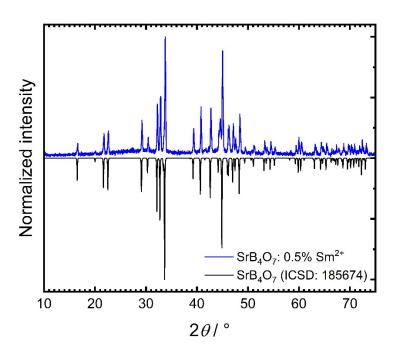
## **Electronic Supplementary Material**

## How to calibrate luminescent crossover thermometers: A note on "quasi"-Boltzmann thermometers

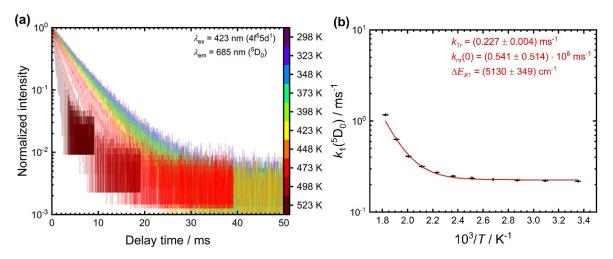
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**Figure S1.** Powder X-ray diffraction pattern (Cu  $K_{\alpha 1}$  radiation,  $\lambda = 1.5406$  Å) of synthesized microcrystalline SrB<sub>4</sub>O<sub>7</sub>: 0.5% Sm<sup>2+</sup> in comparison to a database pattern simulated from single-crystal structural data on SrB<sub>4</sub>O<sub>7</sub> (ICSD depository no.: 185674)<sup>[1]</sup>.



**Figure S2. (a)** Temperature-dependent luminescence decay curves ( $\lambda_{ex} = 423$  nm) of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ -related emission at 685 nm. All curves showed a single exponential decay. **(b)** Temperature evolution of the extracted decay rates  $k_{1}$ . The red line indicates a fit to the sum of  $k_{1r}$  and the non-radiative contribution modelled by eq. (1) in the manuscript. Due to the lack of more high-temperature points,  $k_{nr}(0)$  and  $\Delta E_{X1}$  cannot be reliably determined from the fit.

## Derivation of eq. (4) from eq. (3) in the manuscript

We start with eq. (3) of the manuscript

$$R_{21}(T) = \frac{I_2}{I_1} = C \frac{n_2}{n_1} = C \frac{\alpha_{a2}k_{1r} + (\alpha_{a1} + \alpha_{a2})k_{nr}(0)\exp\left(-\frac{\Delta E_{X1}}{k_B T}\right)}{\alpha_{a1}k_{2r} + (\alpha_{a1} + \alpha_{a2})k_{nr}(0)}.$$
(S1)

The electronic pre-constant C can be defined as

$$C = \frac{k_{2r}}{k_{1r}},\tag{S2}$$

if the two radiative transitions denote the cumulated transitions from the excited states  $|2\rangle$  and  $|1\rangle$  to the different ground levels, respectively (such that no branching ratios need to be considered). In that case, eq. (S1) evolves to

$$R_{21}(T) = \frac{\alpha_{a2}k_{2r}}{\alpha_{a1}k_{2r} + (\alpha_{a1} + \alpha_{a2})k_{nr}(0)} + \frac{k_{2r}}{k_{1r}}\frac{(\alpha_{a1} + \alpha_{a2})k_{nr}(0)}{\alpha_{a1}k_{2r} + (\alpha_{a1} + \alpha_{a2})k_{nr}(0)}\exp\left(-\frac{\Delta E_{X1}}{k_BT}\right),$$
(S3)

and with the abbreviation

$$k_{eff} = \alpha_{a1}k_{2r} + (\alpha_{a1} + \alpha_{a2})k_{nr}(0),$$
(S4)

we finally arrive at eq. (4) of the manuscript

$$R_{21}(T) = \frac{\alpha_{a2}k_{2r}}{k_{eff}} + \frac{k_{2r}\left(\alpha_{a1} + \alpha_{a2}\right)k_{nr}(0)}{k_{eff}}\exp\left(-\frac{\Delta E_{X1}}{k_{B}T}\right) \equiv A + B\exp\left(-\frac{\Delta E_{X1}}{k_{B}T}\right).$$
 (S4)

## References

[1] W. D. Stein, J. Liebertz, P. Becker, L. Bohaty, M. Braden, *Eur. J. Phys. B*, 2012, **85**, 236.