



	Experiment title: Formation, stability and structure elucidation of elusive gold hydrides: in situ PXRD studies of the systems A -Au-H ($A = \text{K}, \text{Cs}$) at pressures up to 12 GPa	Experiment number: CH-6626
Beamline: ID06-LVP	Date of experiment: from: 12/04/23 to: 17/04/23	Date of report: 07/09/2023 <i>Received at ESRF:</i>
Shifts: 15	Local contact(s): Dr. Dmitrii Druzhbin	
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Report:

Aim of the study

The goal of experiment CH-6626 was to explore formation conditions and phase transition behaviour of possible new ternary hydrides in systems A -Au-H ($A = \text{K}; \text{Cs}$) at pressures up to 12 GPa. Solid state gold hydrides have been notoriously elusive. Gold is among the very few metallic elements for which hydrides are unknown, and apparently binary Au hydrides are not even feasible at incredibly high pressures (up to 300 GPa).¹ Surprisingly, a recent theoretical investigation² suggested the existence of thermodynamically stable ternary alkali metal gold hydrides which could develop superconductivity at high pressures. In particular, theoretical calculations in the study show that linear anion AuH_2^- can be stabilized in ternary compounds $AAu\text{H}_2$ ($A = \text{K} - \text{Cs}$) even at ambient pressure towards all conceivable decomposition reactions. GPa pressures, however, would still be required for the synthesis to prevent thermal decomposition of the target hydrides. Using large volume press (LVP) for this purpose is particularly promising, as LVP hydrogenations at GPa pressures have already shown strong potential for accessing novel ternary hydrides.³⁻⁵ At the same time, LVP experiments combined with in situ synchrotron diffraction, in particular those with monochromatic beam at ID06-LVP,⁶ are extremely well suited for the study of hydrogenation reactions as well as phase relations and structures of hydrides at GPa pressures because of the well controllable p , T environment and the possibility to contain complex multi-component samples of several mm^3 .

In a recent beamtime at PETRA III, DESY (August 2022) we investigated the reaction $\text{KH} + \text{Au} + n\text{H}_2$ at pressures $\sim 6, 12$ and 20 GPa using ED-XRD at the beamline P61B-LVP. At all target pressures the formation of a new compound interpreted as ternary hydride $\text{K}_x\text{Au}_y\text{H}_z$ was observed. However, the ED-XRD data would

not allow the elucidation of the structure and phase behavior of this hydride from in situ data. Therefore, during CH-6626 it was crucial to revisit this experiment at ID06 with monochromatic beam in order to obtain necessary structural information for $K_xAu_yH_z$. At the same time, we extended the study at ID06-LVP towards Cs–Au–H system, aiming at producing novel ternary gold hydrides $Cs_xAu_yH_z$ and, in case of success, shedding light on their structures, phase relations and p , T behavior. Experimental details and results of the study are discussed in the next sections.

Technical aspects

Sample preparation for CH-6626 was performed in advance at DESY in an Ar-filled glovebox due to air and moisture sensitivity of the starting materials. Powdered precursor mixtures CsAu:KH and KH:Au (with 1:1 and 2:1 molar ratios, respectively) were pressed into pellets with 1.0 mm OD, $h \sim 0.8$ – 1.1 mm, while pure CsAu precursor was pressed into 0.6 mm OD, $h \sim 1$ mm pellets. Originally proposed CsH could not be synthesized before the experiment due to technical difficulties and therefore was not used. The small pellet diameters were chosen to allow sufficient X-ray beam penetration during the experiment. Along with two pellets of ammonia borane hydrogen source (NH_3BH_3) the samples were enclosed into sodium chloride (NaCl) capsules of either 2.5 or 3 mm OD, ~ 2.6 – 3.6 mm height. The amount of NH_3BH_3 per sample corresponded to $\geq 10 \times$ molar excess of hydrogen with respect to Au, while the complete decomposition of the hydrogen source at target pressures was expected at 200–400 °C.⁷ NaCl (dried under vacuum) was used as sample capsule material due to its ability to form air-tight seal for sensitive materials and resist hydrogen diffusion. In addition, its EOS is well studied⁸ and can be used for p , T evaluation *in situ*.

