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

Supporting Information

Multifunctional Near-Infrared Emitting Cr^{3+}-doped $Mg_4Ga_8Ge_2O_{20}$ Particles with Long Persistent, Photostimulated Luminescence and Photochromism properties

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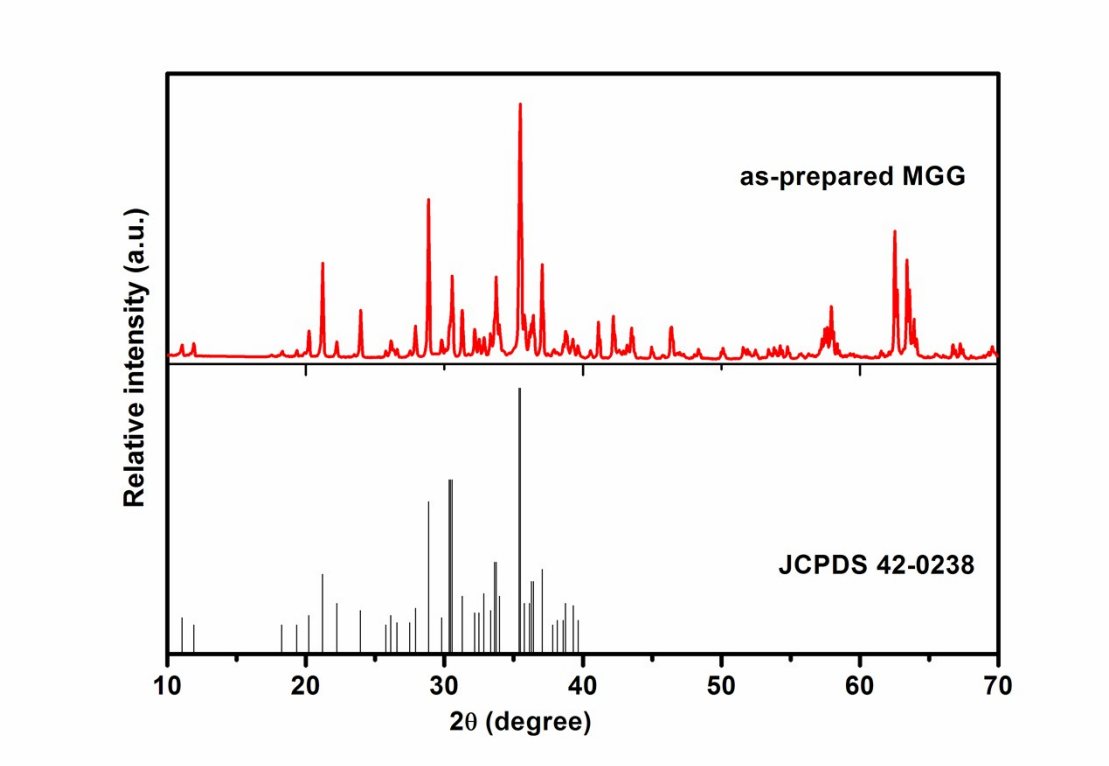
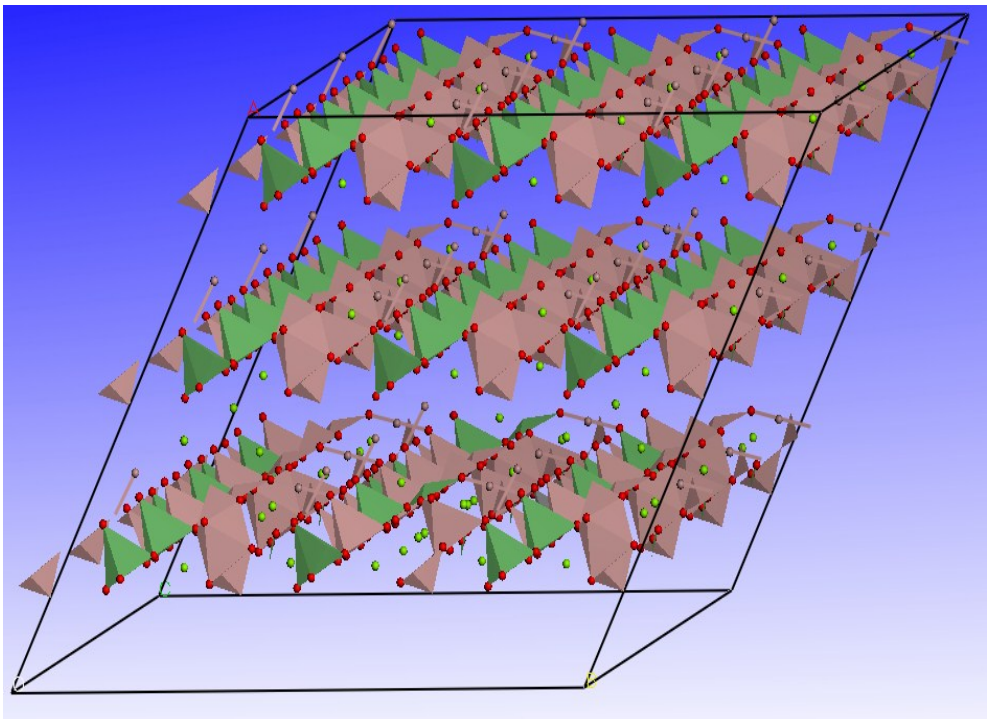


(a)



(b)

Fig. S1 (a) XRD patterns of as-prepared MGG and JCPDS 42-0238. (b) Crystal structure of MGG.

Table S1. Refined structure parameters of $Mg_4Ga_{7.999}Ge_2O_{20}$:0.001Cr^{3+} derived from the Rietveld refinement of X-ray diffraction data

Atoms	Wyckoff position	x	y	z	Frac.	Uiso
Mg1	2i	0.8326	0.8491	0.4573	0.1475	0.000131
Mg2	2i	0.1376	0.1663	0.0509	0.1701	0.001143
Mg3	2i	0.9476	0.9418	0.6633	0.4836	0.000643
Mg4	2i	0.9367	0.9377	0.1678	0.8764	0.000176
Mg5	2i	0.6291	0.6452	0.5741	1.0000	0.001018
Mg6	2i	0.6393	0.6275	0.0559	1.0000	0.001627
Mg7	2i	0.7538	0.7358	0.2515	0.1169	0.001405
Mg8	2d	0.5000	0.0000	0.0000	0.2233	0.002936
Mg9	2g	0.0000	0.5000	0.5000	0.2324	0.003551
Ga1	2i	0.8326	0.8491	0.4573	0.8523	0.000131
Ga2	2i	0.1376	0.1663	0.0509	0.8289	0.001142623
Ga3	2i	0.9476	0.9418	0.6633	0.5159	0.000643499
Ga4	2i	0.9367	0.9377	0.1678	0.1227	0.000176125
Ga5	2i	0.7538	0.7358	0.2515	0.8827	0.001405373
Ga6	2d	0.5000	0.0000	0.0000	0.7764	0.002935995
Ga7	2g	0.0000	0.5000	0.5000	0.7673	0.003551494
Ga8	2i	0.7512	0.3619	0.4231	0.1077	0.003580369
Ga9	2i	0.7606	0.3531	0.9145	0.2793	0.002609996
Ga10	2i	0.6496	0.2514	0.2200	0.0366	0.002585246
Ga11	2i	0.6381	0.2484	0.7172	0.9389	7.04999E-05
Ga12	2i	0.9432	0.5687	0.8033	0.9318	0.002194371
Ga13	2i	0.5698	0.9411	0.6876	0.1499	0.001114623
Ge1	2i	0.7512	0.3619	0.4231	0.8923	0.003580369
Ge2	2i	0.7606	0.3531	0.9145	0.6707	0.002609996
Ge3	2i	0.6496	0.2514	0.2200	0.9534	0.002585246
Ge4	2i	0.6381	0.2484	0.7172	0.0411	7.04999E-05
Ge5	2i	0.9432	0.5687	0.8033	0.0582	0.002194371
Ge6	2i	0.5698	0.9411	0.6876	0.8501	0.001114623
O1	2i	0.6169	0.8632	0.3914	1.0000	0.000887499
O2	2i	0.6278	0.8721	0.8841	1.0000	0.000837499
O3	2i	0.8285	0.0610	0.3025	1.0000	0.000774999
O4	2i	0.8259	0.0551	0.8117	1.0000	0.000862499
O5	2i	0.7214	0.9340	0.6005	1.0000	0.001262498
O6	2i	0.7310	0.9392	0.0689	1.0000	0.001012498
O7	2i	-0.0628	0.1563	0.4905	1.0000	0.000962498
O8	2i	-0.0638	0.1675	-0.0380	1.0000	0.000799999
O9	2i	0.8795	0.6192	0.6232	1.0000	0.000724999
O10	2i	0.8656	0.6211	0.1250	1.0000	0.000974998
O11	2i	0.6756	0.3938	0.7428	1.0000	0.000924998

