals prepared using the ionic liquids were studied using SEM; furthermore, EDX was used to highlight the elemental composition and stoichiometry of the products formed (Table 1, 1-6).

Entries 1-3 in Table 1 show that, at 240 $^\circ\text{C}$, $[\text{P}_{66614}]_2[\text{Zn}_2\text{Cl}_6]$, $[\text{P}_{8884}]_2[\text{Zn}_2\text{Cl}_6]$ and $[\text{P}_{55510}]_2[\text{Zn}_2\text{Cl}_6]$ gave very similar results, yielding products of either micro crystalline or nanosize. From EDX analysis it is evident that zinc selenide has been formed in each case, with the colour of the sample often reflecting the size of the product formed.

Table 1. Morphology and average composition of zinc(II) selenide products synthesised in different ionic liquids, at 240 $^\circ\text{C}$ with a variety of stoichiometries, colours and sizes formed.

No.	Ionic liquid	Reaction times and temperatures tested	Appearance of precipitate	Elemental Analysis from EDX	Size of materials formed
1	$[\text{P}_{66614}]_2[\text{Zn}_2\text{Cl}_6]$	240 $^\circ\text{C}$, 1 min	Black	44% Zn : 56% Se	1-2 μm
2	$[\text{P}_{8884}]_2[\text{Zn}_2\text{Cl}_6]$	240 $^\circ\text{C}$, 1 min	Red	42% Zn : 58% Se	100-200nm
3	$[\text{P}_{55510}]_2[\text{Zn}_2\text{Cl}_6]$	240 $^\circ\text{C}$, 1 min – small scale 240 $^\circ\text{C}$, 1 min (repeated) – large scale 240 $^\circ\text{C}$, 5 min	Red Bright yellow Bright yellow	43% Zn : 57% Se 48% Zn : 52% Se 54% Zn : 46% Se	100-200nm 0.5-1 μM 0.5-1 μM
4	$[\text{P}_{6662}]_2[\text{Zn}_2\text{Br}_6]$	240 $^\circ\text{C}$, 1 min	Red/ black	prod 1: 20% Zn : 80% Se prod 2: 100% Se	200-300 nm 20 μM
5	$[\text{P}_{6664}]_2[\text{Zn}_2\text{Br}_6]$	240 $^\circ\text{C}$, 1 min	Red/ black	prod 1: 20% Zn : 80% Se prod 2: 100% Se	200-300 nm 20 μM
6	$[\text{P}_{6665}]_2[\text{Zn}_2\text{Br}_6]$	240 $^\circ\text{C}$, 1 min	Red/ black	prod 1: 20% Zn : 80% Se prod 2: 100% Se	200-300 nm 20 μM

Chlorozincates

From the SEM image obtained, **Figure 2**, it is evident that the particles produced were in the range of 100-200 nm. The EDX analysis of this product, shown in **Figure 3**, confirms the production of zinc selenide, with the weight percentage of 57.5 % zinc: 42.5 % selenium, which is in very good agreement to the calculated value for standard zinc(II) selenide, of 45% Zn: 55% Se.

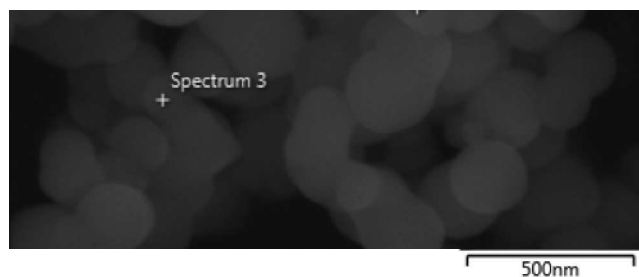


Figure 2. SEM image of the product formed using $[P_{5.5.5.10}]_2[Zn_2Cl_6]$.

