Abundant study of local structure peculiarities in $Cu_{1-y}Zn_yMo_{1-x}W_xO_4$ solid solutions

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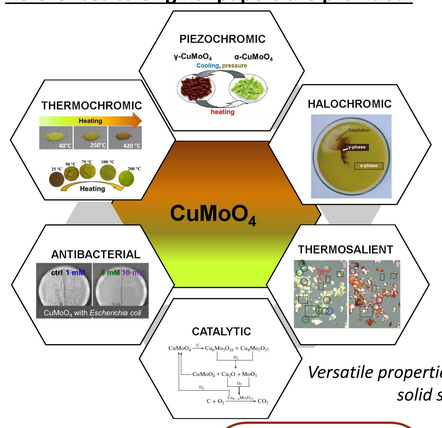
Introduction

The impact of the local atomic structure and lattice dynamics on the thermochromic properties of copper molybdate ($CuMoO_4$) and its solid solutions ($CuMo_{1-x}W_xO_4$ and $Cu_{1-y}Zn_yMoO_4$) was studied using X-ray absorption spectroscopy (**XAS**) and resonant X-ray emission spectroscopy (**RXES**). The experimental results were supported by the reverse Monte-Carlo (**RMC**) simulations coupled with ab initio multiple-scattering calculations.

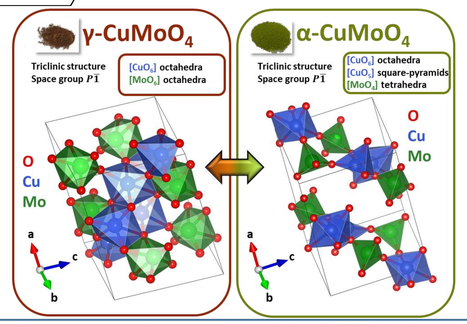
The thermochromic effect of $CuMoO_4$ below room temperature is caused by the α-to-γ structural phase transition whereas above room temperature the α-phase remains unchanged but thermal disorder plays an important role. The control of the α-to-γ phase transition temperature was achieved by chemical doping. Hysteretic type of the transition together with its tunability could be useful for an application of the material as a cheap and robust indicator for monitoring storage or processing conditions of temperature-sensitive products.

References to original papers are provided.



Versatile properties of $CuMoO_4$ and its solid solutions.

Potential application as an indicator for temperature-sensitive products.



Crystal structures and unit cells of low-temperature brownish-red (γ) and high-temperature green (α) $CuMoO_4$ phases.

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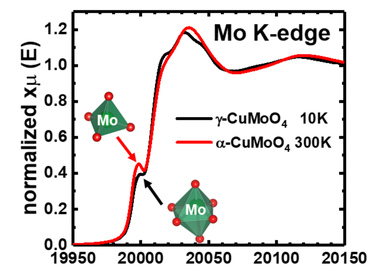
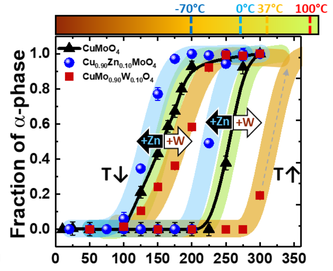
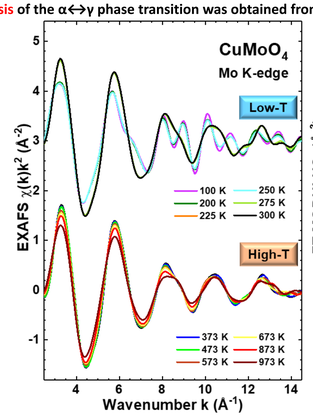
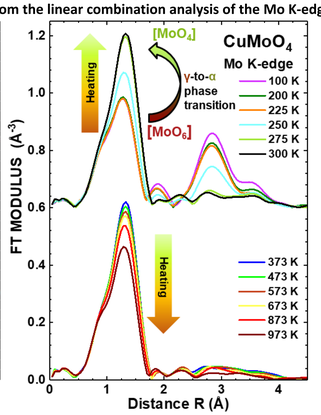
Mo K-edge





Hysteresis of the α↔γ phase transition was obtained from the linear combination analysis of the Mo K-edge XANES.

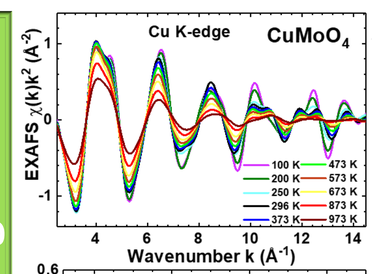


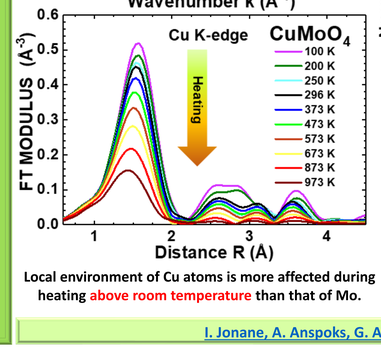


Coordination change from octahedral to tetrahedral was well pronounced in the Mo K-edge EXAFS spectra at low T.

