ELECTRONIC SUPPLEMENTARY INFORMATION

Dysprosium-Activated Scheelite-Type Oxides as Thermosensitive Phosphors

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1. Synthesis of Na_2MoO_4 and Na_2WO_4

High-temperature solid-state reactions were employed to synthesize Na_2MoO_4 and Na_2WO_4. Na_2CO_3 (99.5%), MoO_3 (99.5%), and WO_3 (99.9%) were used as starting materials. All chemicals were purchased from Sigma-Aldrich and used as received. Stoichiometric amounts of the starting materials were mixed with a small volume of acetone and ground in an agate mortar for ~20 min. The unreacted homogeneous mixtures were placed in alumina crucibles and heated at 600 °C under air for 6 and 12 h to obtain Na_2MoO_4 and Na_2WO_4, respectively. After an intermediate grinding, samples were reheated under identical conditions to obtain polycrystalline powders.

2. Rietveld Analyses of $NaLa_{1-x}Dy_x(MO_4)_2$ and $Na_5La_{1-x}Dy_x(MO_4)_4$

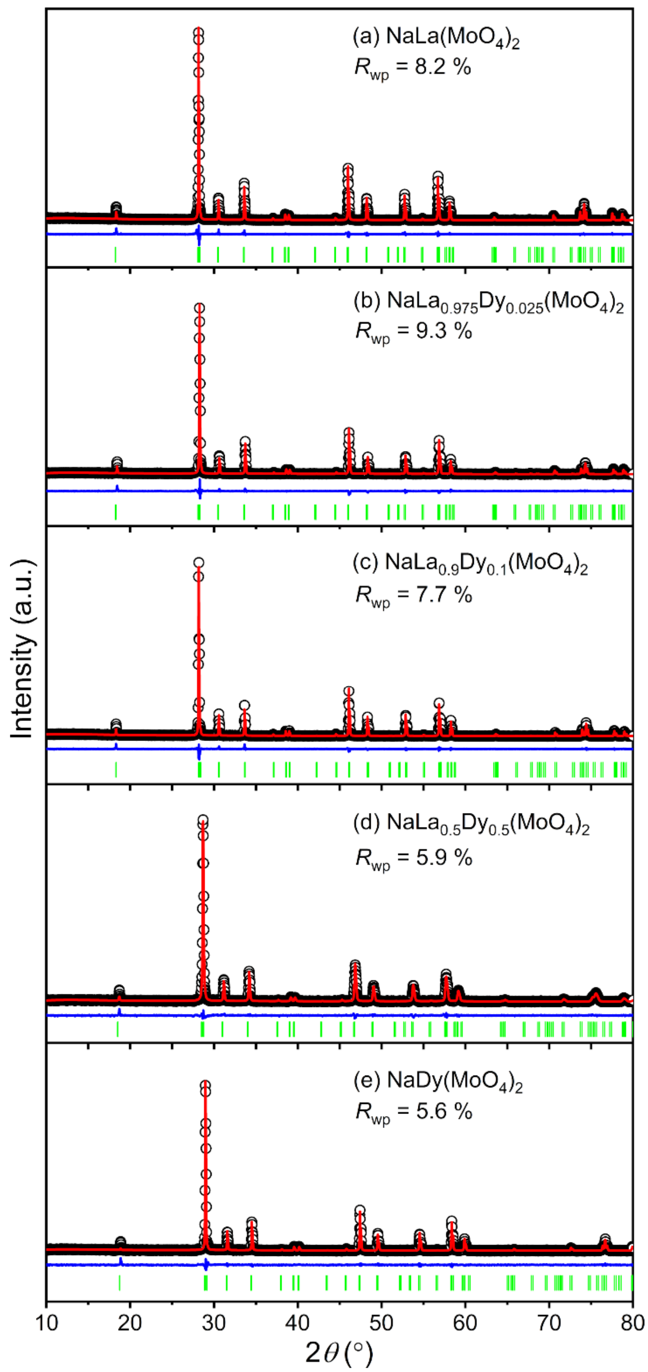

Figure S1. Rietveld analysis of the $NaLa_{1-x}Dy_x(MoO_4)_2$ series. Experimental (○) and calculated patterns (—) are shown along with difference curves (—). Tick marks (|) correspond to the calculated position of the diffraction maxima.

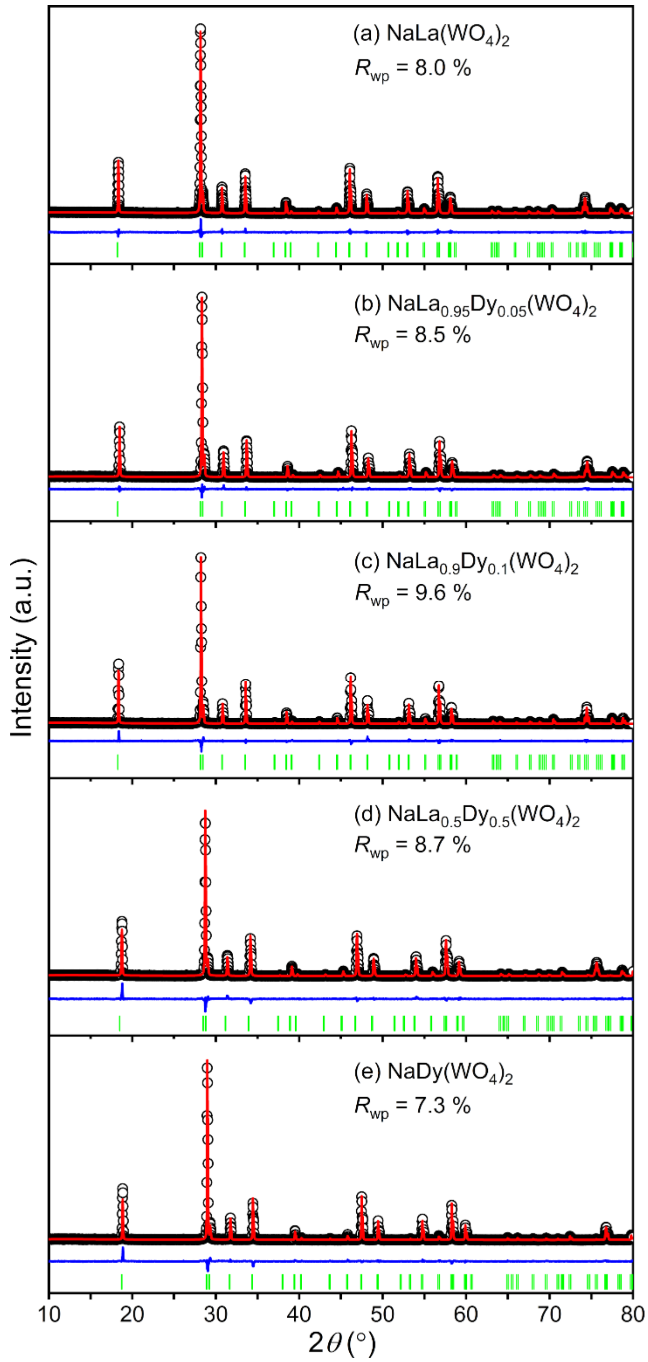

Figure S2. Rietveld analysis of the $NaLa_{1-x}Dy_x(WO_4)_2$ series. Experimental (○) and calculated patterns (—) are shown along with difference curves (—). Tick marks (|) correspond to the calculated position of the diffraction maxima.

