Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Ratiometric and lifetime-based luminescent thermometer exploiting the Co^{3+} luminescence in $CaAl_2O_4:Co^{3+}$ and $CaAl_2O_4:Co^{3+},Nd^{3+}$

K. Kniec[1]*, A. Kochanowska[1], L. Li[2], M. Suta[3], L. Marciniak[1]*

[1]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wroclaw, Poland

[2] Hebei Key Laboratory of Optic-electronic Information and Materials, College of Physics Science and Technology, Hebei University, Baoding 071002, China

[3] Inorganic Photoactive Materials, Institute of Inorganic Chemistry, Heinrich Heine University Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany

* corresponding author: k.kniec@intibs.pl, l.marciniak@intibs.pl

KEYWORDS luminescence thermometry, nanocrystals, cobalt, luminescence, lifetime-based luminescence thermometer

The average decay time of the broad-band luminescence of Co^{3+} was calculated with equation S1:

$$\tau_{avr} = \frac{A_1\tau_1^{\,2} + A_2\tau_2^{\,2}}{A_1\tau_1 + A_2\tau_2} \tag{S1}$$

for a biexponential decay,

$$y = y_0 + A_1 \cdot exp\left(-\frac{x}{\tau_1}\right) + A_2 \cdot exp\left(-\frac{x}{\tau_2}\right) \tag{S2}$$

where: τ_1, τ_2 – decay components of biexponential decay and A_1, A_2 – amplitudes. y_0 denotes an experimental background of the decay curve.

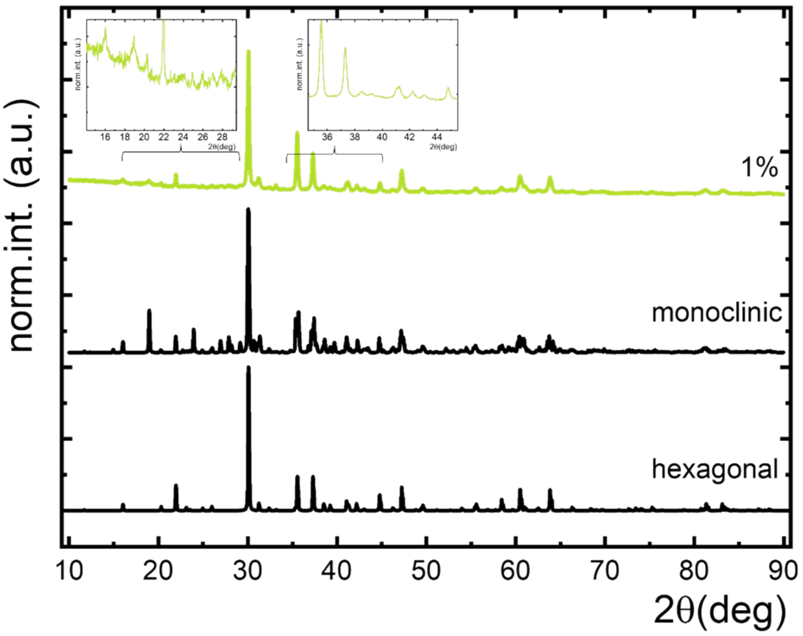


Figure S1. Comparison of the powder X-ray diffraction patterns of $CaAl_2O_4$ doped with 1% Co^{3+} annealed at 850 °C with reference patterns (ICSD 157457 -hexagonal $CaAl_2O_4$ and ICSD 260 – monoclinic $CaAl_2O_4$).

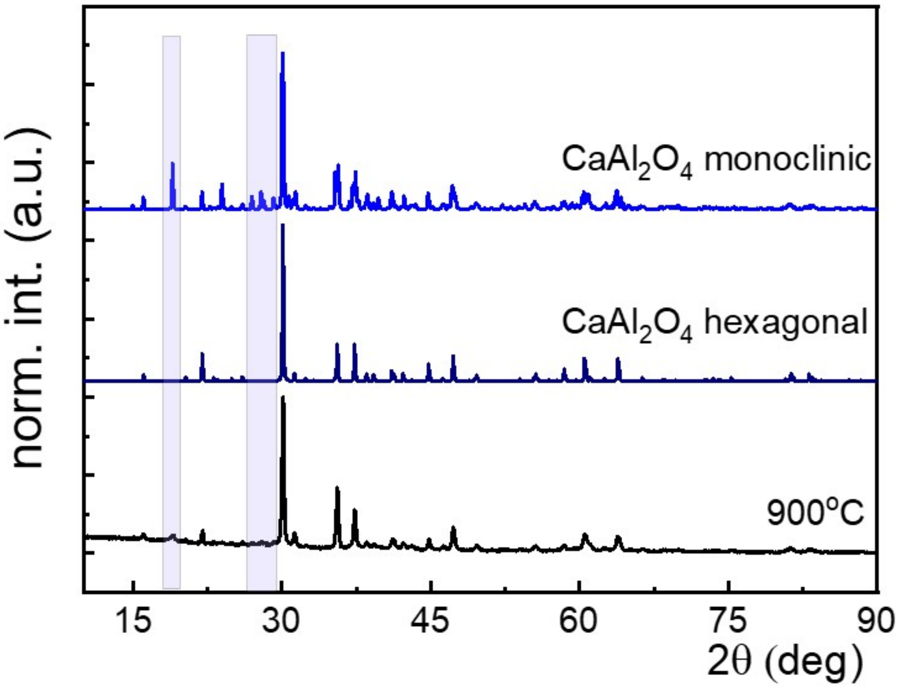


Figure S2. Comparison of powder X-ray diffraction patterns of $CaAl_2O_4$: Co^{3+} annealed at 900 °C with reference patterns (ICSD 157457 -hexagonal $CaAl_2O_4$ and ICSD 260 – monoclinic $CaAl_2O_4$).

