Supporting Information

Achieving high thermal sensitivity from ratiometric $CaGdAlO_4$: Mn^{4+}, Tb^{3+} thermometers

Yuyin Fang[a], Yuanpeng Zhang[b], Yuepin Zhang [*a], and Jianxu Hu[*a]

[a]School of Material Science and Chemical Engineering, Ningbo University, Ningbo, Zhejiang, 315211, China

[b]Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37830, USA

[*]Corresponding authors: Yuepin Zhang (zhangyuepin@nbu.edu.cn) and Jianxu Hu (hujianxu@nbu.edu.cn)

Contents

temperatures for the $CaGdAlO_4$: 0.005 Mn^{4+}/0.06 Tb^{3+} sample.

Figure. S6 Temperature dependent PL spectra for the 0.5 mol% Eu^{3+}/6 mol% Tb^{3+} co-doped $CaGdAlO_4$ sample measured from 298 to 523 K.

References

Table. S1 Crystallographic data of 0.5 mol% Mn^{4+}/*x* mol% Tb^{3+} co-doped $CaGdAlO_4$ phosphors (*x* = 2, 4, 6, 8, 10, 12) from Rietveld refinement.

Sample	0.5% Mn^{4+}/2% Tb^{3+}	0.5% Mn^{4+}/4% Tb^{3+}	0.5% Mn^{4+}/6% Tb^{3+}	0.5% Mn^{4+}/8% Tb^{3+}	0.5% Mn^{4+}/10% Tb^{3+}	0.5% Mn^{4+}/12% Tb^{3+}
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	*I4/mmm*	*I4/mmm*	*I4/mmm*	*I4/mmm*	*I4/mmm*	*I4/mmm*
a (Å)	3.6612(3)	3.6531(4)	3.6425(2)	3.6317(4)	3.6251(1)	3.6017(5)
b (Å)	3.6612(3)	3.6531(4)	3.6425(2)	3.6317(4)	3.6251(1)	3.6017(5)
c (Å)	11.952(1)	11.721(5)	11.518(3)	11.315(6)	11.103(3)	10.915(8)
V (Å^3)	160.21(2)	156.41(8)	152.81(8)	149.23(6)	145.90(8)	141.59(2)
α (deg)	90	90	90	90	90	90
β (deg)	90	90	90	90	90	90
γ (deg)	90	90	90	90	90	90
χ^2	2.51	3.26	3.57	4.35	4.28	3.77
R_p (%)	3.43	4.13	4.35	4.32	3.81	3.06
R_{wp} (%)	4.23	4.71	5.45	5.23	5.41	4.15

Table. S2 Atomic parameters for $CaGdAlO_4$: 0.005 Mn^{4+}/*x* Tb^{3+} phosphors.