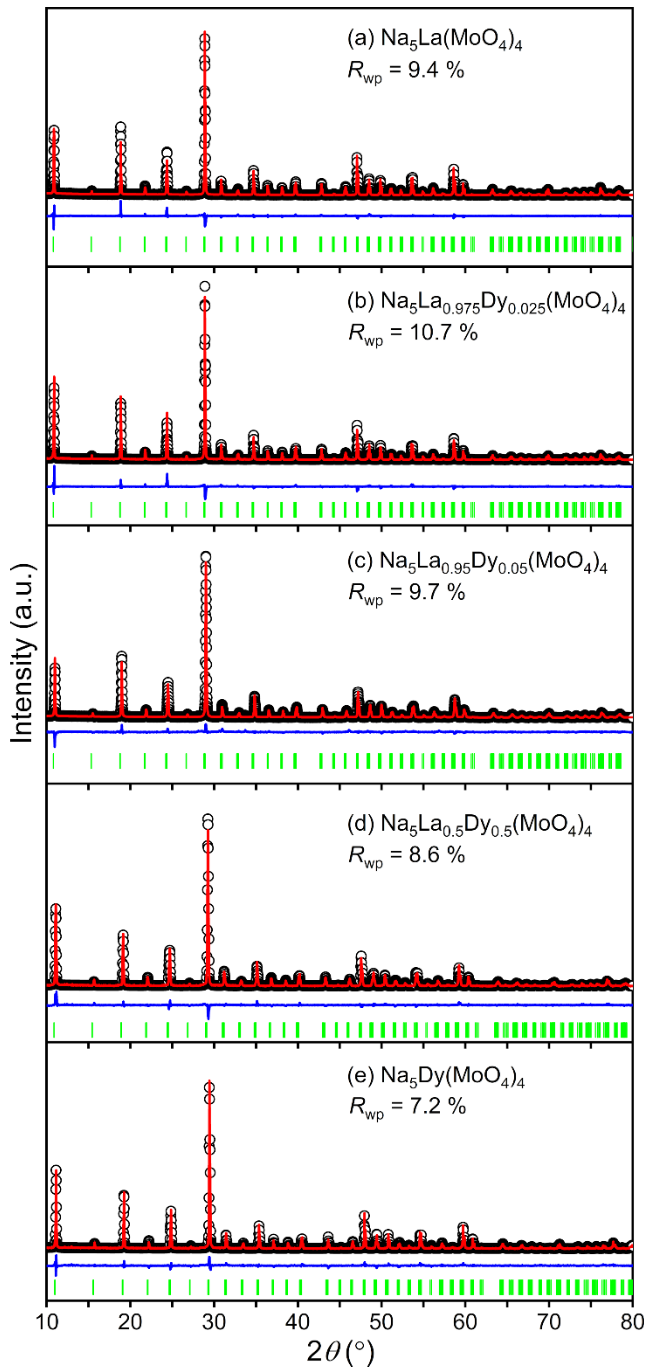

Figure S3. Rietveld analysis of the $Na_5La_{1-x}Dy_x(MoO_4)_4$ series Experimental (○) and calculated patterns (—) are shown along with difference curves (—). Tick marks (|) correspond to the calculated position of the diffraction maxima.

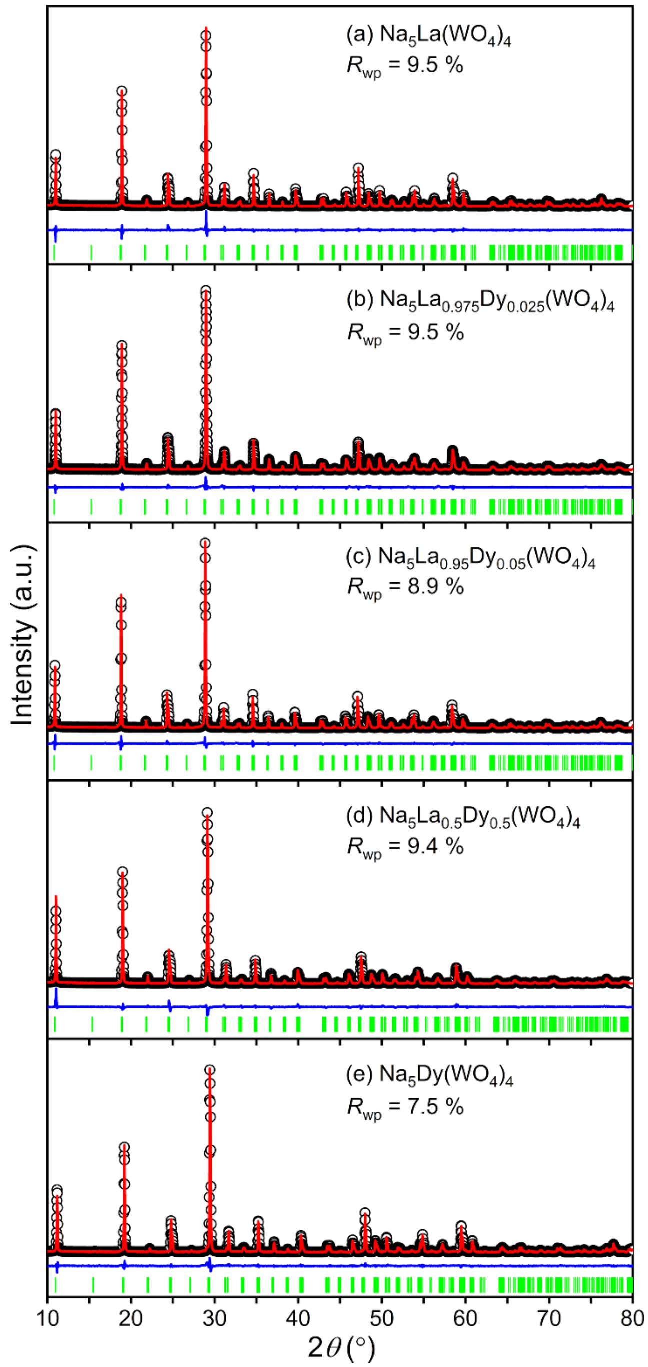

Figure S4. Rietveld analysis of the $Na_5La_{1-x}Dy_x(WO_4)_4$ series. Experimental (○) and calculated patterns (—) are shown along with difference curves (—). Tick marks (|) correspond to the calculated position of the diffraction maxima.

