Supplementary Information

Tetrahedrally coordinated rigid crystal structure enabled partial self-reduction of mixed-valence Europium for optical thermometric application

Zhichao Meng[#], Yan Gao*[#], Ji'an Song, Zelong Jiang, Wei Lv, Qingguang Zeng, Dawei Wen*, Tao Hu*

School of Applied Physics and Materials, Wuyi University, Jiangmen 529020, Guangdong Province, P. R. China
*Corresponding author. E-mail: gaoyan_chn@sina.com (Y. Gao), ontaii@163.com (D.W. Wen), hutaowyu@sina.com (T. Hu).

Fig. S1

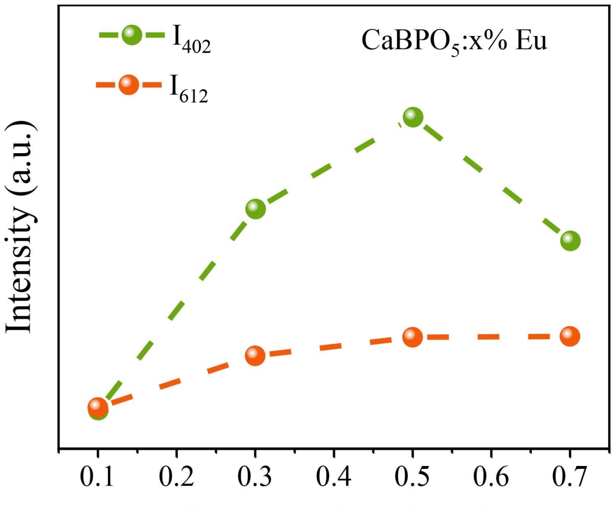

Fig. S1 The luminescence intensity of Eu^{2+} emission at 402 nm and Eu^{3+} emission at 612 nm for the $CaBPO_5$:*x*%Eu (*x* = 0.1, 0.3, 0.5, 0.7) samples.

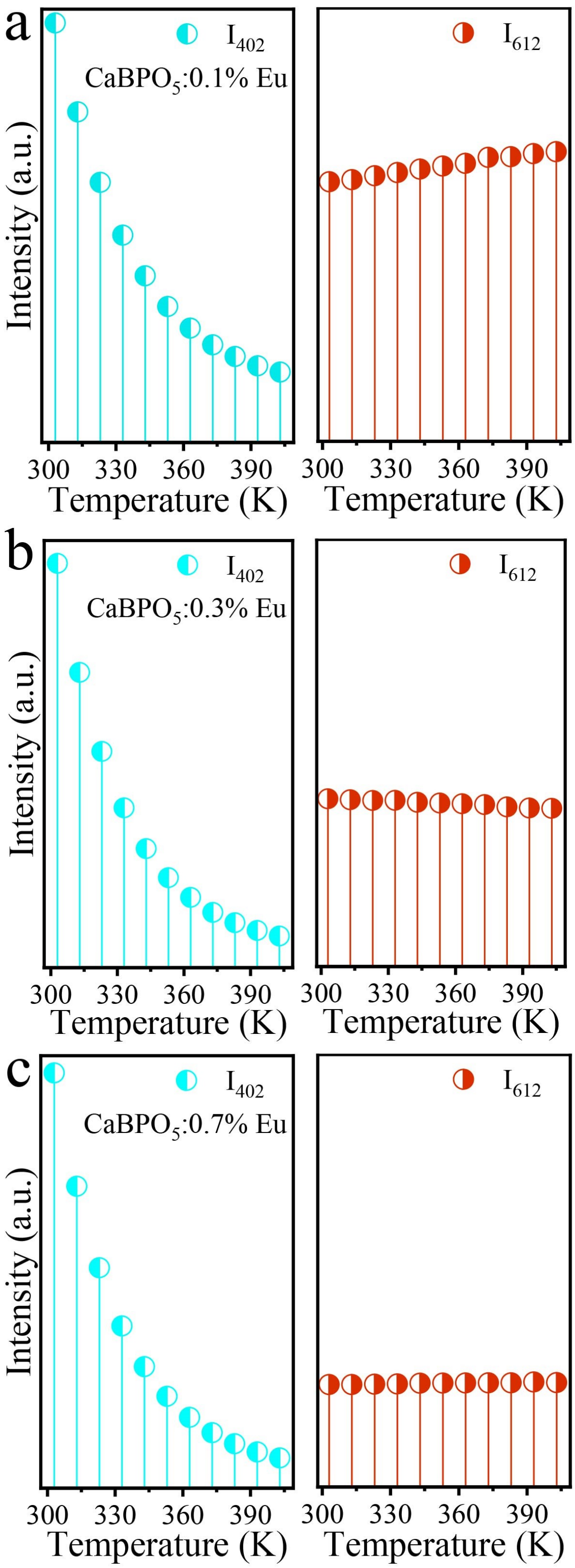

Fig. S2

Fig. S2 (a-c) The emission intensity of Eu^{2+} and Eu^{3+} at different temperatures for the $CaBPO_5$:*x*%Eu (*x* = 0.1, 0.3, 0.7) samples.

