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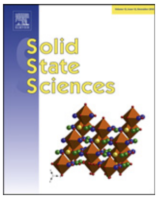

Crystal growth of uranium-containing complex oxides: $Ba_2Na_{0.83}U_{1.17}O_6$, $BaK_4U_3O_{12}$ and $Na_3Ca_{1.5}UO_6$

Irina P. Roof, Mark D. Smith, H.-C. zur Loye*

University of South Carolina, Columbia, SC 29208, USA

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ABSTRACT

Single crystals of complex uranium oxides, $Ba_2Na_{0.83}U_{1.17}O_6$, $BaK_4U_3O_{12}$ and $Na_3Ca_{1.5}UO_6$, were grown out of reactive carbonate melts. The crystal structures the three uranates were determined by single crystal X-ray diffraction. $Ba_2Na_{0.83}U_{1.17}O_6$ crystallizes in the $Fm\bar{3}m$ space group, $a = 8.6173(1)$, with a disordered cubic double perovskite structure. $BaK_4U_3O_{12}$ forms in the cubic $Im\bar{3}m$ space group, $a = 8.7232(1)$, with the asymmetric unit consisting of three metal positions, which shows improvement of the structure refinement from the published results. $Na_3Ca_{1.5}UO_6$ crystallizes in the orthorhombic *Fddd* space group with $a = 6.6573(2)$, $b = 9.6111(3)$ and $c = 20.1155(5)$ in a rock salt superstructure. In all three oxides the U (VI) cation is octahedrally coordinated. While the UO_6 octahedra in $Ba_2Na_{0.83}U_{1.17}O_6$ are undistorted due to oxygen disorder, the UO_6 octahedra in $BaK_4U_3O_{12}$ and $Na_3Ca_{1.5}UO_6$ feature the typical uranyl geometry with four long two short U–O bonds.

1. Introduction

Molten carbonates have proven to be an excellent medium for the growth of high quality single crystals of a wide variety of complex metal oxides. Recently, we extended the use of molten carbonates into the rich uranium chemistry where we were able to grow crystals of several uranium-containing double perovskites, Sr_3UO_6 and Ba_2MUO_6 (M = Cu, Ni, Zn) [1] Uranium-containing oxides have been of interest for decades [2], and simple binary and ternary uranium-containing species, such as alkali metal-uranium oxides, have been extensively studied, analyzed and reviewed [3–5]. This investigation of binary and ternary phases, driven by both fundamental and practical reasons, has resulted in a fairly extensive library of known uranium-containing oxides [6]. Fundamentally, uranium has the interesting ability to form uranyl species that in turn, can organize into low-dimensional materials with chains or layers of the uranium–oxygen polyhedral networks [4]. Alternatively, uranium can also be found in ideal, undistorted octahedral coordination. From a practical standpoint, uranium-containing oxides are important for the nuclear industry, for long-term nuclear fuel storage, for catalytic applications, as well as for the investigation of its radiochemistry [4,7]. For these reasons it is of interest to continue to investigate the structure–property relationships of known oxides and to put a deliberate effort towards the synthesis and characterization of new uranium-containing species.

Solid-state powder synthesis continues to be the most widely used synthetic approach for the preparation of complex uranium oxides, especially if the preparation of larger quantities of the oxides is required. Of course, solid-state preparative methods have their limitations in the discovery process of new oxides, especially with respect to the ease of structure determinations. Consequently, new synthetic approaches are desired that can lead to single crystals of new compositions for structure determinations. It is known that molten carbonates are very effective for the dissolution of simple uranium oxides and for the successive recrystallization of more complex uranium-containing materials [1,5]. Molten flux crystal growth can readily result in high quality single crystals of uranium-containing oxides as well as lead to more precise structure determinations of known compounds that have previously only been prepared as powders. In addition, the relatively low temperature flux method can stabilize kinetic phases, which can promote the formation of new compositions and structures.

Herein, we report on the synthesis of three uranium-containing oxides, $Ba_2Na_{0.83}U_{1.17}O_6$, $Na_3Ca_{1.5}UO_6$, and $BaK_4U_3O_{12}$, all prepared as single crystals in molten carbonate fluxes. $Ba_2Na_{0.83}U_{1.17}O_6$ and $Na_3Ca_{1.5}UO_6$ represent new uranium-containing oxides and their structures are reported for the first time. $BaK_4U_3O_{12}$, on the other hand, was previously prepared in powder form [8] and we are reporting its single crystal structure herein.