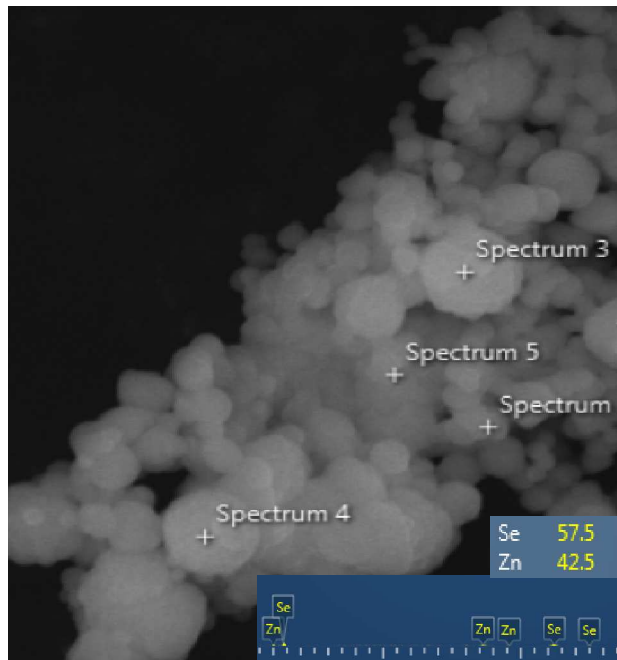


Figure 3. SEM image with EDX analysis of the product formed using $[P_{5.5.5.10}]_2[Zn_2Cl_6]$ in reaction 4b.

As seen in Table 1 for reaction 4.b. the correct stoichiometry of zinc to selenium was evident from the EDX analysis with the size of the particles once again ranging from several hundred nm- 1 μ m, shown in **Figure 3**. The stoichiometry and morphology of the particles shown in **Figure 4**, varied in size, with both micro and nano-crystalline materials produced. The EDX analysis concluded that zinc selenide was formed in each case.

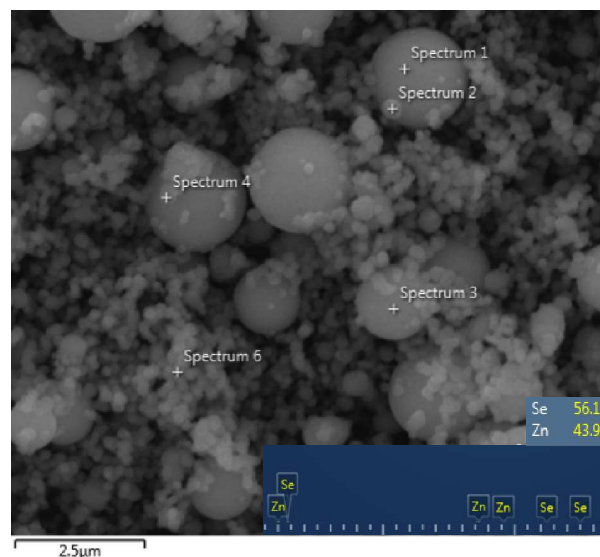


Figure 4. SEM image and EDX analysis of the product formed when using $[P_{8.8.8.4}]_2[Zn_2Cl_6]$.

With regards to the photoluminescence and band gap measurements, all the zinc(II) selenide products formed using the three phosphonium ionic liquids, gave similar if not identical spectra, as seen in **Figure 5**. When compared to the zinc selenide standard, purchased from Sigma Aldrich, the spectra of all the samples were a match, with the main peaks at the same wavelength in each case, **Figure 7**.

