J|A|C|S
COMMUNICATIONS

Preparation and Crystal Growth of $Na_{24}Si_{136}$

Matt Beekman,[†] Michael Baitinger,[‡] Horst Borrmann,[‡] Walter Schnelle,[‡] Katrin Meier,[‡]
George S. Nolas,[*,†] and Yuri Grin[*,‡]

Department of Physics, University of South Florida, Tampa, Florida 33620, and Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

Received May 1, 2009; E-mail: grin@cpfs.mpg.de; gnolas@usf.edu

Intermetallic clathrates[1] constitute a class of materials displaying a variety of intriguing phenomena, such as glasslike thermal conductivity, and wide ranging electrical transport properties, from metals to semiconductors to superconductors.[2] Clathrates are actively investigated due to their potential for thermoelectric power generation[3] as well as for optoelectronics.[4] The unique features of the cage crystal structures are intimately related to their above-mentioned physical properties, offering ideal systems for study of structure−property relationships in crystalline solids.

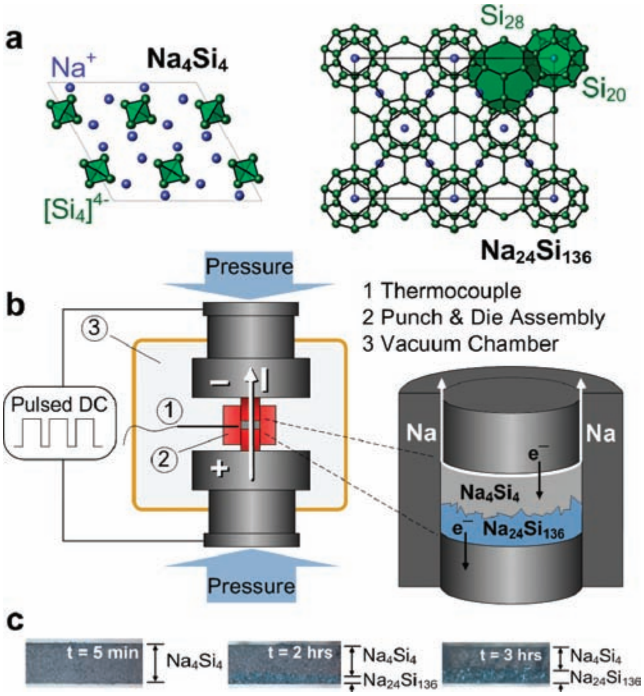

Figure 1. (a) Crystal structures of Na_4Si_4 and clathrate-II $Na_{24}Si_{136}$. Si_{20} and Si_{28} cages and Si_4 tetrahedrons are highlighted. (b) Spark plasma treatment setup. (c) Cross sections of SPS-treated specimens at 600 °C and 100 MPa.

A variety of conventional synthesis techniques have been employed in the preparation and crystal growth of intermetallic clathrates.[5−8] However, the preparation is exceedingly challenging for materials comprised of elemental constituents having greatly differing melting points and/or vapor pressures or where growth from the melt is generally not possible. In many cases such phases can be synthesized in bulk by controlled thermal decomposition of binary or ternary precursors under vacuum or inert atmosphere.[1] Recently, chemical oxidation of such precursors with appropriate agents emerged as a promising technique for the preparation of clathrates that are not accessible by other methods.[9] The clathrate products prepared by these techniques are typically microcrystalline powders.

The spark plasma sintering (SPS) technique has in little more than a decade become a state-of-the-art method for consolidation of polycrystalline materials.[10] Despite the clear role of diffusion-driven material transport within the green body, application of SPS as a method for synthesis of materials, in particular the benefits of the electric field for this purpose, is still in its infancy, especially regarding bulk crystal growth by this processing technique.[10c,d]

In the present work, sodium monosilicide[11] Na_4Si_4 (Figure 1a) was chosen as a reaction precursor for its known high reactivity in promoting the formation of the intermetallic clathrates $Na_{8-x}Si_{46}$ ($0 < x < 1$) and $Na_{24-x}Si_{136}$ ($0 < x < 24$), as evidenced from both thermal decomposition[1,12] and chemical oxidation studies.[9b] Clathrate-II $Na_{24-x}Si_{136}$ is currently of considerable interest due to its intriguing structural and physical properties,[13] yet the synthesis of high quality specimens for physical properties characterization remained challenging.[12]

