

Thermal analysis and phase relations in the pseudobinary system $\text{La}_2\text{W}_2\text{O}_9\text{--Li}_2\text{W}_2\text{O}_7$

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Tetragonal scheelite-like double tungstates belong to the family of $\text{ARE}(\text{WO}_4)_2$ compounds constituted by alkali ($A = \text{Li, Na, K}$) and rare earth ($\text{RE} = \text{Y, Sc, La - Lu}$) cations. The structures are disordered where the alkali and rare earth cations are statistically distributed at the same lattice site. Such cationic distribution strongly influences the optical properties of the materials generating a locally variable crystalline field which leads to the broadening of the absorption and luminescence lines of the dopant ions. This property is highly desired for solid state lasers. The double tungstates $\text{ARE}(\text{WO}_4)_2$ were often described as intermediate phases in the $A_2\text{WO}_4 - \text{RE}_2(\text{WO}_4)_3$ binary systems. However, contradictory results relative to phase diagram for Li-La, about the melting behaviour of $\text{LiLa}(\text{WO}_4)_2$ were observed on the growth of single crystalline fibers for laser applications. In this work, we propose an experimental phase diagram for the $\text{La}_2\text{W}_2\text{O}_9\text{--Li}_2\text{W}_2\text{O}_7$ pseudo-binary section. The construction was based on differential thermal analysis and the phases were determined by X-ray powder diffraction with subsequent Rietveld analysis. The pseudobinary phase diagram $\text{La}_2\text{W}_2\text{O}_9\text{--Li}_2\text{W}_2\text{O}_7$ contains the 1:1 intermediate phase $\text{LiLa}(\text{WO}_4)_2(\text{ss}) = x \text{Li}_2\text{W}_2\text{O}_7 - (1 - x) \text{La}_2\text{W}_2\text{O}_9$ with a homogeneity region $0.48 \leq x \leq 0.546$. $\text{LiLa}(\text{WO}_4)_2$ undergoes peritectic melting at $998 \pm 5^\circ\text{C}$ for $x = 0.48$. A eutectic point exists between $\text{LiLa}(\text{WO}_4)_2$ and $\text{Li}_2\text{W}_2\text{O}_7$ at $722 \pm 5^\circ\text{C}$ and 90mol% $\text{Li}_2\text{W}_2\text{O}_7$.