O12	2i	0.6719	0.4072	0.2414	1.0000	0.000787499
O13	2i	-0.0325	0.7471	0.8212	1.0000	0.001249998
O14	2i	-0.0591	0.7221	0.3372	1.0000	0.000924998
O15	2i	0.7991	0.5060	-0.0837	1.0000	0.001124998
O16	2i	0.7797	0.5338	0.4244	1.0000	0.001087498
O17	2i	0.5854	0.3322	0.5254	1.0000	0.000937498
O18	2i	0.5836	0.3193	0.0402	1.0000	0.000862499
O19	2i	0.4820	0.2155	0.3182	1.0000	0.001224998
O20	2i	0.5331	0.7764	0.1608	1.0000	0.001187498
Cr1	2i	0.8326	0.8491	0.4573	0.0001	3.96249E-05
Cr2	2i	0.1376	0.1663	0.0509	0.0009	0.002666996
Cr3	2i	0.9476	0.9418	0.6633	0.0001	0.003466619
Cr4	2i	0.9367	0.9377	0.1678	0.0013	0.002254246
Cr5	2i	0.7538	0.7358	0.2515	0.0002	0.000996998
Cr6	2d	0.5000	0.0000	0.0000	0.0002	0.004252243
Cr7	2g	0.0000	0.5000	0.5000	0.0011	0.003556869

Crystal system: triclinic

Space group: P-1

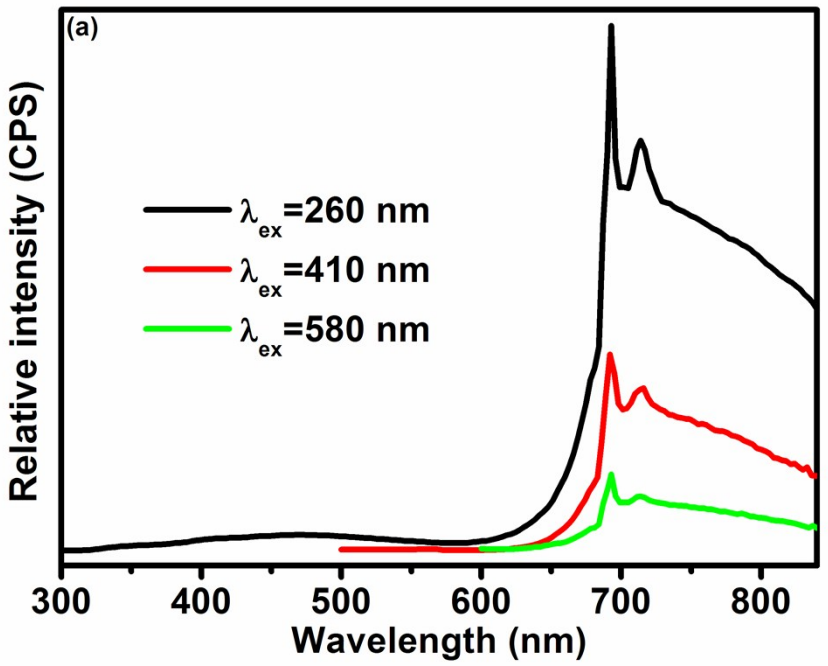
Cell parameters: a=8.843680 Å, b=9.814705 Å, c=10.281434 Å

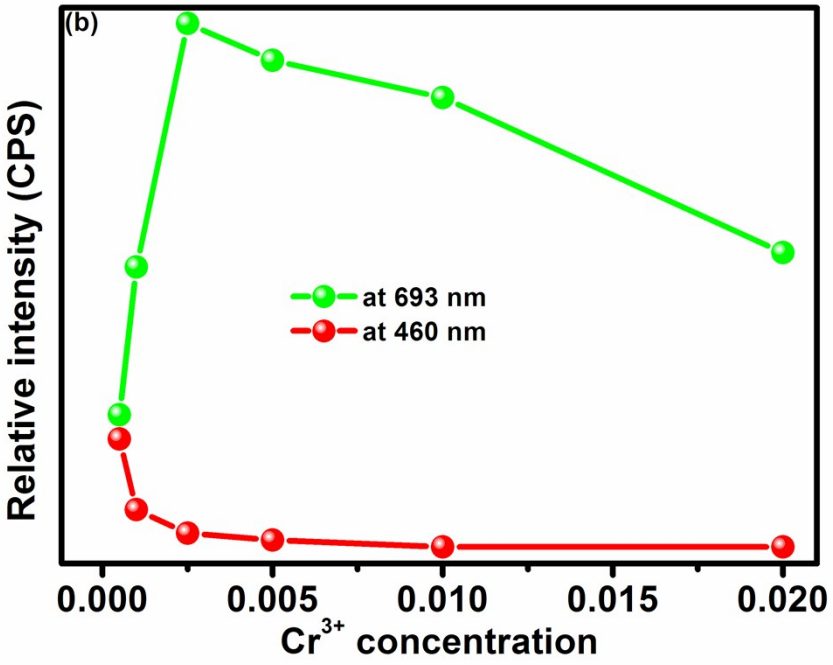
α=63.8062°, β=84.7335°and γ=65.4034°

Cell volume: 724.012 $Å^3$

Z=2

R_{wp}=5.94 %, R_p=4.35 %, χ^2=3.739


(a)
Relative intensity (CPS)
λex=260 nm
λex=410 nm
λex=580 nm
300
400
500
600
700
800
Wavelength (nm)


(b)
Relative intensity (CPS)
at 693 nm
at 460 nm
0.000
0.005
0.010
0.015
0.020
Cr3+ concentration

