



	<b>Experiment title:</b> Exploring the tetragonal distortion in $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ high entropy oxide: a dark field X-ray microscopy investigation	<b>Experiment number:</b>
<b>Beamline:</b> ID06 - HXM	<b>Date of experiment:</b> from: 30/11/2021 to: 06/12/2021	<b>Date of report:</b>  <i>Received at ESRF:</i>
<b>Shifts:</b> 15	<b>Local contact(s):</b> Can Yildirim	
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Martina Fracchia <sup>a</sup> Serena Chiara Tarantino <sup>a</sup> Umberto Cevini <sup>a</sup>  <sup>a</sup> Dipartimento di Chimica, Università di Pavia Via Taramelli 12, Pavia, 27100, Italy		

## Report:

High entropy oxides (HEOs) are an emerging class of materials, where a particular crystal structure can be stabilized starting from a large number of oxide components (five or more, generally). The possibility to obtain a single phase is ascribed to the large value of configurational entropy that compensates for the negative enthalpic contribution. The prototypical high entropy oxide, reported by Rost in 2015, has chemical formula  $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$  and it presents a single-phase rock salt structure. In a recent XRD experiment, where we heated this metastable material up to 900°C, we observed that, above 250 °C, it undergoes a significant deviation from the ideal cubic structure, compatible with an incipient tetragonal distortion. This was evident in the pattern by a massive broadening of all peaks apart from those related to the {111} family. Above 500 °C, a small amount of guggenite is formed, while at higher temperature we observe CuO segregation. While the XRD clarified some aspects, the nature of this distortion was still not clearly addressed. The aim of this experiment was to investigate through dark field X-ray microscopy (DFXM) the distortion occurring upon heating in the rock-salt high entropy oxide (HEO) in the temperature range between 25 and 500 °C. The sample was first studied on a coarse scale, in order to identify and select one representative grain. This allowed to monitor the evolution of a single embedded grain at the different temperatures at the 200 reflection. In both cases, two type of scans were acquired at each temperature value, namely i) a mosaicity scan, with  $2\theta$  fixed and the sample tilted by the two perpendicular angles  $\phi$  and  $\chi$ , that gives information on the internal orientation of the embedded grain

ii) a strain scan, where  $2\theta$  is scanned, and a rocking scan around  $\phi$  is taken for each value of two theta. This gives indication on the lattice strain.

Some of the most significant results are summarized in Fig. 1. Fig. 1 a) shows the mosaicity maps acquired at the 200 reflection at the different temperatures As mentioned above, the mosaicity scan involves the movement of two motors, *i.e.* the tilting of the sample by  $\chi$  and  $\phi$ . The maps can therefore be displayed either as a function of the two angles, or just as a function of  $\chi$  or  $\phi$ . Here we choose to show them as a function of  $\chi$ , that allows a better resolution. In these maps, the color differences (*i.e.* the contrast) indicate the presence of different orientations inside the grain. For each temperature we chose a scale of  $\chi$  in order to give the maximum contrast. The larger the scale, the larger will be the angular spread over which our diffraction signal is extended. At 75 °C the scale is very small, ranging from 0.30° to 0.34°, meaning that the grain is homogeneous. By increasing the temperature, the scale is progressively larger, indicating a significant misorientation inside the grain. This effect intensifies at 500 °C, where the signal is spread over a range of 0.1°, denoting a massive distortion. Fig. 1 b) shows the scale range of  $\chi$  over temperature. It can be observed that an abrupt increase of  $\Delta\chi$  occurs between 250 and 300 °C; at this same region we observed the broadening of the 200 in the XRD patterns.

Very interestingly, as evident from Fig. 1 a), tweed-like textures start to appear inside the grain above 250 °C. Above 400 °C, part of the grain goes out of the diffraction condition, always according to specific directions. It should be noted that the same results, including the formation of the tweeds, are obtained with the strain scan, indicating that the deviation from the cubic structure is accompanied by a strong misorientation and lattice strain. Fig. 1 c) shows the Debye-Scherrer rings of the pellet at the end of the thermal treatment. It can be observed the presence of a peculiar strain-induced diffuse scattering around the 200 diffraction spots, which is not observed for the 111 reflection. This peculiar shape of the 200 spots is typically observed in presence of twin/tweeds.

