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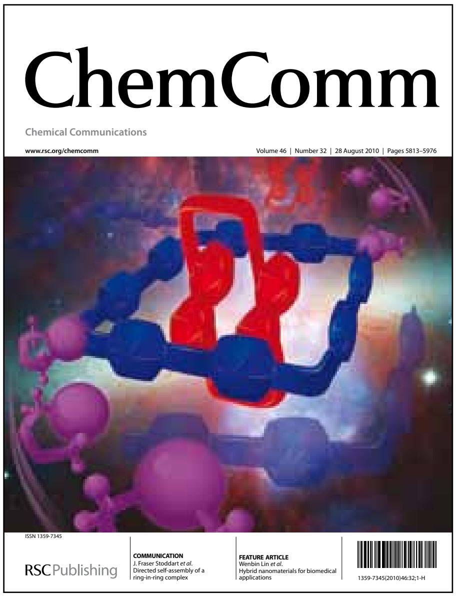

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ARTICLE TYPE

Size Controlled Mechanochemical Synthesis of ZrSi$_2$

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Mechanochemical metathesis reactions were utilized to synthesize nanocrystalline ZrSi$_2$ ranging from 9-30 nm in size. Size was controlled through dilution with CaCl$_2$. A linear relationship was found between diluent concentration and crystallite size. Unlike typical self-propagating metathesis reactions, this reaction did not self-propagate, requiring the input of mechanical energy.

Transition metal silicides, which are refractory, conductive, strong, and relatively inert, offer an attractive choice for reinforcement materials [1, 2]. In particular, nanocrystalline refractory silicides are more desirable due to their novel properties, such as high strength, hardness, and electrical conductivity [2]. Because of these properties and its low electrical resisitivity (13 – 34 μΩ cm)[3] zirconium silicide is used in composites as a reinforcement material [4, 5], in microelectronic devices [6], and potentially in neutron deflectors [7]. Recently, nanoinclusions of conductive materials have been proposed as a route to improved thermoelectric materials.[8, 9] Incorporation of gold nanoparticles in a Bi$_2$Te$_3$ matrix resulted in an improved Power Factor and Figure of Merit. This result shows that a top down approach to improving thermoelectric materials is practical. However, gold is not compatible with thermoelectric materials used at higher temperatures. In particular, the SiGe alloy currently used in radioisotope thermoelectric generators (RTGs) is processed at temperatures above the melting point of gold and nanostructures would be lost. It has been proposed that nanoparticles of silicides can enhance the thermoelectric properties of SiGe.[10] Current approaches to producing silicide inclusions rely on a bottom up approach through the formation of silicides *in situ*, which can be difficult to control.[11] A controllable route to unfunctionalized silicides would allow a top down approach to forming SiGe alloys enhanced with silicide inclusions.

Traditional routes to producing zirconium disilicide include silicothermic reduction [12], electrochemical [13], mechanochemical [14], sintering [15], arc-melting [15], and self-propagating metathesis reactions [16, 17]. However, these reactions are difficult to scale, do not yield pure ZrSi$_2$, and do not allow for control of crystallite size. In addition, some routes require temperatures above 1000ºC.

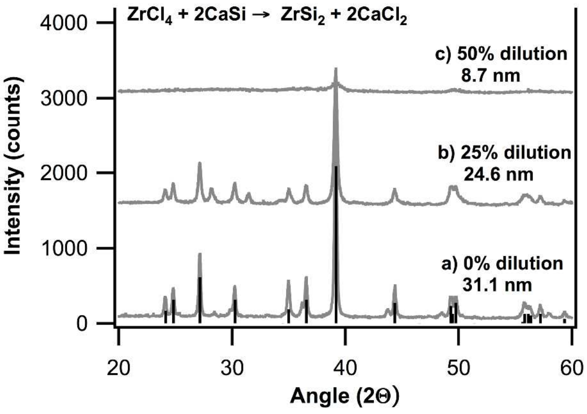

Figure 1. XRD patterns of the mechanochemically synthesized ZrSi$_2$ at different diluent loadings. By adding an inert diluent (CaCl$_2$) the crystallite size can be reduced. All patterns match ZrSi$_2$ (JC-PDS 32-1499).

This study focuses on an alternative synthetic route to ZrSi$_2$ using mechanochemical synthesis via a metathesis reaction. Although mechanochemical methods have been used to prepare a variety of nanomaterials,[18-23] the synthesis of refractory materials by mechanically driven solid-state metathesis has not been investigated thoroughly. This approach involves grinding the starting materials in a high-energy ball mill. By using a diluent, crystallite size is controlled enabling the production of ZrSi$_2$ with sizes dependent on the level of dilution. Although, size control in self-propagating metathesis reaction has been investigated in the past,[24] the extent of control was limited by the need for self-propagation. A mechanochemical approach eliminates this restriction, since self-propagation is not necessary. The continuous input of energy through the grinding process drives the the reaction to completion.