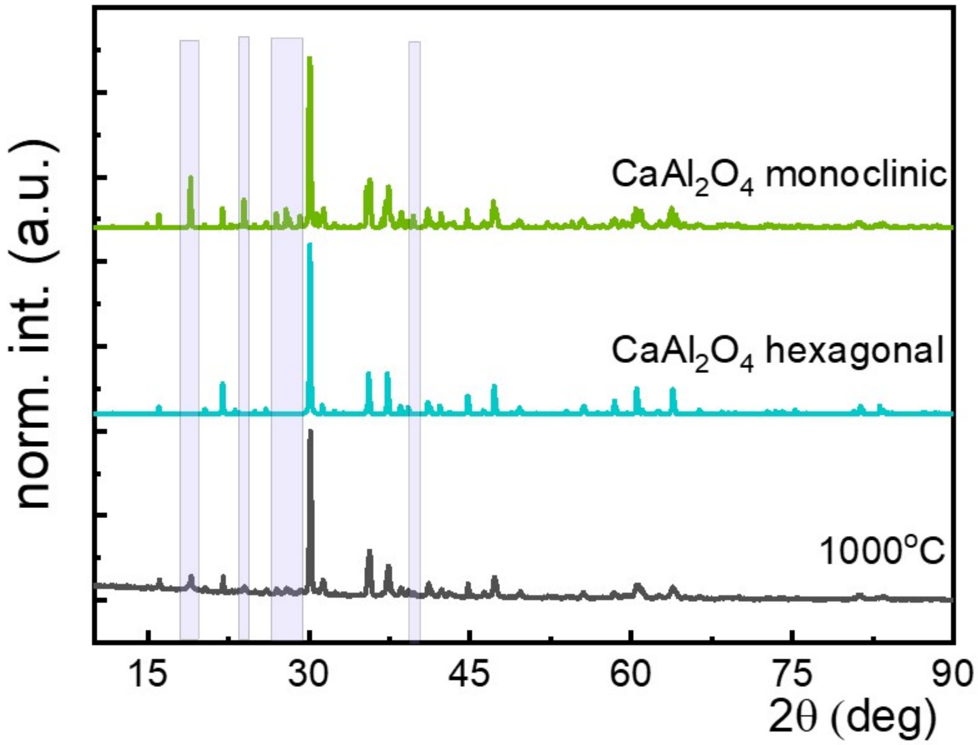


Figure S3. Comparison of powder X-ray diffraction patterns of CaAl$_2$O$_4$: Co^{3+} annealed at 1000 °C with reference patterns (ICSD 157457 -hexagonal CaAl$_2$O$_4$ and ICSD 260 – monoclinic CaAl$_2$O$_4$).

