

Supporting Information

**Topochemical approach for transition metal exchange assisted by copper
extrusion: from Cu_2FeBO_5 to Fe_3BO_5 .**

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S1. Experimental section

The samples were prepared in air, starting from a mixture of $\{2 \text{ CuO} : 0.5 \text{ Fe}_2\text{O}_3 : 0.5 \text{ B}_2\text{O}_3\}$, pressed in the shape of bars, heated at 900°C during 24hrs.

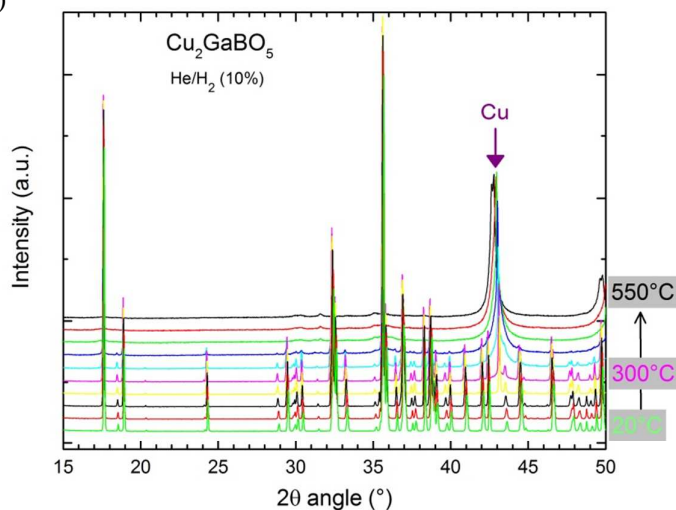
The quality of the samples was checked at room temperature (RT) by X-ray powder diffraction (XRPD) using a PANalytical diffractometer, working with Cu or Co radiations. These data were collected for the as-prepared and annealed samples and they were completed by *in-situ* studies (versus temperature) by means a D8 Bruker diffractometer (Cu $K_{\alpha 1}$) equipped with an Anton-Paar chamber, from RT up to 600°C in air or reducing atmosphere. The diffraction data were processed using the Fullprof software.^[22]

Thermogravimetric measurements (TGA) were done with a SETARAM apparatus, in similar temperature range and atmospheres as XRPD experiments.

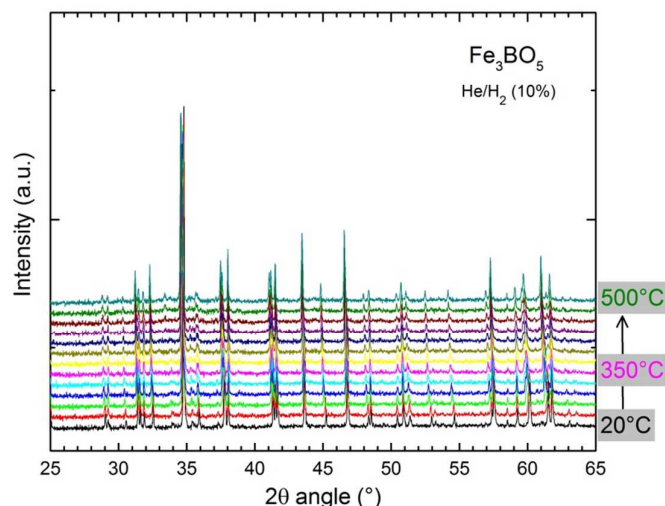
The transmission electron microscopy (TEM) studies, including high-resolution TEM (HRTEM) and electron diffraction (ED), were performed at room temperature with a 300kV high-angle Tecnai G² 30 UT (LaB6) microscope having 0.17 nm point resolution. High-angle annular dark-field scanning TEM (HAADF-STEM), annular bright field STEM (ABF-STEM) experiments and EDX elemental mapping were carried out on an aberration probe and image corrected 200 kV JEM ARM200F microscope equipped with CENTURIO EDX detector and QUANTUM GIF. TEM specimens were prepared by mechanical grinding of the sample in an agate mortar together with ethanol and the obtained suspension was then deposited on a Ni holey carbon grid.

Magnetic properties were characterized versus temperature (from 5 to 300K) in 100Oe (field cooling procedure) in a Quantum Design SQUID magnetometer.

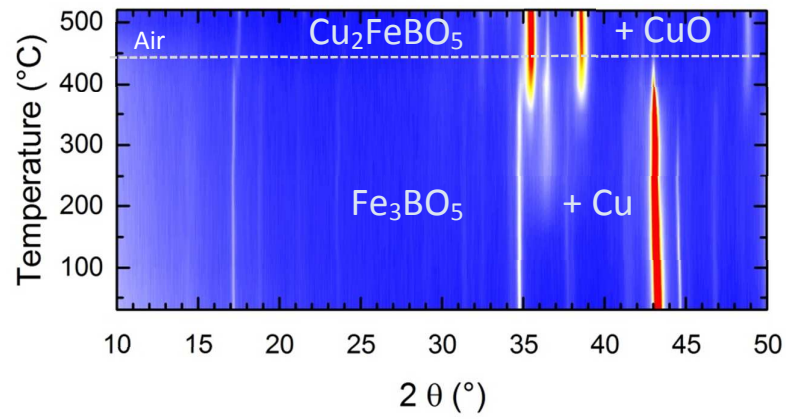
S2. Evolution of the XRPD patterns of Cu_2GaBO_5 versus temperature in reducing atmosphere (*In-situ* experiment, $\lambda=1.5406\text{\AA}$)



S3. Evolution of the XRPD patterns of Fe_3BO_5 versus temperature in reducing atmosphere (*In-situ* experiment, $\lambda=1.5406\text{\AA}$)



S4. : XRPD patterns showing the reversibility of the phenomenon: *in situ* evolution vs. temperature in air of the sample ($\text{Fe}_3\text{BO}_5 + \text{Cu}$) obtained by annealing Cu_2FeBO_5 in He:H_2 $\lambda=1.5406\text{\AA}$)



Cu