$CaGdAlO_4$: 0.005 Mn^{4+}/0.02 Tb^{3+}						
Atom	**Wyck.**	**x/a**	**y/b**	**z/c**	**S.O.F**	**U_{iso}**
Ca1	4e	0.50000(0)	0.50000(0)	0.14821(0)	0.49519(3)	0.00616(1)
Gd1	4e	0.50000(0)	0.50000(0)	0.14821(0)	0.48851(5)	0.00478(2)
Tb	4e	0.50000(0)	0.50000(0)	0.14821(0)	0.01629(2)	0.00146(8)
Al1	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.99305(6)	0.00821(4)
Mn	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.00494(4)	0.00961(6)
O1	4c	0.50000(0)	1.00000(0)	0.00000(0)	1.00000(0)	0.00813(1)
O2	4e	0.50000(0)	0.50000(0)	0.34520(3)	1.00000(0)	0.00162(9)
$CaGdAlO_4$: 0.005 Mn^{4+}/0.04 Tb^{3+}						
Atom	**Wyck.**	**x/a**	**y/b**	**z/c**	**S.O.F**	**U_{iso}**
Ca1	4e	0.50000(0)	0.50000(0)	0.13951(3)	0.49428(3)	0.00751(5)
Gd1	4e	0.50000(0)	0.50000(0)	0.13951(3)	0.46521(7)	0.00892(1)
Tb	4e	0.50000(0)	0.50000(0)	0.13951(3)	0.00405(0)	0.00165(5)
Al1	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.99472(1)	0.00919(1)
Mn	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.00527(9)	0.00249(6)
O1	4c	0.50000(0)	1.00000(0)	0.00000(0)	1.00000(0)	0.00821(5)
O2	4e	0.50000(0)	0.50000(0)	0.36171(5)	1.00000(0)	0.00592(4)
$CaGdAlO_4$: 0.005 Mn^{4+}/0.06 Tb^{3+}						
Atom	**Wyck.**	**x/a**	**y/b**	**z/c**	**S.O.F**	**U_{iso}**
Ca1	4e	0.50000(0)	0.50000(0)	0.14148(6)	0.49135(1)	0.00239(1)
Gd1	4e	0.50000(0)	0.50000(0)	0.14148(6)	0.45128(2)	0.00384(5)
Tb	4e	0.50000(0)	0.50000(0)	0.14148(6)	0.05737(7)	0.00172(0)
Al1	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.99471(1)	0.00187(3)
Mn	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.00529(9)	0.00254(2)
O1	4c	0.50000(0)	1.00000(0)	0.00000(0)	1.00000(0)	0.00232(5)
O2	4e	0.50000(0)	0.50000(0)	0.33171(3)	1.00000(0)	0.00514(3)
$CaGdAlO_4$: 0.005 Mn^{4+}/0.08 Tb^{3+}						
Atom	**Wyck.**	**x/a**	**y/b**	**z/c**	**S.O.F**	**U_{iso}**
Ca1	4e	0.50000(0)	0.50000(0)	0.14227(3)	0.48246(5)	0.00199(1)
Gd1	4e	0.50000(0)	0.50000(0)	0.14227(3)	0.43513(1)	0.00456(8)
Tb	4e	0.50000(0)	0.50000(0)	0.14227(3)	0.08241(4)	0.00381(3)
Al1	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.99493(2)	0.00737(4)

Mn	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.00517(8)	0.00221(5)
O1	4c	0.50000(0)	1.00000(0)	0.00000(0)	1.00000(0)	0.00412(6)
O2	4e	0.50000(0)	0.50000(0)	0.32831(1)	1.00000(0)	0.00635(7)

$CaGdAlO_4$: 0.005 Mn^{4+}/0.10 Tb^{3+}

Atom	**Wyck.**	**x/a**	**y/b**	**z/c**	**S.O.F**	**U_{iso}**
Ca1	4e	0.50000(0)	0.50000(0)	0.14532(7)	0.47983(6)	0.00351(4)
Gd1	4e	0.50000(0)	0.50000(0)	0.14532(7)	0.41846(9)	0.00723(2)
Tb	4e	0.50000(0)	0.50000(0)	0.14532(7)	0.10171(5)	0.00513(6)
Al1	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.99538(4)	0.00824(3)
Mn	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.00462(6)	0.00349(2)
O1	4c	0.50000(0)	1.00000(0)	0.00000(0)	1.00000(0)	0.00279(5)
O2	4e	0.50000(0)	0.50000(0)	0.33254(8)	1.00000(0)	0.00249(7)

$CaGdAlO_4$: 0.005 Mn^{4+}/0.12 Tb^{3+}

Atom	**Wyck.**	**x/a**	**y/b**	**z/c**	**S.O.F**	**U_{iso}**
Ca1	4e	0.50000(0)	0.50000(0)	0.14245(5)	0.49519(1)	0.00824(9)
Gd1	4e	0.50000(0)	0.50000(0)	0.14245(5)	0.40245(2)	0.00572(0)
Tb	4e	0.50000(0)	0.50000(0)	0.14245(5)	0.11740(7)	0.00361(4)
Al1	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.99492(6)	0.00294(5)
Mn	2a	0.00000(0)	0.00000(0)	0.00000(0)	0.00507(4)	0.00162(7)
O1	4c	0.50000(0)	1.00000(0)	0.00000(0)	1.00000(0)	0.00821(3)
O2	4e	0.50000(0)	0.50000(0)	0.33254(8)	1.00000(0)	0.00243(1)

Table. S3 Bond lengths (Å) of metal sites for $CaGdAlO_4$: 0.005 Mn^{4+}/*x* Tb^{3+} phosphors.

