Supplementary Information

Negative Thermal Expansion in $Sc_2Mo_3O_{12}:Sm^{3+}$ for White LEDs and Unveiling the Impact of Phase Transition on Cryogenic Luminescence

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S1. Characterization

The powder XRD patterns were acquired on a Proto-AXRD bench top system in the 2θ range of 10-70° using the Cu Kα line (λ = 1.5406 Å) and a scanning rate of 1°/min. Fourier Transform Infrared Spectroscopy (FTIR) was performed in ATR mode on a Bruker Alpha FTIR spectrometer in the scanning range from 500 to 4000 cm^{-1} using average of 36 scans with a resolution of 4 cm^{-1}. The scanning electron microscopy (SEM) was performed on a SEM (Model: JEOL ICM6000Plus-7E, Japan) system at 15 kV. Rietveld refinement was done on powder XRD patterns by using FullProf software.[1] HT-XRD measurements were done on GNR Explore X-ray Diffractometer with a heating rate of 10 K/min and equilibrium time of 10 minutes. An X-ray Absorption Spectroscopy (XAS) measurement, which comprises of both X-ray Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS)

techniques, have been carried out on undoped and Sm doped $Sc_2Mo_3O_{12}$ at Mo K-edge in transmission mode and Sm L_3-edge in fluorescence mode to probe the local structure. The XAS measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the Indus-2 Synchrotron Source (2.5 GeV, 100 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.[2, 3] PL and PLE spectra were recorded with a continuous Xenon lamp (450 W) source on a FLS 1000 fluorescence spectrometer (Edinburgh Instruments, U.K.), and visible-PMT as the detector. Emission photographs were captured under the excitation wavelength of 270 nm by Nikon camera. Low temperature-dependent PL studies were performed using cryostat assembly with FLS-1000 fluorescence spectrometer and liquid nitrogen as coolant. Temperature-dependent PL spectra at high temperature were measured using an Ocean optics spectrophotometer that has a Maya 2000 PRO with a 280 nm LEDs as excitation source. Differential scanning calorimeter (DSC) measurements were performed on M/s. Mettler Toledo GmbH, Switzerland. A prototype white-LED was fabricated by pasting a mixture of phosphors onto a 280 nm UV LED chip operating at a voltage of 12 V and current of 2 A. The red pc-LEDs were fabricated by combining this optimized red phosphor with a 280 nm UV-LED chip and a 410 nm blue LED chip individually, both operated at a voltage of 12 V and current of 2 A. The temperature-dependent Raman spectroscopy was performed using the Linkam thermal stage (HFS600E) having temperature control accuracy of 1 °C and a heating rate of 10 °C min^{-1}. A sufficient time hold of 5 min is taken at each temperature step for sample temperature stabilization.