Crystal growth and preparation of $Na_{24}Si_{136}$ was achieved by SPS processing of Na_4Si_4 at 550−700 °C for 3 h, under a uniaxial pressure of 100 MPa. The pulsed DC electrical current (with a possible range of 0 to 1500 amperes, depending upon the temperature to be achieved) was sourced through the specimen (green body) and die from the bottom electrode (anode) to the top electrode (cathode), which simultaneously acted for application of uniaxial pressure to the green body (Figure 1b). The specimen, die, punches, and electrodes are enclosed inside a vacuum chamber and maintained under dynamic vacuum (10^{-2} Torr). The whole setup was located inside an argon-filled glovebox for complete protection against oxidation and moisture.

Single-phase products were obtained at 600 °C. The products of reactions at 550 °C contain ca. 5 to 10 mass % of the clathrate-I Na_8Si_{46} (from Rietveld refinement), while reactions performed at 700 °C yield a similar fraction of α-Si. During the spark plasma treatment, a thin film of Na was always observed to condense on the cathode (Figure 1b). The clathrate formation initiates from the anode and progresses toward the cathode (Figure 1c). The bluish crystals of $Na_{24}Si_{136}$, discernible in the bottom portion of the compact, increase in fraction as the reaction is allowed to progress for a longer duration of time. The growth of the $Na_{24}Si_{136}$ crystalline specimens is completely reproducible. The residual Na_4Si_4 precursor, spatially occupying the top part of the SPS compact, is readily removed from the products by washing with ethanol and distilled water under flowing argon allowing isolation of $Na_{24}Si_{136}$.[14] Sizable single crystals are formed (Figures 2, S1). Energy dispersive X-ray spectroscopy detected only Na and Si in the crystals, with the composition $Na_{22(1)}Si_{136}$ in fair agreement with $Na_{24}Si_{136}$ determined from single crystal XRD. The findings above clearly suggest an

---

[†] University of South Florida.
[‡] Max-Planck-Institut für Chemische Physik fester Stoffe.

10.1021/ja903362b CCC: $40.75

influence of the DC electrical current. At this stage we propose that $Na_{24}Si_{136}$ forms by oxidation of Si_4^{4-} at the anode, whereas sodium is reduced at the cathode. Upon oxidation of the Si_4^{4-} cluster anions, the clathrate framework is formed, while simultaneously encapsulating sodium in the resulting Si_{20} and Si_{28} cages of the silicon framework (Figure 1a). The process is driven by the electric field and the evaporation of Na formed at the cathode.

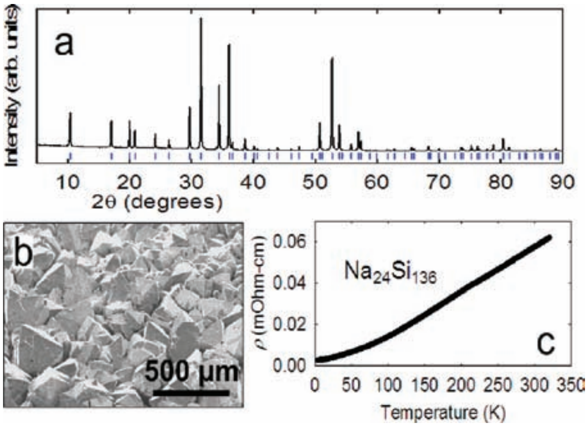

Figure 2. (a) Powder X-ray diffraction pattern (Cu $K_{\alpha1}$ radiation); tick marks represent calculated reflection positions. (b) Scanning electron microscope image of $Na_{24}Si_{136}$ crystals prepared at 600 °C. (c) Electrical resistivity *vs* temperature of as-grown single crystal of $Na_{24}Si_{136}$.

The PXRD pattern of a $Na_{24}Si_{136}$ product (Figure 2a) corroborates the phase purity of the specimen. All reflections are indexed with the cubic lattice of the clathrate-II crystal structure (space group $Fd\bar{3}m$). The unit cell parameter $a = 14.7157(2)$ Å is in general agreement with the previously reported trend[12] extrapolated to $x = 0$.