Sample	0.5% Mn^{4+}/2% Tb^{3+}	0.5% Mn^{4+}/4% Tb^{3+}	0.5% Mn^{4+}/6% Tb^{3+}	0.5% Mn^{4+}/8% Tb^{3+}	0.5% Mn^{4+}/10% Tb^{3+}	0.5% Mn^{4+}/12% Tb^{3+}
Gd1/Ca1-O1	2.4972	2.4813	2.4651	2.4493	2.4297	2.4182
Gd1/Ca1-O1	2.4972	2.4813	2.4651	2.4493	2.4297	2.4182
Gd1/Ca1-O1	2.4972	2.4813	2.4651	2.4493	2.4297	2.4182
Gd1/Ca1-O1	2.4972	2.4813	2.4651	2.4493	2.4297	2.4182
Gd1/Ca1-O2	2.6102	2.5912	2.5713	2.5544	2.5318	2.5149
Gd1/Ca1-O2	2.6102	2.5912	2.5713	2.5544	2.5318	2.5149
Gd1/Ca1-O2	2.6102	2.5912	2.5713	2.5544	2.5318	2.5149
Gd1/Ca1-O2	2.6102	2.5912	2.5713	2.5544	2.5318	2.5149
Gd1/Ca1-O2	2.2823	2.2765	2.2694	2.2617	2.5318	2.2451
Al1-O1	1.8316	1.8309	1.8291	1.8275	1.8301	1.8289
Al1-O1	1.8316	1.8309	1.8291	1.8275	1.8301	1.8289
Al1-O1	1.8316	1.8309	1.8291	1.8275	1.8301	1.8289
Al1-O1	1.8316	1.8309	1.8291	1.8275	1.8301	1.8289
Al1-O2	2.0193	2.0184	2.0210	2.0179	2.0151	2.0162
Al1-O2	2.0193	2.0184	2.0210	2.0179	2.0151	2.0162

Table. S4 Fitting parameters for luminescence intensity ratio (LIR) as a function of temperature for 0.5 mol% Mn^{4+}/*x* mol% Tb^{3+} co-doped samples (*x* = 2, 4, 6, 8, 10, 12).

Samples	*C*	*A*	Δ*E*	R^2
0.5% Mn/2% Tb	30.9911 ± 4.7819	2220.7563 ± 537.8189	0.2344 ± 0.0521	0.9959
0.5% Mn/4% Tb	52.5319 ± 4.6486	3958.8361 ± 849.8703	0.2658 ± 0.0399	0.9965
0.5% Mn/6% Tb	5.2464 ± 1.0890	236637.4286 ± 84252.2053	0.3534 ± 0.1161	0.9846
0.5% Mn/8% Tb	24.0369 ± 2.0439	4907.3641 ± 212.1882	0.1861 ± 0.0378	0.9976
0.5% Mn/10% Tb	8.5154 ± 1.4626	9272.1762 ± 658.8119	0.2625 ± 0.0972	0.9893
0.5% Mn/12% Tb	34.4017 ± 4.4915	726.5455 ± 62.8861	0.1575 ± 0.0498	0.9959

Table. S5 Relative thermal sensitivity of luminescent thermometers based on Mn^{4+}-Ln^{3+} ions.