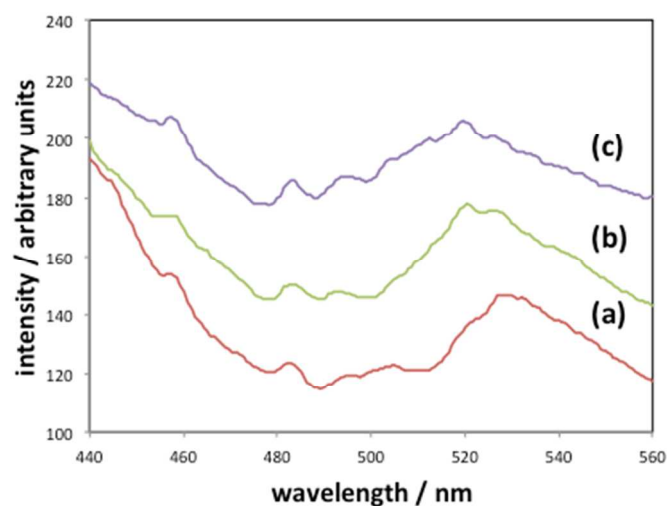


Figure 5. PL measurements of zinc selenides produced by chlorozincates ionic liquids, $[P_{6.6.6.14}]_2[Zn_2Cl_6]$ (a) $[P_{8.8.8.4}]_2[Zn_2Cl_6]$ (b) and $[P_{5.5.5.10}]_2[Zn_2Cl_6]$ (c) excited at 380 nm.

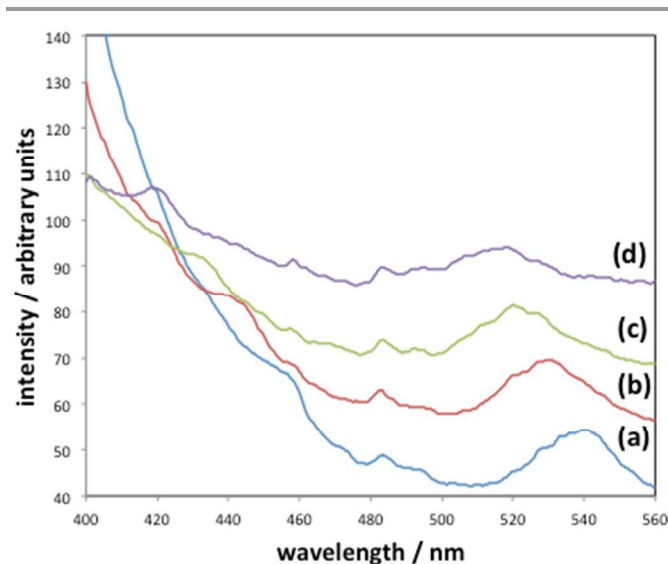


Figure 6. PL measurements of zinc selenide produced by $[P_{66614}]_2[Zn_2Cl_6]$ with varying excitation wavelengths, indicated by lines at 380 nm (a), 370 nm (b), 360 nm (c), 350 nm (d).

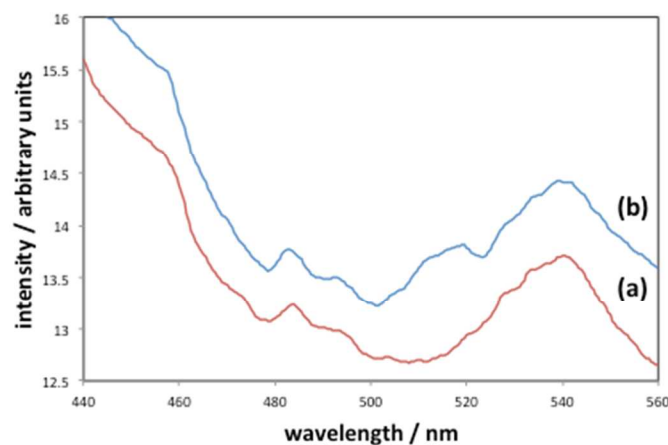


Figure 7. Photoluminescent spectrum of ZnSe standard (a) compared with product formed with $[P_{66614}]_2[Zn_2Cl_6]$ (b) excited at 380 nm.

All the samples were excited at a range of energies, from 380–360 nm in order to produce the photoluminescence spectra shown in **Figure 5** - **Figure 7**. All samples gave similar spectra, with peaks ranging from 416–537 nm. Each sample gave one peak at the exact same point at 482 nm, which indicates a band gap energy of 2.588 eV, which was calculated using the equation $E = h \cdot c / \lambda$.

