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Floating zone growth of complex shear plane phases

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"Wadsley–Roth"-phased crystal structures have defied accurate crystallographic determination since their discovery in 1965. These structurally challenging materials comprise transition-metal oxides whose oxygen vacancies condensed to give rise to intricate structures and short-range order compounded by second-order Jahn–Teller distortions experienced by the d^0 cations. Structural studies have been hampered by the small crystals obtained from annealing, which led to unclear resolutions on the precise space groups of the materials.

Here, PARADIM's Bulk Crystal Growth Facility supported the work of users from the University of Utah using the laser diode floating zone technique and a traveling solvent method to obtain centimeter-sized high-quality crystals of niobium tungstate. The characterization revealed additional symmetry than previously assumed. $Nb_{12}WO_{33}$ crystallizes in *I*2/*m* and $Nb_{14}W_3O_{44}$ in the *I*4/*m* space group. We also find oxygen-deficient (reduced) crystals to have significant twinning and drastically different electrochemical properties when cycled against a lithium anode from their oxidized counterpart.

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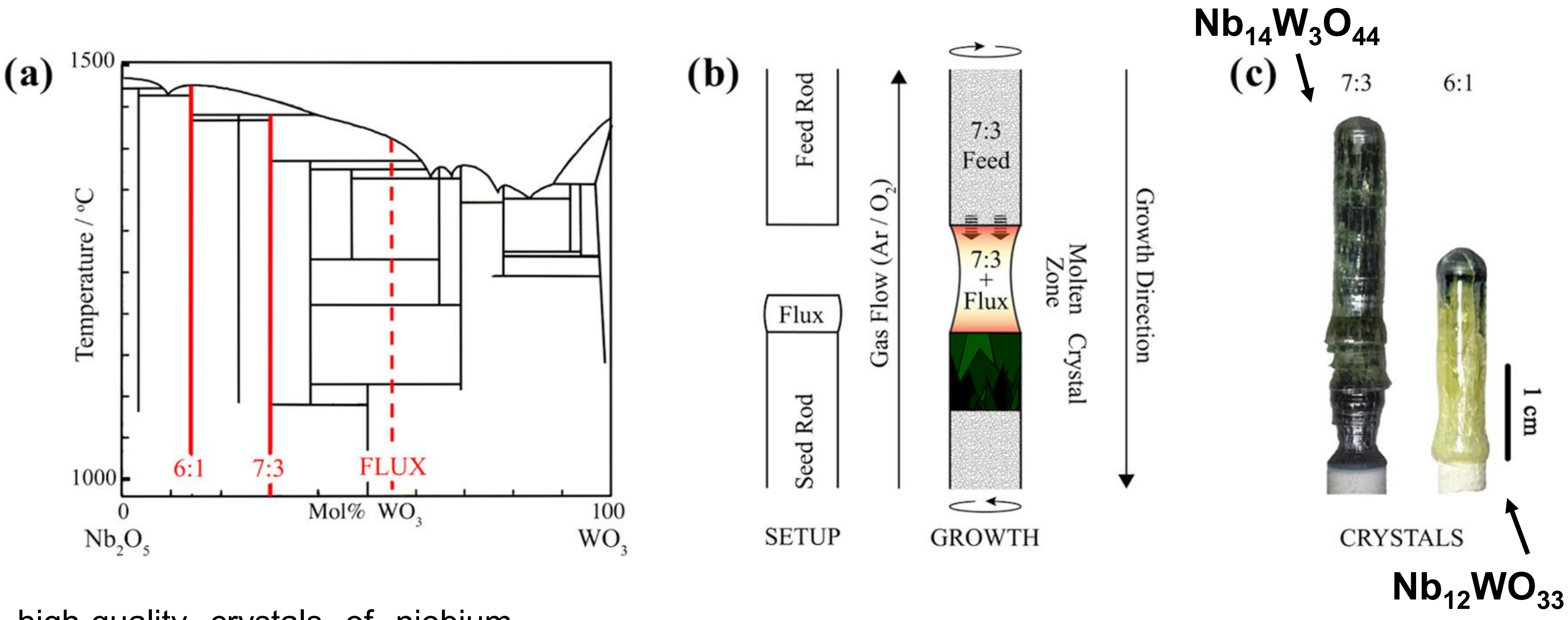

Figure: (**a**) The Nb_2O_5–WO_3 binary phase diagram adapted from ref (36) with line compounds $Nb_{12}WO_{33}$ (6:1) and $Nb_{14}W_3O_{44}$ (7:3) highlighted in red and the 55 wt % WO_3 self-flux shown as a dotted red line. (**b**) Schematic of the laser diode floating zone furnace setup used to grow high-quality crystals of 6:1 and 7:3. Note that the 6:1 growth did not require a flux. **(c)** Photos of the obtained centimeter-sized crystal boules.