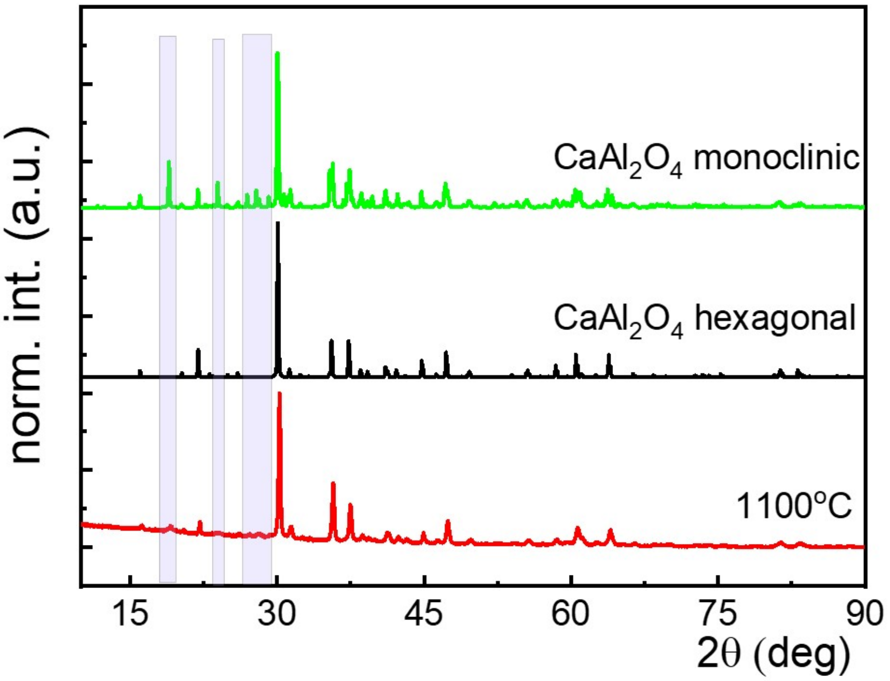
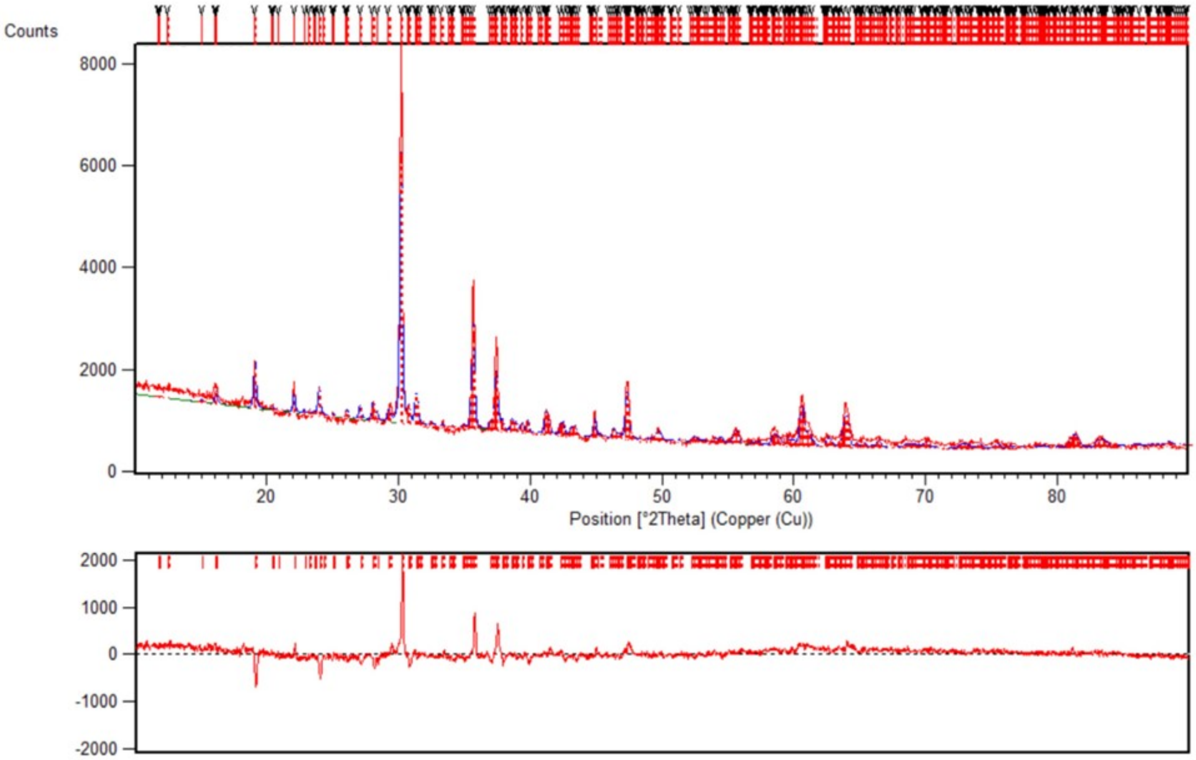
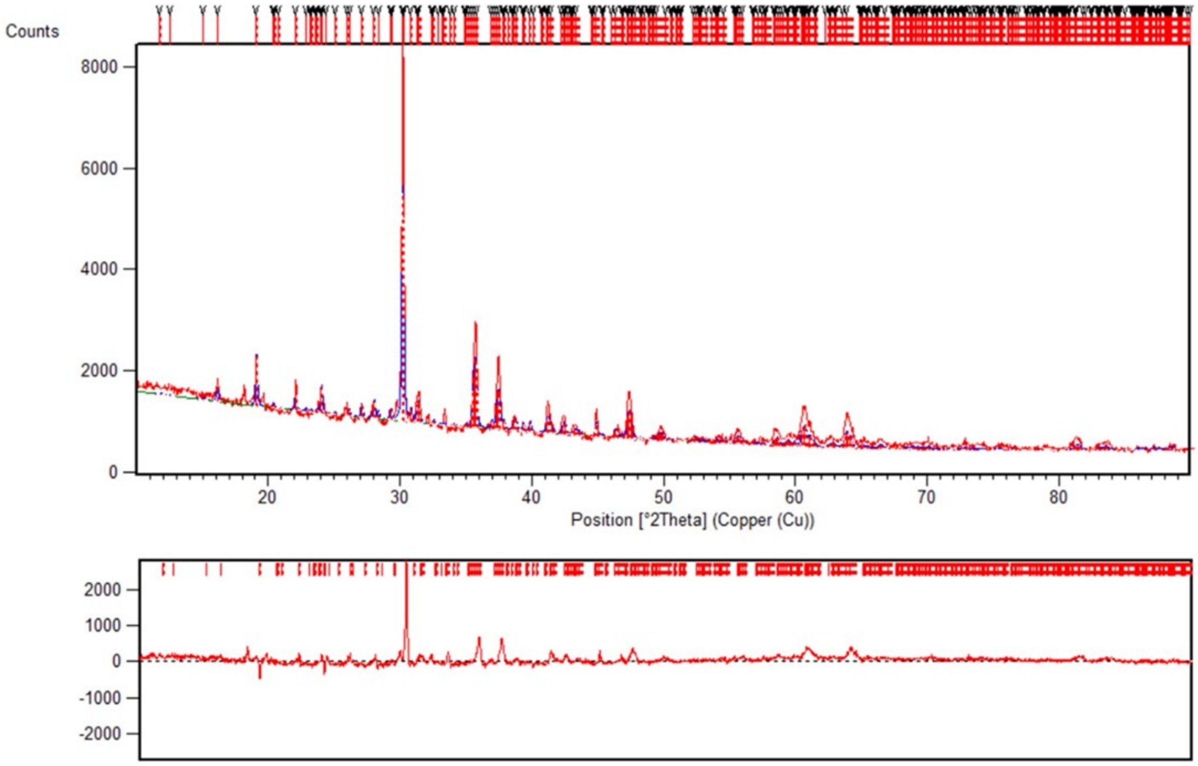


Figure S4. Comparison of powder X-ray diffraction patterns of CaAl$_2$O$_4$: Co^{3+} annealed at 1100°C with reference patterns (ICSD 157457 -hexagonal CaAl$_2$O$_4$ and ICSD 260 – monoclinic CaAl$_2$O$_4$).