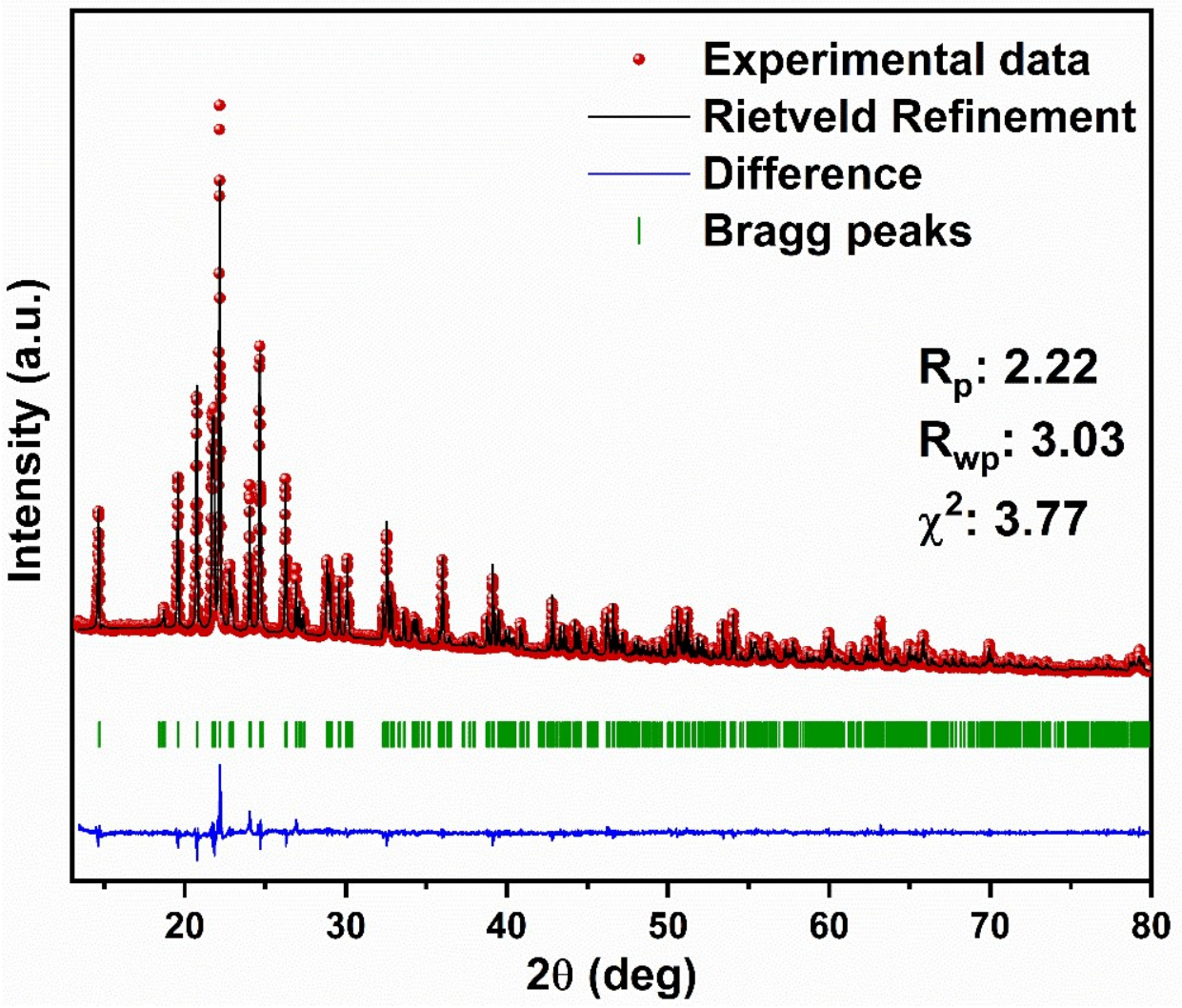

Figure S1: Rietveld fitting of powder XRD patterns of undoped $Sc_2Mo_3O_{12}$ sample at room temperature.

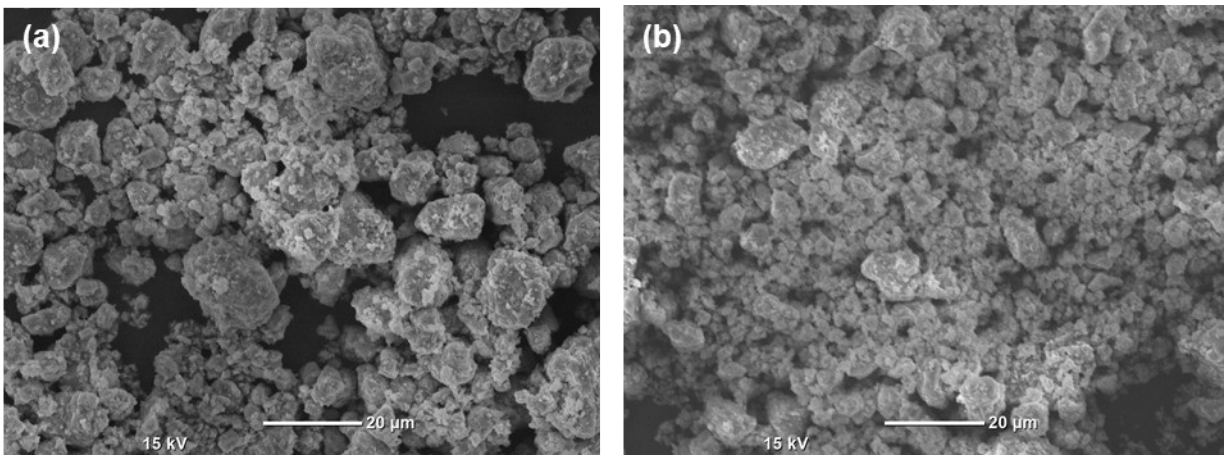

Figure S2: SEM images of (a) SMO:5Sm and (b) SMO:10 Sm phosphors.