Table S1. Structural Parameters of $NaLa_{1-x}Dy_x(MO_4)_2$

$NaLa_{1-x}Dy_x(MoO_4)_2$						
x	0.000	0.025	0.050	0.100	0.500	1.000
a (Å)	5.34288(3)	5.33595(8)	5.33595(7)	5.32531(5)	5.26918(13)	5.21057(8)
c (Å)	11.73410(9)	11.716208(19)	11.7161(2)	11.68853(13)	11.5370(4)	11.3629(2)
V (Å^3)	334.967(5)	334.097(11)	333.586(11)	331.474(7)	320.32(2)	308.504(12)
U_{iso}^M (×100)	0.59(3)	1.67(5)	0.32(2)	1.11(5)	1.50(5)	1.44(6)
U_{iso}^O (×100)	0.91(5)	2.57(8)	1.40(18)	1.66(7)	2.18(8)	2.19(8)
R_{wp} (%)	8.2	9.3	9.1	7.7	5.9	5.6
$NaLa_{1-x}Dy_x(WO_4)_2$						
x	0.000	0.025	0.050	0.100	0.500	1.000
a (Å)	5.35889(3)	5.35603(3)	5.35024(6)	5.34655(5)	5.28785(8)	5.22030(5)
c (Å)	11.66772(9)	11.65948(8)	11.64224(16)	11.63262(14)	11.4875(2)	11.30518(16)
V (Å^3)	335.070(5)	334.476(4)	333.260(9)	332.525(8)	321.206(13)	308.084(9)
U_{iso}^M (×100)	1.16(2)	1.13(3)	0.96(4)	0.94(4)	1.19(5)	1.99(5)
U_{iso}^O (×100)	1.96(4)	1.52(4)	1.48(5)	1.44(6)	1.79(7)	2.89(7)
R_{wp} (%)	8.0	8.5	8.5	9.6	8.7	7.3

Table S2. Structural Parameters of $Na_5La_{1-x}Dy_x(MO_4)_4$

$Na_5La_{1-x}Dy_x(MoO_4)_4$						
x	0.000	0.025	0.050	0.100	0.500	1.000
a (Å)	11.57360(7)	11.57087(8)	11.56736(13)	11.56353(11)	11.48289(19)	11.38693(12)
c (Å)	11.61945(9)	11.61605(12)	11.6153 (2)	11.6116(2)	11.5374(3)	11.43292(19)
V (Å^3)	1556.41(2)	1555.22(3)	1554.17(5)	1552.65(3)	1521.29(6)	1482.42(4)
U_{iso}^{M} (×100)	0.20(3)	1.56(4)	0.55(4)	0.02(4)	1.81(6)	0.76(6)
U_{iso}^{O} (×100)	0.30(5)	2.34(6)	0.82(6)	0.02(7)	2.61(9)	1.14(9)
R_{wp} (%)	9.4	10.7	9.7	9.6	8.6	7.2
$Na_5La_{1-x}Dy_x(WO_4)_4$						
x	0.000	0.025	0.050	0.100	0.500	1.000
a (Å)	11.62533(10)	11.62572(13)	11.62837(12)	11.62419(16)	11.54432(21)	11.44550(13)
c (Å)	11.53952(14)	11.54320(18)	11.54188(17)	11.5362(2)	11.4530(3)	11.35432(18)
V (Å^3)	1559.55(4)	1560.15(5)	1560.68(4)	1558.79(6)	1526.35(7)	1487.41(4)
U_{iso}^{M} (×100)	0.77(4)	1.22(3)	1.22(4)	0.76(3)	1.93(5)	1.03(4)
U_{iso}^{O} (×100)	1.16(6)	1.64(5)	1.88(6)	1.14(5)	2.76(8)	1.49(6)
R_{wp} (%)	9.5	9.5	8.9	9.8	9.4	7.5

