Supporting Information

Transparent glass-ceramics functionalized with $EuSiO_3$ shell constrained BaF_2: Eu^{2+}nanocrystals: Theoretical design and experimental fulfillment towards an efficient spectral converter

Chenhao Wang [#], Di Wang [#], Xiuxia Xu, Pengcheng Li, Zhao Junjie, Xvsheng Qiao, Jincheng Du, Guodong Qian and Xianping Fan*

Chenhao Wang, Pengcheng Li, Xiuxia Xu, Zhao Junjie, Dr. Xvsheng Qiao, Prof. Guodong Qian, Prof. Xianping Fan
State Key Laboratory of Silicon Materials & School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
School of Materials Science and Engineering, Tianjin University, Tianjin, 300350, China

Di Wang,
State Key Laboratory of Silicon Materials, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Prof. Jincheng Du
Department of Materials Science and Engineering, University of North Texas, Denton, Texas 76203-5017, U.S.

[#] Chenhao Wang and Di Wang contribute equally to the study.
*E-mail: qiaoxus@zju.edu.cn; fanxp@zju.edu.cn

Table S1 Composition of the glass samples with BaO/BaF_2 substitution, as well as glass transition temperature (T_g), first crystallization termperature (T_{c1}) and second crystallization termperature (T_{c2}) of the glass samples

Sample	Composition (mol%)	T_g (°C)	T_{c1} (°C)	T_{c2} (°C)	T_{c1}-T_g (°C)	T_{c2}-T_g (°C)
G-F18	$50SiO_2$–$21Al_2O_3$–$18BaF_2$–7NaF-$4EuF_3$	547	606	721	59	174
G-O2F16	$50SiO_2$–$21Al_2O_3$–2BaO–$16BaF_2$–7NaF-$4EuF_3$	552	617	714	65	162
G-O4F14	$50SiO_2$–$21Al_2O_3$–4BaO–$14BaF_2$–7NaF-$4EuF_3$	557	623	730	66	173
G-O6F12	$50SiO_2$–$21Al_2O_3$–$12BaF_2$–6BaO–7NaF-$4EuF_3$	558	630	744	72	186
G-O8F10	$50SiO_2$–$21Al_2O_3$–8BaO–$10BaF_2$–7NaF-$4EuF_3$	558	621	716	63	158

Table S2 Composition of the glass samples with Al_2O_3/BaF_2 substitution, as well as glass transition temperature (Tg), first crystallization termperature (T_{c1}) and second crystallization termperature (T_{c2}) of the glass samples.

Sample	Composition (mol%)	T_g (°C)	T_{c1} (°C)	T_{c2} (°C)	T_{c1}-T_g °C)	T_{c2}-T_g (°C)
G-Al17Ba22	$50SiO_2$–$17Al_2O_3$–$22BaF_2$–7NaF–$4EuF_3$	557	618	724	61	167
G-Al19Ba20	$50SiO_2$–$19Al_2O_3$–$20BaF_2$–7NaF–$4EuF_3$	546	600	721	54	175
G-Al21Ba18	$50SiO_2$–$21Al_2O_3$–$18BaF_2$–7NaF–$4EuF_3$	547	606	721	59	174
G-Al23Ba16	$50SiO_2$–$23Al_2O_3$–$16BaF_2$–7NaF–$4EuF_3$	546	606	717	60	171
G-Al25Ba14	$50SiO_2$–$17Al_2O_3$–$14BaF_2$–7NaF–$4EuF_3$	556	613	750	57	194

Table S3 Composition of the glass samples with different Eu doping, as well as glass transition temperature (T_g), first crystallization termperature (T_{c1}) and second crystallization termperature (T_{c2}) of the glass samples.

