On the Optical Properties of the Solid Solution $LiBaLa_{1-x}Pr_xWO_6$ with x = 0.0 to 1.0

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Background

Tungstates have recently generated high interest in academic and commercial research as potential host structures for rare earth ions. Comprising a sublattice of WO_4^{2-} or WO_6^{6-} moieties this group of inorganic compounds offers unique properties in combination with trivalent lanthanide ions such as Eu^{3+}, Pr^{3+}, or Tb^{3+}. Large unit cells, high refractive indices, high physical, and chemical stability as well as their rather ease of synthesis characterise tunstates [1]. High possible activator concentration and energy transfer from the ligand-to-metal charge transfer (LMCT) can counteract the natural drawback of a low absorption cross section in Ln^{3+} ions.

Phase formation and structure

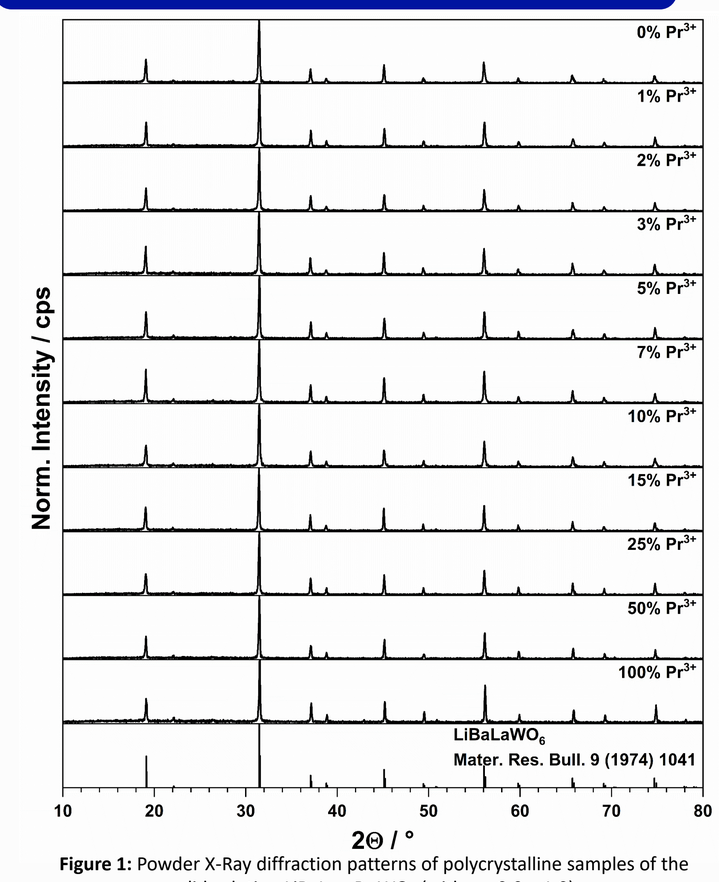

Figure 1: Powder X-Ray diffraction patterns of polycrystalline samples of the solid solution $LiBaLa_{1-x}Pr_xWO_6$ (with x = 0.0 – 1.0).

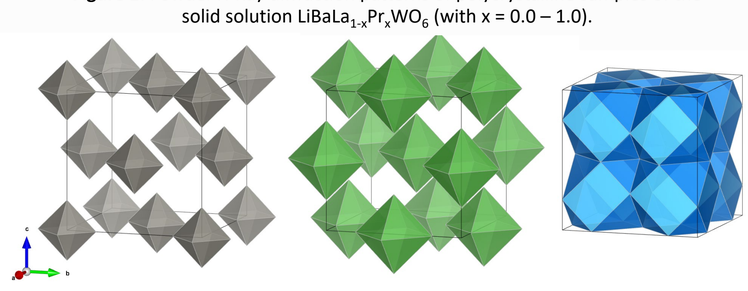

Figure 2: Crystal structure and polyhedra of $LiBaLaWO_6$. [WO_6]-octahedrons in grey, [LiO_6]-octahedrons in (green), [(La,Pr)O_{10}]- and [BaO_{10}]-polyhedrons in green [2].

