Experimental report

06/11/2023

Proposal: 5-23-785 **Council:** 10/2022

Title: Investigation of crystal and magnetic structure of high entropy oxides

Research area: Chemistry

This proposal is a new proposal

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Samples: Dy2(TiZrHfSnNb)2O7
(Y0.9Ca0.1)2(TiZrHfSnSc)2O7
(CoNiCuZn)0.80Fe0.20WO4
Dy2(TiZrHfSnSc)2O7
(CoNiCuZn)0.84Fe0.16WO4
(MgCoNiCuZn)WO4
(CoNiCuZnFe)WO4
(Dy0.975Ca0.025)2(TiZrHfGeSn)2O7
(Dy0.925Ca0.075)2(TiZrHfGeSn)2O7
(CoNiCuZn)0.76Fe0.24WO4

Instrument	Requested days	Allocated days	From	To
D2B	5	2	22/05/2023	24/05/2023
D1B	4	3	12/05/2023	15/05/2023

Abstract:

High entropy is an emergent strategy used for the design of new materials, which has aroused considerable interest over the last years. It was recently applied to rare-earth pyrochlore (A2B2O7) and tungstate (AWO4) oxides. High entropy pyrochlores and tungstates arouse our intention respectively for their oxygen ionic conductivity and for their magnetic properties combined with a surprising structural transition.
For these materials, we want an accurate description of the nuclear structure (position of the oxygens, possible distortion, etc.), and for tungstates, its evolution over the structural transition. Moreover, for tungstate, we also want to refine the magnetic structure at low temperature. 5 days are requested on D2B and another 4 days on D1B, both equipped with an orange cryostat.

Investigation of crystal and magnetic structure of high entropy oxides

High entropy oxide is an emerging concept that challenges the paradigms of material science and has aroused considerable interest over the last years. Similarly, to high entropy alloys, they are characterized by the large number of cations introduced on one or several sub-lattices of the crystal structure, giving rise to a high configurational entropy that drives the materials stability. Thus, this concept opens a new route for design of new material and enables to synthesize new versatile compounds with unique physical properties, highly tunable through substitutions, hole or electron doping, or finely tuning the stoichiometry.

Moreover, in high entropy materials, a cocktail effect has been shown [1], leading to not easily predictable properties as compared to monocationic compounds. The first high entropy oxide, (MgCoCuNiZn)O (rocksalt structure), was reported in 2015 by C.M. Rost et al. [2]. Compounds derived from this seminal composition present interesting physical properties such as colossal dielectric constants [3], high ionic conductivities or [4] an unexpected long-range antiferromagnetic order despite the strong chemical disorder [5]. This emphasizes the complexity and unpredictability of physical properties induced by high entropy.

High entropy tungstate (MWO_4) is a new family of high entropy materials, whose study is still in its very early stage. The monocationic compounds display almost all a monoclinic structure (space group P2/c) with spin chains, combined with antiferromagnetic long-range order with several different magnetic structures [6]. As an exception, because of Jahn Teller effect, $CuWO_4$ crystallises in a triclinic structure (space group P-1). Recently, we successfully synthesized a set of new high entropy tungstates, with various $(M)WO_4$ (M being combinations of cations belonging to Mg, Co, Ni, Cu, Zn, Fe, Ga or Li). Preliminary characterizations showed that $(MgCoNiCuZn)WO_4$ is isostructural to $MgWO_4$, and that it displays a transition with an antiferromagnetic ordering at TN=25K seen on the magnetization curve and confirmed by a preliminary neutron diffraction measurement performed on HRPT@SINQ. Moreover, a structural transition from a monoclinic to a triclinic structure at low temperature was observed by neutron diffraction, that could be linked to the presence of Jahn-Teller distortion around Cu^{2+}.

Outcome of Exp 5-23-785:

This proposal consisted in two experimental parts:

The first part of the experiment was carried on D1B (3 days) to look at the magnetic structure of tungstate HEOx with various cationic compositions on the metallic site. We used an orange cryostat to cool down the sample and worked at a neutron wavelength of 2.52Å. We collected diffractograms at several temperatures: 300, 100, 40, 30, 20, 10 and 2 K (1h counting time) per temperature) guided by magnetization data that showed the occurrence of a magnetic transition at 25K. We further continuously collected data on cooling for few compounds.

Our measurements showed the systematic occurrence of a magnetic transition to a long range ordered antiferromagnetic state in all of the compounds: $(MgCoCuNiZn)WO_4$, $(FeCoCuNiZn)WO_4$, $(CoFeZnNiMg)WO_4$ and $(CoCuniZn)_{0.76}Fe_{0.24}WO_4$, $(CoCuNiZn)_{0.9}Fe_{0.1}WO_4$ and $(CoCuNiZn)_{0.84}Fe_{0.16}WO_4$ (**Fig. 1.a-b**). The precise analysis of the magnetic structure is ongoing.

Our data further revealed the occurrence of the monoclinic to triclinic transition in the compounds that do not contain Fe on the metallic site.