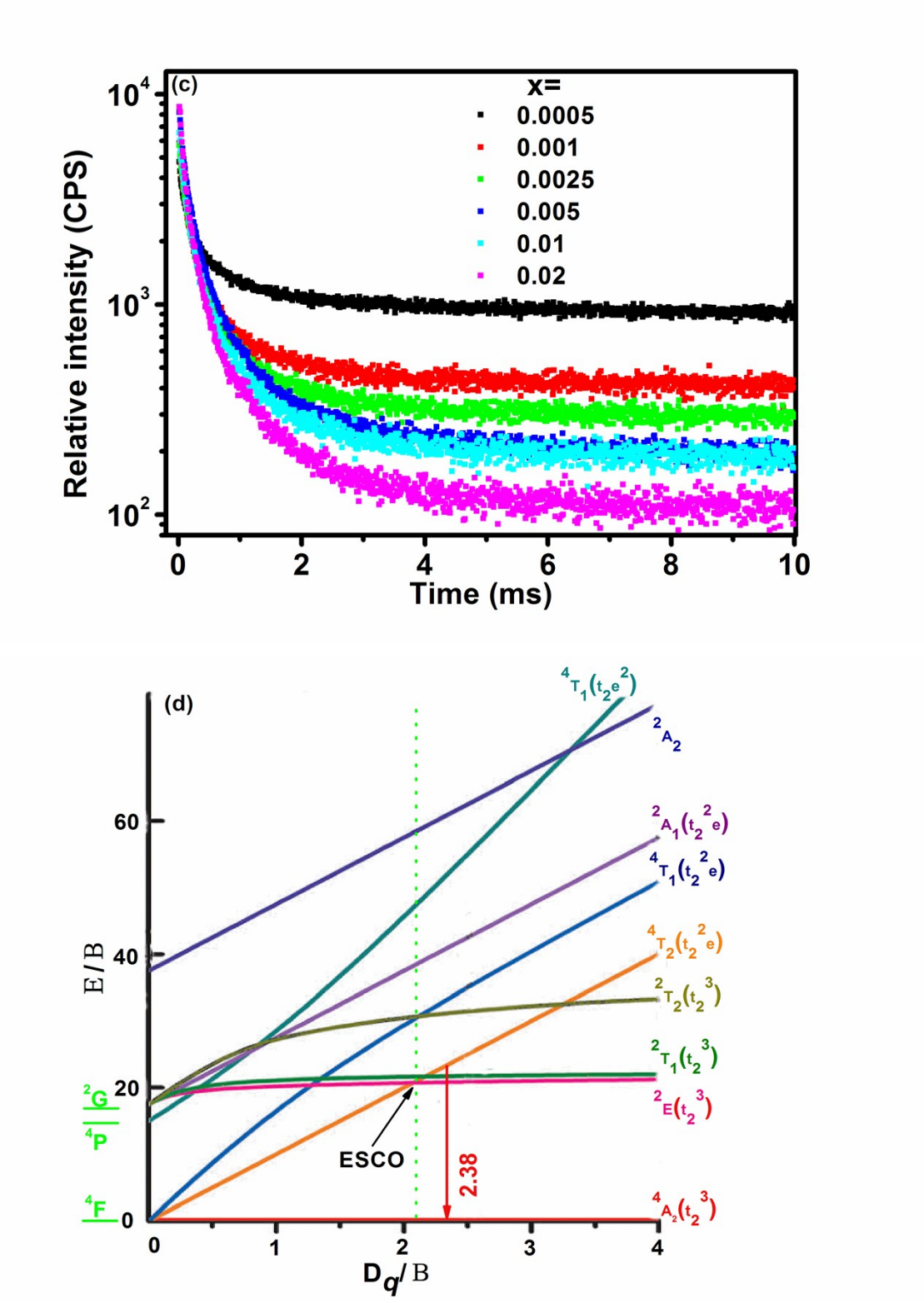


Fig. S2 (a) Emission spectra of sample MGG: 0.0025Cr^{3+} under the excitations with different wavelengths (260, 410 and 580 nm). (b) The dependence of emission intensity at 460 and 693 nm on the Cr^{3+} doping concentrations. (c) The fluorescence lifetime of samples MGG: xCr^{3+} (x=0.0005-0.02) under 260 nm excitation and monitoring emission at 460 nm. (d) Tanabe and Sugano diagram.

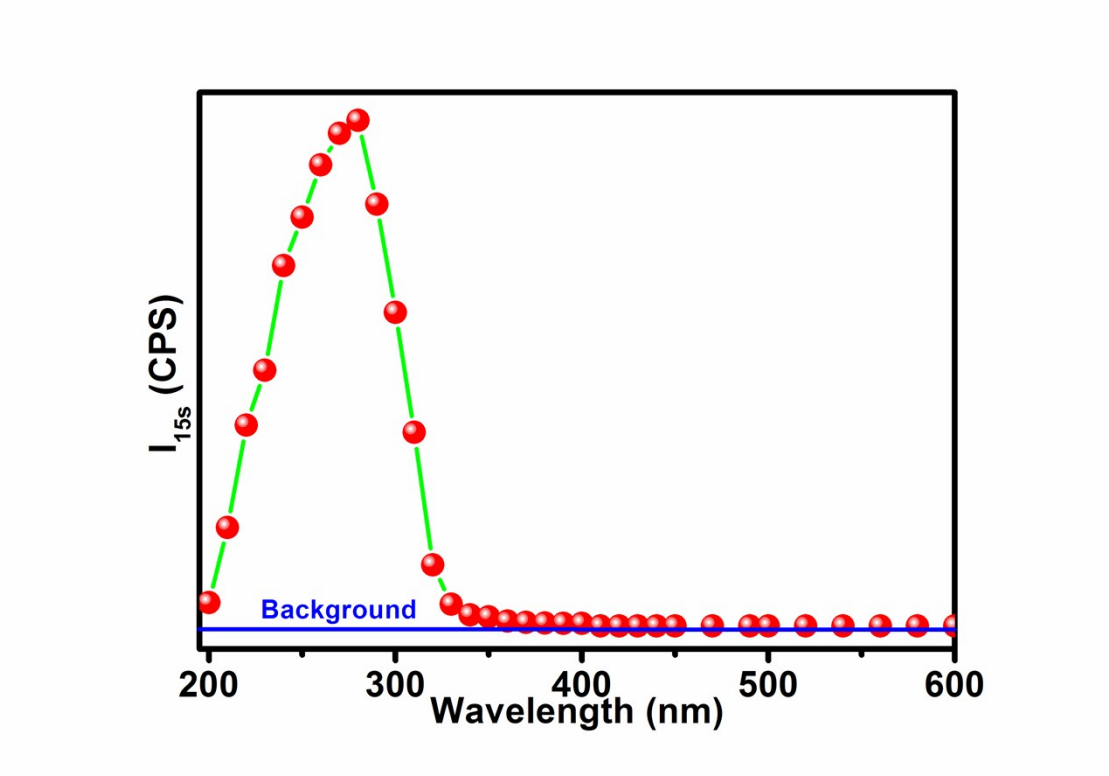


Fig. S3. NIR LPL excitation spectrum.