- **Cubic – double perovskite structure**
- **Space group: *Fm-3m* (# 225)**
- **a = b = c = 8.01422 Å**
- **Cell volume: 0.51473 nm³**

Acknowledgements

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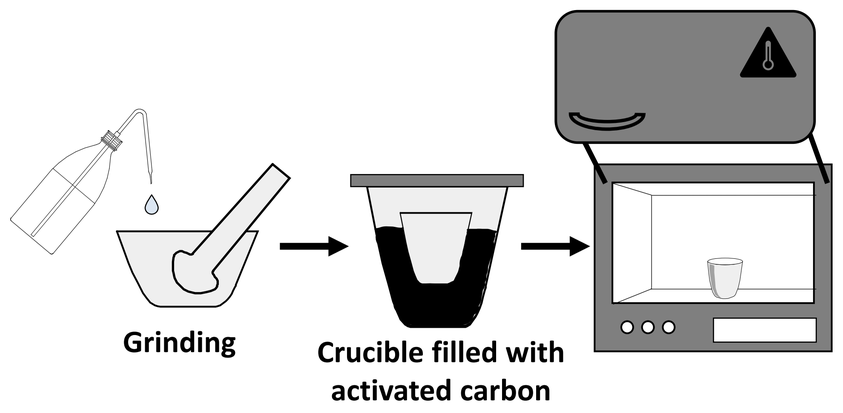
Sample Preparation

Solid State Synthesis

- Li_2CO_3, $BaCO_3$, La_2O_3, $Pr_2(C_2O_4)_3 \cdot 10H_2O$, and WO_3 as educts
- Precalcination of La_2O_3 at 1000 °C
- Li_2CO_3 in an excess of 20 wt-%
- Grinding using an agate mortar
- Annealing at 1150 °C for 10 hours in a reducing CO atmosphere



Optical Properties

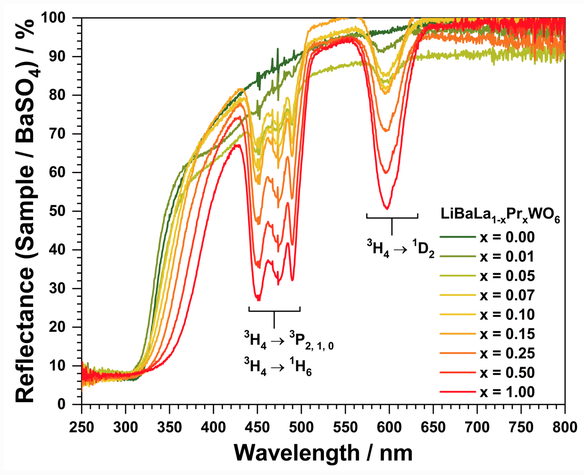


Figure 3: Diffuse reflectance spectra of the solid solution $LiBaLa_{1-x}Pr_xWO_6$ (with x = 0.0 – 1.0).

