Cs_3ReD_{10}, High Pressure Synthesis and Crystal Structure

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Ternary metal hydrides of the general formula $\boldsymbol{A}_x\boldsymbol{M}_yH_z$ – where ***A*** is either an alkali metal or an alkaline-earth metal and ***M*** a transition metal – can be synthesized by the reaction of a mixture of a binary alkali or alkaline-earth metal hydride and the transition metal in an atmosphere of hydrogen at temperatures ranging from 500 K to 900 K. The development of high pressure equipment (permitting the use of hydrogen pressures up to 6000 bar) has made possible the synthesis of hydrogen-rich compounds containing transition metals in a high oxidation state.

The synthesis of Cs_3ReD_{10} succeeds by conversion of CsD and rhenium powder at a deuterium reaction pressure higher than 4000 bar at 875 K in a high pressure autoclave [1]. Instead of the hydrogen compound a completely deuterated compound was synthesized. This offers the opportunity for reliable structure determination by neutron diffraction experiments. The resulting product is a colorless, microcrystalline powder which is extremely sensitive to moisture and air.

The preparation of the ternary deuteride Cs_3ReD_{10} [2] via the reported synthesis path is surprising because the oxidation of rhenium metal in the presence of alkali-metal hydrides with hydrogen succeeded up to the highest oxidation state +7. An analogous reaction with the electronegative homologous element fluorine is not known so far.

The crystal structure determination of Cs_3ReD_{10} was performed by a combination of X-ray investigations and neutron diffraction experiments. The atomic arrangement at room temperature is shown in Fig. 1. The description $[ReD_9]DCs_3$ elucidates the structural relation to the perovskite structure type (space group: $\boldsymbol{Pm\bar{3}m}$, Z = 1, ***a*** = 6.1826(1) Å). The crystal structure corresponds to a framework structure of vertex-sharing cesium octahedra centered by deuterium ions. The $[ReD_9]$-polyhedra are incorporated within the holes of this framework. The coordination of the rhenium atoms can be described crystallographically as a statistical occupation of two 24-fold sites. Below 100 K a phase transition was found which is obviously caused by freezing the mobility of the deuterium atoms. A neutron diffraction experiment at 4 K carried out at the high resolution powder diffractometer HRPD (Rutherford Appleton National Laboratory, UK) shows a splitting of reflections refering to a symmetry reduction.

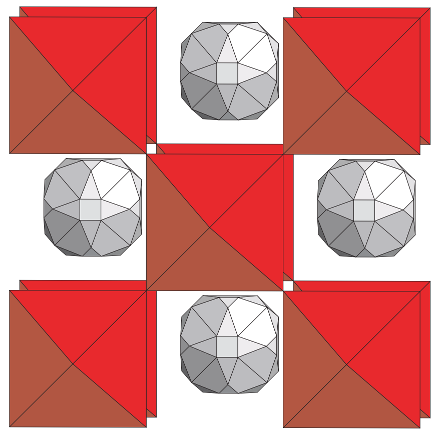

Fig. 1: Cs_3ReD_{10}: projection of the atomic arrangement of the framework structure from deuterium centered vertex-sharing octahedra of cesium atoms as well as $[ReD_9^{2-}]$-units in which the ligands can be described with a statistical occupation of two 24-fold sites.

In the system Cs-Os-D an analogous reaction at a deuterium reaction pressure above 1500 bar at 870 K led to the synthesis of the osmium(VI)-compound Cs_3OsD_9 [3]. At room temperature the determined structure corresponds to that of the rhenium compound ($[OsD_8]$-polyhedra instead of $[ReD_9]$-units) with a distortion of the cubic symmetry. The sequence of the oxidation states of the transition metals, (+7 for rhenium and +6 for osmium) indicates an analogous course as seen for ternary oxides of the 3***d***-metals: +4 for titanium, +5 for vanadium, +6 for chromium, +7 for manganese, +6 for iron, +5 für cobalt, +4 for nickel and +3 for copper. In this context the synthesis of the first ternary tungsten hydride is predicted: Cs_3WD_9?

References

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