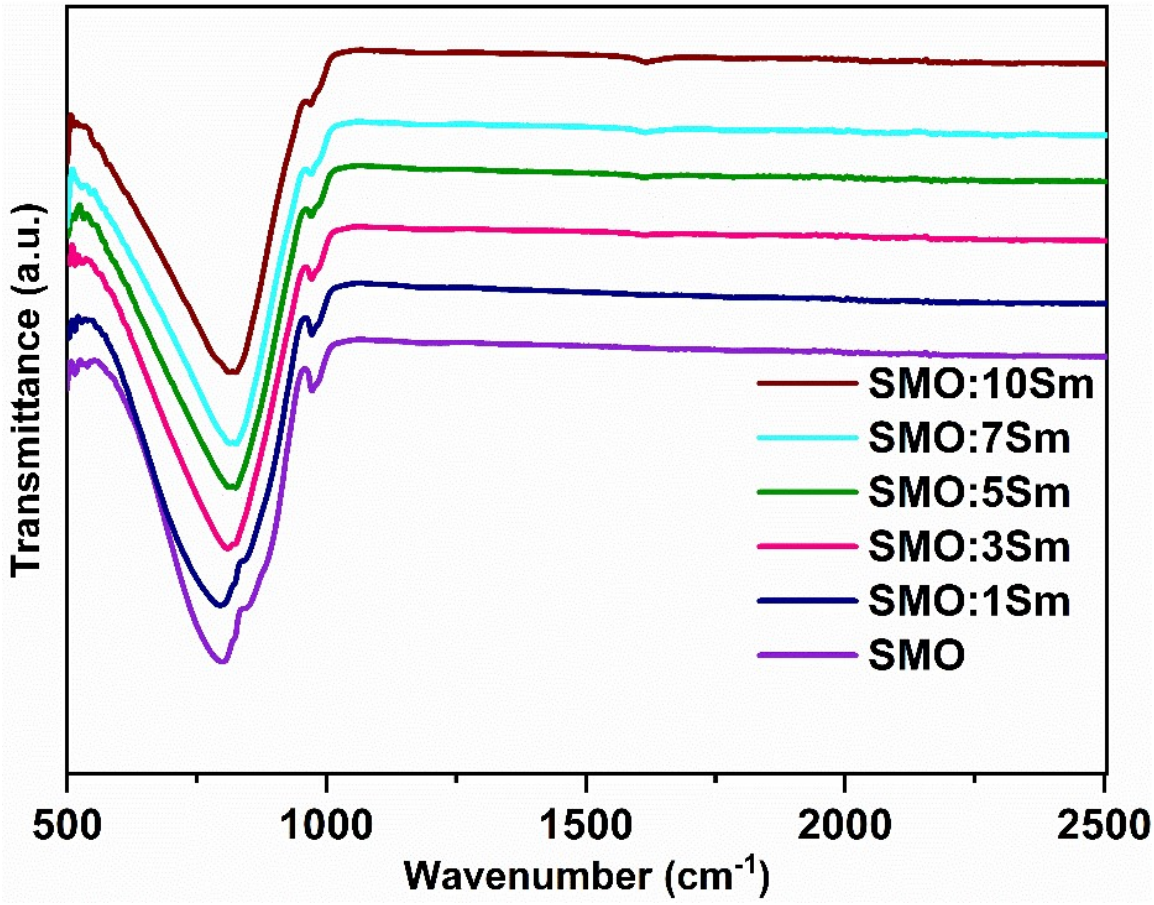

Figure S3: FTIR spectra of $Sc_2Mo_3O_{12}$:*x*Sm^{3+} (*x* = 0, 1, 3, 5, 7 and 10 mol %) phosphors.

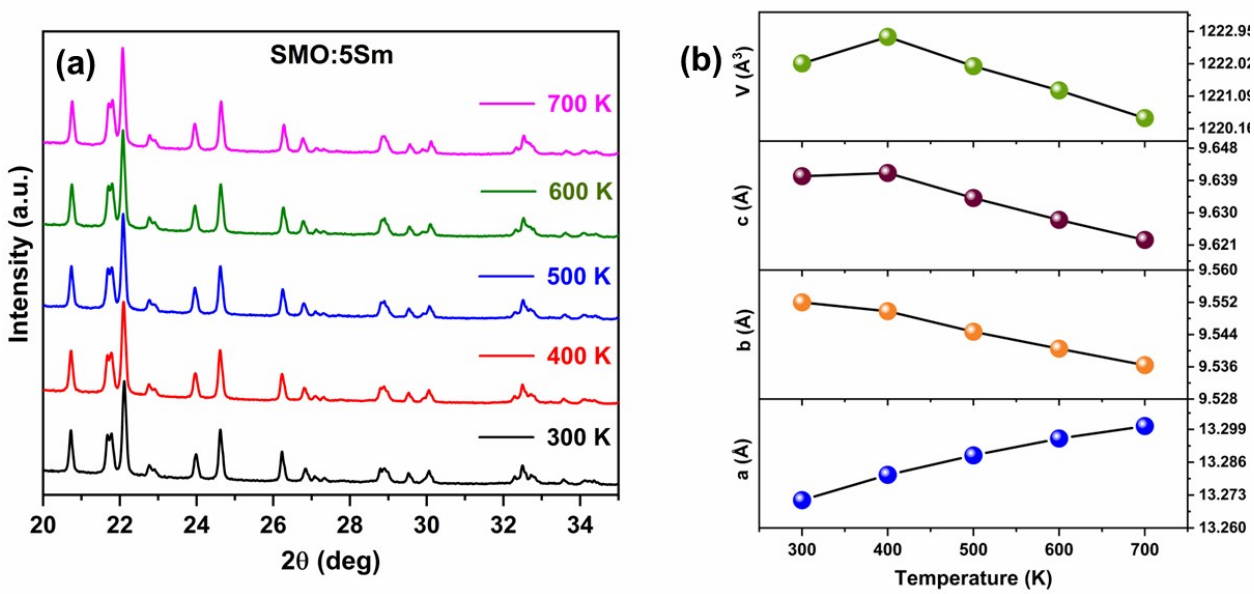

Figure S4: (a) High temperature-dependent XRD patterns of SMO:5Sm sample and (b) Changes in unit cell parameters with temperature in the range of 300 to 700 K.

