ESRF	**Experiment title:** In situ XRD investigation of $Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2}O$ high entropy oxide phase transition during CO catalytic oxidation	**Experiment number**: CH-5675
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Report:

The experiment was supposed be run under CO gas atmosphere. However, preliminary tests in our laboratories revealed that some structural distortions could be induced by heating the specimens even without recurring to reducing agents. Therefore, in order to allow remote control, the experiment has been carried out at atmospheric pressure. X-ray powder diffraction data for Q-space (XRD) and real-space (PDF) analysis were collected at incident energy ~100 keV, placing the detector respectively at 100 and 40 cm far from the sample. The sample-to-detector distances were calibrated with a Cr_2O_3 reference material. The powdered samples were filled into 0.3 mm quartz capillaries, sitting vertically on the goniometer head and spinning during data collection. The temperature on the sample was controlled using a hot air blower, heating by 2 deg/min up to 900 °C. The temperature of the air blower was calibrated using an alumina standard.

Six equimolar samples were investigated: the quinary HEO $(Mg_{0.2}Ni_{0.2}Co_{0.2}Cu_{0.2}Zn_{0.2})O$ and five quaternary samples obtained by removing one of the cations. The specimens are named after the missing cations. As an example, noMg stands for composition $(Ni_{0.25}Co_{0.25}Cu_{0.25}Zn_{0.25})O$.

All samples were checked at room temperature before heating. Impurities of spinel phase were well below 1%wt. Significant broadening of all reflections, except those of {hhh} family are consistent with a tetragonal distortion. However no peak split was revealed at room temperature. Preliminary PDF analysis revealed no obvious signal of lower symmetry, except for some peak broadening. More advanced investigations are ongoing. For the first ramps, data were collected by moving the detector from XRD to PDF position, after collection of a single frame at each position. Later on, we noticed an issue in the detector movement, so we moved to PDF configuration every 75 frames in XRD mode. The change of the actual detector position from the calibrated might prevent a correct PDF analysis of high temperature data.

The sample HEO shows two main effects with temperature, related to the peak broadening of the rock salt peaks, and to the segregation of secondary phases. Indeed, the (200) peak (black circles in Figure 1 left), and those with strong h component, broaden significantly up to ~500 °C. Then, the same peaks narrow, concomitantly with the

segregation of a secondary phase, detected as a very feeble signal, consistent with guggenite $MgCu_2O_3$. Further heating leads to the consumption of guggenite and segregation of CuO. The latter enters rock-salt phase above 800 °C to give a single phase compound. Conversely, the noCu sample shows no peak broadening (empty circles in Fig. 1 Left), nor phase segregations induced by heating. This confirms that Cu does play a major role in the tetragonal-like distortion and in general on the stability of HEO compounds.

On the contrary, noMg shows a rich set of transformations (Fig. 1 middle). Already at room temperature, it exhibits dramatic peak broadening. By increasing temperature, the (200) reflection becomes asymmetric showing a clear split above 250 °C (Fig. right). At ~320 °C a single tetragonal phase, fitted in space group *I*4/*mmm* was observed. Further heating leads to the progressive formation of the original cubic phase, with the concomitant segregation of single component oxides (spinel, zincite and tenorite). The secondary phases are characterized by very broad peaks, suggesting limited crystal dimension, which increased upon further heating. Full single phase is restored above 900 °C. The remaining samples (noZn, noCo and noNi) show a similar tetragonal distortion around 300°C as observed for noMg. However, rather than single element oxides, the tetragonal-distorted rock salt phase consumes to form guggenite, which in turn releases CuO upon heating. Again the rock-salt phase is restored at higher temperature.

To summarize, all the Cu-containing samples undergo upon heating a tetragonal phase transition or important broadening of (h00) reflections. This distortion seems to anticipate the nucleation of a guggenite phase, which is observed to grow with temperature. Guggenite is not observed in noMg and noCu samples, as Mg and Cu are not present. In the former, single element oxides are formed directly after the tetragonal distortion, while in noCu no distortion occurs. Hence, it looks like that the formation of the guggenite phase inhibits the segregation of the single constituent oxides, retarding the formation of CuO. Further studies will investigate the element composition of guggenite, to verify whether other cations do contribute to its formation.

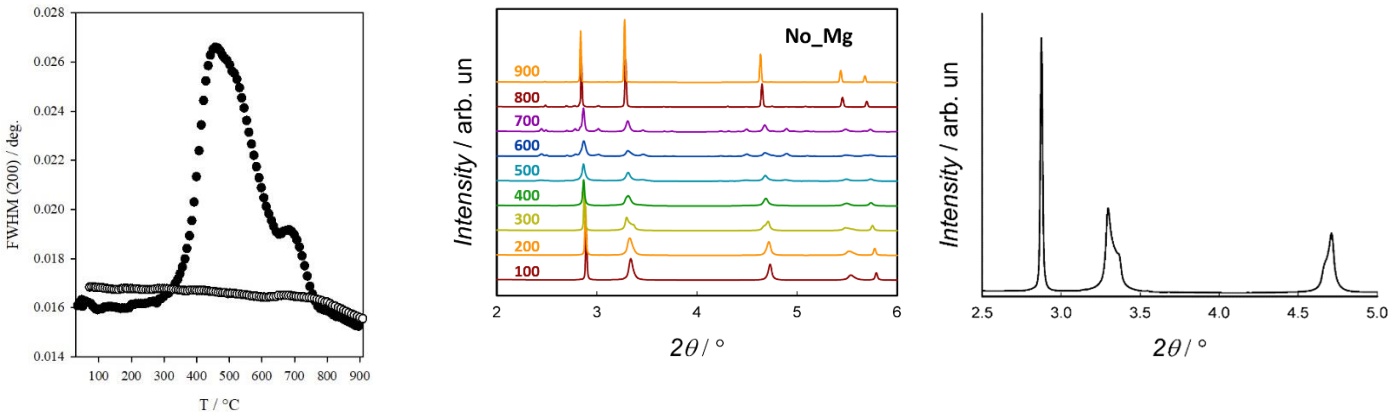

Fig. 1 left: FWHM of (200) for HEO (full circles) and noCu (empty circles). middle: Experimental XRD patterns of noMg upon heating. right: tetragonal pattern of noMg collected at 320 °C.