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Rapid Crystal Growth of Type-II Clathrates $A_8Na_{16}Si_{136}$ (A = K, Rb, Cs) by Spark Plasma Sintering

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Single crystal type-II clathrates $A_8Na_{16}Si_{136}$ (A = K, Rb, and Cs) were grown from NaSi and alkali metal halides by spark plasma sintering (SPS). Single crystal structure refinements indicate that K atoms at the 8*b* crystallographic site are partially occupied ($K_{5.8(1)}Na_{16}Si_{136}$) while Rb in $Rb_8Na_{16}Si_{136}$ and Cs in $Cs_8Na_{16}Si_{136}$ are fully occupied. Our results indicate that SPS can be employed in topochemical ion exchange reactions, thus allowing for the rapid synthesis of single crystals of multinary intermetallic phases that cannot be accessible by traditional crystal growth techniques.

Inorganic clathrates based on group 14 elements have attracted attention due to their interesting structural and physical properties, for example very low thermal conductivities,[1-3] tunable electrical properties and band gaps with modification of composition,[4,5] and second-order ferromagnetic phase transitions.[6-8] As a result, they are of interest for a variety of potential technological applications, including solid state energy conversion,[1-3,9] photovoltaics,[10,11] magnetocalorics,[12-14] superconductivity,[15-17] and as the anode for Li-ion batteries.[18-20]

Due to this scientific interest and technological importance an understanding of the fundamental structural and physical properties of inorganic clathrates is essential. In order to achieve this goal various synthetic techniques have been employed to obtain stable or metastable compositions that are not accessible by conventional solid state reaction or single-crystal growth methods. These include soft chemical routes (chemical oxidation),[21-23] kinetically controlled thermal decomposition,[24,25] high-temperature high-pressure synthesis,[26,27] and spark plasma sintering (SPS).[28,29]

Among the synthetic approaches described above, SPS is unique in that it applies a pulsed DC current to the specimen through a die assembly that is between two electrodes under uniaxial pressure. SPS processing is well established for the consolidation of ceramics, polymers, semiconductors, and nanocomposites due to the fast heating rates and uniform heating through the specimen inside the die assembly.[30-36] Recently crystal growth of binary type-I and -II clathrates, Na_8Si_{48} and $Na_{24}Si_{136}$, by SPS was achieved.[28,29] In this report we demonstrate that ternary type-II clathrate single crystals can be synthesized via ion-exchange and electrochemical oxidation-reduction (redox) reactions between NaSi and ACl (A = K, Rb, Cs) using SPS. This approach will also be of interest for the synthesis and crystal growth of other intermetallic or metastable ternary, and potentially quaternary, compounds.

Single crystals of three type-II clathrates, $K_{5.8(1)}Na_{16}Si_{136}$, $Rb_8Na_{16}Si_{136}$, and $Cs_8Na_{16}Si_{136}$, were synthesized by SPS. The NaSi precursor along with each alkali-metal chloride were ground together in a 1:1 mass ratio and the resulting mixture was loaded in a graphite die assembly. Tantalum foil was placed between the precursor mixture and the graphite die and punches to prevent direct reaction with the die and punches as well as to provide a tight fit of the die assemble. After mounting this assembly into the SPS reaction chamber, the chamber was evacuated and flushed three times with high-purity N_2. Pulsed DC current (with a pulse-on and -off time of 36 and 2 ms, respectively) was sourced through the precursor mixture and die assembly while under a uniaxial pressure of 100 MPa in a vacuum of 10 mTorr. The dwell time at the desired temperature (600 ºC for $K_{5.8(1)}Na_{16}Si_{136}$, 565 ºC $Rb_8Na_{16}Si_{136}$, and 500 ºC for $Cs_8Na_{16}Si_{136}$) for each reaction was 1.5 hr. The product of each reaction was separated from any unreacted NaSi and ACl by washing with ethanol and distilled water.[28] Figure 1 shows the schematic diagram of the SPS experimental setup and an SEM image of $Rb_8Na_{16}Si_{136}$ crystals grown by this approach.