Counts
8000
6000
4000
2000
0
20
30
40
50
60
70
80
Position [°2Theta] (Copper (Cu))
2000
1000
0
-1000
-2000


Counts
8000
6000
4000
2000
0
20
30
40
50
60
70
80
Position [°2Theta] (Copper (Cu))
2000
1000
0
-1000
-2000

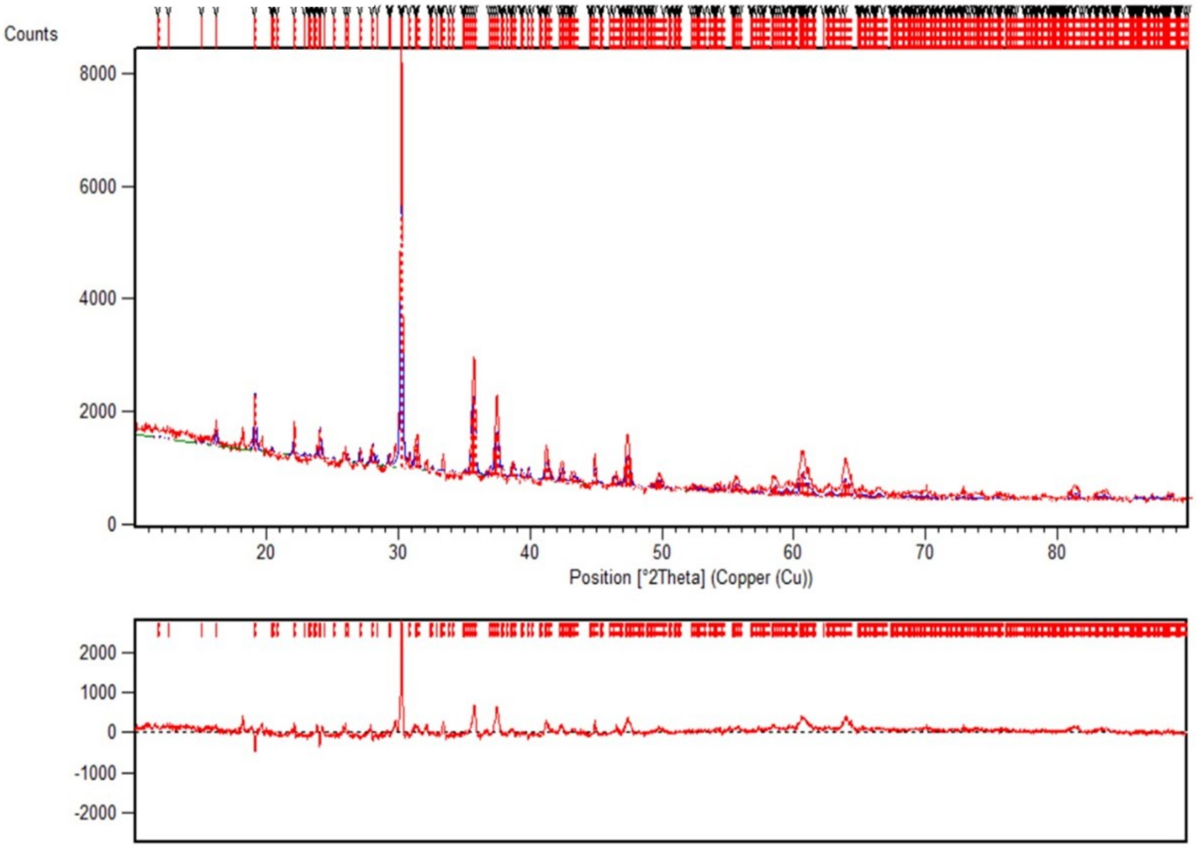


Figure S5. The representative results of the Rietveld refinement of the $CaAl_2O_4:Co^{3+}$ annealed at 1000^{o}C-a); the $CaAl_2O_4:Co^{3+}$ annealed at 1100^{o}C-b); and the $CaAl_2O_4:Co^{3+},Nd^{3+}$ annealed at 1100^{o}C-c)