Host	Ln^{3+}	S_r at 398K (% K^{-1})	Temperature range (K)	Reference
$CaGdMgSbO_6$	Sm^{3+}	0.21	298-573	[1]
$NaLaMgWO_6$	Eu^{3+}	0.79	303-523	[2]
Ca_2LaNbO_6	Eu^{3+}	0.75	298-498	[3]
Ba_2LaNbO_6	Eu^{3+}	2.08	298-498	[3]
$BaLaMgNbO_6$	Dy^{3+}	1.72	230-470	[4]
$SrGdLiTeO_6$	Eu^{3+}	0.95	300-550	[5]
La_2LiSbO_6	Eu^{3+}	0.036	303-523	[6]
$YAlO_3$	Ho^{3+}	0.25	293-563	[7]
$YAlO_3$	Er^{3+}	0.98	293-563	[7]
$Sr_4Al_{14}O_{25}$	Tb^{3+}	2.1	123-523	[8]
$Lu_3Al_5O_{12}$	Tb^{3+}	2.2	270-420	[9]
$Na_4Mg(WO_4)_3$	Tb^{3+}	2.3	200-450	[10]
$CaGdAlO_4$	**Tb^{3+}**	**2.3**	**298-523**	**This work**

Table. S6 Relative thermal sensitivity, temperature uncertainty, and temperature repeatability of the 0.5 mol% Eu^{3+}/6 mol% Tb^{3+} co-doped $CaGdAlO_4$ sample.

Temperature (K)	S_r (% K^{-1})	δT (K)	Repeatability (%)
298	0.144	2.39	99.4
348	0.281	1.95	99.1
398	0.407	1.56	96.1
448	0.404	1.52	98.8
498	0.504	0.95	99.2