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* Corresponding author. Tel.: +1 803 777 6916; fax: +1 803 777 8508.
E-mail address: zurloye@mail.chem.sc.edu (H.-C. zur Loye).

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2. Experimental details

2.1. Crystal growth

Single crystals of $Ba_2Na_{0.83}U_{1.17}O_6$ and $Na_3Ca_{1.5}UO_6$ were grown out of molten sodium carbonate. 1/3 mmol of U_3O_8 (Strem Chemicals, 99.8%), 3 mmol of Ba_2CO_3 (Alfa, 99.95%) or $CaCO_3$ (Alfa, 99.0%) and 12 g of Na_2CO_3 (Mallinckrodt Chemicals, A.C.S grade, 99.5%) flux were loaded into alumina crucibles loosely covered with alumina lids. The charges were placed into a tube furnace and heated to 1050 °C at 600 °C/h. The furnace was held at the target reaction temperature for 24 h, after which time it was cooled to 800 °C at a rate of 15 °C/h and subsequently cooled to room temperature by shutting off the furnace.

Single crystals of $BaK_4U_3O_{12}$ were grown out of molten potassium carbonate. 1/3 mmol of U_3O_8 (Strem Chemicals, 99.8%), 1 mmol of NiO (Alfa, 99.998%), 3 mmol of $BaCO_3$ (Alfa, 99.95%) and 10 g of K_2CO_3 (Alfa, A.C.S. grade, 99%) flux were loaded into an alumina crucible loosely covered with an alumina lid. The charges were placed into a tube furnace and heated to 1050 °C at 600 °C/h. The furnace was held at the target reaction temperature for 24 h, after which time it was cooled to 850 °C at a rate of 20 °C/h, and subsequently cooled to room temperature by shutting off the furnace.

Orange octahedral blocks of $Ba_2Na_{0.83}U_{1.17}O_6$ and $BaK_4U_3O_{12}$, and orange plate crystals of $Na_3Ca_{1.5}UO_6$, were isolated from the flux by dissolving the flux with water and collecting the crystals by vacuum filtration.

2.2. Single crystal X-ray diffraction

Single crystals of $Ba_2Na_{0.83}U_{1.17}O_6$ formed as orange octahedra that exhibited no extinctions when rotated in polarized light. The X-ray diffraction pattern indexed cleanly to a face-centered cubic unit cell with $a \approx 8.62$ Å. Close examination of the diffraction pattern showed no significant non-fit reflections. An X-ray intensity data set was measured at 150(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) [9]. The data collection covered 100% of the reciprocal space to $2\theta_{max} = 75.2°$, with an average redundancy (m3m Laue symmetry) of 41.4, and $R_{int} = 0.0344$ after absorption correction. The raw area detector data were processed, scaled and corrected for absorption effects with the SAINT+ and SADABS programs. [9] Final unit cell parameters were determined by least-squares refinement of 1787 reflections from the data set. Structure solutions, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL [10].

Systematic absences in the intensity data were consistent with an F-centered lattice but indicated no screw axes or glide planes, leaving five possible cubic space groups ($F23$, $Fm\overline{3}$, $F432$, $F\overline{4}3m$, $Fm\overline{3}m$). The compound is best described as a disordered cubic double perovskite (K_2NaAlF_6 structure type) in the space group $Fm\overline{3}m$, with statistical disorder of the oxygen atoms and partial substitution of Na^+ by U^{6+}. Four atomic positions were refined: Ba1 on ¼, ¼, ¼ (Wyckoff site 8*c*); U1 on 0, 0, 0 (site 4*a*); Na1/U1A on ½, ½, ½ (site 4*b*) and O1 on 0, *y*, *z* (site 96*j*). The Ba1 and U1 sites refined normally as shown by the displacement parameters and bond distances for these atoms; the Na1 and O1 sites require further comment.