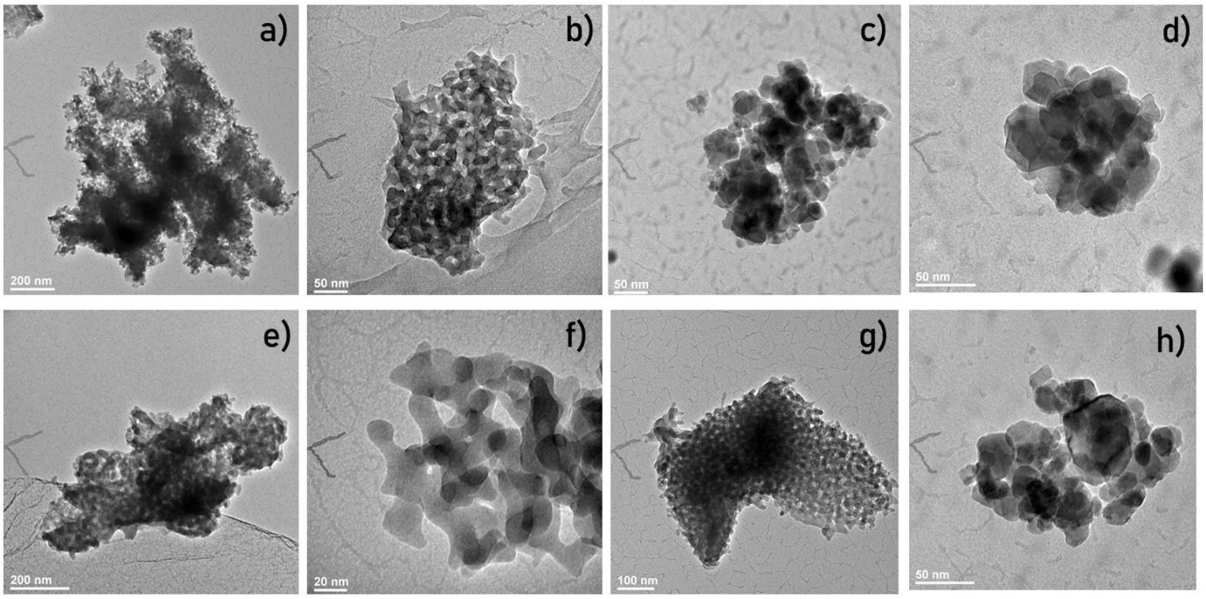


Figure S6. The representative TEM images of $CaAl_2O_4:Co^{3+}$ -a), b), c), d) and $CaAl_2O_4:Co^{3+},Nd^{3+}$ -e), f), g), h) annealed at 850^{o}C -a), -e); 900^{o}C -b), -f); 1000^{o}C -c);-g) and 1100^{o}C -d); -h).

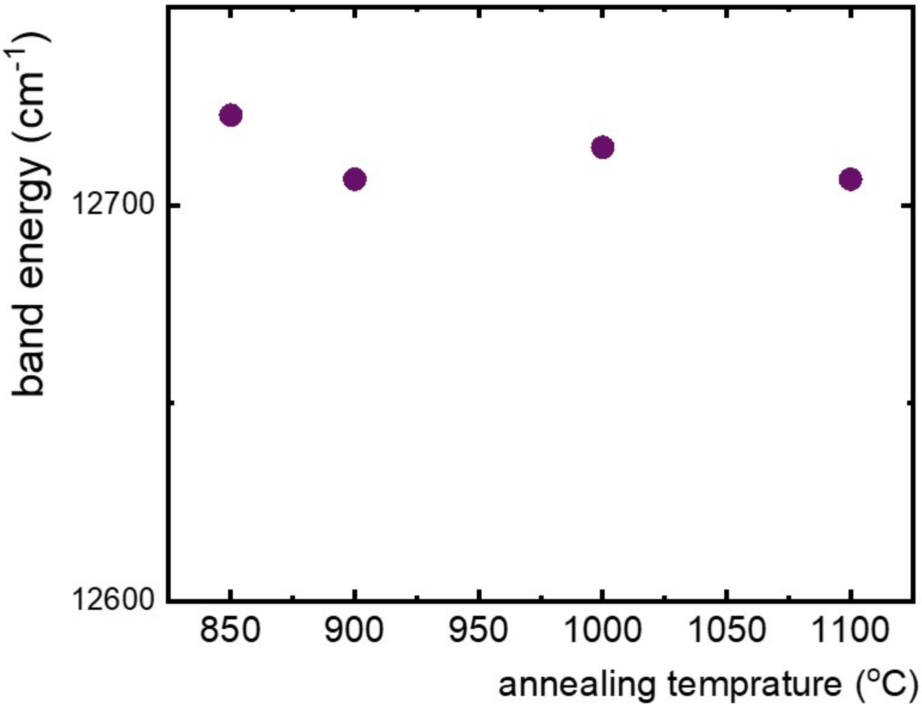


Figure S7. Energy of the maximum of the Co^{3+}-related broad-band emission as a function of annealing temperature of the prepared $CaAl_2O_4$: 0.02% Co^{3+} sample.