Table S1: Lattice parameters for SMO at different temperature from 300 to 700 K

Temperature (K)	a (Å)	B (Å)	c (Å)	V (Å^3)
300	13.2403(3)	9.5426(3)	9.6356(3)	1217.425(045)
400	13.2516(9)	9.5345(9)	9.6282(9)	1216.511(180)
500	13.2615(9)	9.5292(9)	9.6201(9)	1215.720(180)
600	13.2698(15)	9.5244(9)	9.6129(12)	1214.941(240)
700	13.2770(15)	9.5216(9)	9.6071(12)	1214.510(240)

Table S2: Lattice parameters for SMO:5Sm at different temperature from 300 to 700 K.

Temperature (K)	a (Å)	B (Å)	c (Å)	V (Å^3)
300	13.2710(3)	9.5520(3)	9.6402(3)	1222.030(072)
400	13.2810(12)	9.5498(9)	9.6411(9)	1222.793(210)
500	13.2887(12)	9.5447(9)	9.6341(9)	1221.953(210)
600	13.2954(6)	9.5405(6)	9.6280(6)	1221.256(105)
700	13.3003(12)	9.5364(9)	9.6224(9)	1220.461(180)

Table S3: Lifetime values of SMO:Sm samples at 647 nm emission and λ_{ex} = 270 nm and 404 nm, respectively.

λ_{ex} = 270 nm and λ_{em} = 647 nm					
Sample	τ_1 (μs)	%	τ_2 (μs)	%	τ_{av} (μs)
1Sm	452 ± 10.1	17.49	1143.5 ± 4.60	82.51	1022.56 ± 4.19
3Sm	364 ± 3.61	35.8	1020 ± 4.27	64.2	785.15 ± 3.03
5Sm	298.5 ± 2.81	41.6	952.8 ± 4.82	58.4	680.61 ± 3.04
7Sm	274 ± 2.45	43.63	896.05 ± 4.81	56.37	624.65 ± 2.91
10Sm	271 ± 2.21	47.71	892.92 ± 4.89	52.29	596.20 ± 2.77
λ_{ex} = 404 nm and λ_{em} = 647 nm					
Sample	τ_1 (μs)	%	τ_2 (μs)	%	τ_{av} (μs)
1Sm	387 ± 8.16	16.99	1110 ± 3.94	83.01	987.16 ± 3.55
3Sm	303.8 ± 3.84	32.14	905.94 ± 4.26	67.86	712.41 ± 3.14
5Sm	253.1 ± 3.24	39.65	793.33 ± 5.10	60.35	579.13 ± 3.33
7Sm	255.86 ± 2.99	43.7	773.5 ± 5.28	56.31	547.37 ± 3.25
10Sm	220.34 ± 2.29	43.72	714.41 ± 4.29	56.28	498.40 ± 2.62

