ESRF	**Experiment title:** High Pressure synthesis mechanism of the superconducting mercury cuprates	**Experiment number:** Hs- 497
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Report:

Aims of the experiment and scientific background

The superconducting mercury cuprates compounds of general formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2+d}$ (n=l up to 6) exhibit the highest critical temperature of 133 K for the n=3 member. Single phase samples of compounds with n>3 can only be prepared by high pressure-high temperature synthesis. However, the preparation of single phases free from intergrowths becomes increasingly difficult as n increases, and the synthesis process needs to be improved. This synthesis involves the high-pressure reaction of HgO with a precursor which is a pre-reacted mixture of Ba, Ca and Cu oxides. It has been proposed that the formation of each phase proceeds through an intercalation starting from the lower members of the series : the reaction starts with the formation of Hg-1212 and $CaHgO_2$ which ***is*** then converted into higher terms by incorporation of $CaCuO_2$. In this scheme, longer times or higher temperatures favour the formation of higher members of the series. However, there is no direct evidence of this mechanism.

Experimental

We used the ESRF large volume high pressure cell to investigate the -synthesis mechanism of mercury cuprates by in-situ X-ray powder diffraction. In order to reproduce the laboratory synthesis conditions, special gold capsules (diameter 1.4 mm, height 2.8 mm, thickness 50 pm) were prepared to fit with the dimensions of the ESRF cell. The initial mixtures of oxides (precursors) were sealed in these capsules to avoid any reaction with the external medium. High quality diffraction images were recorded at 77 Kev in 80s, using an on-line image plate detector at 1 m from the sample. Despite strong absorption, the presence of very heavy elements in the sample appears to be advantageous, because it leads to a very high diffraction contrast with respect to the signal from the light element gasket. This high in-situ data collection rate gives access to the kinetics of phases formation and chemical reactions.

Results

The first experiments have been focused on the synthesis of $HgBa_2CuO_{4+\delta}$ (Hg-1201). This is a less complex problem, due to the absence of Ca, and thus of the $CaHgO_2$ phase during the reaction process. We have investigated the influence of temperature, dwell time and pressure. All known phases present (HgO, $Ba_2CuO_{3+\delta}$, Au, Hg-1201) can be clearly identified and their proportions can be determined by Rietveld refinement. Experiments have been carried out at 2 and 3 GPa (fig. 1). In all these synthesises the Hg-1201 phase is formed via an intermediate phase. Pure Hg-1201 samples have been' obtained at P=3 GPa. At 2 GPa the intermediate phase remains until the fusion around 950°C. We have also carried out a preliminary experiment on the synthesis of the more complex $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) phase which showed that the Hg-1223 phase is formed via the Hg-1212 phase. This first experiment shows the feasibility of the in-situ diffraction study of the Hg-1223 synthesis.

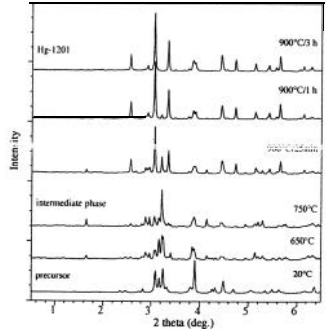

figure 1: X-ray diffractograms collected during the synthesis of Hg-1201 at 3 GPa.

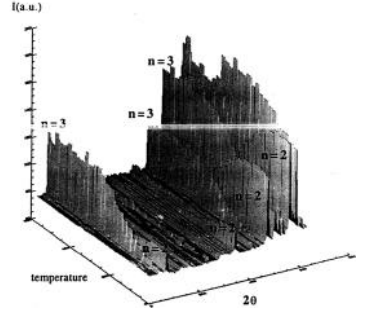

figure 2: 3D representation of diffractograms collected between 1000 and 1200°C during the Hg-1223 synthesis at 4 GPa.