Sample	Composition (mol %)	T_g (°C)	T_{c1} (°C)	T_{c2} (°C)	T_{c1}-T_g °C)	T_{c2}-T_g °C)
G-Eu0.5	$50SiO_2$–$21Al_2O_3$ –$21.5BaF_2$–7NaF–$0.5EuF_3$	545	591	641	46	96
G-Eu1	$50SiO_2$–$21Al_2O_3$ –$21BaF_2$–7NaF–$1EuF_3$	544	592	638	48	94
G-Eu2	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	537	588	680	51	143
G-Eu4	$50SiO_2$–$21Al_2O_3$ –$18BaF_2$–7NaF–$4EuF_3$	547	606	721	59	174
G-Eu6	$50SiO_2$–$21Al_2O_3$ –$16BaF_2$–7NaF–$6EuF_3$	548	617	731	69	183

Table S4 Composition and thermal treatment method of the glass-ceramics samples with thermal treatment at different temperature for 1 hour.

Sample	Composition (mol %)	Treatment Temperature (°C)	Treatment Time (h)
GC-580	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	580	1
GC-600	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	600	1
GC-620	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	620	1
GC-640	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	640	1

Table S5 Composition and thermal treatment method of the glass-ceramics samples with thermal treatment at 580 °C for different time

Sample	Composition (mol %)	Treatment Temperature (°C)	Treatment Time (h)
GC-1 h	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	580	1
GC-2 h	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	580	2
GC-4 h	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	580	4
GC-8 h	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	580	8
GC-16 h	$50SiO_2$–$21Al_2O_3$ –$20BaF_2$–7NaF–$2EuF_3$	580	16

Table S6 The evaluated PL lifetime of Eu^{2+} in the glass-ceramic samples obtained through heat treating G-Eu2 at 580~640 °C for 1 hour.

Sample	GC-580	GC-600	GC-620	GC-640
A1	0.357	0.365	0.342	0.381
t1 [ns]	121.8	109.8	150.6	149.7
A2	0.577	0.577	0.607	0.561
t2 [ns]	732.1	723.8	773.9	727.0
$<\tau>$ [ns]	675.2	670.1	712.3	656.1

Table S7 The evaluated PL lifetime of Eu^{2+} in the glass-ceramic samples obtained through heat treating G-Eu2 at 580 °C for 1 hour ~16 hours.

Sample	GC-1h	GC-2h	GC-4h	GC-8h	GC-16h
A1	0.357	0.372	0.320	0.356	0.360
t1 [ns]	121.8	150.4	113.3	162.2	180.4
A2	0.577	0.585	0.604	0.585	0.587
t2 [ns]	732.1	745.2	706.1	768.0	769.8
<τ> [ns]	675.2	677.5	659.7	698.9	695.7

Table S8 The amounts of different atoms in one simulation cell (atoms in G-Al21Ba18 and G-Eu4 are the same as G-F18).

Sample	Si	Al	Na	La	F	O	Ba
G-F18	1000	840	140	80	1100	3260	360
G-O2F16	1000	840	140	80	1020	3300	360
G-O4F14	1000	840	140	80	940	3340	360
G-O6F12	1000	840	140	80	860	3380	360
G-O8F10	1000	840	140	80	780	3420	360
G-Al17Ba22	1000	680	140	80	1260	3020	440
G-Al19Ba20	1000	760	140	80	1180	3140	400
G-Al23Ba16	1000	920	140	80	1020	3380	320
G-Al25Ba14	1000	1000	140	80	940	3500	280
G-Eu0.5	1000	840	140	10	1030	3260	430
G-Eu1	1000	840	140	20	1040	3260	420
G-Eu2	1000	840	140	40	1060	3260	400
G-Eu6	1000	840	140	120	1140	3260	320

Table S9 The performance of the another OSCs with spectral converting glass-ceramics as filters.