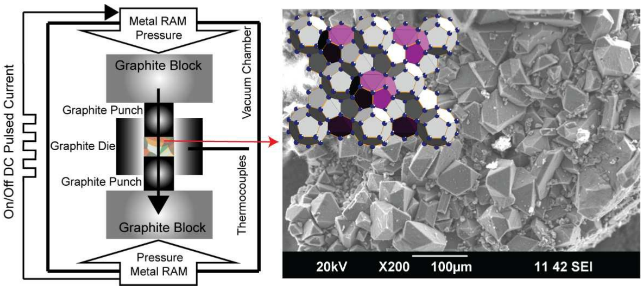

FIGURE 1. Schematic diagram of the SPS approach (left). SEM image of single crystals grown by SPS together with the type-II crystal structure ($Rb_8Na_{16}Si_{136}$ crystals are shown) composed of Si_{28} (purple) and Si_{20} (gray) polyhedra encapsulating Rb and Na, respectively (right).

Figure 2 shows SEM images of the single crystal morphologies and powder XRD patterns from crushed single crystals for each clathrate specimen. Crystals of up to 100 µm on each side were obtained at 550 ºC for $K_{5.8(1)}Na_{16}Si_{136}$ (Fig. 2(a)) and $Rb_8Na_{16}Si_{136}$ (Fig. 2(c)), while smaller crystals were obtained for $Cs_8Na_{16}Si_{136}$ (Fig. 2(e)). The powder XRD patterns from the crushed single crystals are in excellent agreement with that of the simulated patterns, also shown in Figure 2. The compositions of each specimen were determined by single-crystal XRD. The crystallographic details, atomic positions, and anisotropic displacement parameters can be found in the supporting information and CIF file. Energy dispersive spectroscopy results, obtained from six to eight data sets from four different crystals for each SPS run, corroborated these results.

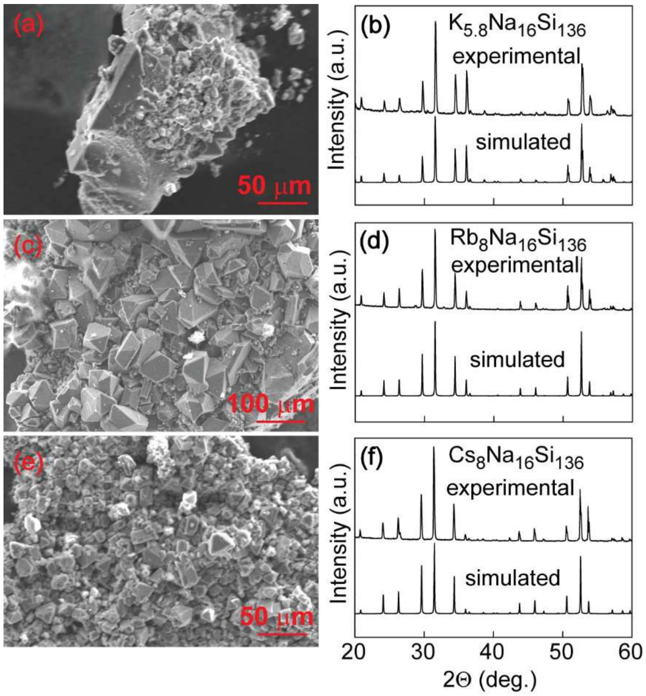

FIGURE 2. SEM images of the clathrate single crystals and powder XRD patterns from crushed single crystals for (a) and (b) $K_{5.8(1)}Na_{16}Si_{136}$, (c) and (d) $Rb_8Na_{16}Si_{136}$, and (e) and (f) $Cs_8Na_{16}Si_{136}$, along with their simulated powder pattens.

Clathrates can have a wide range of stoichiometries for the guest atom sites, hence site occupancy refinement was carried out for all alkali metal sites. The atomic displacement parameters (ADPs) of Rb in $Rb_8Na_{16}Si_{136}$ and Cs in $Cs_8Na_{16}Si_{136}$ are relatively small with U_{eq} = 0.0296 Å^2 and U_{eq} = 0.0168 Å^2, respectively, and very similar to those previously reported.[37-39] The potassium atoms in $K_{5.8(1)}Na_{16}Si_{136}$ have room temperature ADP values that are 2 to 3 times larger (U_{eq} = 0.0695 Å^2) implying that the K atom is either disordered over several close sites or that the position is partially occupied. Our results indicate that the K atoms likely partially occupy the Si_{28} polyhedra[25] while possessing a more dynamic disorder inside the Si_{28} polyhedra, as compared with that of Rb and Cs in the other clathrates,[37-40] due to its relatively smaller ionic size (details in the SI). A fragment of the crystal structure of $K_{5.8(1)}Na_{16}Si_{136}$ depicting the Si_{28} and Si_{20} polyhedra is shown in Figure 3.