The experiments at ID06-LVP were performed with 10/5 and 14/8 multianvil assemblies depending on target pressure. The sample capsules along with MgO plugs of the same OD were loaded into graphite heaters (3.2 or 4 mm OD for 10/5 and 14/8 setups, respectively). The heaters and the two outer ZrO_2 plugs (3.2 or 4 mm OD) were then enclosed inside 10 or 14 mm OEL Cr-doped MgO octahedra. The passage of the current was ensured by topping the heaters with molybdenum (Mo) foils (4mm OD), which, in turn, were in contact with Mo leads (1 mm OD, $h=1.6$ mm) inserted into the outer ZrO_2 plugs. The octahedra were then positioned between eight gasketed 32 mm WC anvils (5 or 8 mm TEL). To minimize the contribution of assembly materials to PXRD data, X-ray transparent SiBCN cylinders as well as MgO or BCN rectangles were inserted along the beam into the octahedra and the gaskets, respectively. The outer side of the tungsten carbide cubes was insulated with epoxy sheets, apart from the copper foil contacts at the cubes adjacent to the Mo leads.

Samples were brought to target pressure in 6–12 GPa range and heated using Delta Elektronika SM6000 power supply by regulating the power. Angle-dispersive PXRD data ($\lambda=0.233933$ Å) were collected continuously during compression, decompression (8–30 sec/pattern) and heating (3 sec/pattern) using a customized DECTRIS PILATUS3 X CdTe 900K-W-ESRF detector placed at an azimuth angle of 270°. The new detector system was highly advantageous for our experiments as it allowed to acquire the data with very good signal-to-noise ratio at extremely high time resolution and thus detect the slightest changes in the patterns on heating, while accessing wide 2θ range (~ 1.5 – 13.8°) essential for structural characterization. The heating rate and duration were adjusted depending on the observed changes in the diffraction and lasted up to 9 hours in order to drive the reactions to completion and study phase transition behaviour of the products. Temperatures were estimated based on power – temperature calibrations performed earlier at DESY, P61B, using type C thermocouple. Heating was terminated either by temperature quenching or slow cooling, and the samples were further decompressed and recovered at ambient conditions.

Results

During 15 shifts allocated for CH-6626 5 experiments were performed: 2 runs each were dedicated to Cs–Au–H and K–Cs–Au–H systems, respectively, while one run was used for the K–Au–H system study. All of the experiments ran successfully.

The first two experiments focused on Cs–Au–H and K–Cs–Au–H systems at ~ 6 GPa starting pressure and T up to ~ 550 °C. In both runs a highly complex behaviour of the precursor upon heating and hydrogenation was observed via PXRD, such as multiple phases appearing and replacing each other as well as undergoing temperature-dependent changes. At the same time, when CsAu:KH mixture was tested at ~ 8.5 GPa in a further experiment, heating to ~ 450 °C yielded a more clear pattern with only one major phase present, whose reflections could be indexed to a primitive trigonal unit cell. It is not clear whether hydride compounds have formed in these experiments, or if KH participated in the reactions during CsAu:KH mixture hydrogenations.

