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Hydroflux synthesis and crystal structure of new lanthanide tungstate oxyhydroxides

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ABSTRACT

Single crystals of $Na_5Ln(OH)_6WO_4$ where *Ln* = Er, Tm, and Yb were grown out of a NaOH hydroflux. The crystals were characterized by single crystal X-ray diffraction and were found to crystallize in the monoclinic space group *I*2/*a*. The lattice parameter ranges for the three structures are $a = 11.2024(7)$ Å −11.2412(6) Å, $b = 16.1850(10)$ Å−16.2220(10) Å, and $c = 11.9913(7)$ Å−12.0323(7) Å while the β angle range is 101.999(2)°−102.025(2)°.

1. Introduction

A recent surge in the use of the hydroflux method to synthesize crystals has proven that this method is adaptable and can be used for the creation of crystals of complex structures that contain diverse elements, including alkali and alkaline earth elements, lanthanides, arsenic, manganese, cobalt, nickel, copper, silicon, and tungsten. The hydroflux method is quite general and can be used to grow single crystals of oxides, hydroxides, oxyhydroxides, and hydrated oxides [1–7]; where it exemplifies one important approach for the preparation of single crystals of thermally unstable phases.

The hydroflux method uses a very high water content hydroxide flux as the "high" temperature solution in which crystals are grown. By using a wet hydroxide flux, the dwelling temperature needed for the reactions is lowered from a range of 320–1300 °C in hydroxide flux reactions [8] to 180–230 °C in hydroflux reactions [1–6]. The amount of water added is important as it controls the acid–base chemistry of the flux when it is molten, following the Lux-Flood concept of oxo-acidity [9–11]. Because the hydroflux is a melt and not simply an aqueous solution, there is no significant pressure buildup in the reaction vessel.

While a significant number of complex oxides containing tungsten are known, there are very few reports of tungsten containing oxyhydroxides, especially of those also containing an alkali and a lanthanide cation [12,13]. Looking at early transition metal examples, there are many instances of single crystals grown as oxides and a few examples of oxyhydroxides. These oxides and oxyhydroxides include but are not limited to $NaLnTiO_4$ (*Ln* = La, Pr, Nd) [14], $K_2Hf_2O_5$ and $K_4Hf_5O_{12}$ [15], $A_5(VO_4)_3(OH)$ (A = Sr, Ba) [16], $LnKNaMO_5$ (*Ln* = La, Pr, Nd, Sm, Eu, Gd, Tb; M = Nb, Ta) [17–19], $Ln_4Na_2K_2M_2O_{13}$ (*Ln* = Nd, Sm, Eu, Gd; M = Nb, Ta) [20], $Rb_4Al_2Nb_{35}O_{70}$ [21], $Li_3Al(MoO_4)_3$ [22], $Cs_{0.33}MoO_3$ and $CsFe(MoO_4)_2$ [23], $KBaMnO_4$ [6], $K_2Ba(MO_4)_2$ (M = Cr, Mo, W) [3], Ba_2MgWO_6 and Ba_2ZnWO_6 [24], $Sr_2Mn(OH)_6$ and $Ba_2Mn(OH)_6$ [1]. Herein we present the hydroflux crystal growth of a series of new tungsten containing oxyhydroxides and report their crystal structures.

2. Experimental section

2.1. Sample preparation

2.1.1. Reactants

Er_2O_3, Tm_2O_3, and Yb_2O_3 (99.9%) were purchased from Alfa Aesar. WO_3 (99.8%) was purchased from Alfa Aesar, $Na_2SiO_3 \cdot 9H_2O$ (99.9%) was purchased from EM Science, and NaOH (ACS grade) was purchased from Macron.

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Table 1
Crystallographic data for $Na_5Er(OH)_6WO_4$, $Na_5Tm(OH)_6WO_4$, and $Na_5Yb(OH)_6WO_4$.

Formula	$Na_5Er(OH)_6WO_4$	$Na_5Tm(OH)_6WO_4$	$Na_5Yb(OH)_6WO_4$
Formula weight	632.11	633.78	637.89
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*I* 2/*a*	*I* 2/*a*	*I* 2/*a*
a (Å)	11.2412(6)	11.2257(7)	11.2024(7)
b (Å)	16.2074(9)	16.2220(10)	16.1850(10)
c (Å)	12.0323(7)	12.0133(8)	11.9913(7)
β (°)	102.025(2)	101.999(2)	102.021(2)
V (Å^3)	2144.1(2)	2139.9(2)	2126.5(2)
Z	8	8	8
Density (mg/m^3)	3.916	3.935	3.985
Absorption coefficient (mm^{-1})	18.734	19.219	19.792
Crystal size (mm^3)	0.12 × 0.10 × 0.05	0.12 × 0.10 × 0.05	0.12 × 0.10 × 0.05
2 theta range (°)	4.28 to 70.24	4.28 to 70.20	4.29 to 70.38
Reflections collected	25,482	32,799	22,728
Data/restraints/parameters	4633/6/181	4691/6/183	4537/6/183
R (int)	0.0368	0.0359	0.0335
GOF (F^2)	1.063	1.036	1.022
R indices (all data)	$R_1 = 0.0374$	$R_1 = 0.0415$	$R_1 = 0.0400$
	$wR_2 = 0.0636$	$wR_2 = 0.0525$	$wR_2 = 0.0616$