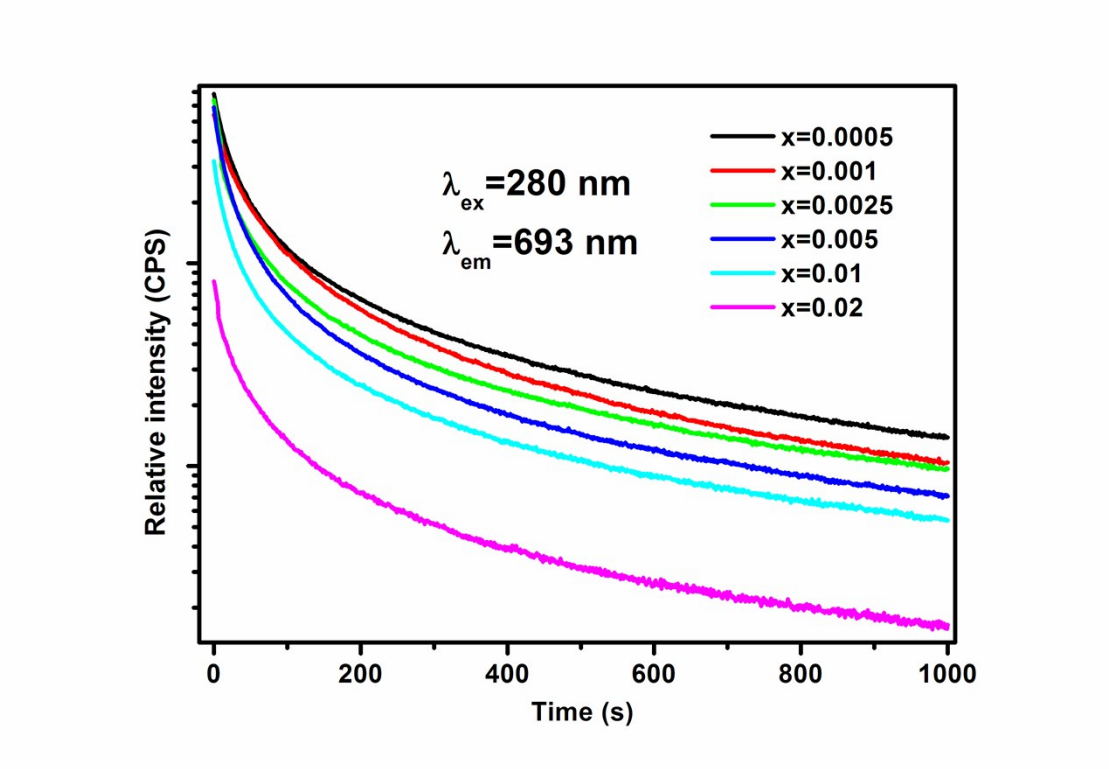


Fig. S4. LPL decay curves recorded at 693 nm emission for MGG: xCr^{3+} (x=0-0.02) LPPs after the stoppage of the 280 nm irradiation.

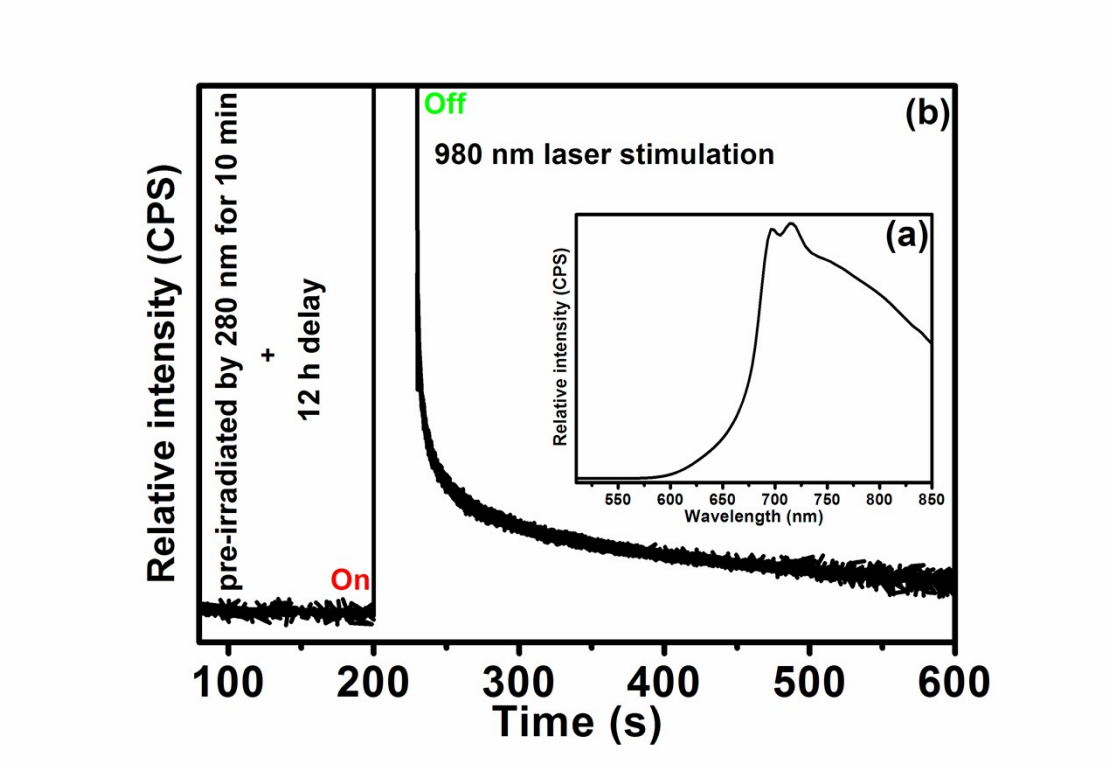


Fig. S5. (a) PSPL spectrum of MGG: 0.0005Cr^{3+}. (b) PSPL decay curves monitored at 693 nm obtained through the 980 nm laser stimulation on a 12 h decayed MGG: 0.0005Cr^{3+} sample with pre-irradiation by 280 nm light for 10 min.