The bond distances from the 4*b* site to oxygen are ca. 2.3 Å and indicate this position to be primarily occupied by sodium; however 100% sodium occupancy resulted in a displacement parameter of zero ($Å^2$) along with large residual electron density buildup. Introduction of partial uranium mixing on this site yielded a sensible displacement parameter and a flat electron density map. For refinement stability, the total Na1/U1A-site occupancy was constrained to unity and the constituent atoms assigned a common displacement parameter. The refined values are 0.826(5) Na1/0.174 (5) U1A. This occupancy distribution results in a nearly electroneutral crystal, assuming all uranium atoms are present as U^{6+}. There remains an excess negative charge of −0.13, which may be caused by model limitations or oxygen atom vacancies.

The oxygen atom site in the K_2NaAlF_6 structure type is 24*e* (*x*, 0, 0), generating a non-tilted system of corner-shared octahedral (Na−O−Al angles ≡ 180°). However a huge oblate anisotropic displacement parameter was observed for oxygen refined on *x*, 0, 0. A model with O1 shifted slightly off the 24*e* site, onto the 96*j* site (0, *y* ,*z*) gave a more reasonable displacement parameter. This implies a four-fold disorder of the oxygen atoms about a position of site symmetry 4 mm, corresponding to four-fold disorder of the UO_6/NaO_6 octahedral tilt system. The disorder was not resolved by lowering the crystal symmetry. Several structure solutions and refinement were undertaken in various lower-symmetry space groups ($Fm\overline{3}$, $F23$, $I4/m$, $I2/m$, $P1$); in each case an oxygen atom displacement parameter several times larger than the remaining atoms was observed, even in space groups allowing for a ordered tilt system (i.e. U−O−Na/U angle ≠ 180°). In all cases this could be alleviated by refining a split oxygen atom position (disorder). The persistence of the oxygen atom disorder down to space group *P*1 (No.1) implies a genuine disorder not imposed by twinning or falsely high crystallographic symmetry.

For the final refinement cycles O1 was refined anisotropically with fixed ¼-occupancy. The metal atom displacement parameters are isotropic by crystallographic symmetry. The largest residual electron density map extrema ($e^-/Å^3$) are +2.98 and −2.01, both located <0.6 Å from Ba1.

$BaK_4U_3O_{12}$: X-ray diffraction intensity data from an irregular fragment cleaved from a large orange block crystal were measured at 294(2) K on a Bruker SMART APEX diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) [9]. The data collection covered 100% of reciprocal space to $2\theta_{max} = 80.2°$, with an average reflection redundancy of 37.7 and $R_{int} = 0.041$ after absorption correction. The raw area detector data frames were processed and corrected for absorption effects with the SAINT+ and SADABS programs. [9] The reported unit cell parameters were determined by least-squares refinement of 4724 reflections from the data set. Difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL [10].

The compound crystallizes in the space group $Im\overline{3}m$ (#229) of the cubic system. The previously published coordinates of "$K_8Ba_2U_6O_{24}$" [8] were used as a starting model for refinement. However a satisfactory refinement was only achieved with potassium occupying the six-coordinate 2*a* site instead of barium, and a 75/25 mixture of K and Ba occupying the 8*c* site instead of 100% K. The asymmetric unit consists of three metal and two oxygen atom positions: U1 on Wyckoff site 6*b*, K1 on site 2*a*, a 75/25 mixture of K/Ba on site 8*c*, O1 on site 12*e* and O2 on site 12*d*. The occupancies for K and Ba on the 8*c* sites were constrained to sum to unity; the final refined values are: $K_2 = 0.750(6)$, $Ba_2 = 0.250(6)$, exactly satisfying electroneutrality (assuming U^{6+}). All atoms were refined with anisotropic displacement parameters. Trial refinements of site occupancy parameters showed no deviation from unity occupancy for K1 and U1. The largest difference map extrema are +0.98 and −1.36 $e^-/Å^3$, located 0.61 and 0.75 Å from U1 and K1, respectively. The large disk-shaped displacement ellipsoids of the oxygen atoms indicate some perovskite tilt system disorder, which could not be resolved.

$Na_3Ca_{1.5}UO_6$: X-ray diffraction intensity data from an orange plate crystal were measured at 150(2) K on a Bruker SMART APEX diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) [1]. The data collection covered 100% of reciprocal space to $2\theta_{max} = 75.6°$, with an average reflection redundancy of 8.8 and $R_{int} = 0.032$ after