The crystal structure of the $Na_{24}Si_{136}$ clathrate was investigated in detail on the prepared single crystals. The low residuals of the structure refinement ($R1 = 0.015$ ($I > 4\sigma I$), Table S1) are indicative of the high quality of the acquired data.[15] All silicon framework sites are found to be completely occupied, and both sodium sites show full occupancy within the standard deviations, giving the chemical composition $Na_{24}Si_{136}$. A very large atomic displacement parameter was observed for Na2 centered in the Si_{28} cage. A difference Fourier map calculated with Na2 removed from the model shows only a broadly smeared, essentially spherical residual density with a clear maximum at the center of the cage (Figure S2). Although no improvement in the residuals was obtained implementing a split model for the description of the electron density within the cages (Tables S1−S5), it reflects rather a thermal motion ("rattling"[2,3,5−7,13]). In light of previous high resolution transmission electron microscopy investigations[16] on $Na_{24-x}Si_{136}$ specimens prepared by thermal decomposition of Na_4Si_4, which revealed a significant amount of {111} twins and stacking defects, it is noteworthy that the growth of large crystals without such defects is achieved by the spark plasma treatment.

Accurate measurements of electrical transport on $Na_{24-x}Si_{136}$ were previously highly challenging,[1b,13] due to difficulties in preparation of dense specimens, free from detrimental grain boundary effects. The temperature dependence and magnitude of the electrical resistivity measured on a single crystal (Figure 2c) indicate metallic behavior for $Na_{24}Si_{136}$, as expected for a filled silicon clathrate, and constitute the intrinsic electrical behavior of $Na_{24}Si_{136}$ free from interfacial and grain boundary contributions.

To summarize, the spark plasma treatment is identified as the first route for the synthesis and crystal growth of completely filled intermetallic clathrate-II $Na_{24}Si_{136}$. The reported process, we believe, is an electrochemical variant of the redox reactions of precursor phases.[9] Understanding the mechanism of such processes should be the focus of further investigations. The approach demonstrated herein also reveals a new general method for the preparation and crystal growth of materials.

Acknowledgment. M.B. and G.S.N. acknowledge support from US DOE Grant No. DE-FG02-04ER46145. M.B. also acknowledges support from DAAD. The authors would like to acknowledge R. Cardoso Gil, R. Koban, P. Scheppan, and S. Müller for their support and technical assistance as well as B. Böhme for useful discussions.