According to literature³⁰ for zinc selenide hollow microspheres, there are three main emission bands centres, found at 425 nm (2.91 eV), 440 nm (2.82 eV) and 460 nm (2.69 eV). The first two emissions are blue shifted and are attributed to the quantum size effect of zinc selenide nanoparticles. The emission at 2.69 eV, corresponds to the bulk emission of ZnSe, which is a value similar to what we have reported, at 2.59 eV.

The main peaks found in each sample, give an indication of a band gap between 2.31 eV and 2.99 eV, with 2.67 eV the value reported in the literature.¹ The main hump/ broad peak evident in all materials analysed was found between 520 - 540 nm,

which equates to a band gap of 2.39 eV, but could be assigned to an emission caused by Se defects.³⁰

The PXRD patterns of the zinc selenide products, produced from all the chlorozincate ionic liquids, $[P_{66614}]_2[Zn_2Cl_6]$, $[P_{8884}]_2[Zn_2Cl_6]$ and $[P_{55510}]_2[Zn_2Cl_6]$ as seen in **Figure 8**, indicate phase compositions and purity of compounds. The PXRD patterns of the prepared samples indicate products with high crystallinity.³⁰ The spectra produced matched the pattern of zinc selenide (JCPDS 15-0105, space group: $P6_3mc$)³¹, exhibiting a nearly pure hexagonal wurtzite structure. The PXRD spectra of the products formed using the chlorozincate ionic liquids, indicates that the same product is formed regardless of the scale of the reaction, or the time, as indicated from spectra, (a), (b) and (c) in **Figure 8**.

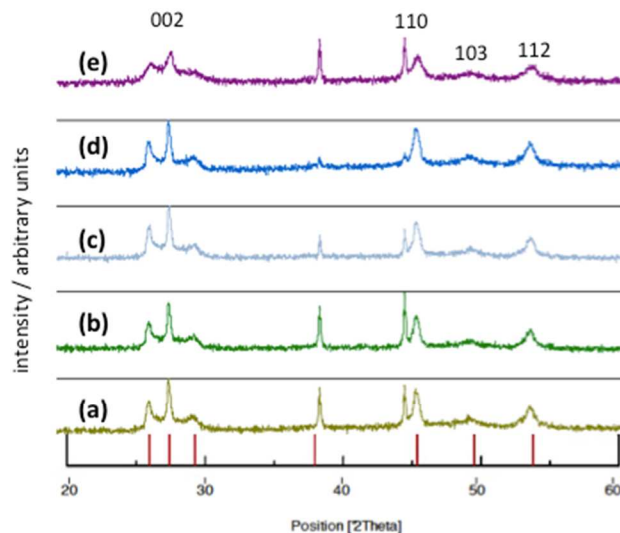


Figure 8. PXRD spectra of the zinc(II) selenide products formed, using the chlorozincate ionic liquids $[P_{55510}]_2[Zn_2Cl_6]$ small scale, 1 min (a), repeated reaction using $[P_{55510}]_2[Zn_2Cl_6]$ for reproducibility, large scale, 1 min (b) repeated reaction using $[P_{55510}]_2[Zn_2Cl_6]$ for reproducibility, 5 min (c) $[P_{8884}]_2[Zn_2Cl_6]$ (d) and $[P_{66614}]_2[Zn_2Cl_6]$ (e).

Bromozincates

Entries 4-6 in Table 1 indicate the formation of a zinc polyselenide product using the bromozincate ionic liquids, $[P_{6662}]_2[Zn_2Br_6]$, $[P_{6664}]_2[Zn_2Br_6]$, and $[P_{6665}]_2[Zn_2Br_6]$. The materials produced were both nano- and micro-sized. The EDX analysis of the products formed when using the bromozincate ionic liquids indicated a weight percentage of zinc: selenium of 20%:80%, which is higher than the weight percentage calculated for standard zinc selenide (55% zinc: 45% selenium), but this could be due to the amount of elemental selenium impurity found in the product. From the EDX analysis it was revealed that the larger particles were elemental selenium, and the smaller particles were zinc selenide.