Zirconium disilicide was prepared by ball milling a stoichiometric amount of zirconium (IV) chloride (Strem Chemicals, 99.6%) with calcium silicide (CaSi) (GFS Chemicals, Inc., 99.5%), or mechanochemically synthesized CaSi in an argon environment. Calcium chloride (Bryant Lab, Inc.) was used as a diluent to control the size of the ZrSi$_2$ crystallites. Milling experiments were carried out using 8000M and 8000D SPEX CertiPrep mixer/mills. Three 440c stainless steel balls (1.27-cm dia., 8g ea.) were used as the milling media. Commercial calcium silicide contains a significant amount of iron impurities.

In order to reduce these impurities,[25] calcium silicide was mechanochemically prepared from the elements using a method similar to that reported for Mg_2Si.[26] One gram of calcium (granules, redistilled -6 mesh, 99.5% Alfa Aesar) was added in three increments to a stoichiometric quantity of silicon (Virgin poly fines 99.999%, Alfa Aesar, ground and sieved to -270 mesh under argon). Grinding for 30 minutes in a steel SPEX vial followed each calcium addition. Size controlled $ZrSi_2$ was prepared by milling 2 g reaction masses for 8 h in 30-minute increments, followed by 30 min of cooling to reduce wear on the mill's motor. The product was isolated in an argon environment to prevent oxygen contamination.

Formamide (Aldrich, 99%) and N,N-dimethylformamide (DMF, Acros, 99.8% extra dry) were used to wash away the calcium chloride by-product. The formamide was dried over molecular sieves (4-8 mesh, Acros) prior to use. The reaction mass was transferred to a 100-mL serum vial along with 15 mL of formamide, crimped with a cap and septum, and centrifuged at 3000 rpm using an RC-5 Superspeed Refrigerated Centrifuge. The supernatant was decanted in an argon atmosphere and this process was repeated twice. N,N-dimethyl formamide (in three 15 mL portions) was used to rinse off the remaining formamide. The DMF was removed by heating under vacuum inside a glove box.

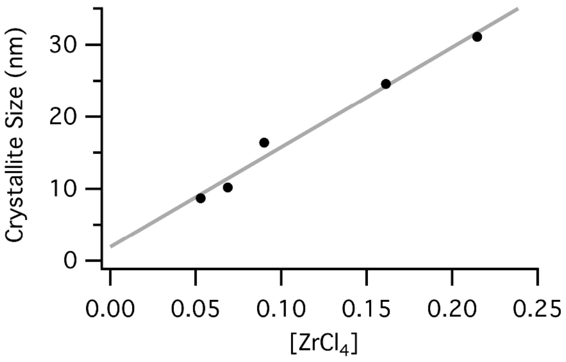

Figure 2. Control of the average crystallite size in the mechanochemical synthesis of $ZrSi_2$. The concentration of $ZrCl_4$ is expressed in terms of moles/liter of free volume.

Mechanochemical routes to zirconium silicide from the elements have been reported, however these routes required long reaction times [14] or yield impure materials [27]. Synthesis by a mechanically driven metathesis reaction (Equation 1) remedies these deficiencies. Zirconium silicide has been previously synthesized via a self-propagating solid-state metathesis (SSM) reaction at elevated temperatures. This is the first time such a reaction has been performed at nominally ambient conditions.

$$ZrCl_4 + 2CaSi \rightarrow ZrSi_2 + 2CaCl_2 \tag{1}$$

An added benefit, to this approach, is that it is possible to scale mechanochemical reactions through modification of mill design.[28] The crystallite size of $ZrSi_2$ was controlled by the addition of an inert diluent, $CaCl_2$. Figure 1 shows the XRD patterns of $ZrSi_2$ at different diluent loadings. Size analysis was performed using the Scherrer method. As the diluent amount was increased, the crystallite size decreased. This allowed for the preparation of nanocrystalline materials ranging from 9-30 nm. Figure 2 shows that the crystallite size of $ZrSi_2$ obtained is dependent upon the concentration of $ZrCl_4$ used. The reactor volume is fixed at 65 mL and concentration is defined as moles of reagent per liter of free volume of the vessel (total volume excluding the volumes of the milling media and reactants). This has been successfully applied to the kinetic analysis of the mechanochemical formation of alkaline earth carbides.[25] As $ZrCl_4$ concentration was increased, the crystallite size of the synthesized $ZrSi_2$ increased linearly. This analysis approach is a departure from the typical mechanochemical reaction analysis, which characterizes reactions in terms of ball to reactant ratios.[29] Although this method takes into account the increase in the kinetic energies available by using more or larger balls, it does not take into account the restriction in motion by increased ball volumes. The analysis presented here takes both into account for a single ball material. The addition of $CaCl_2$ reduced the effect of Ostwald ripening and resulted in smaller crystallite sizes. It is important to note that none of these reactions self-propagate. The continuous input of energy from milling is required for the reaction to go to completion.