3. Variable-Temperature Spectra of $NaLa_{1-x}Dy_x(MO_4)_2$ and $Na_5La_{1-x}Dy_x(MO_4)_4$

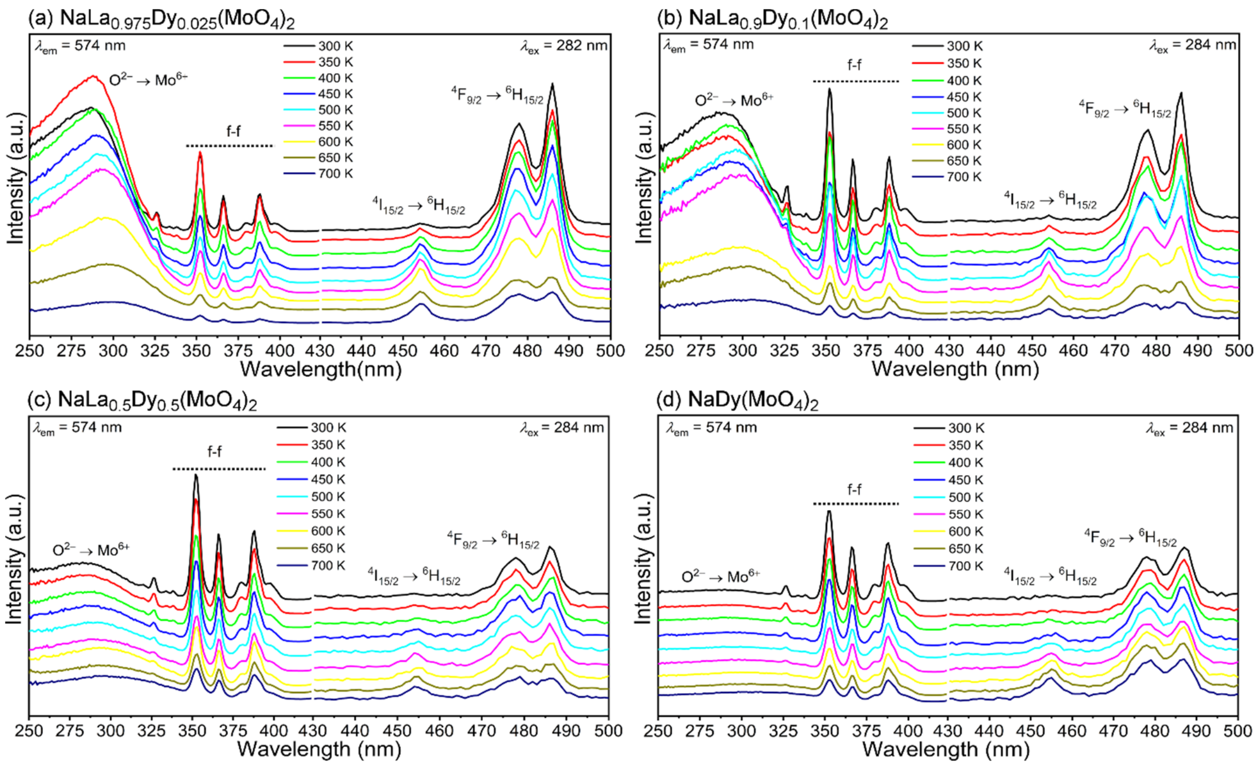

Figure S5. Temperature-dependent excitation and emission spectra of the $NaLa_{1-x}Dy_x(MoO_4)_2$ series in the 300–700 K temperature range.

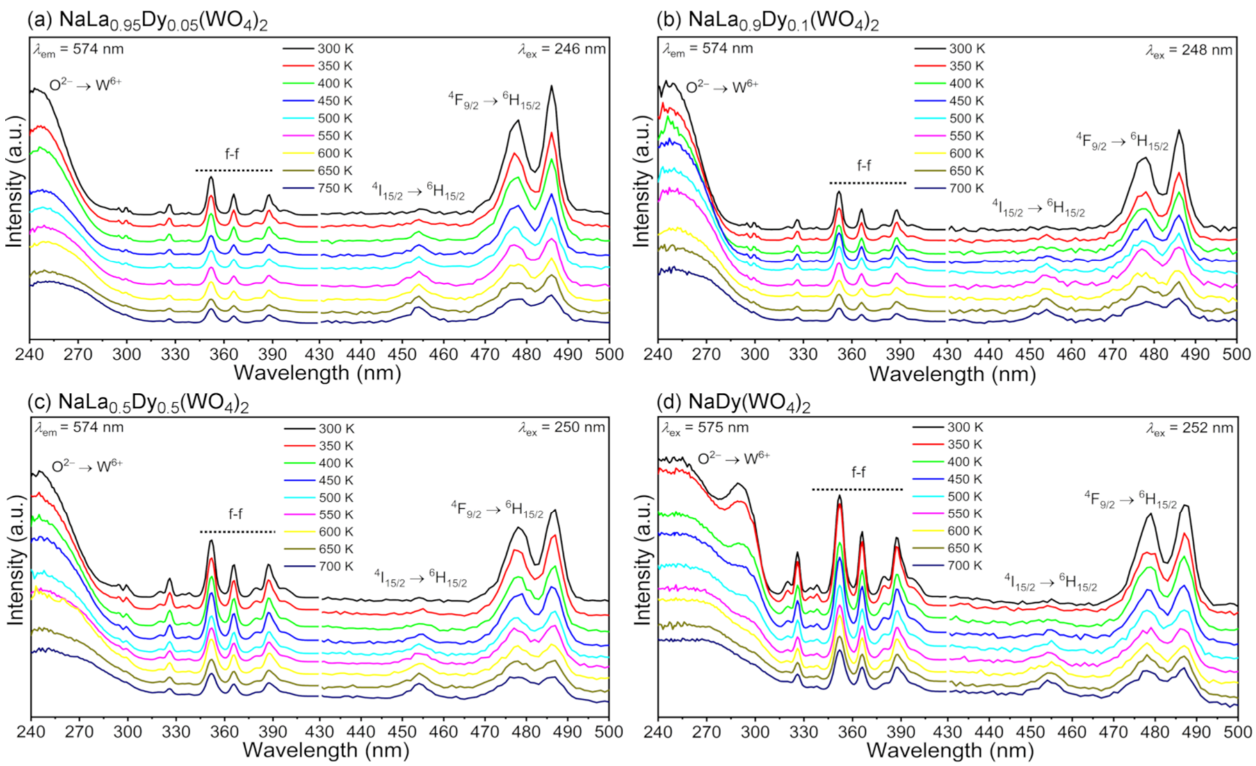

Figure S6. Temperature-dependent excitation and emission spectra of the $NaLa_{1-x}Dy_x(WO_4)_2$ series in the 300–700 K temperature range.

