ESRF	**Experiment title:** Structural studies of sulphur polyhydrides up to 200 GPa	**Experiment number**: HC-2790
Beamline: ID27	**Date of experiment**: from: 30/09/2016 to: 05/10/2016 from: 12/12/2016 to: 16/12/2016	**Date of report**: 02/02/2016
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Report:

Recently, astonishing superconductive properties of sulphur hydride have been unveiled at high pressure, with a critical temperature (Tc) of 200 K at 150 GPa [1]. The current interpretation is that H_3S could be formed by decomposition of H_2S under pressure and might be responsible for the observed superconductivity Several experimental works tried to determine the structures of these dissociation products at 150 GPa, including H_3S, but the results were of poor quality due to the complexity of the multi-phase x-ray diffraction (XRD) patterns [3, 4].

The aim of this proposal was to investigate the stable compounds in H-S systems under pressure. We therefore performed a detailed structural study of the sulphur hydrides synthesized directly under pressure by laser heating mixtures of $S+H_2$ up to 160 GPa. A major goal was to synthesize a pure H_3S compound around 150 GPa and refine its structure. We have carried out three experiment at 300 K, in different pressure ranges. The sample was annealed using a YAG laser, at various pressures (see Table 1). The heating temperature was kept below 1300 K. The pressure was measured using the Au equation of state The volume was measured using angular-dispersive x-ray diffraction. The conditions of the experiments are summarized in **Table 1**.

Name	culet diameter (μm)	Pressure range (GPa)	T (K)	P laser annealing (GPa)
Run 1	150	75-123	300	75, 100, 123
Run 2	100	100-135	300	100
Run 3	100	75-160	300	75

Table 1: Conditions of the three experimental runs.

The measurements of *V* vs. *P* for sulfur III and Cccm-H_3S at 300 K are plotted in **Figure 1**, together with the cell parameters vs. *P* and our data at different pressures. The laser heating process initiated a chemical reaction between sulfur and hydrogen, as one can see in run 2 where XRD data points were taken before laser heating. This reaction leads to the formation of an hydride, namely H_3S. Indeed, the diffraction peaks obtained could be indexed with the Cccm symmetry, which is consistent with theoretical studies [2] and experimental ones [3, 4]. The increase in volume is of about +7 A^3, which corresponds to +2.3 A^3 per atom of hydrogen. Again, this result is in strong agreement with other experimental works on hydrides [5]. The Vinet EoS fit of our data is also consistent with the predicted one for Cccm-H_3S [2]. However, we did not witness any phase transition up to 160 GPa, which is at odds with previous studies. H_3S is expected to metallize around 100 GPa, with a transition to the R3m structure [2]. Our results show that the Cccm insular phase remains stable at least up to 160 GPa. Eventually, the study of the evolution of the lattice parameters as

a function of pressure could indicate a weak phase transition occurring at 100 GPa, as the a and b parameters start to diverge. Yet, both XRD patterns are very close, as one can see on **Figure 1**, and the Cccm structure can fit both.

This successful experiment shows the feasibility and good reproducibility of the synthesis of pristine H_3S. Moreover, a study of its crystal structure shows that the Cccm symmetry remains stable up to 160 GPa. The main implication of this finding is that H_3S might not be the one responsible for the high Tc observed at 150 GPa in H_2S [1].

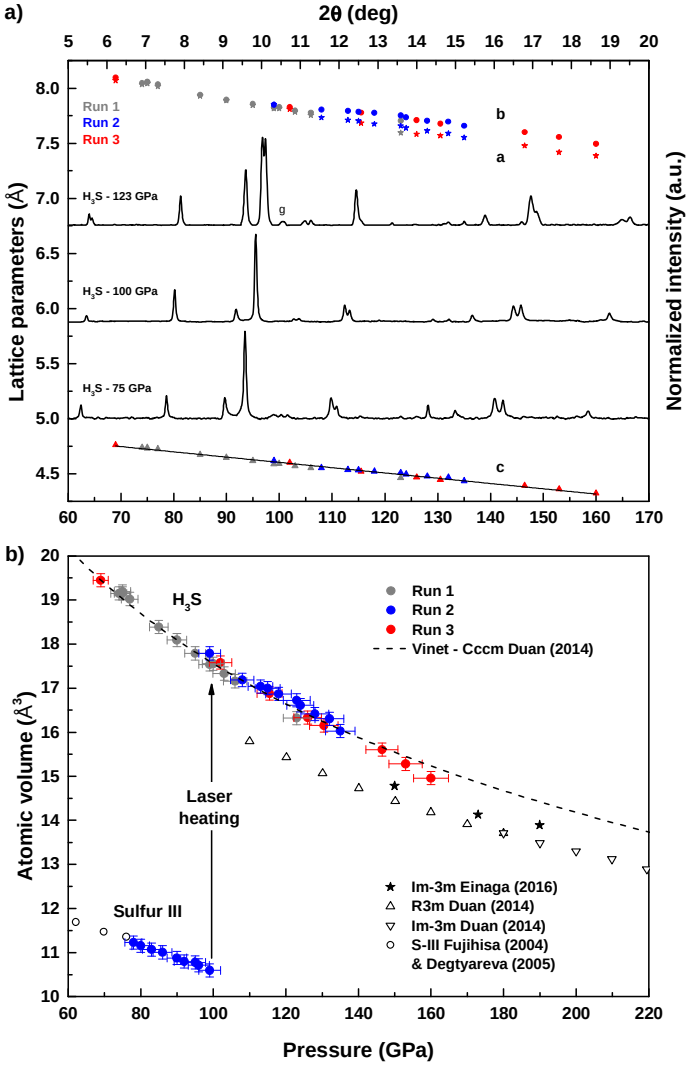

Figure 1: (a) Evolution of the lattice parameters as a function of pressure, together with three XRD diagrams taken at 75, 100 and 123 GPa. At 100 GPa, a phase transition from H_3S-I4/mcm to H_3S-Cccm might occur, though the Cccm symmetry succeeds in fitting the data below 100 GPa as well.
(b) Atomic volume as a function of pressure, for the three different runs. Our experimental data is plotted together with theoretical data from [6] and experimental data from [3, 7, 8]. There is a strong agreement between our data and the theoretical and extrapolated equation of state (EoS) of H_3S-Cccm, and a clear discrepancy with the EoS of H_3S-R3m.

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