Supporting Information

Rapid Crystal Growth of Type-II Clathrates

$A_8Na_{16}Si_{136}$ (A = K, Rb, and Cs) by Spark Plasma Sintering

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Characterization and Refinement

Powder X-ray diffraction (XRD) data of the crushed single crystals were collected with a Bruker D8 Focus diffractometer in Bragg-Brentano geometry using Cu Kα radiation and a graphite monochromator.   Energy dispersive X-ray analysis (EDX) of the single crystals was accomplished with an Oxford INCA X-Sight 7582 M equipped scanning electron microscope (SEM, JEOL JSM-6390LV). Single crystal XRD data for the three clathrate compositions were collected using a Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu Kα INCOATEC Imus micro-focus source (λ = 1.54178 Å). The initial cubic cell constants and orientation matrix were obtained by using APEX2 (Difference Vectors method).[1]   Data integration and reduction were performed using SaintPlus 6.01.[2]   An empirical absorption correction was performed by multi-scan method implemented in SADABS.[3] The initial input files for solving the crystal structure were prepared by XPREP implemented in APEX2.[1] The

structure was solved using SHELXS-97 (direct methods)[4] and refined using SHELXL-97 (full-matrix least-squares techniques)[4] contained in the WinGX program package.[5]

Several crystals were selected for investigation of the crystal uniformity and to determine the unit cell parameters. The compositions crystallize in the cubic space group $Fd\bar{3}m$ (#227), with one independent position for the alkali metal on the crystallographic 8b site, one for Na on the 16c site, and three for Si atoms on 96g, 32e, and 8a sites. The atomic parameters during refinement were standardized by using the program STRUCTURE TIDY.[6] No additional symmetry was found using the ADDSYM[7] algorithm in the PLATON[8] program of packages.

Initially the site occupancy refinement for $K_{5.8(1)}Na_{16}Si_{136}$ resulted in K possessing an abnormally large ADP (U_{eq} = 0.105 Å^2) while the minimum (-1.50 e / Å^3) residual peaks were very close to that of the K atomic site (wR2 and R1 for $K_{5.8(1)}Na_{16}Si_{136}$ were 0.0949 and 0.0289, respectively). The site occupancy factors for K were therefore refined while the occupancies of the other sites were fixed. This resulted in a stoichiometry of $K_{5.8(1)}Na_{16}Si_{136}$ with wR2 and R1 being 0.0434 and 0.0168, respectively, and the minimum residual peak being away from the K atom with an ADP value (U_{eq} = 0.0695 Å^2) 2 or 3 times larger for K than that of Rb and Cs in the other clathrate compositions. Truncation errors (2Θ = 144.6º) or an error in using empirical absorption corrections for irregular shaped geometries are always possible however a split site model and mixed site model (Na/K at one site) did not result in an improvement of these refinement results.

References

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