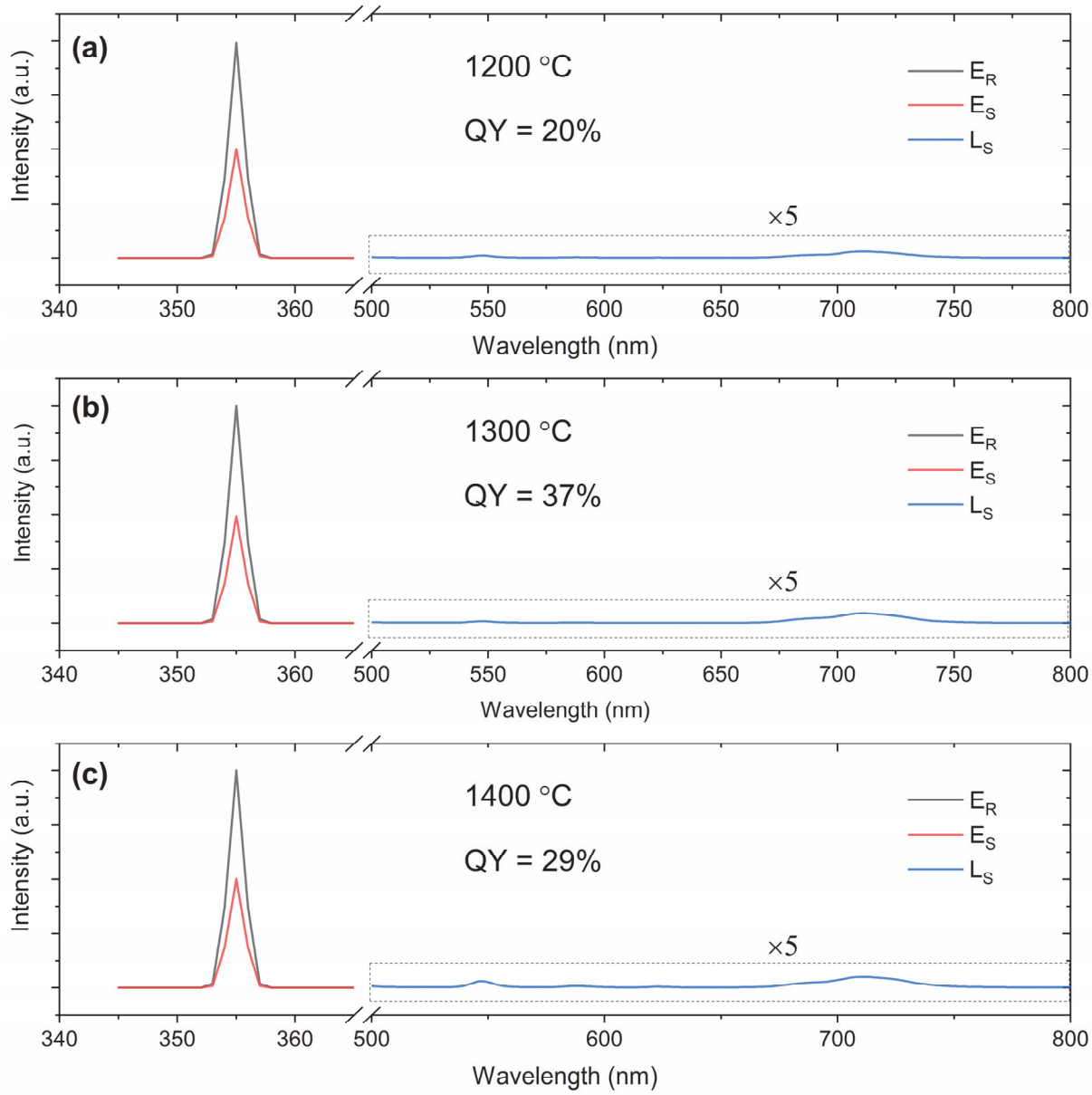

Fig. S1 (a)-(c) External quantum yields of the 5 mol% Mn^{4+}/2 mol% Tb^{3+} co-doped $CaGdAlO_4$ sample annealed at 1200, 1300, and 1400 °C. The signal from the sample was amplified by a factor of 5 for clarity in the plot.

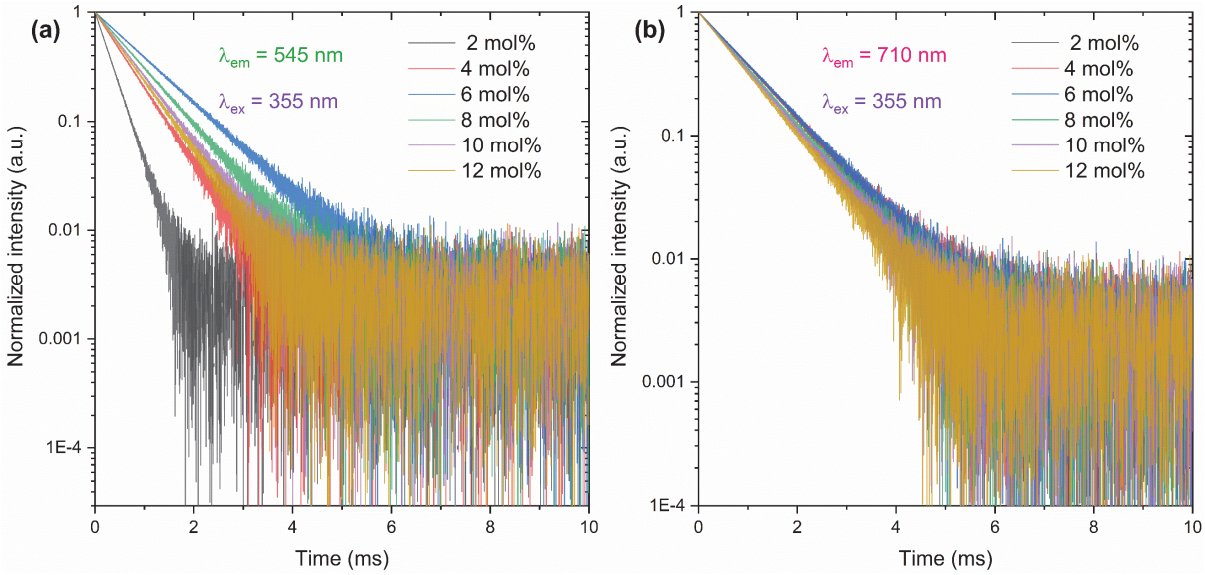

Fig. S2 Decay curves of (a) Tb^{3+} monitored at 545 nm and (b) Mn^{4+} monitored at 710 nm under 355 nm excitation.