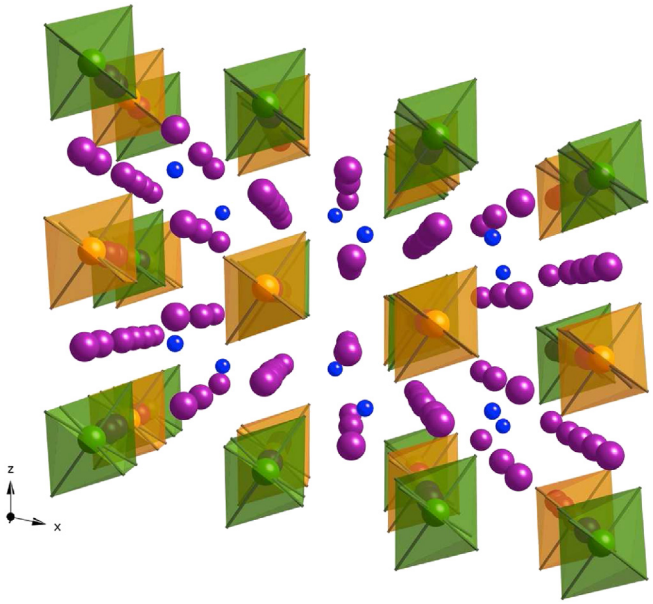

Fig. 2. Crystal structure of $Na_5Yb(OH)_6WO_4$, which is representative of the three title compounds where the alternating isolated lanthanide polyhedra are shown. *Ln*(1) is shown in orange, *Ln*(2) is shown in green, tungsten is shown in blue, sodium is shown in purple, and oxygen and hydrogen are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.1.2. Synthesis

Crystals of $Na_5Ln(OH)_6WO_4$ where *Ln* = Er, Tm, and Yb were grown in a hydroflux. Na_2SiO_3 (2.93 mmol), Ln_2O_3 (0.3 mmol), and WO_3 (0.7 mmol) were put into a hydroflux of NaOH (9.5 g) and H_2O (7 g) and were placed into a 23 mL PTFE-lined stainless steel autoclave. The autoclaves were loaded into a programmable oven at a temperature of 230° C. The oven was programmed to hold at 230° C for 12 h before cooling to 80° C at a rate of 0.1° C/min. The flux was then washed away from the crystals by sonication in methanol. Crystals were kept in methanol to prevent the degradation of the crystals that occurs in moisture over a period of weeks.

2.2. Characterization

2.2.1. Single crystal X-ray diffraction

Crystals of all compounds formed as colorless (Tm, Yb) and pink (Er) rod crystals that decompose in methanol over a period of weeks, presumably due to moisture sensitivity. Intensity data for each were collected at 100(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å) [25]. The data collections covered >98.7% of reciprocal space to $2\theta_{max} = 70°$, with an average reflection redundancies of at least 4.7. The raw area detector data frames were reduced and corrected for absorption effects with the SAINT+ and SADABS programs [25]. Final unit cell parameters were determined by least-squares refinement of large sets of reflections taken from the data sets. An initial structural model was obtained with direct methods [26]. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2014 [26] using the ShelXle interface [27].

The compounds are isostructural and crystallize in the monoclinic system. The space group *I*2/*a* (No. 15) was consistent with the pattern of systematic absences in the intensity data and was confirmed by structure solution. The asymmetric unit consists of one tungsten atom, two unique lanthanide atoms, six sodium atoms, 10 oxygen atoms and six hydrogen atoms. Tungsten W(1), sodium atoms Na(1)–Na(4) and all oxygen and hydrogen atoms are located on general positions (Wyckoff site 8*f*). Both lanthanide atoms *Ln*(1) and *Ln*(2) and sodium atoms Na(5) and Na(6) are located on two-fold axes (site 4*e*). In the Tm and Yb crystals, sodium atom Na(6) is disordered over two 4*e* sites with occupancies Na(6A)/Na(6B) = 0.839(5)/0.161(5) and 0.843(5)/0.157(5), respectively (constrained to sum to one). For *Ln* = Er, no two-fold disorder was observed for Na(6). Only one electron density peak is observed in this region, corresponding to the major Na(6A) site in the *Ln* = Tm and Yb crystals. From trial refinement models site Na(6A) refined to an occupancy factor of 0.98(1), and was fixed at full

Fig. 1. Crystal images of the average size of $Na_5Er(OH)_6WO_4$ (left), $Na_5Yb(OH)_6WO_4$ (center), and $Na_5Tm(OH)_6WO_4$ (right) crystals where the scale bar below the crystals denotes mm increments.