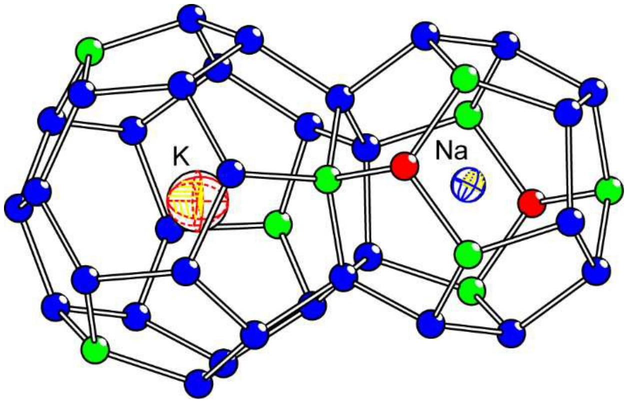

FIGURE 3. Hexakaidekahedron (Si_{28}) and dodecahedron (Si_{20}) with corresponding alkali metal atoms in $K_{5.8(1)}Na_{16}Si_{136}$. Thermal ellipsoids for K (8*b*) and Na (16*c*) are 90 % probability. Blue, green, and red atoms indicate Si on the 96*g*, 32*e*, and 8*a* crystallographic sites, respectively.

Beekman et al[28] proposed that the driving mechanism for $Na_{24}Si_{136}$ crystal growth from NaSi by SPS is an electrochemical redox reaction caused by the applied electrical current passing through the specimen during SPS. In that reaction the NaSi precursor acts like a solid electrolyte that is capable of sodium transport toward the cathode. Our results also suggest an influence on the crystal growth by the pulsed DC current; however, in this process an electrochemical redox reaction occurs simultaneously with an ion-exchange reaction. Considering that the reaction occurs completely, we postulate that the reaction process is as follows: 136 NaSi + 8 ACl → $A_8Na_{16}Si_{136}$ + 8 NaCl + 112 Na. Here, tetrahedral Si_4^{4-} units from the NaSi precursor start to oxidize to form Si_{136}^{24-} at the anode while elemental Na is formed by reduction of Na^+ ions at the cathode through an electrochemical redox reaction. During this process Na^+ ions also react with ACl to form NaCl allowing K, Rb or Cs, together with the remaining Na atoms, to be available for encapsulation in the resulting polyhedra of the clathrate framework. Our results also indicate that reaction time does not substantially affect the yield or size of the single crystals. We note that the polycrystalline ternary silicide compound Li_3NaSi_6[41] was synthesized by this approach when using LiCl and NaSi mixtures as the precursor, instead of lithium containing clathrate crystals.

Conclusions

Single crystals of a new ternary type-II clathrate, $K_{5.8(1)}Na_{16}Si_{136}$, as well as $Rb_8Na_{16}Si_{136}$ and $Cs_8Na_{16}Si_{136}$ type-II clathrates were synthesized by using a mixture of NaSi and ACl as the precursor for ion-exchange/electrochemical redox reactions by SPS. Our SPS synthetic approach can reproduce these crystals easily and rapidly. The K atom in $K_{5.8(1)}Na_{16}Si_{136}$ was refined at the center of the Si_{28} hexakaidekahedra without static disorder. This approach may also be applied to the synthesis and crystal growth of other multinary intermetallic compositions in addition to multinary clathrates.

Notes

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† Electronic Supplementary Information (ESI) available: Characterization and crystallographic data in CIF format (CSD 428367 for $K_{5.8(1)}Na_{16}Si_{136}$, CSD 428368 for $Rb_8Na_{16}Si_{136}$, and CSD 428369 for $Cs_8Na_{16}Si_{136}$). The data may be obtained free of charge by contacting F.I.Z. Karlsruheat +49 7247 808 666 (fax) or crysdata@fiz-karlsruhe.de (email). See DOI: 10.1039/c000000x/

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Single crystals of clathrate–II $A_8Na_{16}Si_{136}$ (A = K, Rb, Cs) were synthesized by spark plasma sintering by simultaneous electrochemical redox and ion–exchange reactions.