	Experiment title: Search for New Perovskite Oxyhydrides in K–M–O–H (M=Ti, V) systems: In Situ Study at Extreme Conditions Using LVP at Beamline ID06	Experiment number: CH-5246
Beamline: ID06-LVP	Date of experiment: from: 20/09/17 to: 23/09/17	Date of report: 27/02/2018
Shifts: 12	Local contact(s): Wilson A. Crichton	<i>Received at ESRF:</i>
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Report

1. Aim of the study

The main goal of the experiment CH-5246 was to explore whether it is possible to produce oxyhydrides in the systems K–Ti–O–H and K–V–O–H under high pressure and high temperature. Oxyhydrides are a newly developed class of compounds often based on classic ($\text{ABO}_{3-x}\text{H}_x$) or double-layered ($\text{A}_2\text{BO}_{4-x}\text{H}_x$) perovskite structures. $[\text{BX}_6]^{n-}$ octahedral units contain both oxide and hydride anions, and the interactions of B metal with the mixed anion environment can aid in developing new materials with tunable magnetic and transport properties [1]. Recent calculation studies have predicted a stable perovskite oxyhydride KTiO_2H , which is expected to have piezoelectric properties comparable to those of PbTiO_3 and would be the first oxyhydride with A^+/B^{4+} combination of metal ions [2]. A number of oxyhydrides were successfully produced by direct synthesis at high pressure in a multianvil press [3,4]. Large volume press at ID06 provides a unique opportunity to collect time-resolved in situ PXRD during the reactions in multicomponent systems at GPa pressures in combination with a stable heating over a wide range of temperatures, which would not be feasible in a DAC. The mapping of p,T space during synthesis in an LVP could allow accessing new oxyhydrides and optimizing their production conditions. In addition, extending the study to the K–V–O–H system was proposed, as monovalent potassium could help stabilizing a variety of vanadium oxidation states, increasing the chance of producing a stable oxyhydride structure. The experimental details and the outcome of the study are discussed below.

2. Technical aspects

Initially we proposed to perform the synthesis by reacting mixtures of vanadium and titanium oxides with potassium oxide (K_2O) in the presence of hydrogen fluid. However, during the experimental planning we found that K_2O is not available commercially, while synthesizing potassium oxide with low amount of impurities is a rather challenging procedure. Instead, we employed KH (potassium hydride) as a source of potassium and hydrogen. KH powder was synthesized at the MMK department of Stockholm University

specifically for CH5246. Absence of K_2O reduced the number of possible compositions due to lack of available oxygen (i.e. K_2VO_3H stoichiometry and proposed compositions with mixed oxidation states of titanium and vanadium). On the other hand, using KH was advantageous since the homogeneous mixtures of ABO_2H compositions, which were of the primary interest for this study, could be prepared easily. At the same time, sample preparation became easier and less time-consuming since the hydrogen source was omitted from the experimental setup.

Sample preparation was handled entirely in the glove box. Potassium hydride (KH) powder was mixed in an agate mortar with either titanium dioxide (TiO_2) or vanadium dioxide (VO_2) in a 1:1 molar ratio. Mixtures were pressed into pellets of 2 mm OD and ~2.5 mm height. The sample pellets were afterwards hermetically sealed inside the capsules made of dry NaCl (~ 3.8 mm height, 3 mm OD). NaCl was chosen as a capsule material as it can provide an efficient air- and moisture-tight seal for highly sensitive materials. In addition, the NaCl EOS [5] is convenient for evaluating pressure and temperature during in situ PXRD studies.