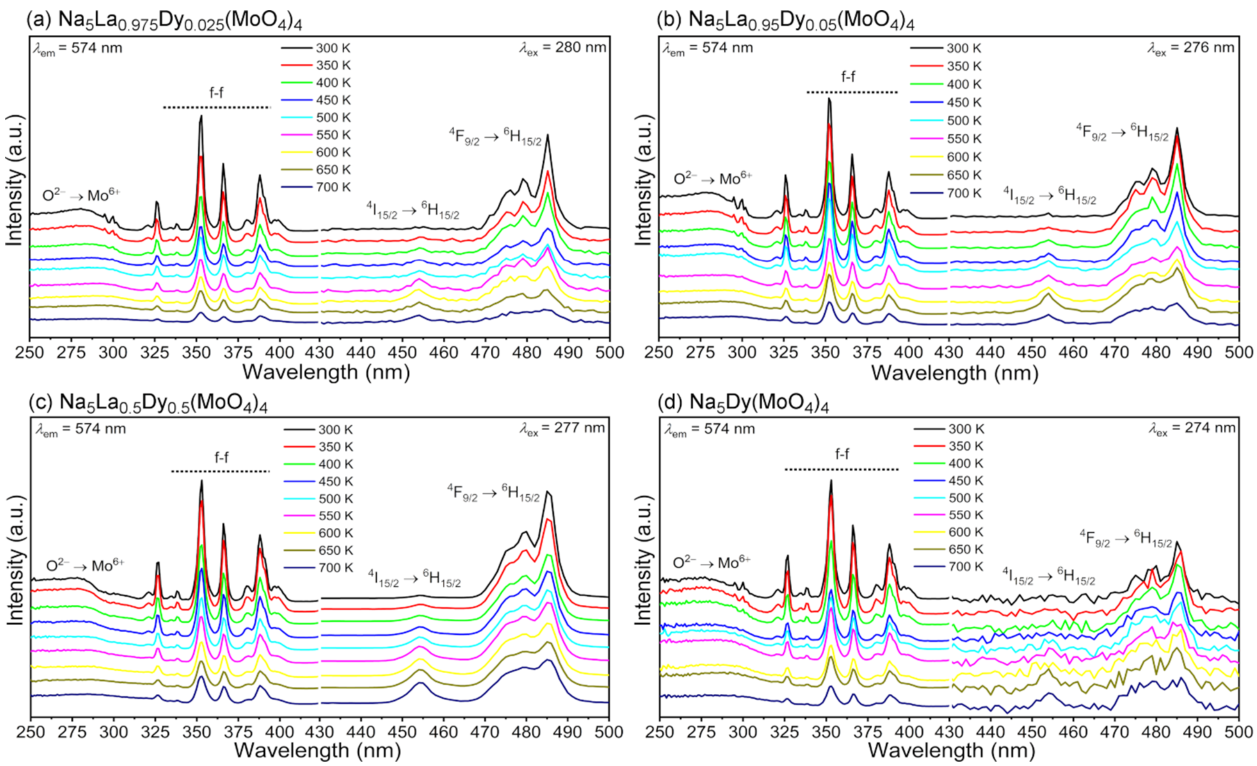

Figure S7. Temperature-dependent excitation and emission spectra of the $Na_5La_{1-x}Dy_x(MoO_4)_4$ series in the 300–700 K temperature range.

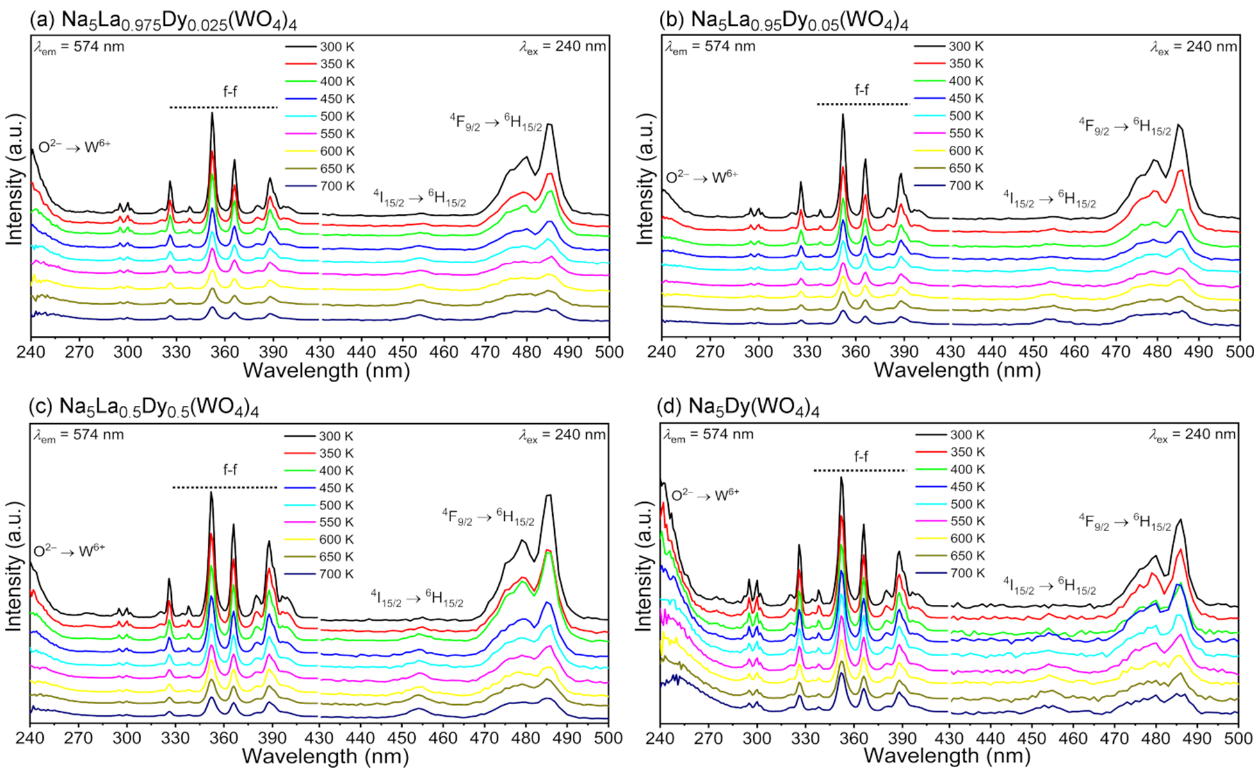

Figure S8. Temperature-dependent excitation and emission spectra of the $Na_5La_{1-x}Dy_x(WO_4)_4$ series in the 300–700 K temperature range.