Supporting Information Available: Experimental details, crystallographic data, safety recommendations; Figures S1−S3; Tables S1−S5; supporting references. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kasper, J. S.; Hagenmuller, P.; Pouchard, M.; Cros, C. *Science* **1965**, *150*, 1713. (b) Cros, C.; Pouchard, M.; Hagenmuller, P. *J. Solid State Chem.* **1970**, *2*, 570.
(2) (a) Cohn, J. L.; Nolas, G. S.; Fessatidis, V.; Metcalf, T. H.; Slack, G. A. *Phys. Rev. Lett.* **1999**, *82*, 779. (b) Hermann, R. P.; Keppens, V.; Bonville, P.; Nolas, G. S.; Grandjean, F.; Long, G. J.; Christen, H. M.; Chakoumakos, B. C.; Sales, B. C.; Mandrus, D. *Phys. Rev. Lett.* **2006**, *97*, 017401. (c) Kawaji, H.; Horie, H.-O.; Yamanaka, S.; Ishikawa, M. *Phys. Rev. Lett.* **1995**, *74*, 1427.
(3) (a) Nolas, G. S.; Cohn, J. L.; Slack, G. A.; Schujman, S. B. *Appl. Phys. Lett.* **1998**, *73*, 178. (b) Nolas, G. S.; Slack, G. A.; Schujman, S. B. In *Semiconductors and Semimetals*; Tritt,T. M., Ed.; Academic Press: San Diego, 2000; Vol. 69, pp 255−300. (c) Paschen, S.; Carrillo-Cabrera, W.; Bentien, A.; Tran, V. H.; Baenitz, M.; Grin, Yu.; Steglich, F. *Phys. Rev. B* **2001**, *64*, 214404.
(4) Gryko, J.; McMillan, P. F.; Marzke, R. F.; Ramachandran, G. K.; Patton, D.; Deb, S. K.; Sankey, O. F. *Phys. Rev. B* **2000**, *62*, R7707.
(5) Sales, B. C.; Chakoumakos, B. C.; Jin, R.; Thompson, J. R.; Mandrus, D. *Phys. Rev. B* **2001**, *63*, 245113.
(6) (a) Condron, C. L.; Martin, J.; Nolas, G. S.; Piccoli, P. M. B.; Schultz, A. J.; Kauzlarich, S. M. *Inorg. Chem.* **2006**, *45*, 9381. (b) Neiner, D.; Okamoto, N. L.; Condron, C. L.; Ramasse, Q. M.; Yu, P.; Browning, N. D.; Kauzlarich, S. M. *J. Am. Chem. Soc.* **2007**, *129*, 13857. (c) Suekuni, K.; Avila, M. A.; Umeo, K.; Fukuoka, H.; Yamanaka, S.; Nakagawa, T.; Takabatake, T. *Phys. Rev. B* **2008**, *77*, 235119.
(7) Christensen, M.; Abrahamsen, A. B.; Christensen, N. B.; Juranyi, F.; Andersen, N. H.; Lefmann, K.; Andreasson, J.; Bahl, C. R. H.; Iversen, B. B. *Nat. Mater.* **2008**, *7*, 811.
(8) Yamanaka, S.; Enishi, E.; Fukuoka, H.; Yasukawa, M. *Inorg. Chem.* **2000**, *39*, 56.
(9) (a) Guloy, A. M.; Ramlau, R.; Tang, Z.; Schnelle, W.; Baitinger, M.; Grin, Yu. *Nature* **2006**, *443*, 320. (b) Böhme, B.; Guloy, A. M.; Tang, Z.; Schnelle, W.; Burkhardt, U.; Baitinger, M.; Grin, Yu. *J. Am. Chem. Soc.* **2007**, *129*, 5348. (c) Böhme, B.; Aydemir, U.; Ormeci, A.; Schnelle, W.; Baitinger, M.; Grin, Yu. *Sci. Techn. Adv. Mat.* **2007**, *8*, 410.
(10) (a) Tokita, M. *J. Soc. Powder Tech. Jpn.* **1993**, *30*, 790. (b) Munir, Z. A.; Anselmi-Tamburini, U.; Ohyanagi, M. *J. Mater. Sci.* **2006**, *41*, 763. (c) Omori, M. *Mater. Sci. Eng., A* **2000**, *287*, 183. (d) Schmidt, J.; Boehling, N.; Burkhardt, U.; Grin, Yu. *Sci. Technol. Adv. Mat.* **2007**, *8*, 410.
(11) (a) Witte, J.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1964**, *327*, 260. (b) Goebel, T.; Prots, Yu.; Haarmann, F. *Z. Kristallogr. NCS* **2008**, *223*, 187.
(12) (a) Ramachandran, G. K.; Dong, J. J.; Diefenbacher, J.; Gryko, J.; Marzke, R. F.; Sankey, O. F.; McMillan, P. F. *J. Solid State Chem.* **1999**, *145*, 716. (b) Reny, E.; Gravereau, P.; Cros, C.; Pouchard, M. *J. Mater. Chem.* **1998**, *8*, 2839. (c) Horie, H.; Kikudome, T.; Teramura, K.; Yamanaka, S. *J. Solid State Chem.* **2009**, *182*, 129.
(13) Beekman, M.; Nolas, G. S. *J. Mater. Chem.* **2008**, *18*, 842.
(14) See Safety Recommendations S3.
(15) Crystallographic data: space group $Fd\bar{3}m$; $a = 14.7157(2)$ Å; Na1 in 16(c) 0 0 0, $U_{eq} = 0.0214(2)$ Å; Na2 in 8(b) 3/8 3/8 3/8, $U_{eq} = 0.110(2)$ Å; Si1 in 8(a) 1/8 1/8 1/8, $U_{eq} = 0.0084(2)$ Å; Si2 in 32(e) xxx, $x = 0.21797(3)$, $U_{eq} = 0.00880(8)$ Å; Si3 in 96(g) xxz, $x = 0.06735(2)$, $z = 0.37133(3)$, $U_{eq} = 0.00863(8)$ Å; cf. Tables S1−S5.
(16) Nistor, L.; van Tendeloo, G.; Amelinckx, S.; Cros, C. *Phys. Status Solidi A* **1994**, *146*, 119.

JA903362B