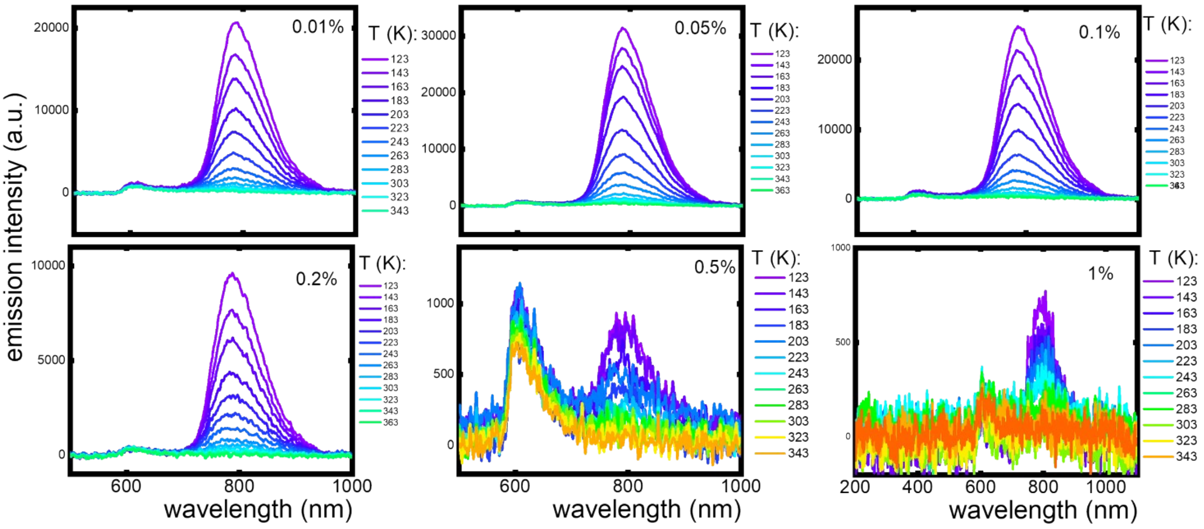


Figure S8. Temperature-dependent emission spectra of $CaAl_2O_4$ activated with Co^{3+} ions with varying doping fraction (emission spectra obtained upon λ_{exc}=445 nm using 590 longpass filter, artificial band at 600 nm results from experimental conditions).

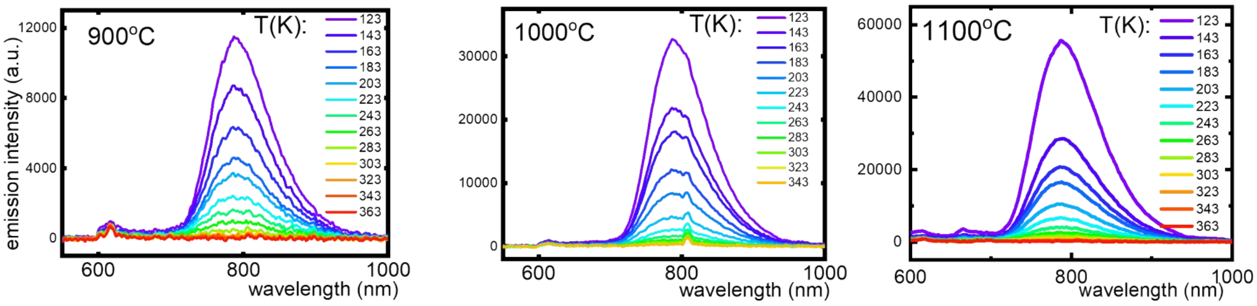


Figure S9. Temperature dependence of $CaAl_2O_4$: 0.02% Co^{3+} ions prepared by annealing at varying temperatures (emission spectra obtained upon λ_{exc}=445 nm using 590 longpass filter, artificial band at 600 nm and 800 nm results from experimental conditions).

$$\ln\left(\frac{I_0}{I_{em}}-1\right)=-\Delta E_a\cdot\frac{1}{k_BT} \qquad \text{(Eq. S3)}$$

where I_0 corresponds to the initial emission intensity (at 123 K) and k_B is Boltzmann constant

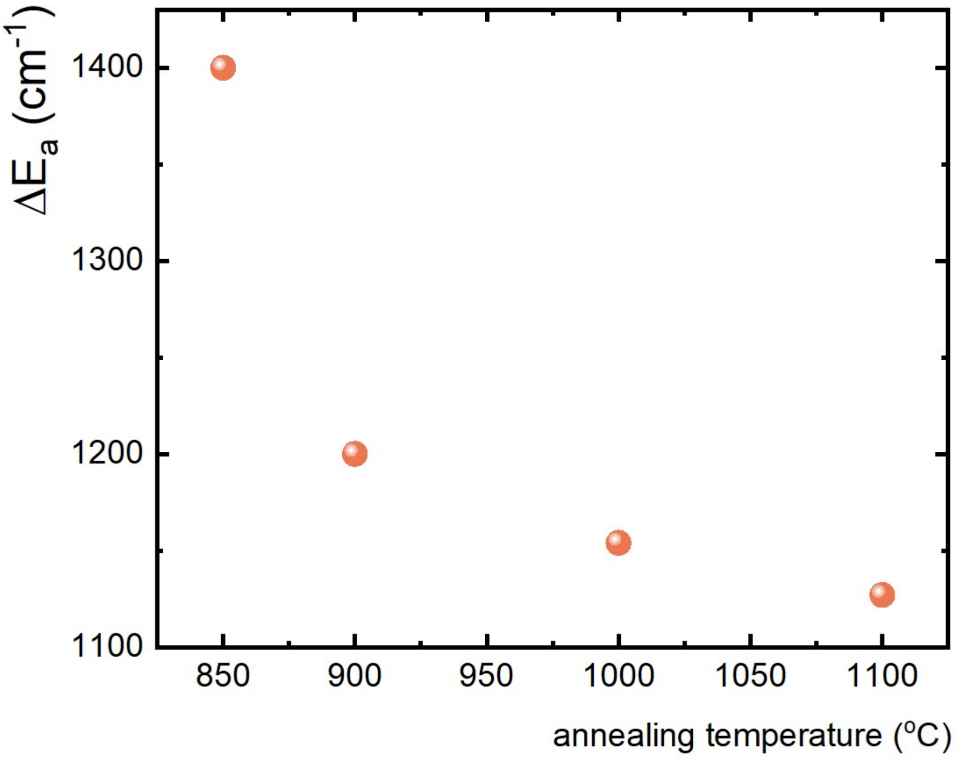


Figure S10. The dependence of the derived thermal crossover activation barrier on the annealing temperature of the prepared $CaAl_2O_4$: 0.02% Co^{3+} powders.