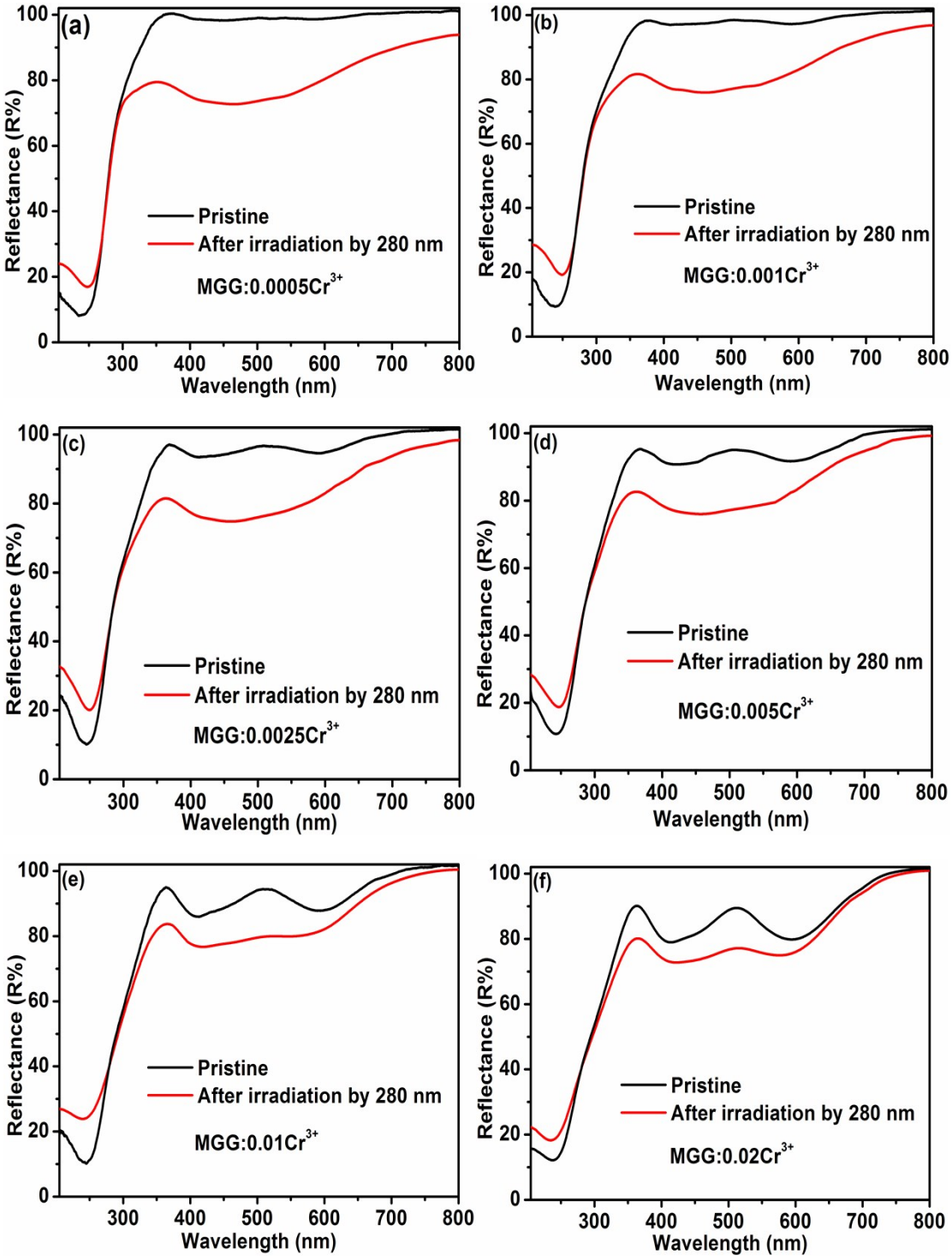
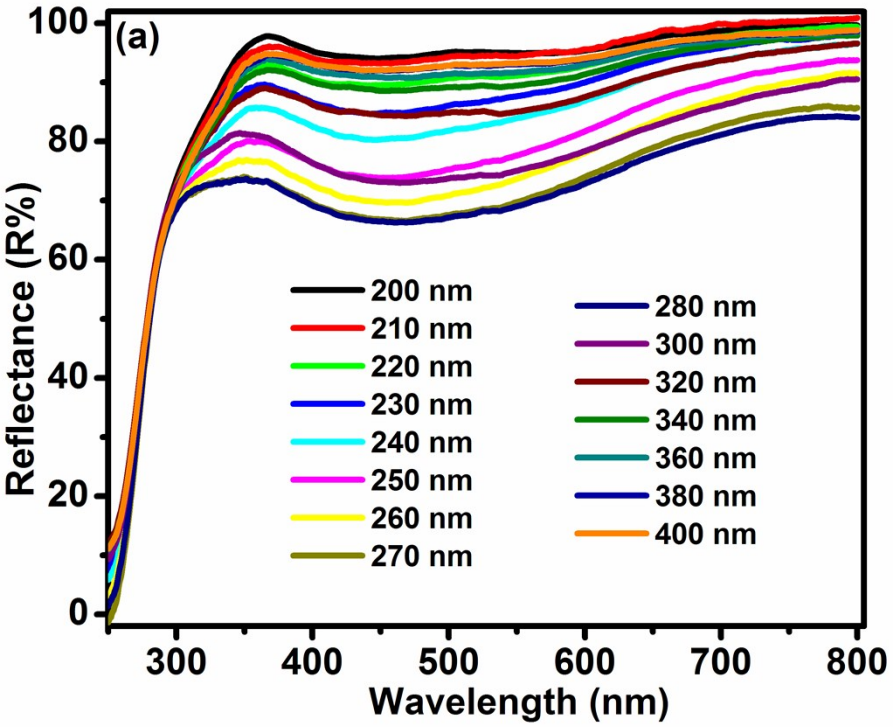
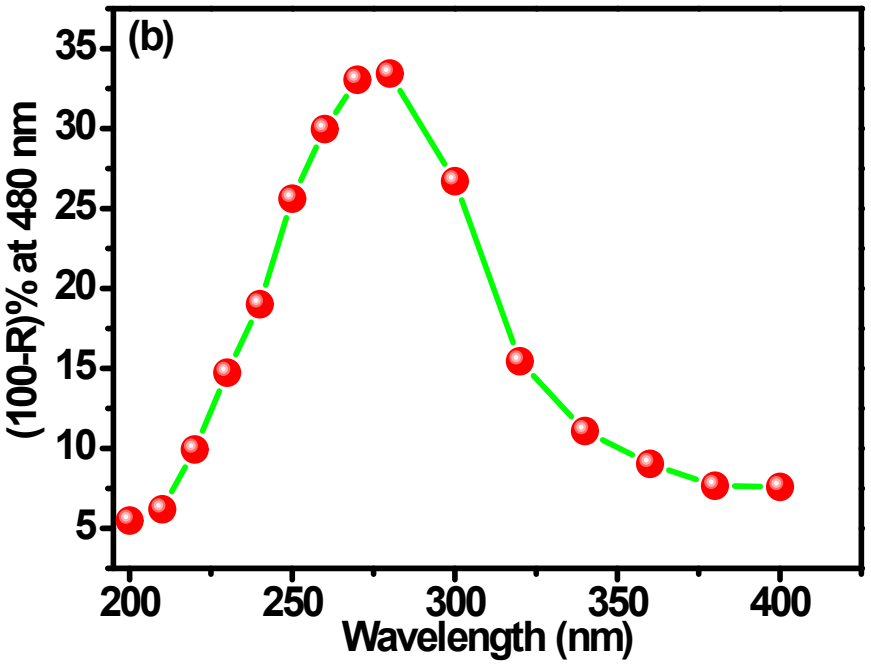
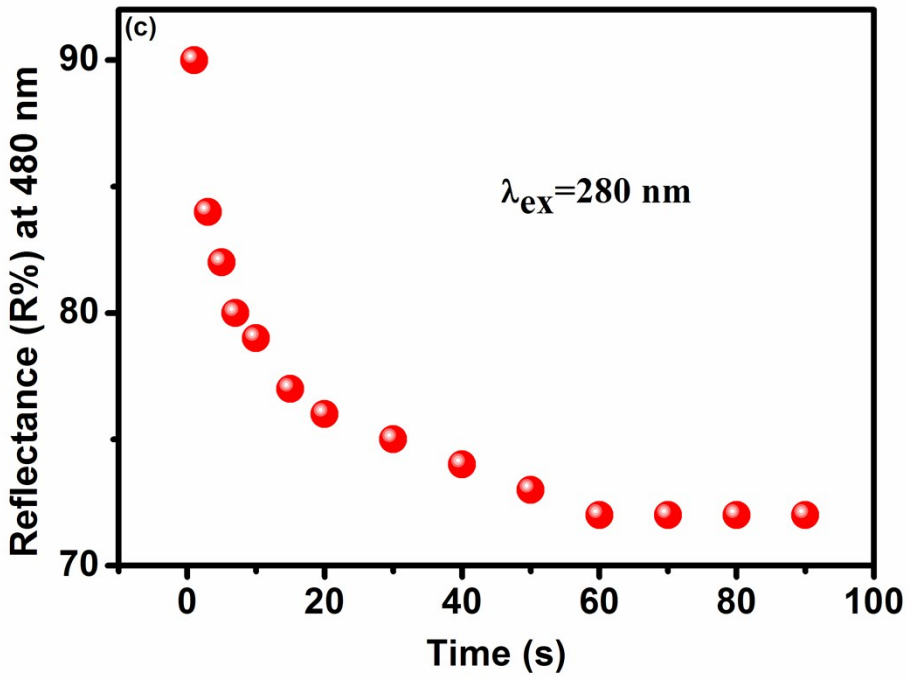
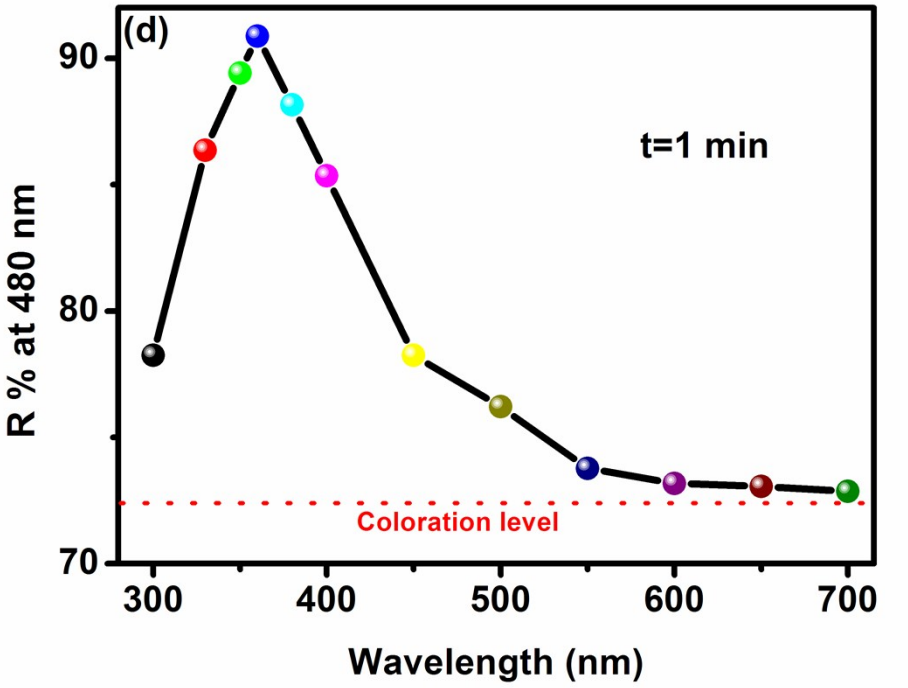


