Experimental report

07/02/2023

Proposal:	**5-21-1170**	**Council:**	4/2021
Title:	Transition oxometallate hydrides: a new compound class		
Research area:	Chemistry		

This proposal is a new proposal

Main proposer:	**Nathalie KUNKEL**
Experimental team:	
Local contacts:	Clemens RITTER

Samples: Rb3MoO4D
Rb3WO4D
Cs3MoO4D
Cs3WO4D

Instrument	Requested days	Allocated days	From	To
D2B	2	2	24/09/2021	26/09/2021

Abstract:

Due to the reductive nature of hydrogenation reactions, mixed hydridic oxoanions are difficult to realize. The reductive atmosphere tends to reduce the oxoanions, hindering access to such materials. However, we were able to synthesize four compounds of new mixed anionic hydrides, the oxometallate hydrides, by applying reaction control. Such a combination of hydrides with transition oxometallate anions, like tungstates or molybdates are to the best of our knowledge not realized so far. Here we present the first four representatives of this class: Rb3MoO4H, Rb3WO4H, Cs3MoO4H, Cs3WO4H. This new class of materials complements previous studies and are of fundamental interest. This study is expected to open up a wide variety of possible new similar compounds.

EXPERIMENTAL REPORT FOR PROPOSAL 5-21-1170

Transition oxometallate hydrides: a new compound class

The allocation of beamtime allowed to record neutron powder patterns of the unprecedented transition oxometalate hydrides A_3MO_4H (A = Rb, Cs; M = Mo, W) at room temperature as well as 4K.

This resulted in the following publication.

Expanding the hydride chemistry: antiperovskites A_3MO_4H (A = Rb, Cs; M = Mo, W) introducing the transition oxometalate hydrides

Alexander Mutschke*, Annika Schulz, Marko Bertmer, Clemens Ritter, Antti J. Karttunen, Gregor Kieslich and Nathalie Kunkel*, *Chem. Sci.*, **2022**, *13*, 7773-7779

Abstract of the manuscript

The four compounds A_3MO_4H (A = Rb, Cs; M = Mo, W) are introduced as the first members of the new material class of the transition oxometalate hydrides. The compounds are accessible via a thermal synthesis route with carefully controlled conditions. Their crystal structures were solved by neutron diffraction of the deuterated analogues. Rb_3MoO_4D, Cs_3MoO_4D and Cs_3WO_4D crystallize in the antiperovskite-like K_3SO_4F-structure type, while Rb_3WO_4D adopts a different orthorhombic structure. ^2H MAS NMR, Raman spectroscopy and elemental analysis prove the abundance of hydride ions next to oxometalate ions and experimental findings are supported by quantum chemical calculations. The tetragonal phases are direct and wide band gap semiconductors arising from hydride states, whereas Rb_3WO_4H shows a unique, peculiar valence band structure dominated by hydride states.

Experimental Report

Solid-state reactions of alkaline metal (Rb, Cs) with dry quasibinary oxometalate salts A_2MO_4 (A = Rb, Cs; M = Mo, W) under 20 bar hydrogen pressure at 528 K to 600 K yield the first representatives of the transition oxometalate hydrides A_3MO_4H. First structural models were obtained from X-ray diffraction data by the use of the program Jana2006[1]. Raman, FTIR and MAS-NMR spectroscopy in combination with DFT calculations show good agreement with the initial structural models and undermine the simultaneous presence of hydride next to oxometalate ions.

To confirm the initial structural models obtained by powder X-ray diffraction and to clarify the hydride positions, neutron powder diffraction of the deuterided analogues was performed with the aid of Dr. Clemens Ritter (Grenoble, ILL) at the instrument D2B. The experiment was performed with a wavelength of 1.594 Å. Low temperature measurements at 4K to reduce the Debye-Waller factor were performed by the use of a cryofurnace. The obtained data was evaluated and refined by the Rietveld method by the use of the program FullProf[2]. An exemplary Rietveld refinement plot of Cs_3WO_4D is shown in Fig 1.