In order to remove the diluent and by-product ($CaCl_2$), the product required a washing step under argon to prevent surface oxidation. The solvent must be polar enough to dissolve $CaCl_2$, but not possess –OH groups. Past reports have used dilute acid to remove by-products and obtain a pure silicide product [13, 30]. However, washing with water or aqueous acids introduces

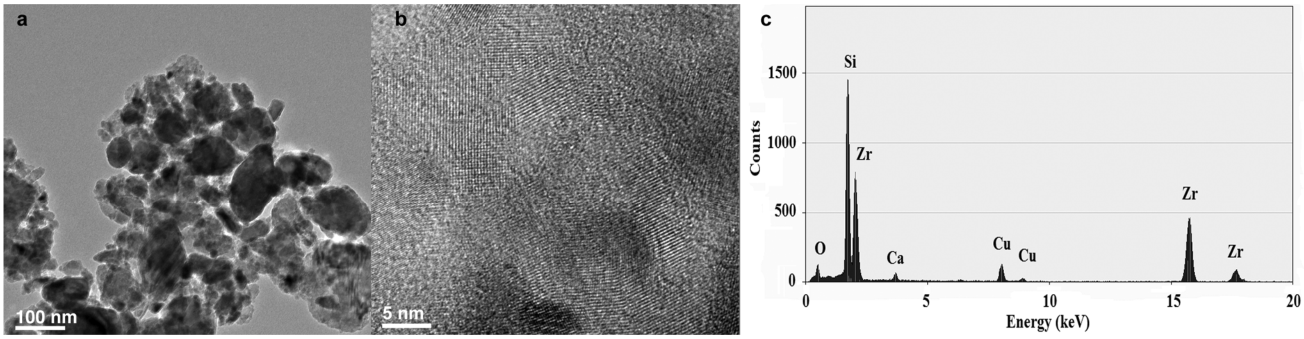

Figure 3. Transmission electron microscope images of $ZrSi_2$ prepared mechanochemically from a reaction diluted 50 mass% with $CaCl_2$. The material was isolated air-free using formamide: a) particles range from 100 nm to 20 nm; b) each particle is composed of crystalline regions as small as 5 nm in diameter; c) elemental analysis shows that calcium chloride was effectively removed. The remaining calcium is due to calcium oxide in the starting material.

surface oxides and hydroxides. It is known that $ZrSi_2$ forms a stable colloid in water due to surface oxidation. [31] Using an alternative washing method, which produces a material suitable for conductive composites, minimized surface oxidation. With a high dielectric constant, formamide is the preferred solvent for $CaCl_2$ removal. Dimethylformamide can also be used, but the removal of $CaCl_2$ is much less efficient due to its lower polarity. The $CaCl_2$ by-product was completely removed when formamide was used as an extraction solvent. The EDS spectrum, Figure 3, has no detectable chlorine peaks implying an upper limit of 1 at% for the chlorine content. A small amount of CaO impurity was also present; this may be due to the presence of CaO in the commercially obtained CaSi. Figure 3 also shows a TEM image obtained from a reaction with 50% diluent loading. Mechanically driven reaction can suffer from iron contamination when steel is used for the media and reaction vessel. Using iron-free milling materials such as alumina and tungsten carbide can eliminate this. However, there were no measureable iron peaks in the EDS spectrum, implying an upper limit for iron contamination of 1 at%. The particle size ranged from 20 nm to 100 nm with crystalline regions as small as 5 nm.

In conclusion, unfunctionalized zirconium disilicide nanomaterials of varying sizes were synthesized through a mechanochemical metathesis reaction. The crystallite sizes ranged from 9 to 30 nm depending on the amount of diluent used. Removal of the diluent and salt product using formamide resulted in isolation of polydisperse nanoparticles without capping groups or a passivating oxide layer. Oxygen-free $ZrSi_2$ could be produced by utilizing ultrapure CaSi. This would allow for nanoelectroceramic particles of the desired size to be incorporated into a composite as a reinforcement material for the improvement of high temperature thermoelectric materials and a variety of other applications.

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Notes and references

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‡ Powder X-ray diffraction (PXRD) was performed using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu $K_{\alpha1}$ = 1.5418Å). Diffractograms were collected from 5 to 80 degrees 2θ using 0.010-degree steps and 0.3 seconds of dwell time.

Transmission electron spectroscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) were performed using an FEI Technai F30 transmission electron microscope operating at an accelerating voltage of 300 kV.