4. Thermometric Performance of $NaLa_{1-x}Dy_x(MO_4)_2$ and $Na_5La_{1-x}Dy_x(MO_4)_4$

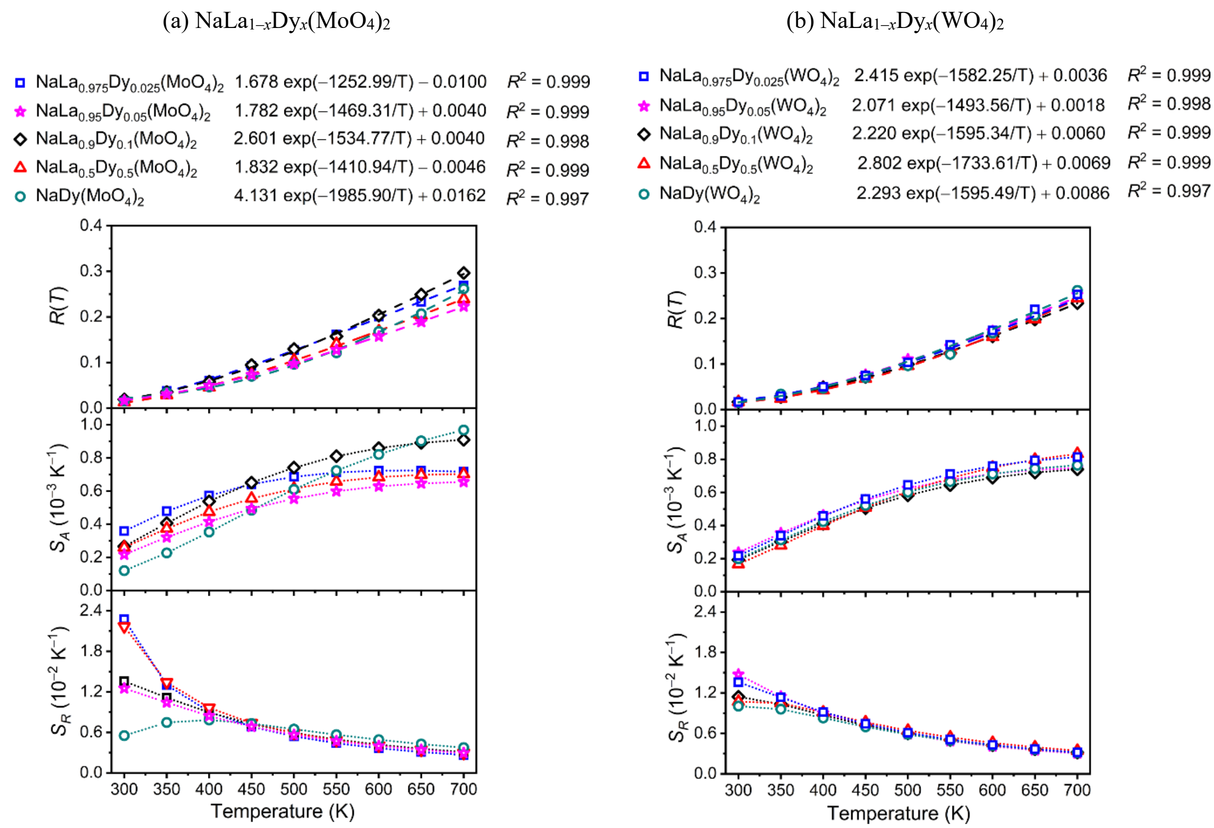

Figure S9. Luminescence intensity ratio ($R(T)$), absolute sensitivity (S_A), and relative sensitivity (S_R) of phosphors belonging to the $NaLa_{1-x}Dy_x(MO_4)_2$ series. Analytical expressions used to fit experimental $R(T)$ values are given. The corresponding fits are depicted as dashed lines and R^2 residuals are given. Dotted lines shown in $S_A(T)$ and $S_R(T)$ plots are guides-to-the-eye.

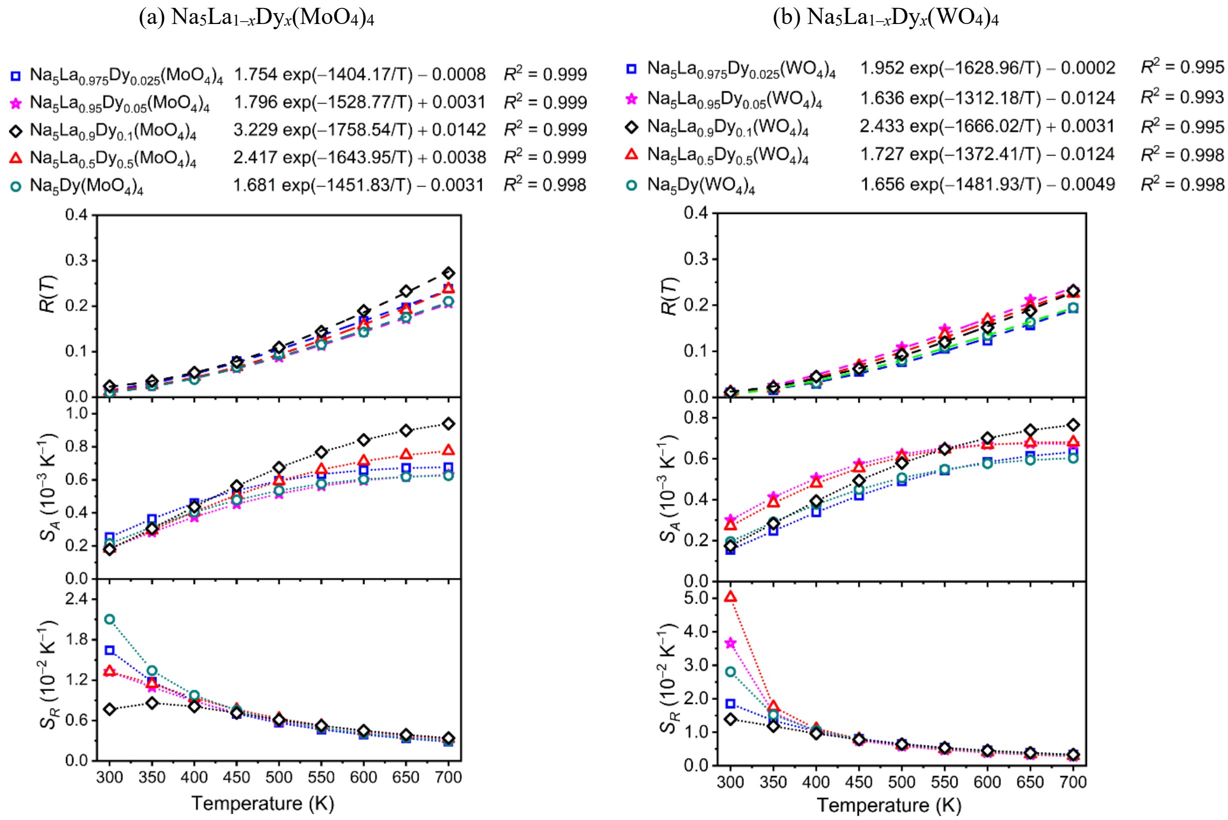

Figure S10. Luminescence intensity ratio ($R(T)$), absolute sensitivity (S_A), and relative sensitivity (S_R) of phosphors belonging to the $Na_5La_{1-x}Dy_x(MO_4)_4$ series. Analytical expressions used to fit experimental $R(T)$ values are given. The corresponding fits are depicted as dashed lines and R^2 residuals are given. Dotted lines shown in $S_A(T)$ and $S_R(T)$ plots are guides-to-the-eye.

