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XAS and RXES studies of phase transitions in $CuMo_{1-x}W_xO_4$ solid solutions

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$CuMo_{1-x}W_xO_4$ solid solutions are multifunctional materials demonstrating remarkable properties, including thermochromic, piezochromic, halochromic, thermosalient and catalytic. Therefore, the structure-property relationship must be understood to learn how to control their functionality.
At atmospheric pressure, pure $CuMoO_4$ exists in two phases – low-temperature γ-phase with dark brown colour and high-temperature α-phase with green colour. The phase transition has a hysteretic behaviour. Furthermore, it is possible to tailor the properties of the molybdate by applying external pressure or by modifying its composition. Depending on the tungsten content, $CuMo_{1-x}W_xO_4$ solid solutions can be obtained in phases isostructural to high-pressure $CuMoO_4$.
To understand the relationship between structural and thermochromic properties in $CuMo_{1-x}W_xO_4$ solid solutions, we performed temperature and composition-dependent X-ray absorption spectroscopy study at the Cu and Mo K-edges and W L_3-edge. Analysis of the Mo K-edge X-ray absorption near-edge structure (XANES) allowed us to determine the hysteresis of the phase transitions. Extended X-ray absorption fine structure (EXAFS) spectra were interpreted using reverse Monte Carlo modelling. The sensitivity of the resonant X-ray emission spectroscopy (RXES) was further used to study the α-to-γ phase transition in $CuMo_{1-x}W_xO_4$ from a tungsten perspective. We extracted information on the crystal-field-induced splitting of the 5d(W) states from the W 2p3d RXES plane by analysing the high-energy resolution fluorescence detected X-ray absorption near-edge structure and off-resonant X-ray emission spectra. The experimental results were interpreted using ab initio calculations.
It was found that an increase of tungsten content promotes the coordination change of molybdenum atoms from tetrahedral to octahedral which is accompanied by the material's colour change from greenish to brownish.
This study demonstrates the possibilities of the XAS and RXES techniques to probe coordination changes in functional thermochromic materials with controllable properties on the example of $CuMo_{1-x}W_xO_4$.

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