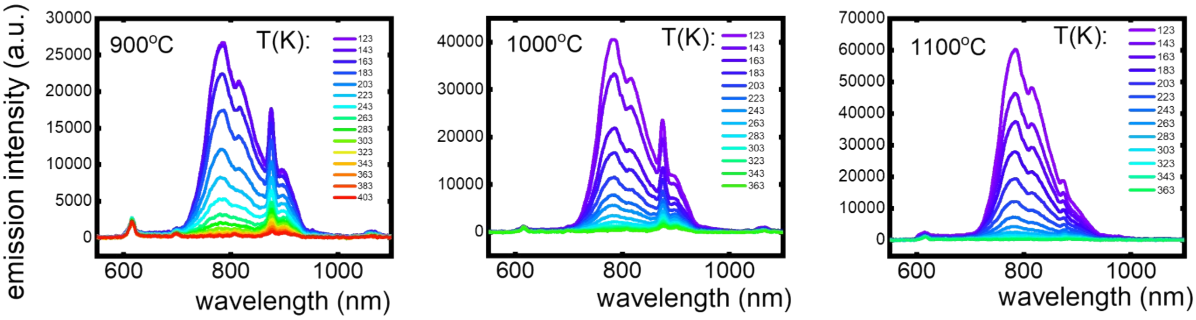


Figure S11. Temperature dependence of the emission spectra of $CaAl_2O_4$:Co^{3+}, Nd^{3+} prepared by varying annealing temperatures (emission spectra obtained upon λ_{exc}=445 nm using 590 longpass filter, artificial band at 600 nm and 800 nm results from experimental conditions).

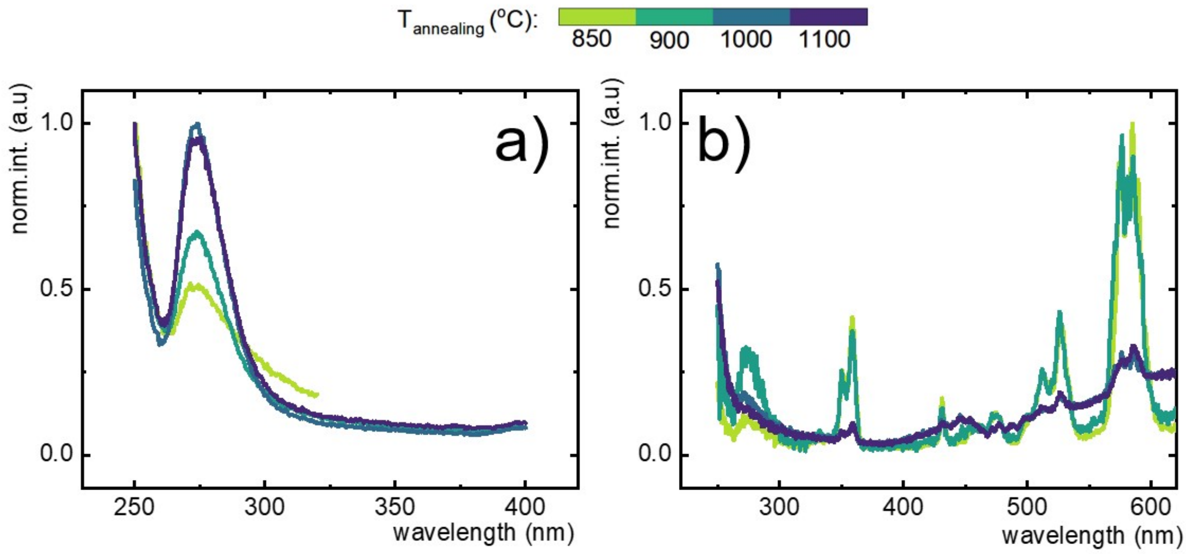


Figure S12. Excitation spectra upon detection of the Nd^{3+}-related emission (λ_{em}=1064 nm) of $CaAl_2O_4$: 0.02%Co^{3+}, 1%Nd^{3+} at 123 K and 303 K – a) and – b), respectively.

