s6.m2.o5 **High-pressure synthesis of the high-Tc mercury cuprates : an in-situ synchrotron diffraction study**. P. Bordet, S. LeFloch, C. Bougerol-Chaillout, M.F. Gorius, A. Prat, M. Mezouar*, *Laboratoire de Cristallographie CNRS, BP166, 38042, Grenoble Cedex 9, France, * ESRF, BP220, 38043 Grenoble France*
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High-pressure high temperature (Hp-HT) synthesis techniques have been extensively used in the past few years for the discovery of new oxide materials, particularly high-Tc superconducting oxides. However, tuning the many synthesis parameters (starting material composition and oxidation state, pressure, temperature, gradients, etc...) can be very complex and time consuming, since the only way to control the reactions is to analyze the products a posteriori. This was particularly true in the case of the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (Hg-12(n-1)n) series of high-Tc cuprates, where the member obtained depends on precise oxidation state of the precursor material, and temperature range chosen.

We have undertaken an in-situ synchrotron diffraction study of the Hp-HT synthesis of the Hg-1201 and Hg-1223 compounds at the ID30 beamline of the ESRF, using the Paris-Edinburgh large volume pressure cell. The combination of a high energy of 77 keV and fast 2D detector allowed us to obtained high quality diffraction spectra on the time scale of a minute up to ≈ 1500°C and 6GPa. The synthesis conditions used in the laboratory belt type apparatus were carefully reproduced (gold capsule, starting compositions, pressure and temperature). We could then determine the pressure and temperature stability ranges of the various phases involved in the reaction process, as well as the kinetics of reactions.

The main effect of increasing pressure was always to increase the reaction temperatures. The application of pressure first lead to amorphization of the starting materials, which progressively recrystallize at ≈400°C.

Starting from a stoichiometric mixture of HgO and Ba_2CuO_{3+x}, single phase Hg-1201was obained. The reaction involved a yet unknown intermediate phase. We also studied the growth of single crystals of this phase in a Hg-Ba-O flux. We were able to determine the flux melting point and the best temperature range for the Hg-1201crystal growth.

In the case of Hg-1223, starting from a HgO, $BaCuO_2$ and Ca_2CuO_3 stoichiometric mixture, we observed the existence of several new intermediate phases such as $Ca_{0.76}Hg_{1.24}O_2$ (structure determined later on by combined TEM and XRD on a sample prepared in the laboratory) and (Ca,Hg)O. The Hg1212, Hg1223 and Hg1234 were successively formed on increasing temperature, until melting of the gold capsule. The temperature range for single phase Hg-1223 is not larger than 30°C, whatever pressure used.

Notes