Fig. S6. The DRS of the pristine and UV (280 nm) irradiated samples MGG: xCr^{3+} (x=0.0005-0.02): (a) x=0.0005, (b) x=0.001, (c) x=0.0025, (d) x=0.005, (e) x=0.01 and (f) x=0.02.


(a)
Reflectance (R%)
Wavelength (nm)
200 nm
210 nm
220 nm
230 nm
240 nm
250 nm
260 nm
270 nm
280 nm
300 nm
320 nm
340 nm
360 nm
380 nm
400 nm


(b)
(100-R)% at 480 nm
Wavelength (nm)


(c)
90
80
70
Reflectance (R%) at 480 nm
λex=280 nm
0
20
40
60
80
100
Time (s)


(d)
90
80
70
R % at 480 nm
t=1 min
Coloration level
300
400
500
600
700
Wavelength (nm)

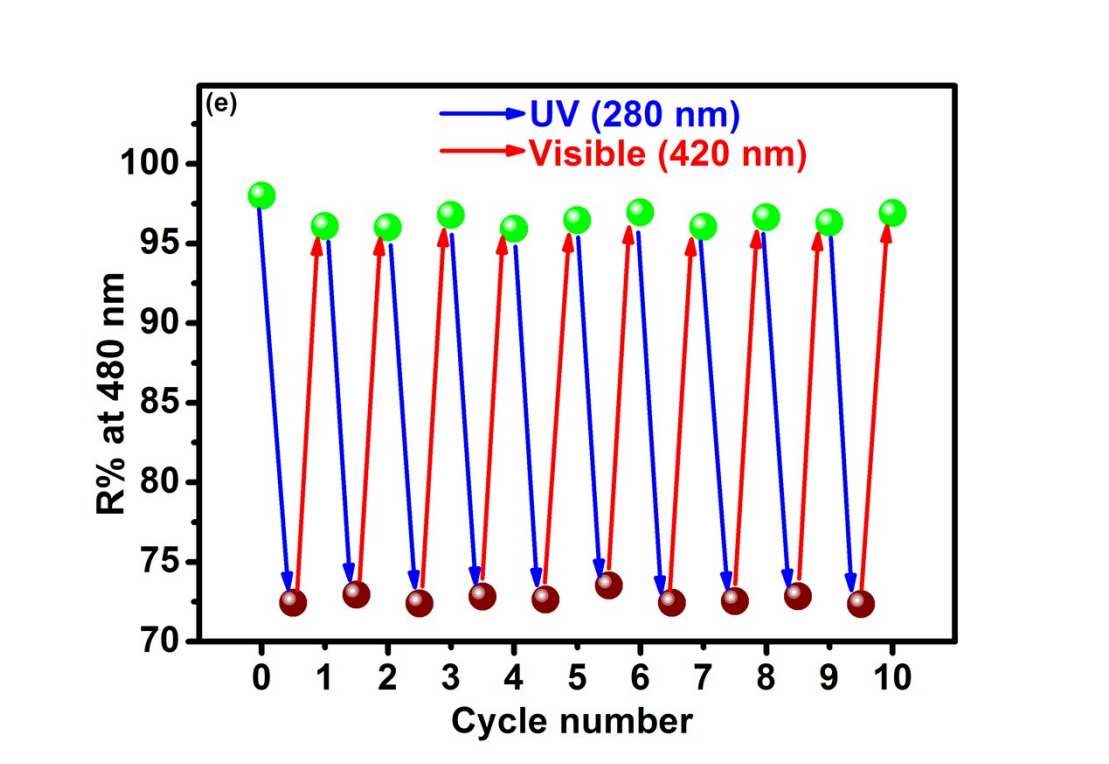


Fig. S7. (a) DRS of sample MGG: 0.0005Cr after irradiation with various wavelengths (200-400 nm). (b) The dependence of the (100-R) % values on the wavelengths according to (a). (c) DRS intensity at 480 nm of MGG: 0.0005Cr after 280 nm irradiation with various durations (0-90 s). (d) The dependence of values (R%) at 480 nm as a function of bleaching light wavelengths (300-700 nm) for sample MGG: 0.0005Cr with pre-irradiation by 280 nm for 3 min. (e) DRS intensity changes at 480 nm by alternating 280 and 420 nm light irradiations.