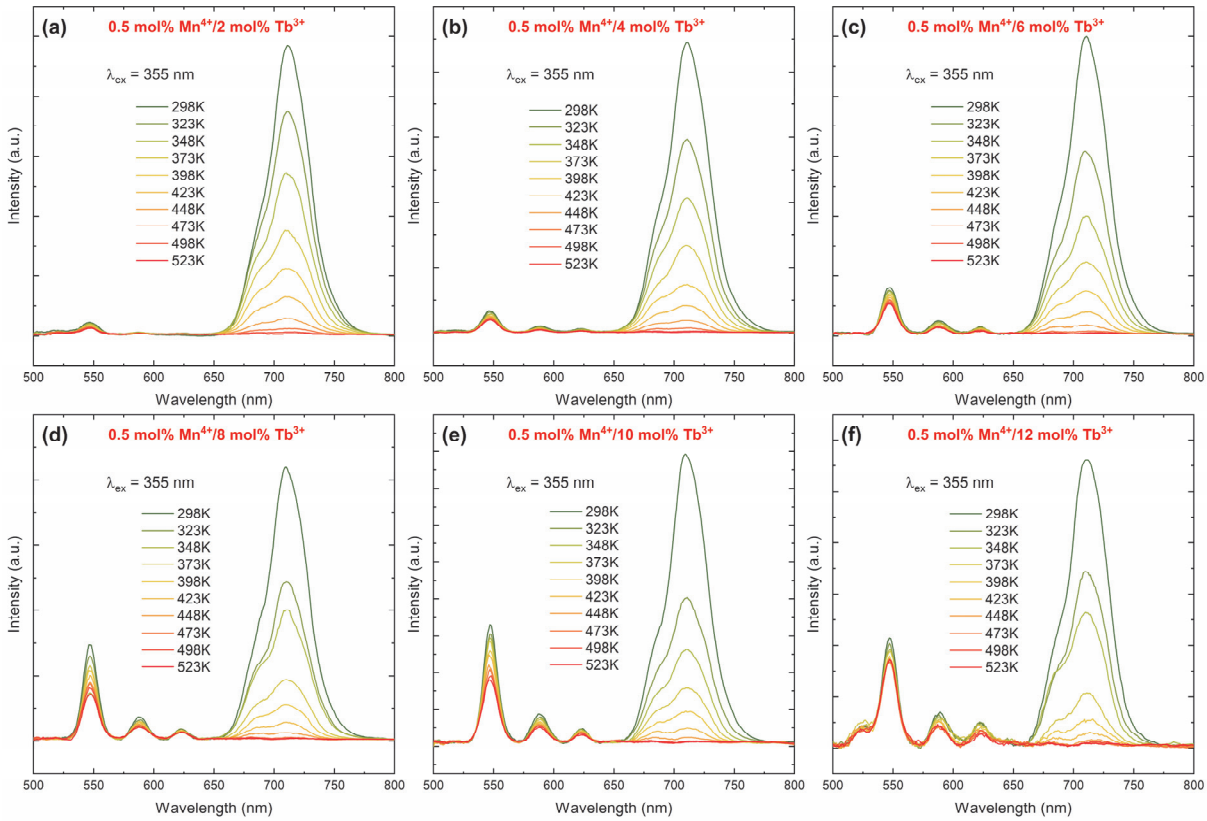

Fig. S3 (a)-(f) Temperature dependent PL spectra for 0.5 mol% Mn^{4+}/*x* mol% Tb^{3+} (*x* = 2, 4, 6, 8, 10, 12) co-doped $CaGdAlO_4$ phosphors measured in from 298 to 523 K.