1. I.-J. Shon, J.-H. Park, J.-K. Yoon and H.-K. Park, *Mater. Res. Bull.*, 2009, **44**, 1462-1467.
2. I.-Y. Ko, J.-H. Park, J.-K. Yoon, K.-S. Nam and I.-J. Shon, *Ceram. Int.*, 2010, **36**, 817-820.
3. V. S. Neshpor and G. V. Samsonov, *Dokl. Akad. Nauk SSSR*, 1960, **134**, 1337-1338.
4. A. Memarpour, V. Brabie and P. G. Joensson, *ISIJ Int.*, 2010, **50**, 1612-1621.
5. O. N. Grigoriev, B. A. Galanov, V. A. Kotenko, S. M. Ivanov, A. V. Koroteev and N. P. Brodnikovsky, *J. Eur. Ceram. Soc.*, 2010, **30**, 2173-2181.
6. K. Pomoni and J. Salmi, *J. Phys. D: Appl. Phys.*, 1991, **24**, 727-730.
7. I.-J. Cho, K.-T. Park, S.-K. Lee, H. H. Nersisyan, Y.-S. Kim and J.-H. Lee, *Chemical Engineering Journal*, 2010, **165**, 728-734.
8. Y. Ma, R. Heijl and A. C. Palmqvist, *Journal of Materials Science*, 2012, 1-12.
9. H. J. Kim, in *47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit 9th Annual International Energy Conversion Engineering Conference*, AIAA/ASME/SAE/ASEE, San Diego, CA, 2011, vol. Manuscript ID: 1027521.
10. N. Mingo, D. Hauser, N. P. Kobayashi, M. Plissonnier and A. Shakouri, *Nano Letters*, 2009, **9**, 711-715. KumakuraKumakura
11. W. Luo, H. Li, Y. Yan, Z. Lin, X. Tang, Q. Zhang and C. Uher, *Intermetallics*, 2011, **19**, 404-408.
12. A. V. Tkachenko and T. Y. Kosolapova, *Powder Metallurgy and Metal Ceramics*, 1968, **7**, 178-181.
13. V. V. Malyshev, N. N. Uskova and V. I. Shapoval, *Powder Metall. Met. Ceram.*, 1997, **36**, 289-292.
14. Y. Bing K, *Journal of Alloys and Compounds*, 1998, **268**, 266-269.
15. J. Canel, J. Zaman, J. Bettembourg, F. M. Le and S. Poissonnet, *Int. J. Appl. Ceram. Technol.*, 2006, **3**, 23-31.
16. I. P. Parkin, *Chemical Society Reviews*, 1996, **25**, 199-207.
17. R. M. Jacubinas and R. B. Kaner, *Mater. Res. Soc. Symp. Proc.* , 1994, **322**, 133-137.
18. E. Ivanov and C. Suryanarayana, *Journal of Materials Synthesis and Processing*, 2000, **8**, 235-244.
19. P. G. McCormick, T. Tsuzuki, J. S. Robinson and J. Ding, *Advanced Materials*, 2001, **13**, 1008-1010.
20. P. Baláž, E. Boldižárová, E. Godočıková and J. Briančin, *Materials Letters*, 2003, **57**, 1585-1589.
21. C. Chakurov, V. Rusanov and J. Koichev, *Journal of Solid State Chemistry*, 1987, **71**, 522-529.
22. J. Ding, T. Tsuzuki, P. G. McCormick and R. Street, *Journal of Alloys and Compounds*, 1996, **234**, L1-L3.
23. J. Ding, T. Tsuzuki, P. G. McCormick and R. Street, *Journal of Physics D: Applied Physics*, 1996, **29**, 2365.
24. R. A. Janes, M. Aldissi and R. B. Kaner, *Chemistry of Materials*, 2003, **15**, 4431-4435.
25. S. M. Hick, C. Griebel and R. G. Blair, *Inorg. Chem.*, 2009, **48**, 2333-2338.
26. S. K. Bux, M. T. Yeung, E. S. Toberer, G. J. Snyder, R. B. Kaner and J.-P. Fleurial, *Journal of Materials Chemistry*, 2011, **21**, 12259-12266.
27. P. Matteazzi, F. Miani, G. Le Caër and E. Bauer-Grosse, *Euromat 91; Proceedings of the 2nd European Conference on Advanced Materials and Processes*, 1992, **2**, 359.
28. A. V. Dushkin, *Chem. Sust. Dev.*, 2004, **12**, 251-273.
29. C. Suryanarayana *Progress in Materials Science*, 2001, **46**, 1-184.
30. A. M. Nartowski and I. P. Parkin, *Polyhedron*, 2002, **21**, 187-191.
31. E. Wedekind, *Zeitschrift fuer Chemie und Industrie der Kolloide*, 1911, **7**, 249-251.