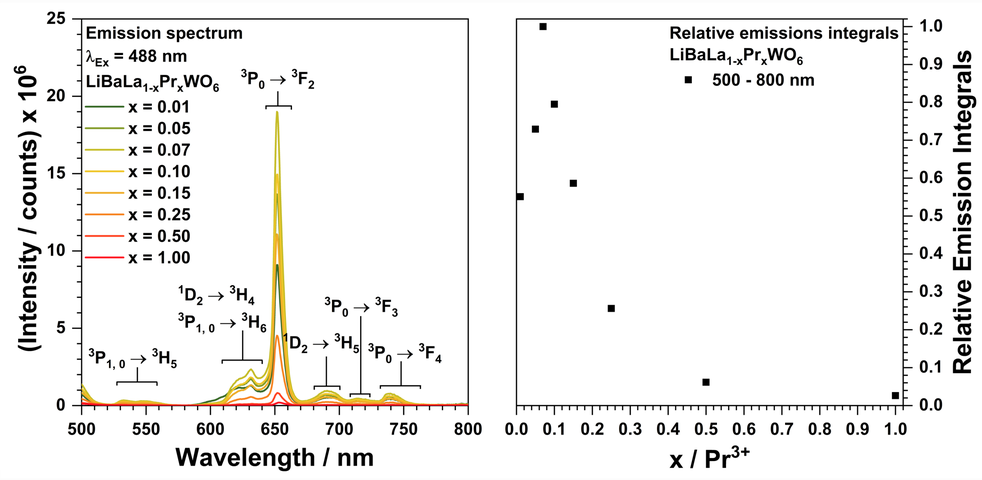


Figure 4: Emission spectra of the solid solution $LiBaLa_{1-x}Pr_xWO_6$ (with x = 0.0 - 1.0) upon 488 nm excitation (left). The respective emission integrals of the polycrystalline samples (right).

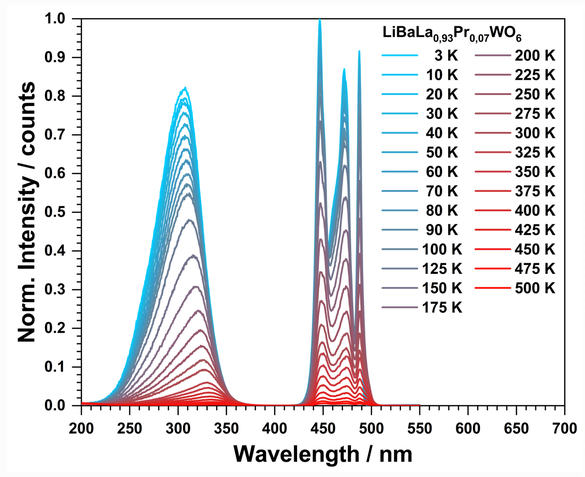


Figure 5: Temperature dependent relative excitation spectra of $LiBaLa_{1-x}Pr_xWO_6$ between 3 and 500 K. The emission maximum at 651 nm was monitored.

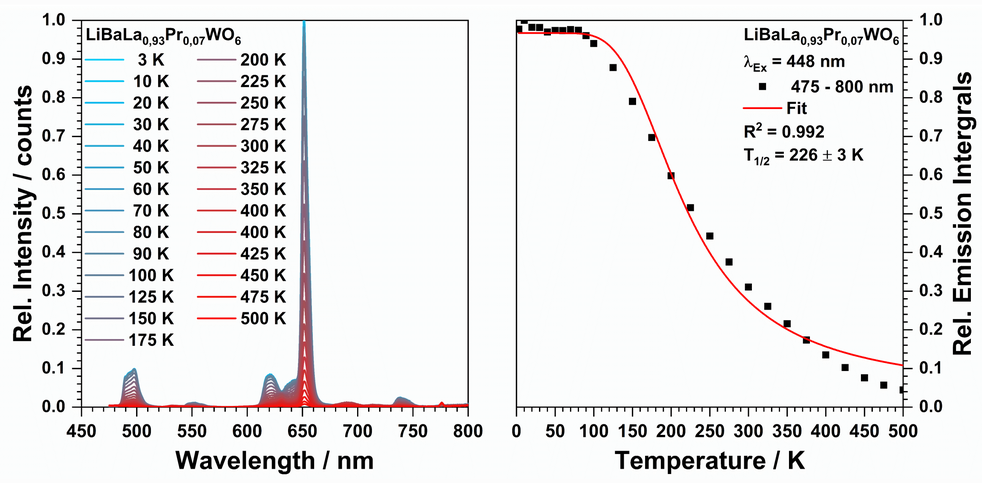


Figure 6: Temperature dependent relative emission spectra of $LiBaLa_{1-x}Pr_xWO_6$ between 3 and 500 K upon 448 nm excitation (left). The respective relative emission integrals and the resulting fit after applying the Struck-Fonger equation.