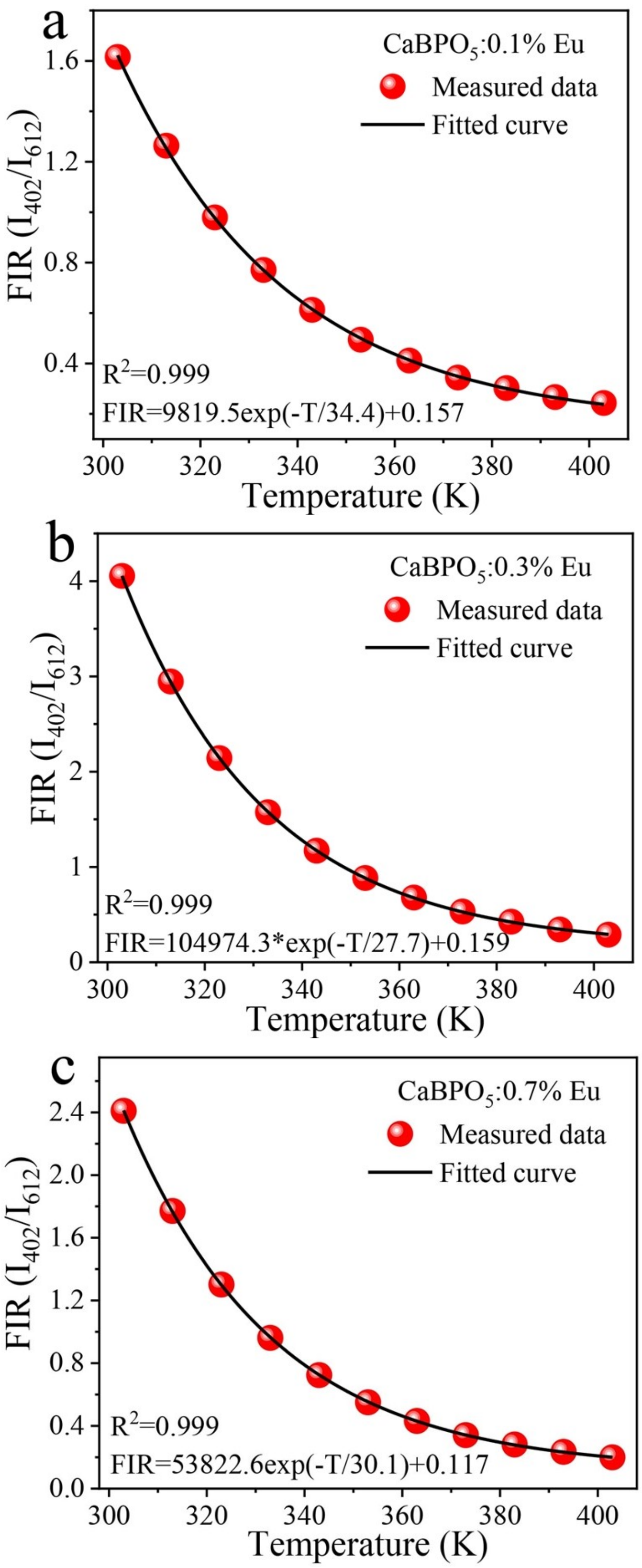

Fig. S3

Fig. S3 (a-c) Experimentally measured and Eq. 4 fitted plots of FIR (I_{402}/I_{612}) versus temperature for the $CaBPO_5$:*x*%Eu (*x* = 0.1, 0.3, 0.7) samples.

To convert the HRBE-scheme into a VRBE-scheme, the ground state of Eu^{2+} $E_{4f}(7,2+,A)$ in VRBE was calculated by the following equation:[1]

$$E_{4f}(7,2+,A) = -24.92 + \frac{18.05 - U(6,A)}{0.777 - 0.0353U(6,A)} \qquad \text{Equation S1}$$

where $U(6,A)$ is the Coulomb repulsion energy between a 4f-electron in Eu^{2+} and in Eu^{3+}. The value of $U(6,A)$ was estimated by the centroid shift ε_c of Ce^{3+} according the following equation:[2]

$$U(6,A) = 5.44 + 2.834 \times e^{-\varepsilon_c/2.2} \qquad \text{Equation S2}$$

The centroid shift was calculated according to the Equation S3:[3]

$$\varepsilon_c = 1.79 \times 10^{13} \sum_{i=1}^{N} \frac{\alpha_{SP}^{O}}{(R_o - 0.6\Delta R)^6} \qquad \text{Equation S3}$$

Where R_O is the distance between Ce^{3+} and the coordinating ions O^{2-} based on DFT structural relaxation, ΔR is the radii difference between Ce^{3+} and the replaced ion (Ca^{2+} in this case), α_{sp}^{O} is the polarizability of O^{2-}. α_{sp}^{0} can be calculated using the average electronegativity x_{av} of cations in the host:

$$\alpha_{SP}^{o} = 0.33 + \frac{4.8}{x_{av}^2} \qquad \text{Equation S4}$$

References

1 P. Dorenbos, Lanthanide 4f-electron binding energies and the nephelauxetic effect in wide band gap compounds, *J. Lumin.*, 2013, **136**, 122-129.

2 P. Dorenbos, Ce^{3+} 5d-centroid shift and vacuum referred 4f-electron binding energies of all lanthanide impurities in 150 different compounds, *J. Lumin.*, 2013, **135**, 93-104.

3 A. A. Setlur, D. G. Porob, U. Happek and M. G. Brik, Inhomogenous Broadening, Charge Compensation, and Luminescence Quenching in Ce^{3+}-Doped Sr_3AlO_4F Phosphors, *ECS J. Solid State Sci. Technol.*, 2016, **5**, R3089.