

# Role of lithium diffusion on thermal expansion of $\text{Li}_{0.4}\text{WO}_3$ bronze studied by neutron elastic and quasi-elastic scatterings

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Diffusion of interstitial cations in ionic conductors plays roles on the thermal expansion [1,2], which is of prime importance for the functionality of materials at a given temperature. We report the anomalous lattice thermal expansion of  $\text{Li}_{0.4}\text{WO}_3$  bronze. The polycrystalline sample was produced by solid state synthesis at low pressure and 973 K. The sample was characterized by time-of-flight neutron powder diffraction (NPD) and quasi-elastic neutron scattering (QENS). The as-synthesized  $\text{Li}_{0.4}\text{WO}_3$  crystallized in the  $Im\bar{3}$  space group [3], where the  $6b$  Wyckoff position is found to be partially occupied by lithium and the  $2a$  site to be vacant. At the  $6b$  position four planar oxygen atoms construct a small aperture of 26.7 pm, and the  $2a$  site a larger cavity of 39.5 pm for possible lithium diffusion. Temperature-dependent NPD data Rietveld refinements showed that the  $\text{Li}^+$  cations preferentially diffuse between 300 K and 500 K from the  $6b$  into the  $2a$  site, which supports the ionic conductivity of some  $\text{Li}_x\text{WO}_3$  bronzes at high temperatures [4] as well as diffusion-based phase transition at ambient condition [3]. Thus, at this temperature regime a statistical equilibrium (dynamic disorder) exists between two sites. With increasing temperature, the occupancy of lithium at the  $2a$  site increases and that of the  $6b$  site decreases. QENS data analysis followed by modelling provides more insights on the lithium diffusion. A sharp minimum of thermal expansion coefficient is observed at 425 K, which does not show high-temperature saturation. The low-temperature metric expansion can be modelled using a single Debye term. The take-off departure of the model line from the observed data is explained in terms of Li-dynamics and high-temperature anharmonicity. Indeed, using an additional Debye spectrum with a low-perturbed quantum anharmonicity term the evolution of the metric parameter can better be modelled [5]. While understanding Li-diffusion mechanism is essential for its full potential as solid electrolyte, the dynamics of lithium in tungsten bronzes and the associated thermal expansion anomaly would shed more lights on relevant studies.

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