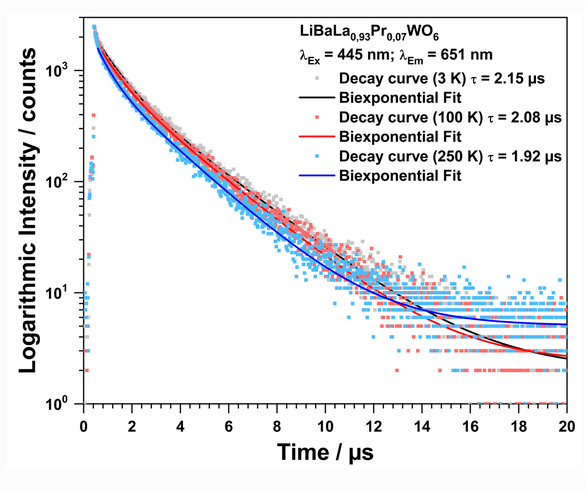


Figure 7: Temperature dependent decay measurements between 3 and 250 K upon excitation at 445 nm by using a flash lamp.

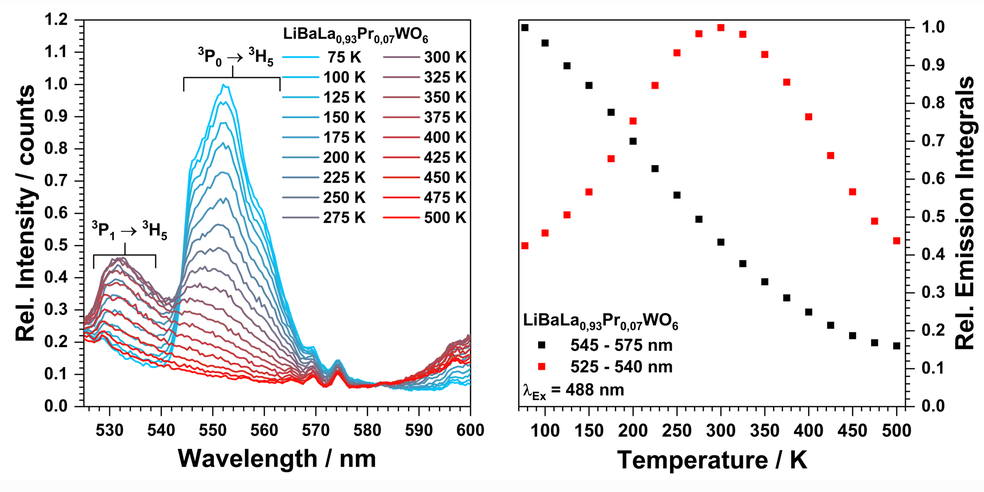


Figure 8: Temperature dependent relative emission spectra of $LiBaLa_{1-x}Pr_xWO_6$ between 75 and 500 K (left) and the respective relative emission integrals (right)

Results

- **Reflectance: Red shift of absorption edge due to Pr^{3+} doping. Novel (Pr^{3+}-W^{6+} ↔ Pr^{4+}-W^{5+}) MMCT**
- **Doping by 7 atom-% Pr^{3+} resulted in the most efficient phosphor sample**
- **Emission maximum at 652 nm, due to hypersensitive, parity forbidden $^3P_0$ → $^3F_2$ transition of Pr^{3+}**
- **Stable emission intensity below 100 K and $T_{1/2}$-value of 226 K**
- **Radiative lifetime at 3 K: 2.15 µs**
- **Thermal population of the $^3P_1$ from the $^3P_0$ with subsequent radiative relaxation into the $^3H_5$ state**

References

[1] T. Pier, T. Jüstel, J. Lumin. 262 (2023) 119958
[2] L.H. Brixner, Mater. Res. Bull. 9 (1974) 1041