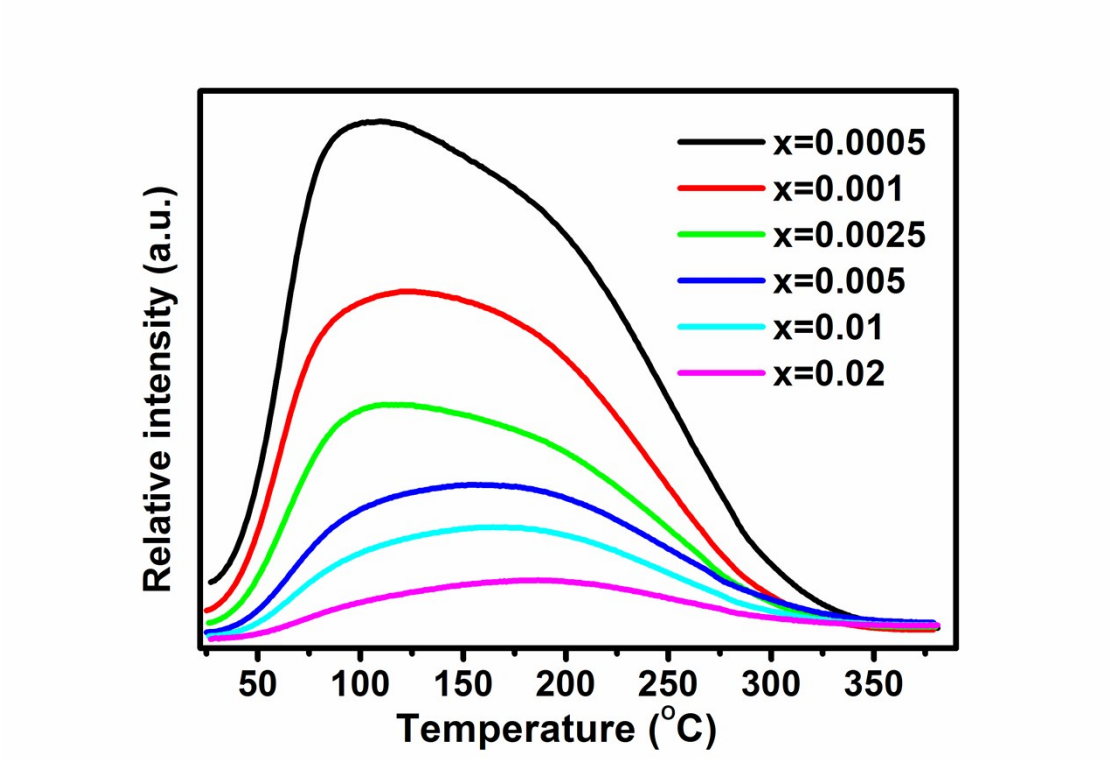


Fig. S8. TL glow curves of samples MGG: xCr (x=0.0005-0.02) 3 min after the pre-irradiation by UV light (280 nm) for 5 min.

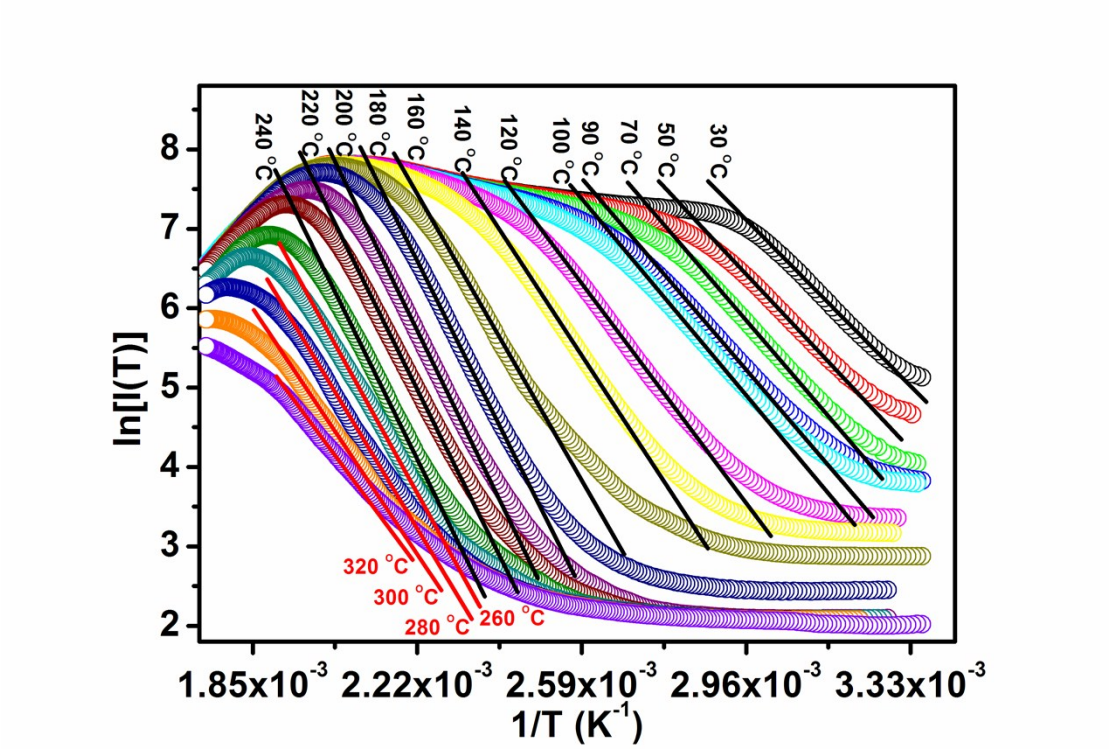


Fig. S9. Initial rise method analysis on the TL glow curves of sample MGG: 0.0005Cr as a function of temperatures based on eqn (4).

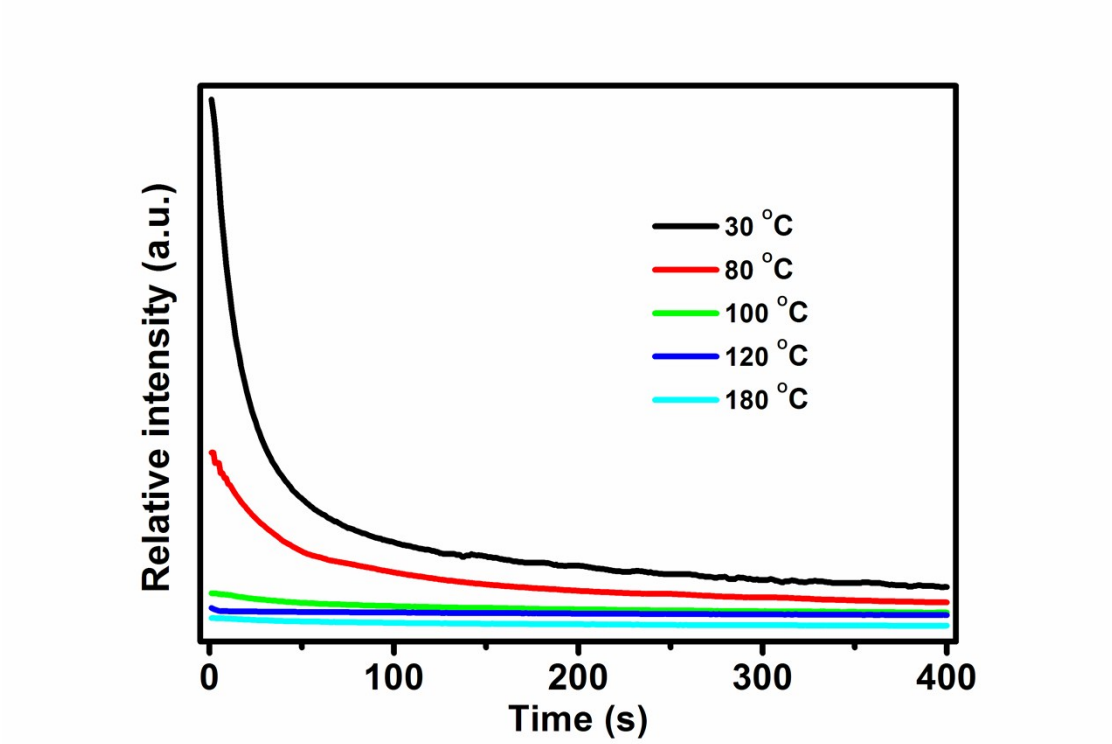


Fig. S10. NIR LPL decay curves of UV (280 nm) pre-irradiated sample MGG: 0.0005Cr for 5 min recorded after 10 s preheating at a certain temperature at the beginning of the 3 min delay duration time and then cooling down to room temperature.