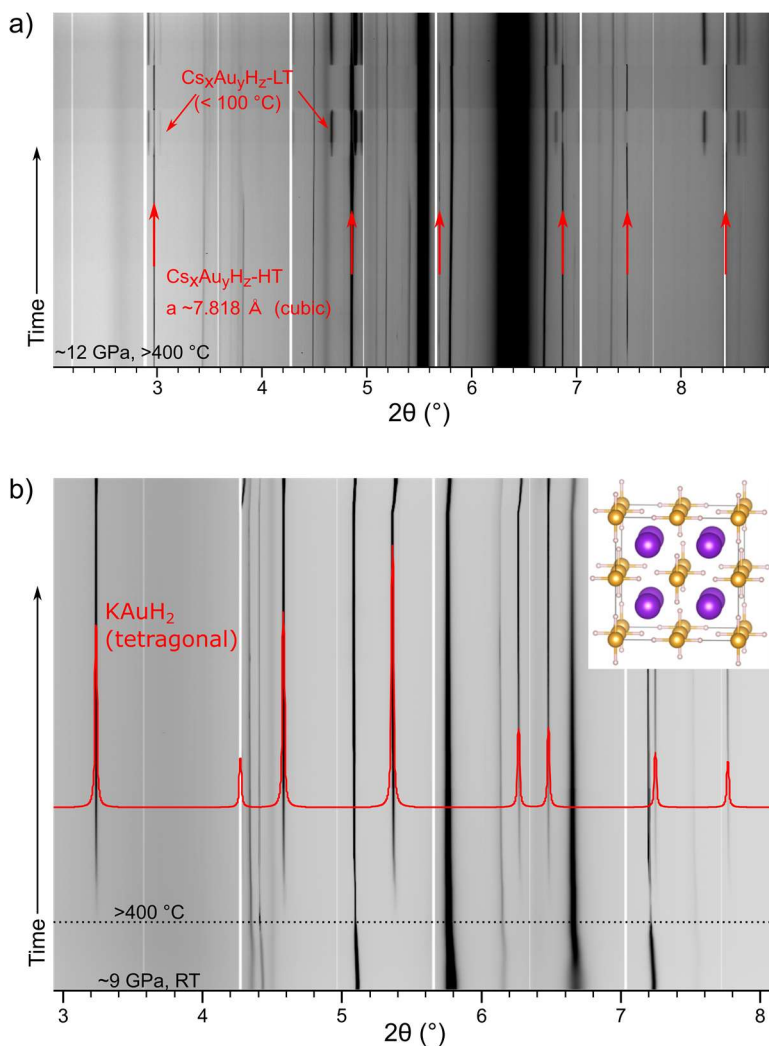


Figure 1. PXR D data collected at ID06-LVP during CH-6626. (a) CsAu hydrogenation run at ~12 GPa. Transition between high T and low T $\text{Cs}_x\text{Au}_y\text{H}_z$ phases is visible. (b) Formation of tetragonal KAuH_2 upon hydrogenation of 2KH:1Au mixture at ~9 GPa. Predicted KAuH_2 structure (ref. 2) is shown in inset, and its calculated PXR D (red) is displayed over experimental data.

Hydrogenation of pure CsAu at 12 GPa resulted in yet another, completely different, situation: above 400 °C the formation of a cubic phase was observed, which upon cooling below 100 °C underwent instantaneous reversible transition to a low symmetry form (see Fig. 1a). The character of the transition is consistent with our earlier observations for ternary complex transition metal hydrides,^{4,5} suggesting the formation of a ternary $\text{Cs}_x\text{Au}_y\text{H}_z$ compound. In addition, a phase transition in CsAu was observed in all relevant experiments during compression at RT above ~1.5 GPa. Data analysis for the above experiments is yet to be concluded. Additional theoretical calculations are required as well in order to unravel the structures observed in the 12 GPa run.

The hydrogenation of 2KH:1Au mixture was performed at ~9 GPa. The experiment was consistent with our earlier observations at P61B, PETRA III: ternary K–Au–H phase started to grow above 400 °C at 9 GPa (Fig 1b). At ID06-LVP the ADXR D data could be collected in a wide range of 2θ with a resolution of 3 sec/pattern, which allowed us to successfully separate and index the relevant reflections to a tetragonal unit cell. The theoretically predicted structure model for the tetragonal ($I4/mcm$) high pressure polymorph of KAuH_2 matched very well to the observed intensities of the new K–Au–H phase. The compound remained stable on cooling and decompression to ambient p . Diffraction of recovered sample measured in August 2023 at ambient p , T , however, differed drastically from the *in situ* observations, suggesting further transition or decomposition of

the sample. Data analysis and further characterizations of the sample are in progress.

Overall, during CH-6626 we have observed the formation of at least two novel ternary phases in the proposed A -Au-H systems (A =K, Cs). Further experiments at ID06-LVP would be extremely beneficial for this project. At least one publication focusing on K–Au–H system is already being planned, as well as further data analysis, ex situ characterization of the samples and theoretical calculations are needed to unravel the Cs–Au–H structures and prepare further papers using CH-6626 results.

References

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