ESRF	**Experiment title:** **Structure and colossal dielecric properties of CaCu3Ti4O12**	**Experiment number**: HE-3384
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Report:

SR powder X-ray diffraction patterns of $CaCu_3Ti_4O_{12}$ (CCTO) have been measured using the high resolution diffraction beamline ID-31. The experiment covered the temperature range from 10 K to 973 K.

Low temperature behaviour

The main goal of the proposal was to study possible changes of the CCTO crystal structure and/or crystalline microstructure associated with the colossal dielectric constants observed below 100 K [1-3]. The SR powder diffraction patterns of CCTO measured at low temperatures below 100 K do not show evidence of any clear peak splitting, but there are subtle effects associated with some peakshape assymetry. These effects which maybe due to some microstrain changes are still under study and there is no clear conclusion at the moment.

High temperature behaviour

The high temperature measurements have shown an unusual and unexpected effect. The first powder CCTO sample was sealed in air inside a standard borosilicate glass capillary (this sample will be referred to as : “in-situ”). SR powder diffraction measurements were performed at temperatures between 100°C and 700°C in 100°C intervals. Suprisingly, above 500°C the appearance of several weak peaks is observed, see Fig. 1a, possibly indicating the presence of a new phase. The positions and intensities of these peaks agree well with those expected for pure bcc Cu [4]. The capillary

containing CCTO warmed "in-situ" was cooled down to RT and remeasured. The Cu phase clearly remains as shown in Fig. 1b

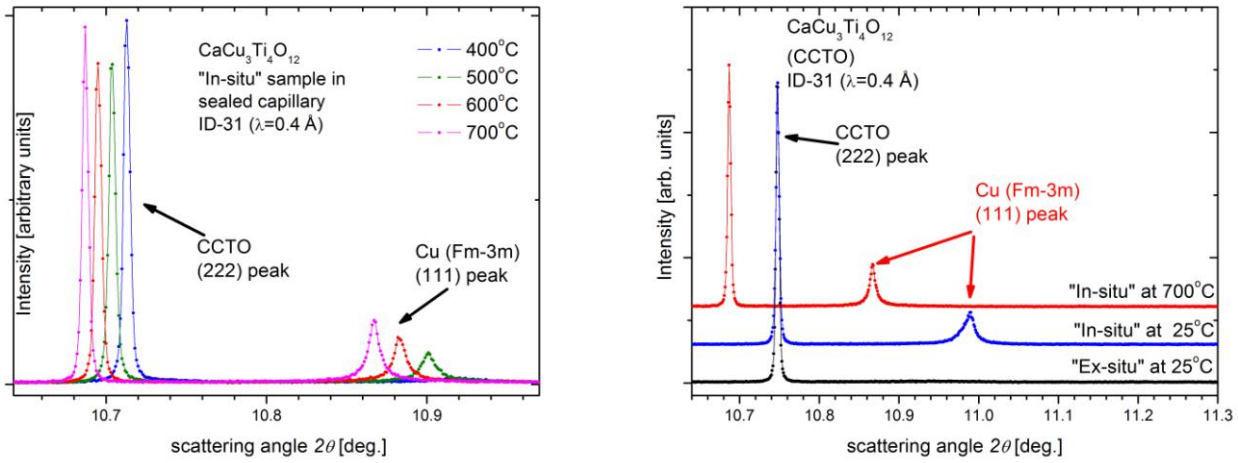

Fig. 1 Selected area of the SR powder diffraction patterns measured for $CaCu_3Ti_4O_{12}$ (CCTO) samples at different temperatures and conditions. Left panel (a) shows results for sealed CCTO ("in-situ" sample) at different temperatures **(increase of the Cu content)**. Right panel (b) compares the results for "in-situ" CCTO sample at 700°C and after cooling to RT **(Cu phase present)** with the results of the "ex-situ" CCTO sample annealed in an open oven **(Cu phase absent).**

Another part of the same CCTO powder batch was placed in an open crucible and annealed in an oven at 800°C for 2 hours and slowly cooled in the oven down to RT (this sample will be referred to as "ex-situ"). The "ex-situ" CCTO sample was measured with SR powder diffraction and there was no trace of the Cu phase (see Fig. 1b).

The unusual phase separation and redox chemistry identified in the $CaCu_3Ti_4O_{12}$ samples will require additional investigations with emphasis on compositional changes in the $CaCu_3Ti_4O_{12}$ phase in order to correlate its physical property with its composition and structure.

References

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