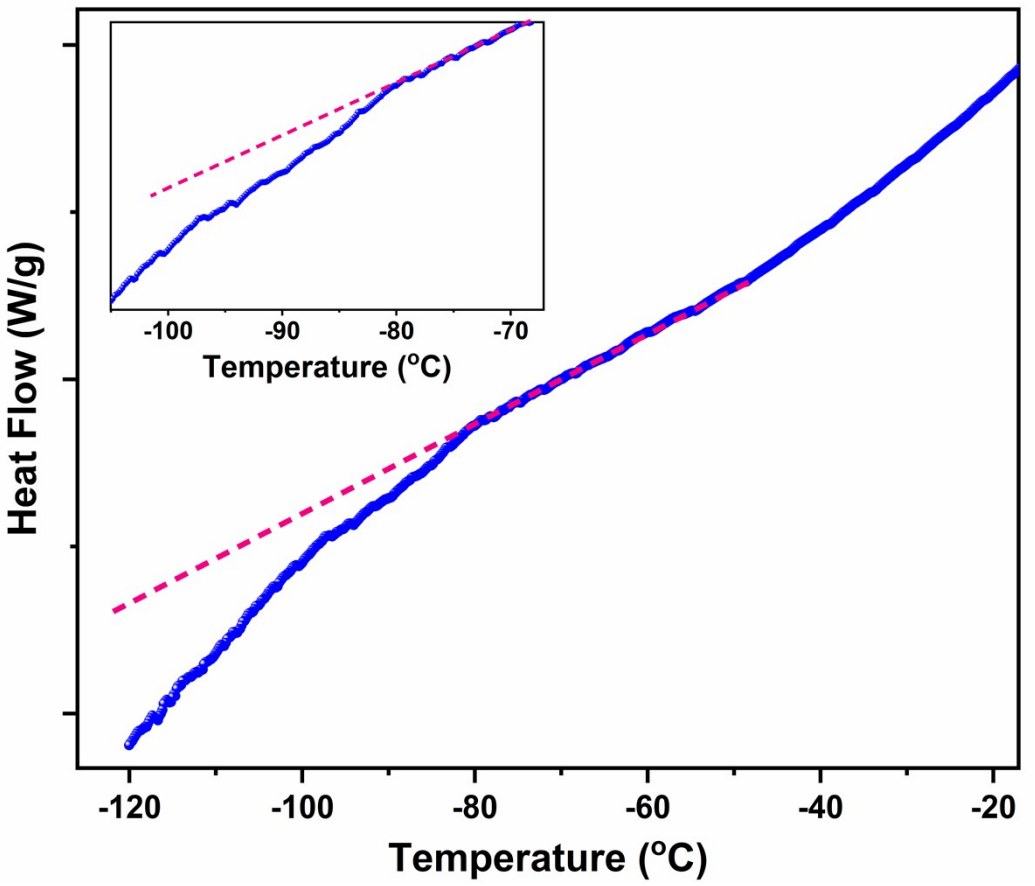

Figure S5: DSC Curve showing the phase transition.

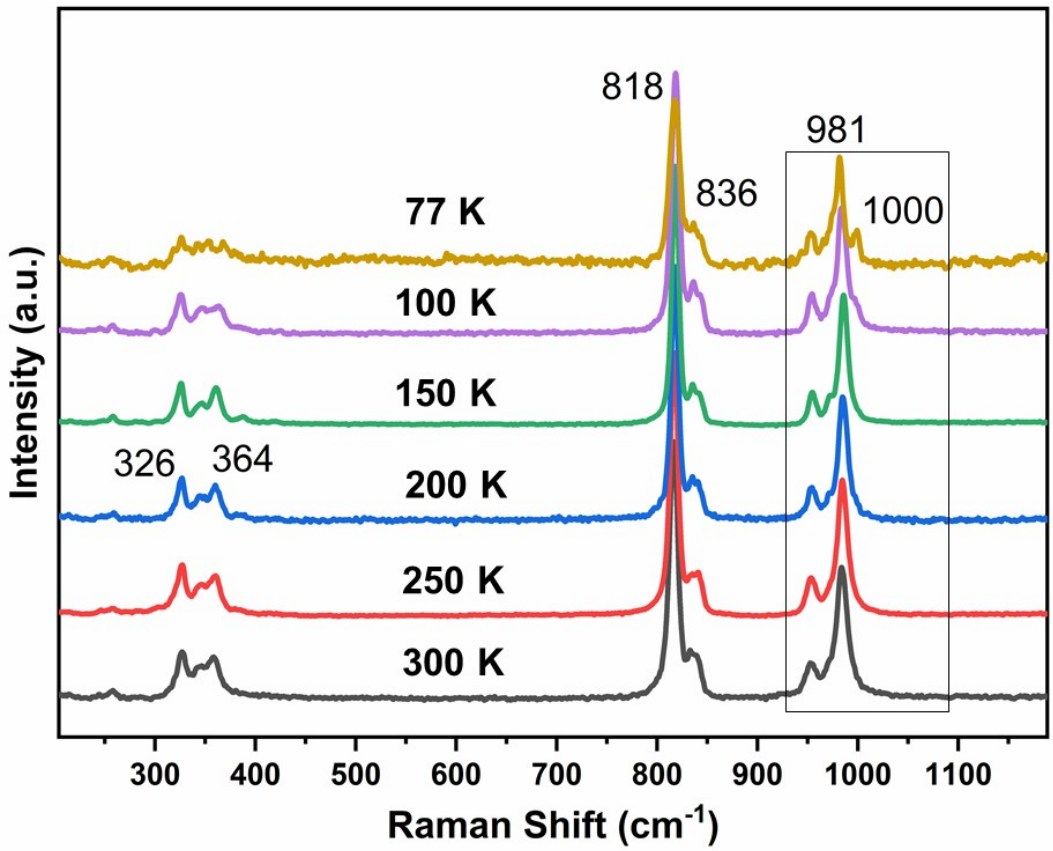

Figure S6: Raman spectra of $Sc_2Mo_3O_{12}$:5Sm at different temperatures.