[1] J. W. Yeh, Annales de Chimie 31(6), 633-648 (2006),
[2] C. M. Rost et al., Nat. Commun. 6, 8485 (2015)
[3] D. Bérardan et al., Phys. Status Solidi Rapid Res. Lett. 10, 328 (2016)
[4] D. Bérardan et al., J. Mater. Chem. A Mater. Energy Sustain. 4, 9536 (2016)
[5] M.P. Jimenez-Segura, Appl. Phys. Lett. 114, 122401 (2021)
[6] H. Weitzel, J. Magn. Magn. Mater. 4, 265-274 (1977)

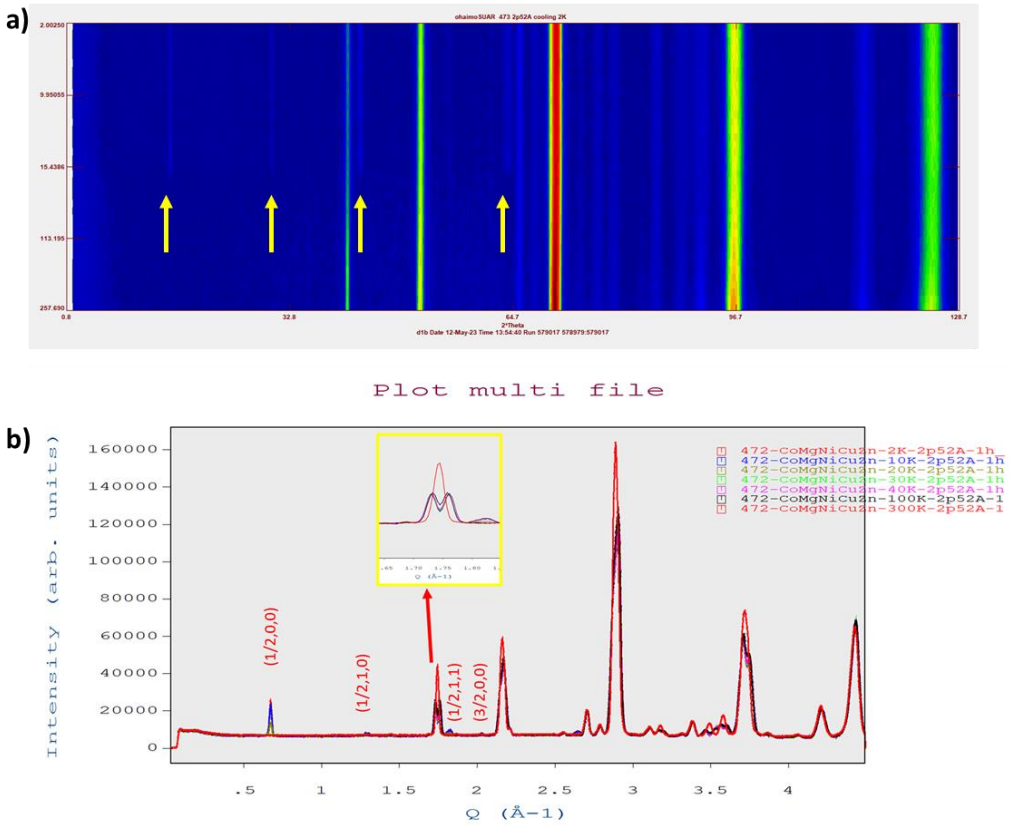

Fig.1. a) Map of the diffracted intensity collected on cooling in $(MgCoCuNiZn)WO_4$. The yellow arrows indicate antiferromagnetic peaks. **b)** Superposition of the diffractograms collected at 300, 100, 40, 30, 20 10 and 2K in $(MgCoCuNiZn)WO_4$. The magnetic peaks are indexed. The inset shows a Nuclear Bragg peak splitting due to the transition from a monoclinic to a triclinic structure.

The second part of the experiment was carried on D2B (2 days) in the following compounds: $(MgCuZnNiCo)WO_4$, $(FeCuZnNiCo)WO_4$ and $(FeMgZnNiCo)WO_4$. The aim of this experiment was to investigate the structural transition previously observed in $(MgCoNiCuZn)WO_4$. We used a wavelength of 1.594 Å and collected diffractograms at both room temperature (outside the orange cryostat in air) and low temperature (3.5K) using an orange cryostat. Additional measurements at 70, 100 and 150K were done in $(MgCuZnNiCo)WO_4$ and data were further collected at 170K in $(FeCuZnNiCo)WO_4$.

The high-resolution diffraction experiment confirmed that the monoclinic to triclinic transition only occurs in the compounds that do not contain Fe on the metallic site. A lower limit for the structural transition temperature can be given as 150K where $(MgCuZnNiCo)WO_4$ already exhibits the characteristic triclinic peak splitting (Fig.2). The precise structure analysis is an ongoing work.

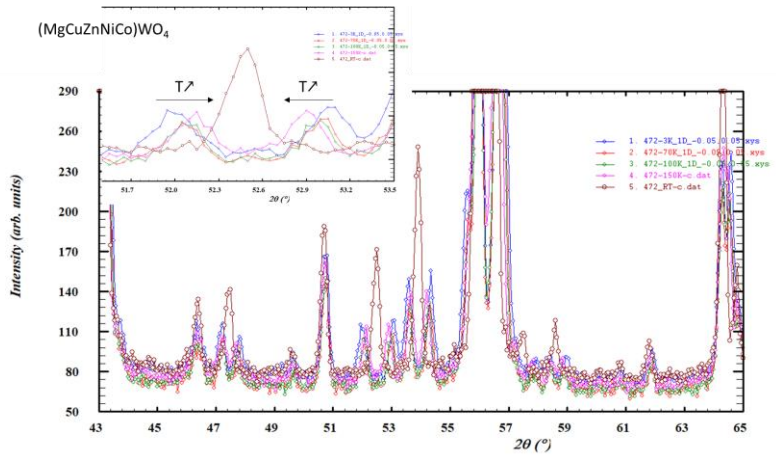

Fig.2. Superposition of the diffractograms collected at 300, 150, 100, 70 and 3K in $(MgCoCuNiZn)WO_4$. The inset shows a Nuclear Bragg peak splitting due to the transition from a monoclinic to a triclinic structure.

[1] J. W. Yeh, Annales de Chimie 31(6), 633-648 (2006),
[2] C. M. Rost et al., Nat. Commun. 6, 8485 (2015)
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