Low-temperature X-ray absorption spectroscopy study of $CuMoO_4$ and $CuMo_{0.90}W_{0.10}O_4$ using advanced reverse Monte-Carlo simulations

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Copper molybdate ($CuMoO_4$) is one of the most interesting transition-metal molybdates that exhibits thermochromic, piezochromic, tribochromic, photoelectrochemical and also promising catalytic and antibacterial properties. Specific atomic and electronic structure makes it as perspective inorganic compound in wide range of chromic-related applications. Currently six different structural phases of $CuMoO_4$ are known. At ambient pressure and below 300 K, $CuMoO_4$ exists in two phases: brownish-red γ-$CuMoO_4$ and green α-$CuMoO_4$. The hysteretic-type transition from the γ-to-α phase occurs in the temperature range of 230-280 K upon heating, whereas the α-to-γ transition occurs between 120 and 200 K upon cooling. Phase transition temperature can be changed by applying external pressure or by modifying composition.

Thermochromic phase transition was studied in $CuMoO_4$ and $CuMo_{0.90}W_{0.10}O_4$ using the Cu and Mo K-edge and W L_3-edge X-ray absorption spectroscopy in the temperature range of 10-300 K. Theoretical calculations of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were performed to shed light on details of the phase transition. Recently developed reverse Monte-Carlo method based on evolutionary algorithm (RMC/EA) was used to reconstruct structural model of the material consistent with experimental EXAFS data for several edges simultaneously. The RMC/EA method is based on iterative random changes of atomic coordinates within 3D structure model of the material. In each iteration theoretical and experimental EXAFS spectra were compared in k and R space simultaneously using Morlet wavelet transform. EA operations significantly improve the convergence and the speed of simulations and make feasible calculations for materials with complex structures like $CuMoO_4$.

The analysis of XANES showed thermochromic phase transition with well-evidenced hysteretic behavior. By substituting 10% of Mo atoms with W in $CuMoO_4$, γ-to-α phase transition temperature was increased by ≈25 K. RMC/EA study allowed us to reconstruct radial distribution functions and extract structural parameters as a function of temperature. Besides, we were able to extract the Wyckoff positions of atoms in the unit cell from the results of RMC/EA fits: they are in good agreement with the known experimental diffraction data.

RMC/EA study for $CuMo_{0.90}W_{0.10}O_4$ showed that simultaneous analysis of three metal atom edges is required to obtain reliable structural information. The obtained results allowed us to understand better the connection between structural and optical properties in $CuMoO_4$ and $CuMo_{0.90}W_{0.10}O_4$.

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