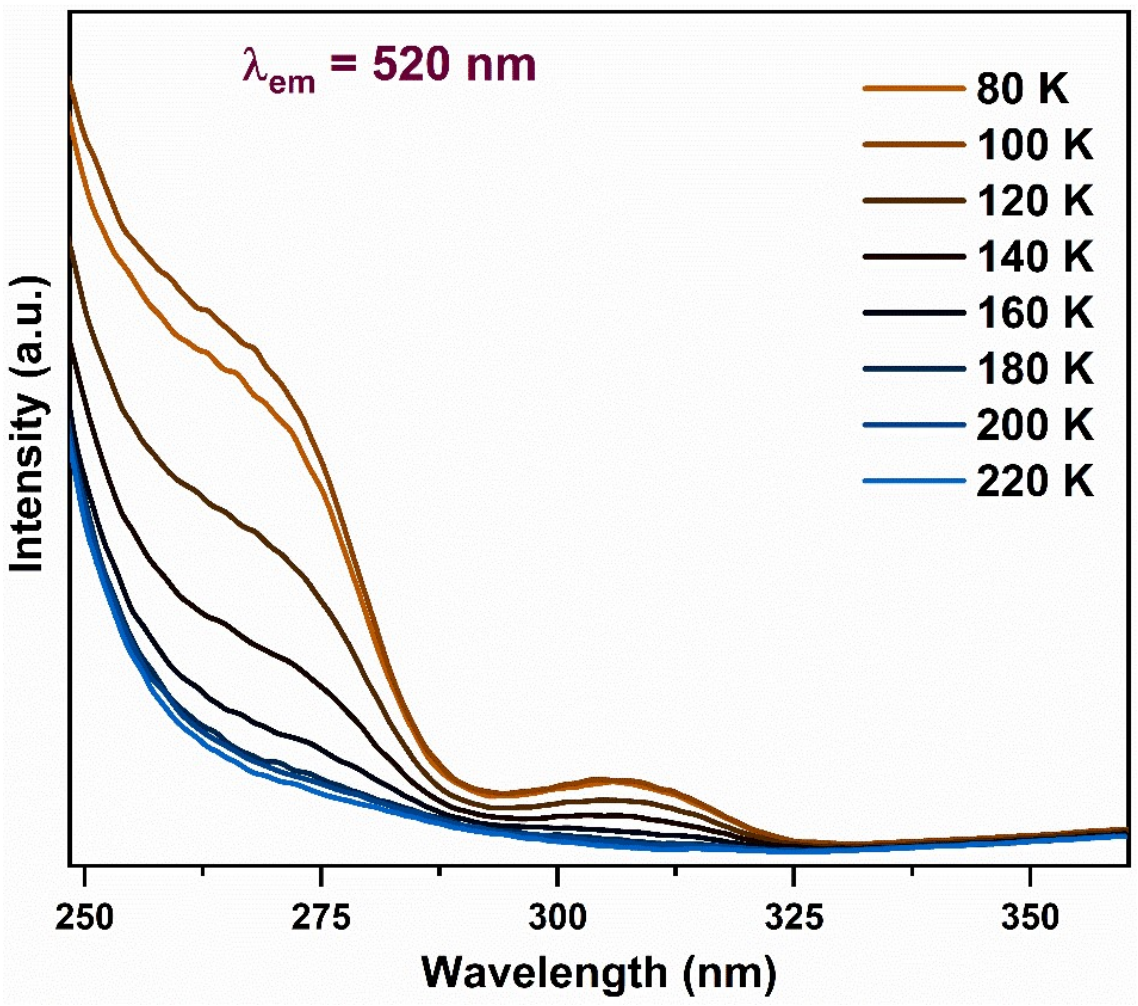

Figure S7: Temperature-dependent PL excitation spectra of SMO:5Sm sample monitored at 520 nm emission in the range of 80 to 300 K.