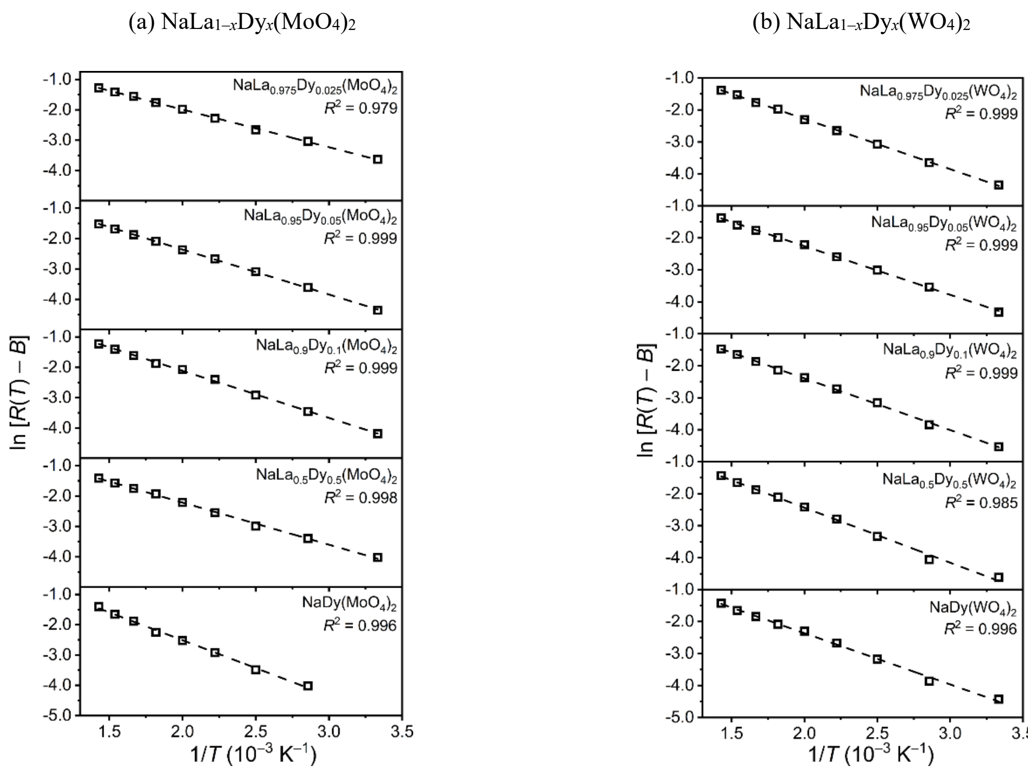

Figure S11. Arrhenius-type plots for phosphors belonging to the $NaLa_{1-x}Dy_x(MO_4)_2$ series. Linear fits are depicted as dashed lines and R^2 residuals are given.

(a) $Na_5La_{1-x}Dy_x(MoO_4)_4$ (b) $Na_5La_{1-x}Dy_x(WO_4)_4$

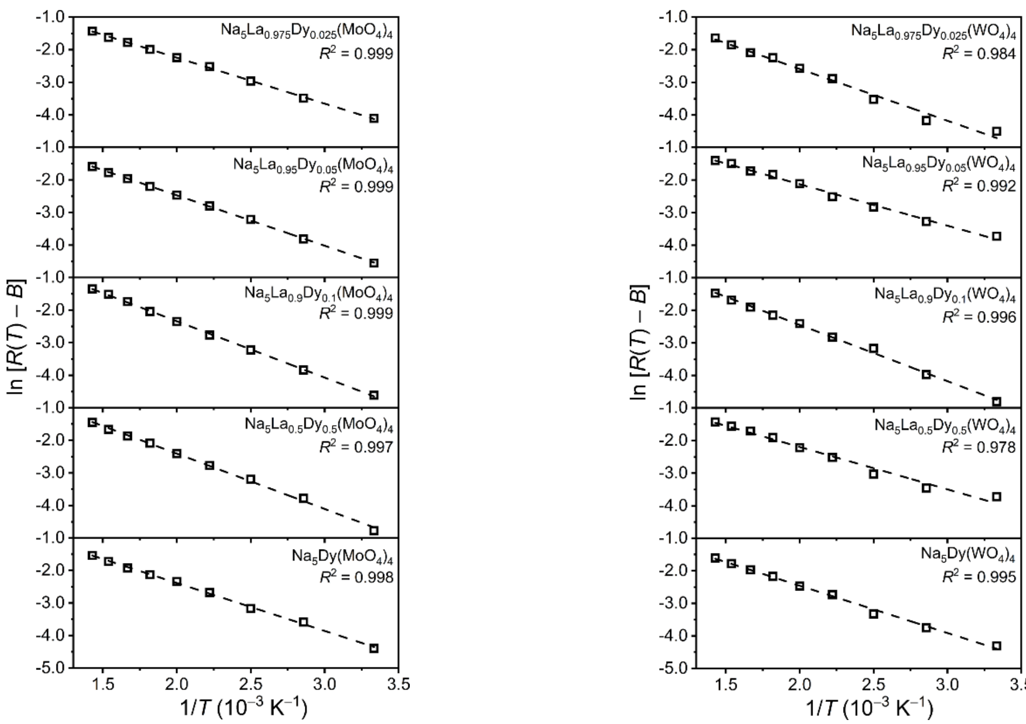

Figure S12. Arrhenius-type plots for phosphors belonging to the $Na_5La_{1-x}Dy_x(MO_4)_4$ series. Linear fits are depicted as dashed lines and R^2 residuals are given.

Table S3. Experimental and Calculated Energy Gap Between Thermally Coupled Levels of Dy^{3+}

Composition	ΔE_{exp} (cm^{-1})	ΔE_{fit} (cm^{-1})	$\Delta E_{fit} - \Delta E_{exp}$ (cm^{-1})
$NaLa_{0.975}Dy_{0.025}(MoO_4)_2$	1222	871	–351
$NaLa_{0.95}Dy_{0.05}(MoO_4)_2$	1234	1021	–213
$NaLa_{0.9}Dy_{0.1}(MoO_4)_2$	1217	1067	–150
$NaLa_{0.5}Dy_{0.5}(MoO_4)_2$	1227	981	–246
$NaDy(MoO_4)_2$	1218	1380	162
$NaLa_{0.975}Dy_{0.025}(WO_4)_2$	1242	1100	–142
$NaLa_{0.95}Dy_{0.05}(WO_4)_2$	1227	1038	–189
$NaLa_{0.9}Dy_{0.1}(WO_4)_2$	1233	1109	–124
$NaLa_{0.5}Dy_{0.5}(WO_4)_2$	1218	1205	–13
$NaDy(WO_4)_2$	1264	1109	–155
$Na_5La_{0.975}Dy_{0.025}(MoO_4)_4$	1207	976	–231
$Na_5La_{0.95}Dy_{0.05}(MoO_4)_4$	1235	1063	–172
$Na_5La_{0.9}Dy_{0.1}(MoO_4)_4$	1230	1222	–8
$Na_5La_{0.5}Dy_{0.5}(MoO_4)_4$	1240	1143	–97
$Na_5Dy(MoO_4)_4$	1195	1009	–186
$Na_5La_{0.975}Dy_{0.025}(WO_4)_4$	1229	1132	–97
$Na_5La_{0.95}Dy_{0.05}(WO_4)_4$	1199	912	–287
$Na_5La_{0.9}Dy_{0.1}(WO_4)_4$	1253	1158	–95
$Na_5La_{0.5}Dy_{0.5}(WO_4)_4$	1210	954	–256
$Na_5Dy(WO_4)_4$	1253	1030	–223

