

MS21-P12 Hysteresis in the solid-state phase transition in DL-NorvalineJun Xu¹, Anthony Linden¹, Hans-Beat Bürgi^{1,2}

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DL-Norvaline is an artificial and non-polar amino acid with chemical formula $C_5H_{11}NO_2$. DSC measurements show that it undergoes two temperature-dependent phase transitions, at about 188 K and 153 K.^{1,2} It shows substantial disorder with three principal conformations of the propyl side chain in the room-temperature β -phase (A, B, C) and two main conformations (B, D) in the intermediate-temperature α -phase.³ The structure of the low-temperature phase is still unknown, due to crystal delamination before the γ -phase is observed.³

We have found that the onset of the β to α phase transition can be delayed and is dependent on the cooling rate. Three crystals instantly cooled from room temperature, and nine crystals rapidly cooled within a few minutes, go through the first phase transition near 188 K. Slow cooling of 5 crystals in steps of 20 K from 300 K to 140 K and waiting 10 hours at each temperature during an X-ray data collection, reveals that the onset of the phase transition occurs only at lower temperatures, sometimes as low as 140 K, and in one case no transition occurred at all. The sluggish phase transition correlates with a different temperature dependence of the atomic displacement and site occupation parameters for the three molecular conformations, compared with those observed following fast cooling. As the temperature decreases, the population of the A conformation in the β -phase grows at the expense of the population of the B conformation, while that of the C conformation remains fairly constant.

In contrast, the populations of the B and D conformations in the α -phase remain constant across the measured temperature range (140-180 K).

Crystals that were rapidly cooled below 188 K transformed to the α -phase, but further rapid cooling to 140 K, which is below the temperature expected for transformation to the γ -phase, did not reveal any significant change of the unit cell or structural parameters, so no evidence for the formation of the γ -phase could be obtained.

References:

- 1 Chatzigeorgiou, P. et al., J. Phys. Chem. B 2010, **114**, 1294-1300.
- 2 Ren, P. et al., J. Phys. Chem. B 2011, **115**, 2814-2823.
- 3 C.H. Görbitz, J. Phys. Chem. B 2011, **115**, 2447-2453.

Keywords: Hysteresis**MS21-P13** Determination of the crystal structure, composition and water uptake of the mixed ionic-electronic conductor

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The presented work on proton conducting materials will show new results on the structural characterization of substituted lanthanum tungstate: $La_{3-4}W_{1-x}Re_xO_{12-\delta}$ with $0 \leq x \leq 0.2$ in two different conditions (dry(Ar), wet-D₂O(Ar)). Among the specimen series measured, the specimen without substitution ($La_3WO_{12-\delta}$) and the one with highest Re-substitution level ($x = 0.2$) will be in the focus of the presentation. Their comparison will be achieved considering neutron diffraction results, due to the insufficient contrast between W ($Z = 74$, $b = 4.86$ fm) and Re ($Z = 75$, $b = 9.2$ fm) against X-Rays.

The structural model of the undoped system $La_3WO_{12-\delta}$ recently suggested will be thoroughly analyzed, independently confirmed, and taken as starting point to determine the position of Re atoms in the crystal structure. Anharmonic vibrations of the oxygen anions are for the first time found in LaWO-based systems and shortly discussed.

Neutron diffraction data was obtained from D2B (ILL, Grenoble), HRPT (SINQ, Villigen) and FIREPOD (BERII, Berlin) in the temperature range between 1.5 K and 1200 K.

Three models will be presented for the Re-substituted system within the $Fm-3m$ space group: Re substituting W on the main W position (Wyckoff site 4a), Re substituting W on the shared La/W position (Wyckoff site 48h) and Re substituting W statistically on both sites. Substitution amount in the shared sites is reached refining site occupancy factors in a single-atom-per-site approach (average neutron scattering length). Restraining of the site occupancy factors according to electron probe micro-analysis composition was mandatory to decrease the degrees of freedom.

Notwithstanding the low Re amount (~1 atom per unit cell out of 32 cations and 55 oxygen anions) and the close neutron scattering length of Re to the main element La ($Z = 57$, $b = 8.24$ fm), the very details of the structure were unambiguously determined by the combination of thermogravimetry, neutron diffraction and electron probe micro-analysis. Surprisingly, even one single Re atom in such a large unit cell ($\approx 1400 \text{ \AA}^3$) strongly influences the water uptake. This peculiar feature will be discussed in relation to the stoichiometry, the oxygen site occupancy factors and the bond lengths in wet and dry specimens.

Keywords: mixed ionic-electronic conductor, Re-substituted lanthanum tungstate, neutron diffraction, water uptake