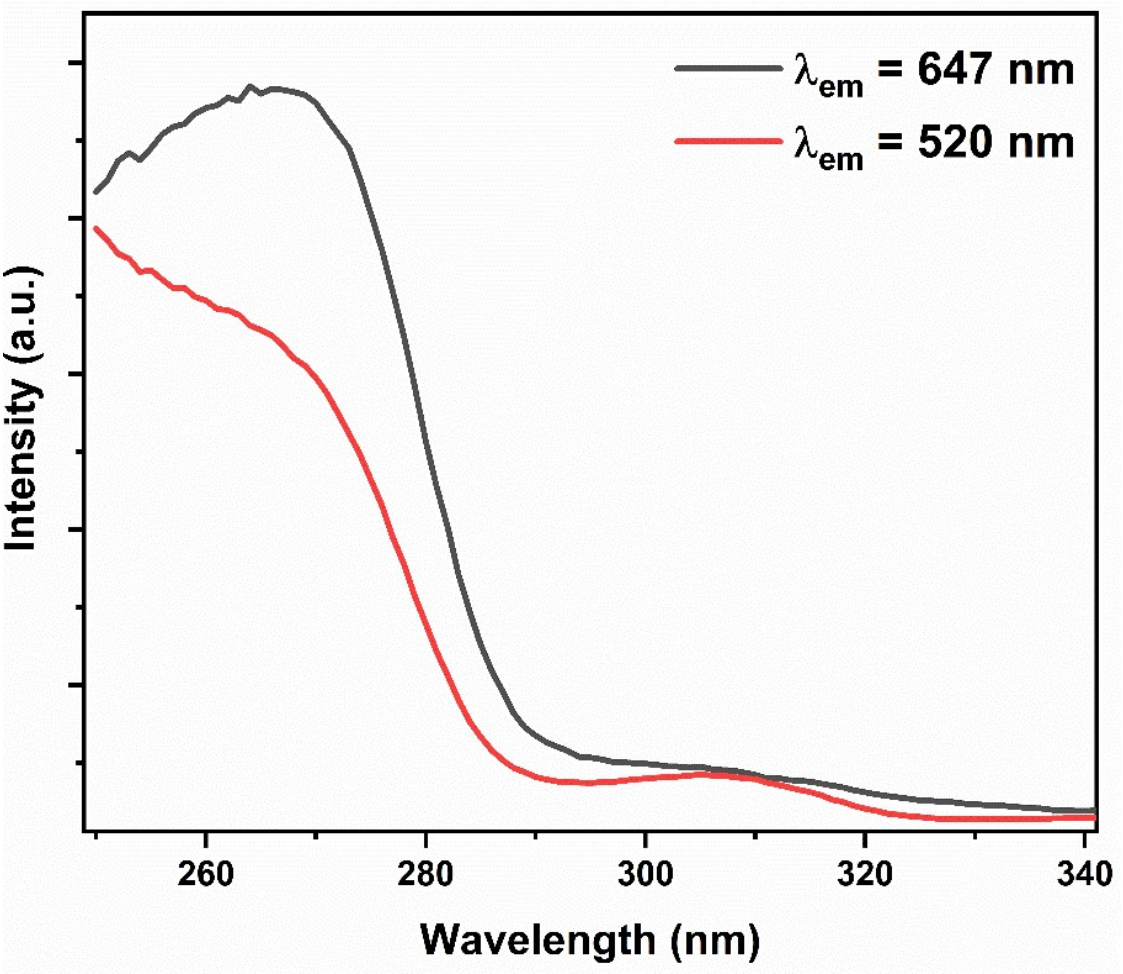

Figure S8: Excitation spectrum acquired at host emission (520 nm) and Sm^{3+} emission (647 nm).