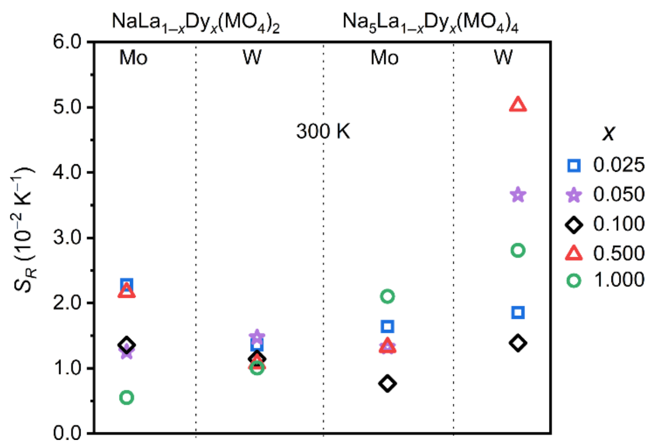

Figure S13. Map of relative sensitivity values at 300 K as a function of host composition and Dy^{3+} concentration.

Table S4. Repeatability of $NaDy(MoO_4)_2$ at 700 K

Cycle #	*R*(350 K)	*R*(700 K)
1	0.03740	0.26476
2	0.03680	0.26672
3	0.03836	0.26638
4	0.03902	0.26159
5	0.03605	0.25586
6	0.03513	0.25507
7	0.03496	0.26408
8	0.03888	0.26166
9	0.04002	0.26370
10	0.04093	0.25978
⟨*R*(700 K)⟩		0.26196

Table S5. Repeatability of $Na_5La_{0.5}Dy_{0.5}(WO_4)_4$ at 350 K

Cycle #	*R*(350 K)	*R*(700 K)
1	0.01953	0.21956
2	0.02004	0.21657
3	0.02021	0.21530
4	0.01959	0.20966
5	0.02163	0.21205
6	0.02179	0.21392
7	0.02136	0.21019
8	0.02122	0.21029
9	0.02188	0.21067
10	0.02184	0.20738
⟨*R*(350 K)⟩	0.02091	

Table S6. Temperature Resolution of $NaDy(MoO_4)_2$ at 700 K

Spectrum #	R(700 K)	Calculated T [a]	Spectrum #	R(700 K)	Calculated T [a]
1	0.26898	710.80255	26	0.25939	701.10351
2	0.27030	712.13266	27	0.27039	712.22242
3	0.25419	695.78642	28	0.26785	709.66535
4	0.24905	690.51080	29	0.25020	691.69456
5	0.25146	692.98239	30	0.24556	686.90002
6	0.25817	699.85871	31	0.25922	700.92676
7	0.26716	708.97478	32	0.25876	700.45376
8	0.25215	693.69335	33	0.25344	695.02166
9	0.26268	704.44389	34	0.27016	711.99329
10	0.25637	698.01943	35	0.25350	695.08239
11	0.26245	704.20789	36	0.26460	706.38526
12	0.25282	694.38391	37	0.26062	702.35029
13	0.25451	696.11411	38	0.26127	703.01185
14	0.24975	691.22516	39	0.26710	708.91073
15	0.26687	708.67517	40	0.25543	697.05638
16	0.25072	692.22657	41	0.24551	686.84588
17	0.25934	701.04886	42	0.25833	700.01542
18	0.25510	696.71591	43	0.25884	700.53738
19	0.26155	703.29918	44	0.26067	702.39642
20	0.25894	700.63958	45	0.25563	697.26751
21	0.27099	712.82284	46	0.27383	715.66822
22	0.26033	702.05381	47	0.26527	707.06551
23	0.26579	707.59089	48	0.26601	707.81352
24	0.25822	699.90434	49	0.25427	695.87480
25	0.26222	703.97587	50	0.26697	708.77451
			Mean	0.25966	701.34253
			Standard Deviation	0.00698	7.10856
			ΔT	7.1	7.1

[a] Calculated using $R(T) = 4.131 \exp(-1985.90/T) + 0.0162$

Table S7. Temperature Resolution of $Na_5La_{0.5}Dy_{0.5}(WO_4)_4$ at 350 K

Spectrum #	R(350 K)	Calculated T [a]	Spectrum #	R(350 K)	Calculated T [a]
1	0.02255	351.86990	26	0.02252	351.77547
2	0.02225	351.08964	27	0.02225	351.07979
3	0.02196	350.33916	28	0.02251	351.77072
4	0.02258	351.94231	29	0.02258	351.93311
5	0.02249	351.70913	30	0.02272	352.28972
6	0.02275	352.37755	31	0.02274	352.36214
7	0.02281	352.54111	32	0.02282	352.54922
8	0.02241	351.49645	33	0.02310	353.27866
9	0.02226	351.11792	34	0.02297	352.94396
10	0.02271	352.26827	35	0.02255	351.87291
11	0.02246	351.62455	36	0.02249	351.71568
12	0.02244	351.58084	37	0.02270	352.25040
13	0.02235	351.35685	38	0.02269	352.22576
14	0.02235	351.33882	39	0.02249	351.70458
15	0.02264	352.09624	40	0.02257	351.91770
16	0.02263	352.07796	41	0.02255	351.87005
17	0.02250	351.72238	42	0.02259	351.96703
18	0.02293	352.83334	43	0.02288	352.70255
19	0.02264	352.10291	44	0.02281	352.52395
20	0.02264	352.09170	45	0.02281	352.52985
21	0.02285	352.62492	46	0.02231	351.24184
22	0.02277	352.42179	47	0.02237	351.40244
23	0.02276	352.39538	48	0.02257	351.92618
24	0.02206	350.58876	49	0.02262	352.05415
25	0.02256	351.88964	50	0.02247	351.64619
			Mean	0.02258	351.94063
			Standard Deviation	0.00022	0.57482
			ΔT (K)	0.58	0.57

[a] Calculated using $R(T) = 1.727 \exp(-1372.41/T) - 0.0124$