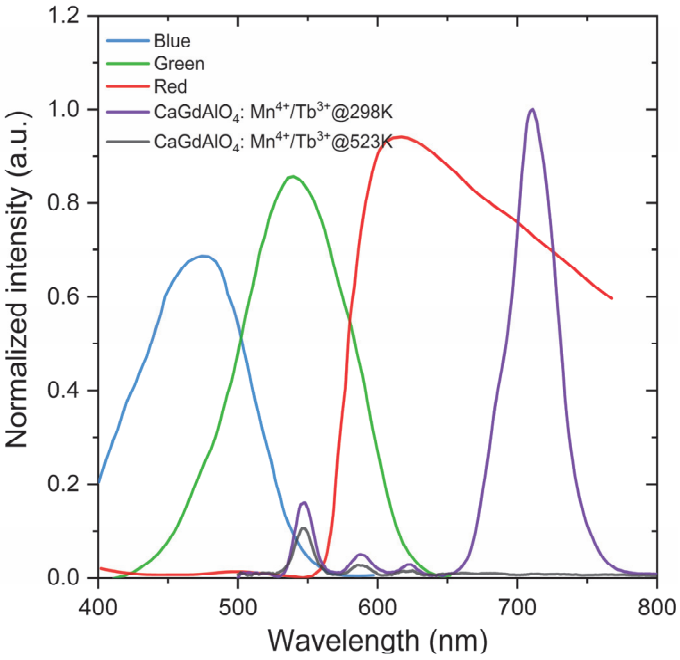

Fig. S4 Comparison of the normalized PL spectra of the $CaGdAlO_4$: 0.005 Mn^{4+}/0.06 Tb^{3+} sample at 298 and 523 K with the colour filter curves of commercial digital camera.

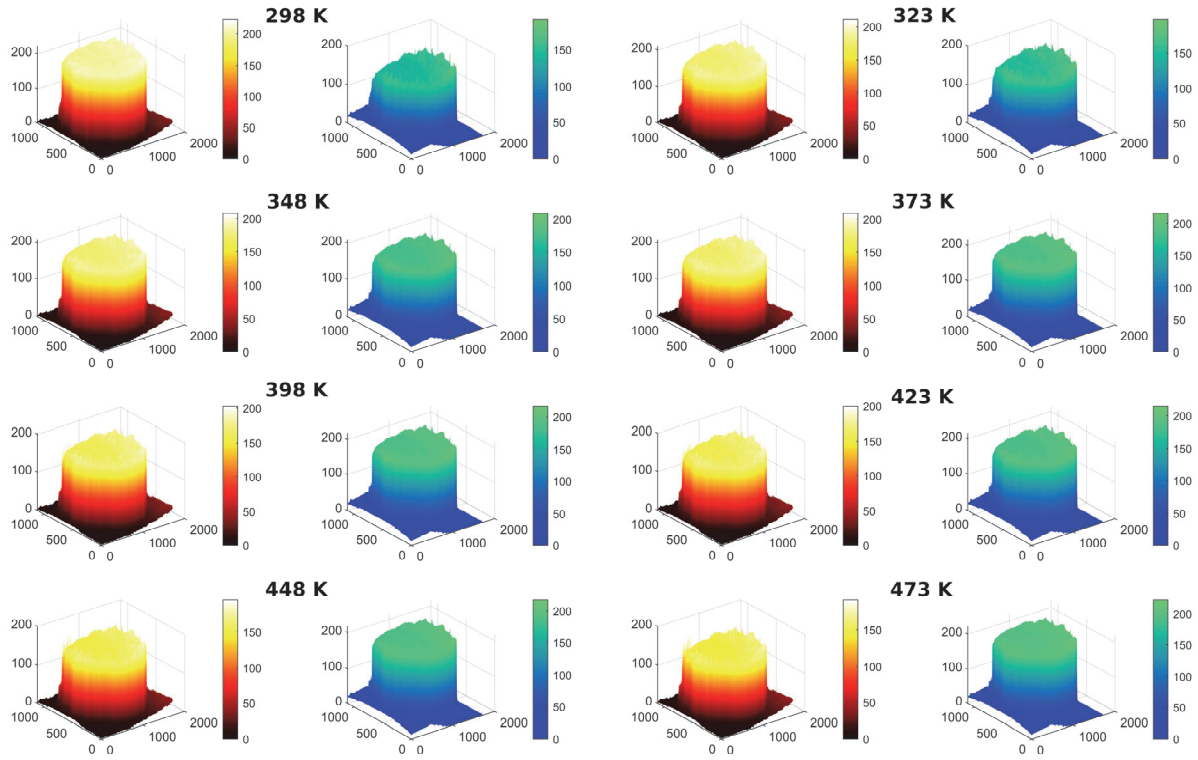

Fig. S5 Red and green channels extracted from the digital images captured at different temperatures for the $CaGdAlO_4$: 0.005 Mn^{4+}/0.06 Tb^{3+} sample.