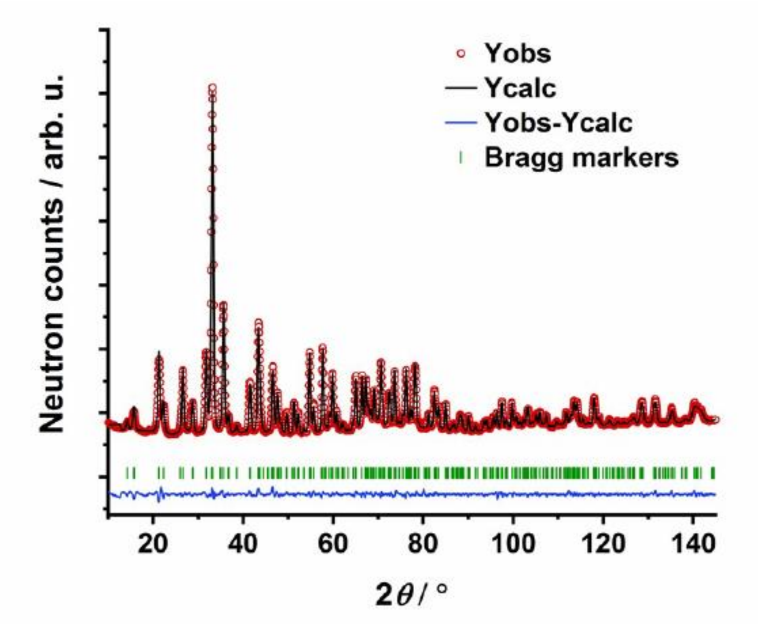
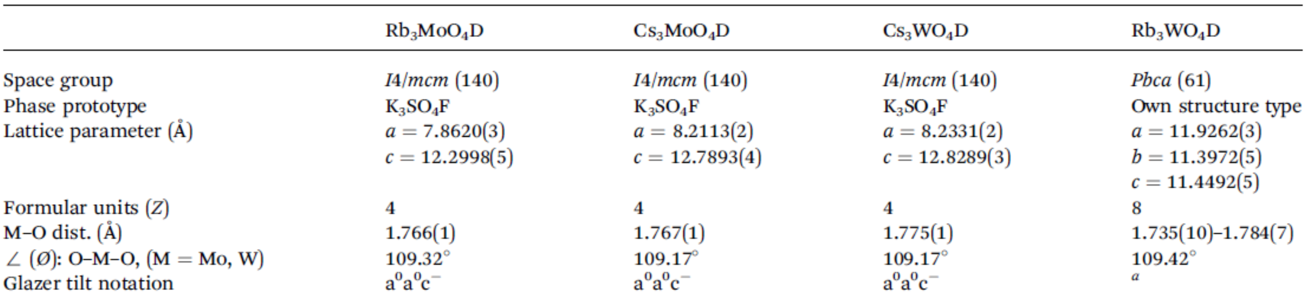


Figure 1. Rietveld refinement plot of Cs_3WO_4D (*I*4/*mcm*, 140) at room temperature based on neutron diffraction data. R_{wp} 2.04%, R_{exp} 0.87%.

With the aid of neutron powder diffraction, the structures could be unambiguously solved and completed. A quick overview of the structures is listed in table 1. Additionally, $Rb_3WO_4H(D)$ was determined to crystallize in an unprecedented perovskite-like structure type (Fig. 2). It was also found that the three tetragonal crystallizing structures preserve the structure up to 4K and do not undergo any phase transitions. The low thermal displacement parameters however allowed for a better, refined structural solution. However, $Rb_3WO_4H(D)$ was found to undergo a phase transition at low temperatures. The structural solution of this low temperature polymorph is yet pending. Overall, the low temperature data of all four compounds and the mentioned phase transition is object to a further, ongoing study.

Table 1. Crystal structure data of the four compounds at room temperature.



	Rb_3MoO_4D	Cs_3MoO_4D	Cs_3WO_4D	Rb_3WO_4D
Space group	*I*4/*mcm* (140)	*I*4/*mcm* (140)	*I*4/*mcm* (140)	*Pbca* (61)
Phase prototype	K_3SO_4F	K_3SO_4F	K_3SO_4F	Own structure type
Lattice parameter (Å)	$a = 7.8620(3)$ $c = 12.2998(5)$	$a = 8.2113(2)$ $c = 12.7893(4)$	$a = 8.2331(2)$ $c = 12.8289(3)$	$a = 11.9262(3)$ $b = 11.3972(5)$ $c = 11.4492(5)$
Formular units (*Z*)	4	4	4	8
M–O dist. (Å)	1.766(1)	1.767(1)	1.775(1)	1.735(10)–1.784(7)
∠ (Ø): O–M–O, (M = Mo, W)	109.32°	109.17°	109.17°	109.42°
Glazer tilt notation	$a^0a^0c^-$	$a^0a^0c^-$	$a^0a^0c^-$	[a]

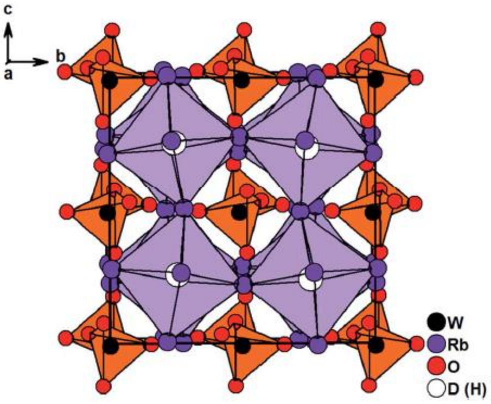


Figure 2. Schematic of the crystal structure of $Rb_3WO_4H(D)$ at room temperature.

Literature

[1] V. Petříček, M. Dušek, L. Palatinus, *Z. Kristallogr. Cryst. Mater.* **2014**, *229*.

[2] J. Rodríguez-Carvajal, *Physica B* **1993**, *192*, 55‑69.