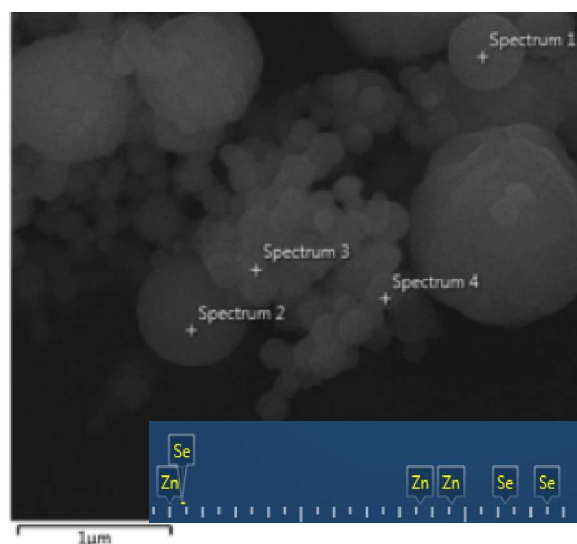


Figure 9. SEM image of the zinc poly selenide product formed when using ionic liquid, $[P_{6662}]_2[Zn_2Br_6]$.

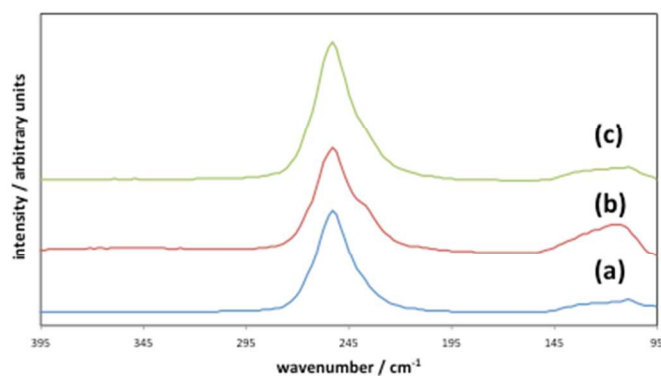


Figure 10. Raman spectrum of the products formed from $[P_{6662}]_2[Zn_2Br_6]$ (a), $[P_{6664}]_2[Zn_2Br_6]$ (b), and $[P_{6665}]_2[Zn_2Br_6]$ (c).

All the zinc selenide products formed when using the bromozincate ionic liquids, gave similar spectra, with the largest peak evident, found at 253 cm^{-1} , **Figure 10**, which is characteristic of a zinc-selenium vibration, confirming the presence of zinc-selenium bonds. The vibration for selenium-selenium bonds, are normally found at 256 cm^{-1} , indicative of amorphous selenium, with selenium S8 rings found at 254 cm^{-1} , which is a similar peak to $\alpha\text{-Se}^{32}$. Therefore, Raman alone could not indicate the presence of zinc selenide, as the vibrations for both Zn-Se and Se-Se are almost identical, and has been used in conjunction with SEM and EDX analysis to confirm the production of the presence of both a zinc selenide and pure selenium.

Conclusions

A novel route towards the synthesis of zinc(II) selenide has been successfully developed. It involves inexpensive phosphonium ionic liquids used in a safe ionothermal procedure. The reaction only employs one temperature of

$240\text{ }^\circ\text{C}$, and does not require several hours with considerable heating and calcining of reagents. The need for VOCs (Volatile Organic Compounds) in their preparation has also been eliminated. To our knowledge, this is the first example of using ionic liquids, namely chlorozincates with the ionothermal approach, together with the microwave reactor in order to prepare zinc(II) selenide.

From the combination of SEM, EDX, Raman, PXRD and Photoluminescence analysis, it is conclusive that zinc selenide has been produced in each case, implementing phosphonium chloride ionic liquids, with a range of alkyl chain lengths attached. With regards to the bromozincate experiments, a variety of both polyselenides, zinc selenide, with residual selenium has been produced; further purification, or a change in reaction temperature could be implemented to modify this.

The novel microwave-assisted ionothermal synthesis of zinc(II) selenide, using a range of chlorozincate phosphonium ionic liquids, has allowed for a more simple, less time consuming and elegant way to make this semiconductor material.

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