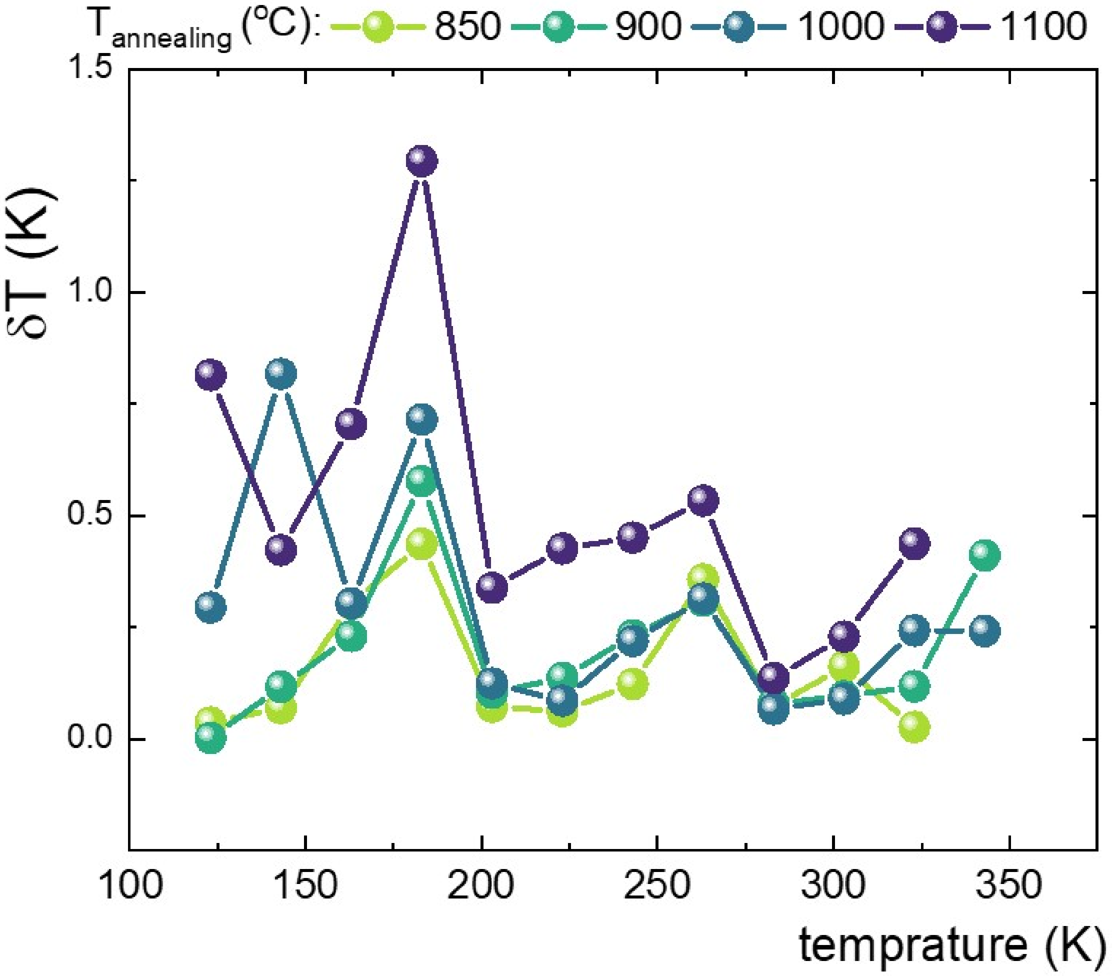


Figure S13. The statistical temperature uncertainty of the conceptualized ratiometric Co^{3+}, Nd^{3+} -co-doped $CaAl_2O_4$ luminescence thermometers.

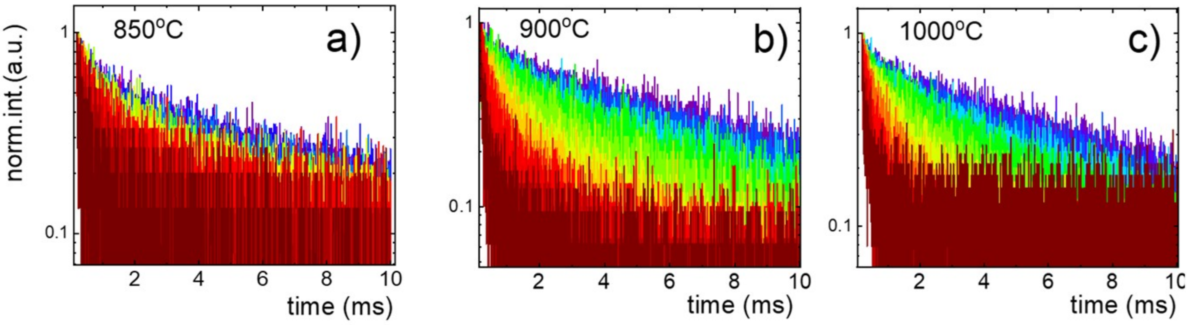


Figure S14. Temperature-dependent time-resolved luminescence of 0.02%Co^{3+} -doped $CaAl_2O_4$ (λ_{exc}=266 nm) λ_{em}=800 nm) annealed at 850°C -a), 900°C -b) and 1000°C -c).

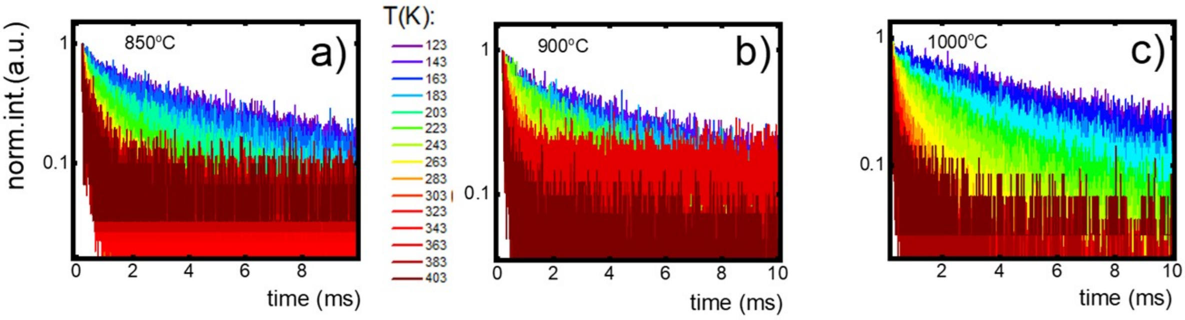


Figure S15. Temperature-dependent time-resolved luminescence of 0.02%Co^{3+}, 1%Nd^{3+}-co -doped $CaAl_2O_4$ (λ_{exc}=266 nm) λ_{em}=800 nm) annealed at 850°C -a), 900°C -b) and 1000°C -c).

.