All the samples were compressed and heated using 14/8 multianvil assemblies analogous to those used during experiment CH-4899 with the only difference being the addition of C-type thermocouple to the set up. In each run the thermocouple junction was located on top of the sample capsule along with an Al_2O_3 plate (0.25 mm thick, 2 mm OD) added for sample protection. Further details of the sample preparation (excluding the addition of hydrogen source) and the 14/8 assembly could be found in the report for CH-4899 experiment. Samples were pressurized to 8-10 GPa and heated using Delta Elektronika SM6000 power supply by regulating the power. Angle-dispersive PXRD patterns ($\lambda=0.22542$ Å) were collected with a Detection Technology X-Scan series1 linear pixelated detector placed at an azimuth angle of 270° . During compression and decompression, a pattern would be saved each 32 seconds, while on heating collection speed was 3.2 sec/pattern. The speed and duration of the heating was adjusted based on the observed changes in the diffraction. In successful runs, heating lasted up to 5 hours in order to drive the reaction to completion.

3. Results and discussion

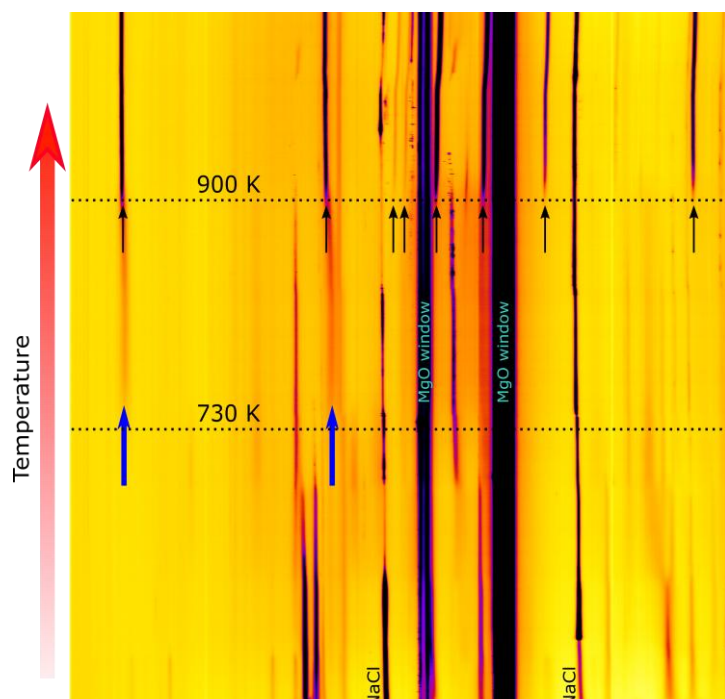


Figure 1. Compilation of PXRD data collected on heating in system I at 9 GPa. Disordered and ordered phases are marked by blue and black arrows, respectively.

Formation of the theoretically predicted oxyhydrides was not observed in any of the two tested $K-M-O-H$ systems at applied p,T conditions. However, a different type of compounds has been unexpectedly obtained. The preliminary results for each system, denoted further as I and II, will be discussed below.

During the heating of the system I at 9 GPa (Figure 1) two diffuse peaks appeared in the PXRD at 730 K (blue arrows). Further heating lead to rapid sharpening of the diffuse peaks along with simultaneous appearance of additional set of reflections at about 900 K (marked by black arrows). The final array of peaks could be indexed to hexagonal lattice. Preliminary analysis of the data suggested the final structure to be a non-stoichiometric ternary oxide. The diffuse peaks preceding its crystallization most probably belong to a poorly ordered precursor. The diffraction data following the decompression revealed a phase transition to a structure of lower symmetry.

The behaviour of system II on heating at 8.5 GPa was similar to that of system I. A stable intermediate was identified as K_2MO_3 . The final ternary oxide structure, however, could not be produced as well-ordered individual compound, as the peaks of K_2MO_3 were still present after prolonged heating, and temperature quenching lead to strong broadening of some of the peaks.

Ex-situ analysis of the recovered samples as well as further evaluation of the in situ PXRD data is ongoing. Future plans include XAS measurements, elemental analysis as well as continuing in situ PXRD studies at

ID06-LVP as in house research to further explore synthesis and structure of these new members of this exciting oxide family.

References

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