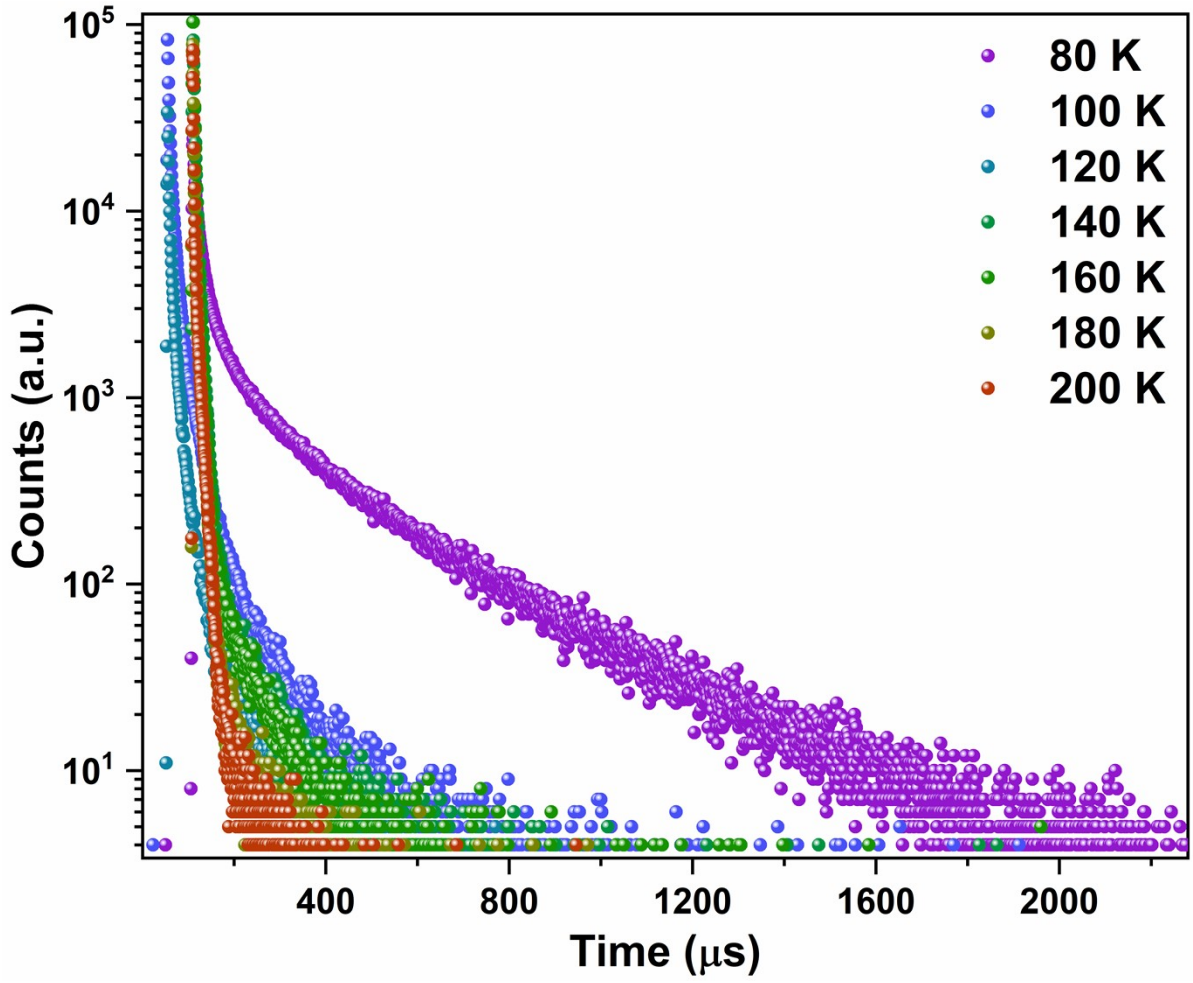

Figure S9: Temperature-dependent decay profiles of SMO:5Sm sample for 520 nm emission excited at 270 nm.

Table S4: Temperature-dependent Lifetime values of SMO:Sm samples at 647 nm emission and λ_{ex} = 270 nm from 80 to 300 K.

T (K)	τ_1 (μs)	%	τ_2 (μs)	%	τ_{av} (μs)
80	237.43 ± 4.80	24.7	1382.14 ± 10.87	75.3	1099.40 ± 8.27
100	244.7 ±11.61	18.4	1380.9 ± 15.95	81.6	1171.84 ± 13.19
120	305.9 ± 8.22	20.7	1410.3 ± 12.29	79.3	1181.69 ± 9.89
140	272.63 ± 8.75	22.3	1380.6 ± 14.40	77.7	1133.52 ± 11.36
160	232.36 ± 7.00	23.2	1288.2 ± 12.89	76.8	1043.24 ± 10.03
180	245.71 ± 6.30	27.2	1296.89 ± 13.27	72.8	1010.97 ± 9.81
200	228.46 ± 6.14	25.4	1224.36 ± 11.75	74.6	971.20 ± 8.90
220	223.4 ± 5.43	28.6	1218.65 ± 12.17	71.4	934.01 ± 8.83
240	243.75 ± 6.06	30.1	1209.46 ± 13.15	69.9	918.78 ± 9.37
260	250.37 ± 5.30	33.3	1249.46 ± 13.19	66.8	917.26 ± 8.98
280	216.2 ± 4.16	32.1	1113.67 ± 9.60	67.9	825.58 ± 6.66
300	177.02 ± 3.98	34.6	687.13 ± 7.37	65.4	510.63 ± 5.01

Table S5: Temperature-dependent Lifetime values of SMO:Sm samples at 647 nm emission and λ_{ex} = 404 nm from 80 to 300 K.

T (K)	τ_1 (μs)	%	τ_2 (μs)	%	τ_{av} (μs)
80	222 ± 16.53	19.2	1183.6 ± 29.13	80.8	998.97 ± 23.75
100	207 ± 15.76	18.5	1118.5 ± 25.94	81.5	949.87 ± 21.34
120	266.03 ± 17.82	24.4	1135.12 ± 28.54	75.6	923.06 ± 22.01
140	169.42 ± 11.36	19.0	1030.1 ± 20.78	81.0	866.66 ± 16.97
160	239.5 ± 8.62	27.6	1199.4 ± 20.52	72.4	934.47 ± 15.05
180	188.67 ± 14.27	19.8	998.99 ± 25.49	80.2	838.55 ± 20.64
200	163.65 ± 9.80	20.7	954.3 ± 18.46	79.3	790.63 ± 14.78

220	184.95 ±10.69	23.2	975.28 ± 21.24	76.8	791.92 ± 16.50
240	204.6 ± 11.27	27.5	1007 ± 26.17	72.5	786.34 ± 19.22
260	204.1 ± 10.56	28.4	1014.3 ± 26.97	71.6	784.20 ± 19.54
280	206.15 ± 11.01	32.4	883.8 ± 30.63	67.6	664.24 ±21.01
300	170.4 ± 10.52	30.7	661.5 ± 21.42	69.3	510.73 ± 15.19

References

1. Rodríguez-Carvajal, J., Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B: Condensed Matter* 1993, 192, (1), 55-69.

2. Basu, S.; Nayak, C.; Yadav, A.; Agrawal, A.; Poswal, A.; Bhattacharyya, D.; Jha, S.; Sahoo, N. In *A comprehensive facility for EXAFS measurements at the INDUS-2 synchrotron source at RRCAT, Indore, India*, Journal of Physics: Conference Series, 2014; IOP Publishing: 2014; p 012032.

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