Finally, it should be here noted that i) the same experiment was repeated for  $\text{Mg}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}\text{Zn}_{0.25}\text{O}$ , *i.e.* the high entropy oxide without copper. In this case, no tweed-like texture was ever observed in the mosaicity and strain maps. ii) a mosaicity/strain map was acquired for the sample  $\text{Cu}_{0.25}(\text{Mg}, \text{Ni}, \text{Co}, \text{Zn})_{0.75}\text{O}$ , *i.e.* the same high entropy oxide with an excess of copper. In this case, even at room temperature, we observe a tweed-like texture coupled to strain-induced diffuse scattering at the 200 diffraction spots. It is therefore natural to think that copper is the main responsible for the deviation of the ideal cubic structure, and that fluctuations in copper composition may result into the formation of the twee-like domains. However, the data are still under analysis and this assumption can be considered preliminary.

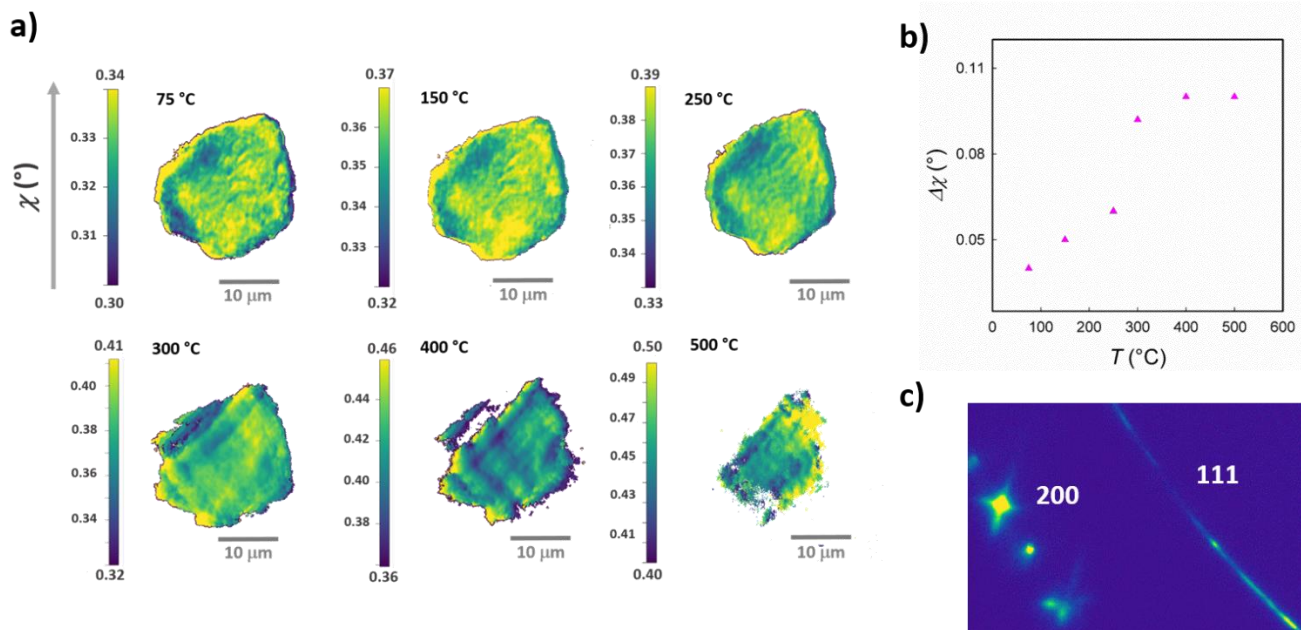


Fig. 1: a) Mosaicity maps as a function of  $\chi$  for high entropy oxide  $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$  at different temperatures. b) Variation of the  $\chi$  scale range at different temperature. c) Zoom of the Debye-Scherrer rings for  $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$  after the thermal treatment.