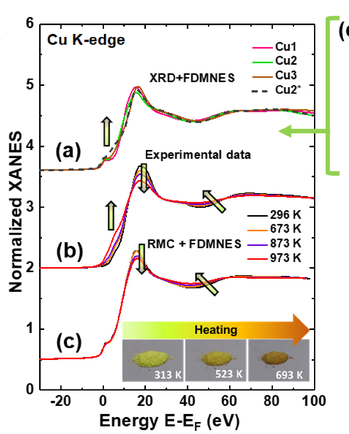
I. Jonane, A. Cintins, A. Kalinko, R. Chernikov, A. Kuzmin, Low Temp. Phys. 44 (2018) 568-572;
I. Jonane, A. Cintins, A. Kalinko, R. Chernikov, A. Kuzmin, Rad. Phys. Chem. 175 (2020) 108112;
I. Pudza, A.Anspoks, A. Cintins, A. Kalinko, E. Welter, A. Kuzmin, *Materi. Today Commun.* 28 (2021) 102607;

Cu K-edge





Local environment of Cu atoms is more affected during heating above room temperature than that of Mo.

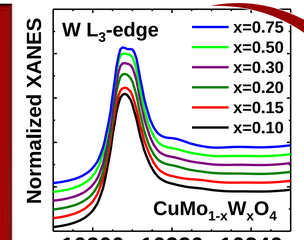


(a) The XANES spectra calculated for non-equivalent atoms (d) in the average structure of $CuMoO_4$. (b) The experimental XANES at selected temperatures. (c) The averaged XANES spectra calculated for the reverse Monte-Carlo (RMC) structure models at selected temperatures. (e) Illustration of correlation reduction in atomic motion between copper and axial oxygen.

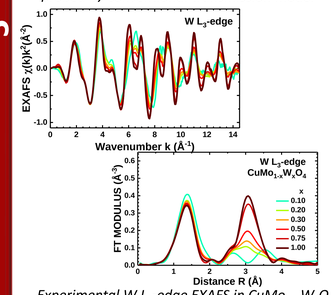
Thermal disorder affects strongly not only the Cu K-edge EXAFS, but also XANES region.

I. Jonane, A. Anspoks, G. Aquilanti, A. Kuzmin, Acta Mater. 179 (2019) 26-35;

W L_3-edge

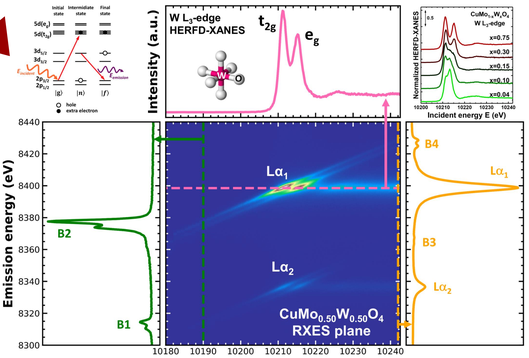


Experimental W L_3-edge XANES in $CuMo_{1-x}W_xO_4$ probed by conventional transmission mode.

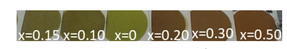


Experimental W L_3-edge EXAFS in $CuMo_{1-x}W_xO_4$.

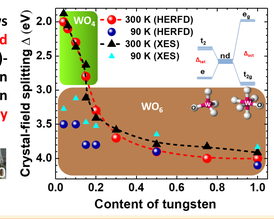
The advantage of RXES and HERFD-XANES



The analysis of the RXES plane allows one to determine the crystal field splitting parameter Δ for the 5d(W)-states and provides valuable information on the coordination of tungsten atoms in the material due to the high energy resolution.



$CuMo_{1-x}W_xO_4$ samples.



I. Pudza, A. Kalinko, A. Cintins, A. Kuzmin, Acta Mater. 205 (2021) 116581;

Conclusions:

- The Mo K-edge XAS spectra are strongly sensitive to the coordination of Mo atoms. The analysis of the experimental data allowed us to reconstruct the hysteresis of the α-to-γ phase transition in $CuMoO_4$ and its solid solutions.
- Data analysis of EXAFS spectra at all metal edges simultaneously by RMC method, allows one to follow the temperature variation of the local environment in low symmetry materials.
- At low temperatures, γ→α phase transition occurs gradually, the Mo coordination changes from strongly distorted octahedral to less distorted tetrahedral.
- At high temperatures, the reduction of correlation in atomic motion between Cu and axial O atoms in CuO_6 octahedra occurs.
- The analysis of the RXES plane provides useful bulk sensitive information on the coordination of tungsten atoms and allows one to determine the crystal-field splitting parameter Δ for the 5d(W)-states. Preference of tungsten ions to form the octahedral environment, as compared to molybdenum ions, was evident.