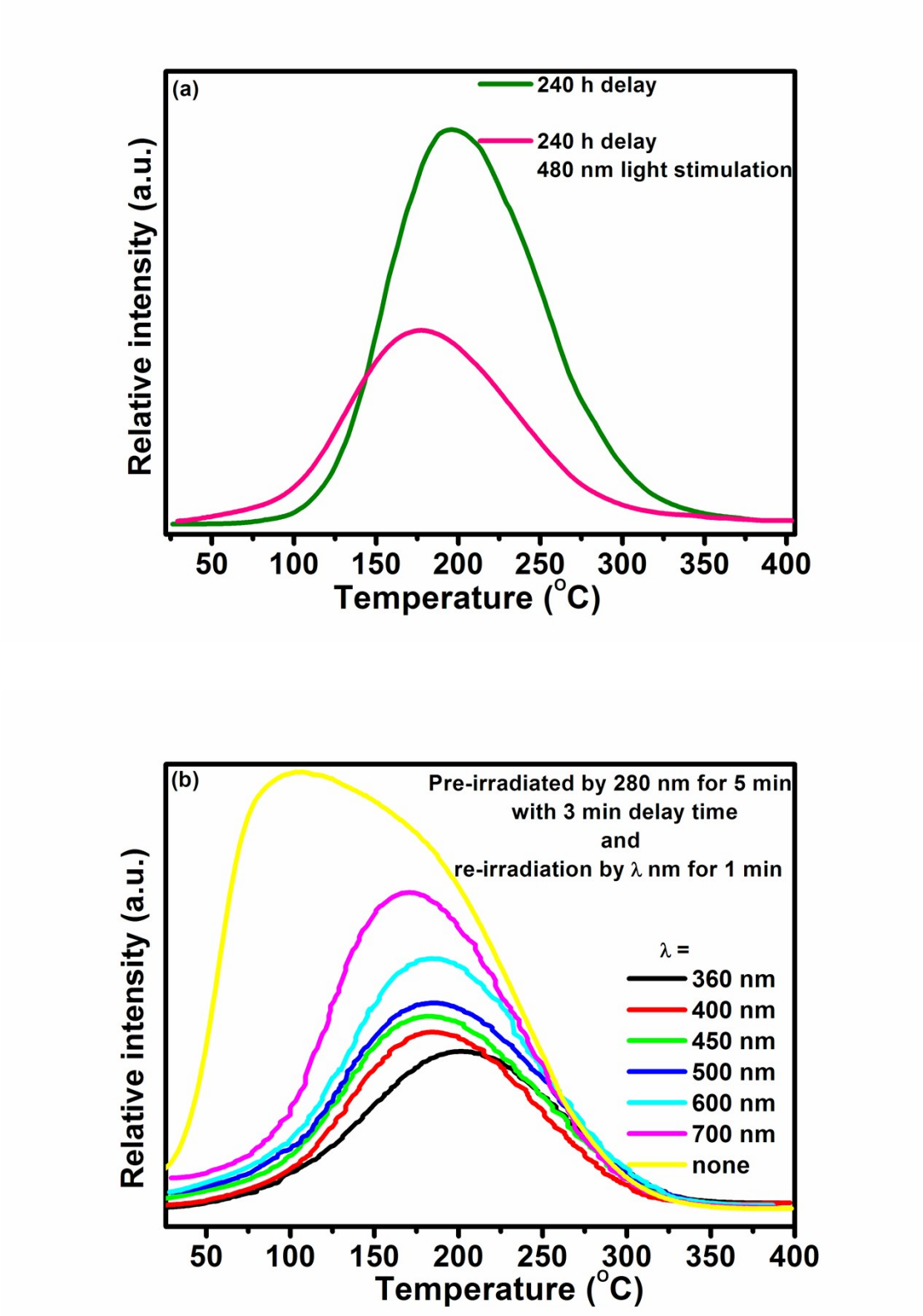


Fig. S11. TL glow curves of sample MGG: 0.0005Cr after irradiation at 280 nm for 10 min at 240 delay time with (lower) and without (upper) 480 nm light stimulation. (b) TL glow curves of sample MGG: 0.0005Cr without and with light stimulations by different wavelengths (360-700 nm). The sample is pre-irradiated by 280 nm for 5 min with 3 min delay time.

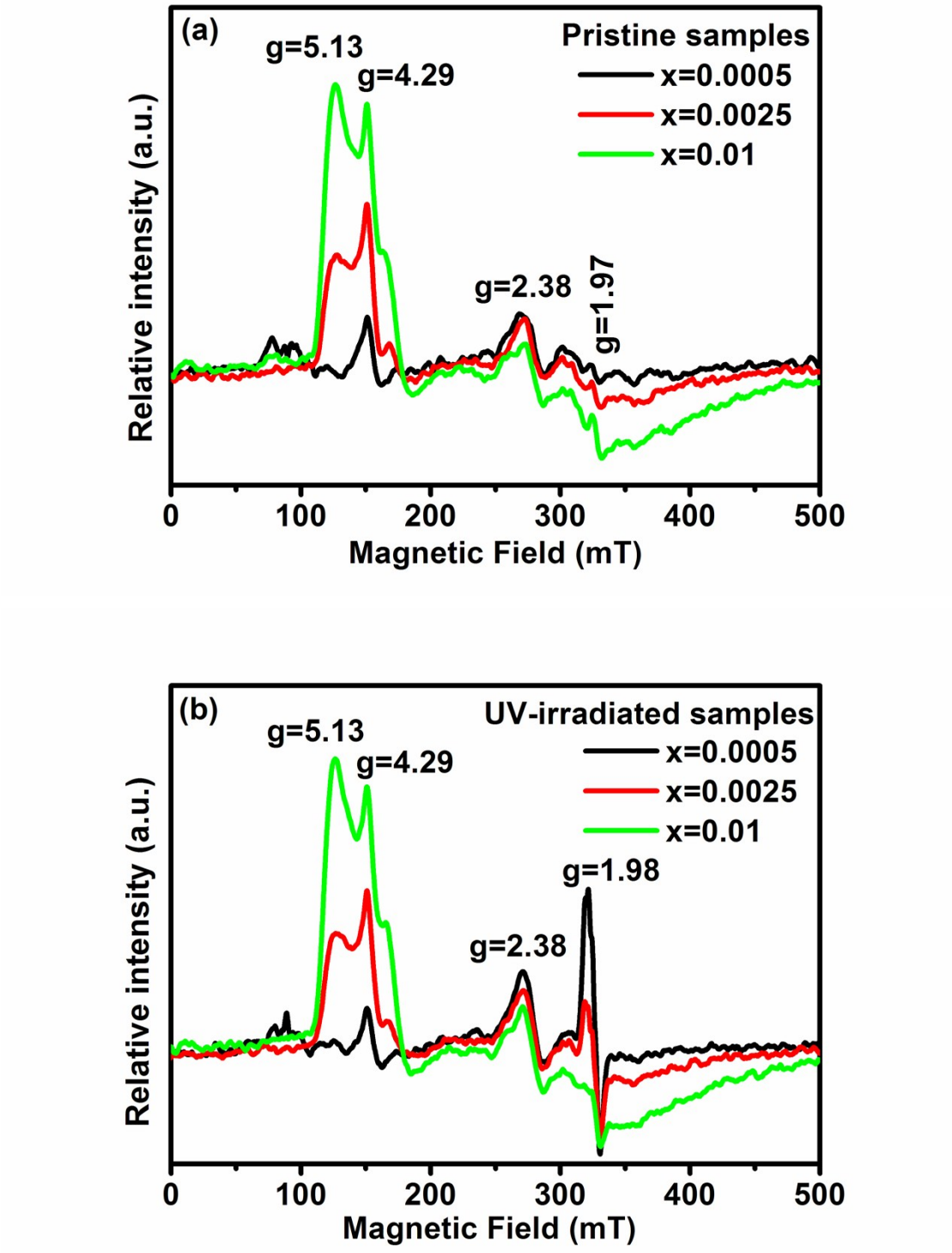


Fig. S12. ESR spectra of the pristine (a) and UV- (280 nm) irradiated (b) samples MGG: xCr (x=0.0005, 0.0025 and 0.01).