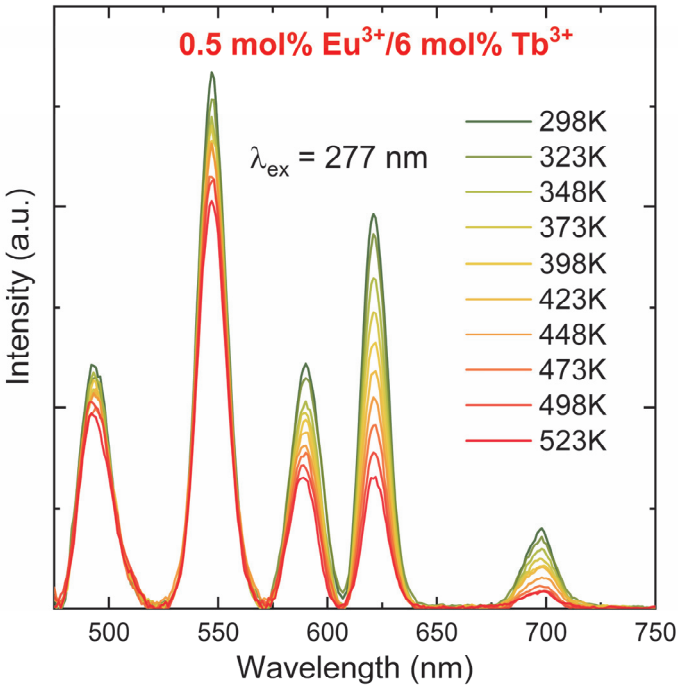

Fig. S6 Temperature dependent PL spectra for the 0.5 mol% Eu^{3+}/6 mol% Tb^{3+} co-doped $CaGdAlO_4$ sample measured from 298 to 523 K.

References

1 J. Liao, M. Wang, L. Kong, J. Chen, X. Wang, H. Yan, J. Huang and C. Tu, *J. Lumin.*, 2020, **226**, 117492.
2 H. Zhou, N. Guo, M. Zhu, J. Li, Y. Miao and B. Shao, *J. Lumin.*, 2020, **224**, 117311.
3 P. Wang, J. Mao, L. Zhao, B. Jiang, C. Xie, Y. Lin, F. Chi, M. Yin and Y. Chen, *Dalton Trans.*, 2019, **48**, 10062-10069.
4 Y. Lin, L. Zhao, B. Jiang, J. Mao, F. Chi, P. Wang, C. Xie, X. Wei, Y. Chen and M. Yin, *Opt. Mater.*, 2019, **95**, 109199.
5 L. Li, G. Tian, Y. Deng, Y. Wang, Z. Cao, F. Ling, Y. Li, S. Jiang, G. Xiang and X. Zhou, *Opt. Express*, 2020, **28**, 33747-33757.
6 Y. Song, N. Guo, J. Li, R. Ouyang, Y. Miao and B. Shao, *Ceram. Int.*, 2020, **46**, 22164-22170.
7 D. Chen, W. Xu, S. Yuan, X. Li and J. Zhong, *J. Mater. Chem. C*, 2017, **5**, 9619-9628.
8 W. Piotrowski, K. Trejgis, K. Maciejewska, K. Ledwa, B. Fond and L. Marciniak, *ACS Appl. Mater. Interfaces*, 2020, **12**, 44039-44048.
9 C. Xie, L. Zhao, B. Jiang, J. Mao, Y. Lin, P. Wang, X. Wei, M. Yin and Y. Chen, *J. Am. Ceram. Soc.*, 2019, **102**, 7500-7508.
10 D. K. Amarasinghe and F. A. Rabuffetti, *Inorg. Chem.*, 2021, **60**, 3165-3171.