Filter glass	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	$J_{calc.}$ (mA cm^{-2})
Quartz glass	0.840	23.54	0.7183	14.18	23.48
Sample GC-Eu2	0.839	24.22	0.7191	14.62	24.15

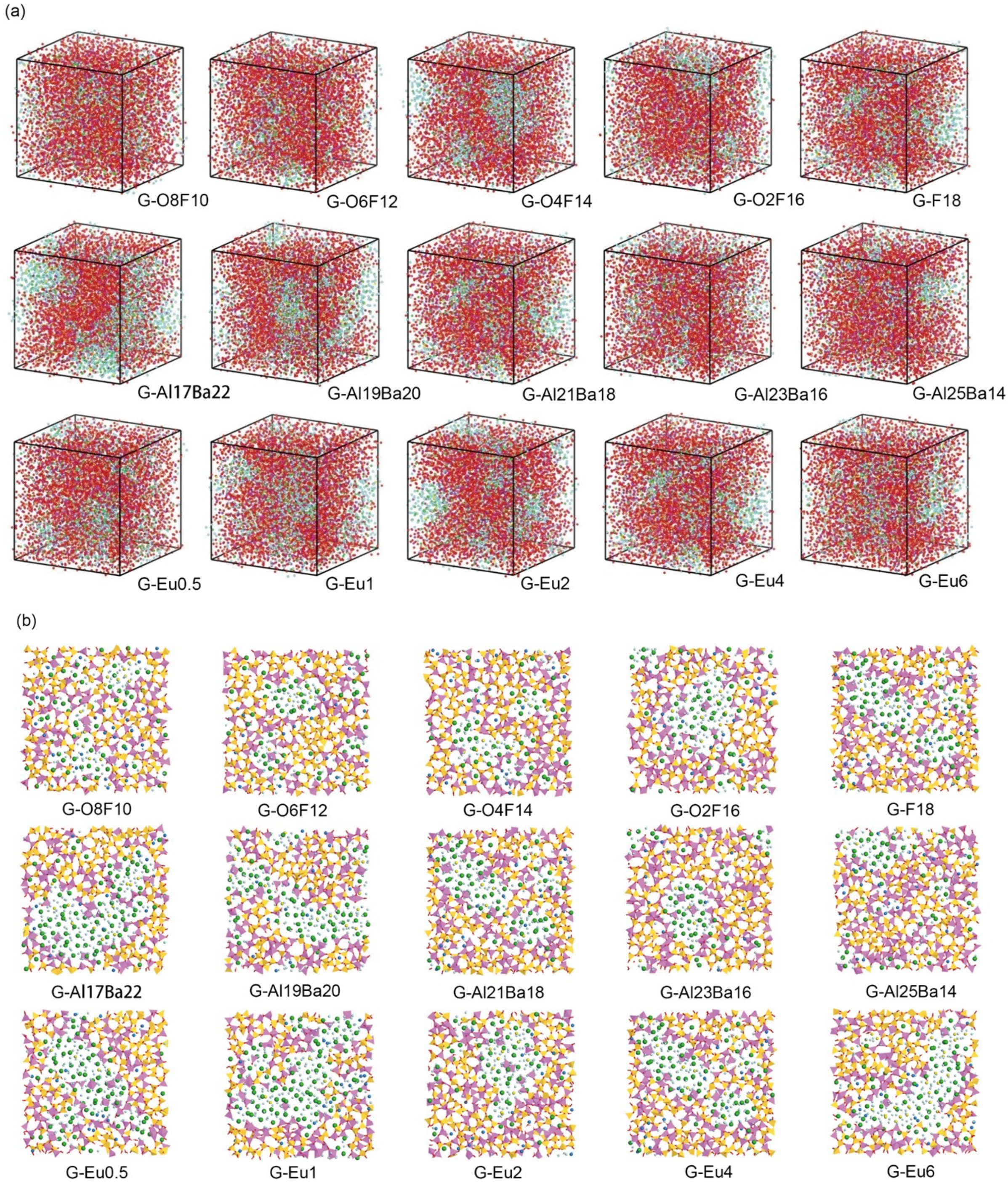

Figure S1 Molecular dynamic (MD) simulated structures for all the investigated glass samples list in Table 1~3 (a). Snapshots from MD simulations for all the investigated glass samples list in Table 1~3 (b).

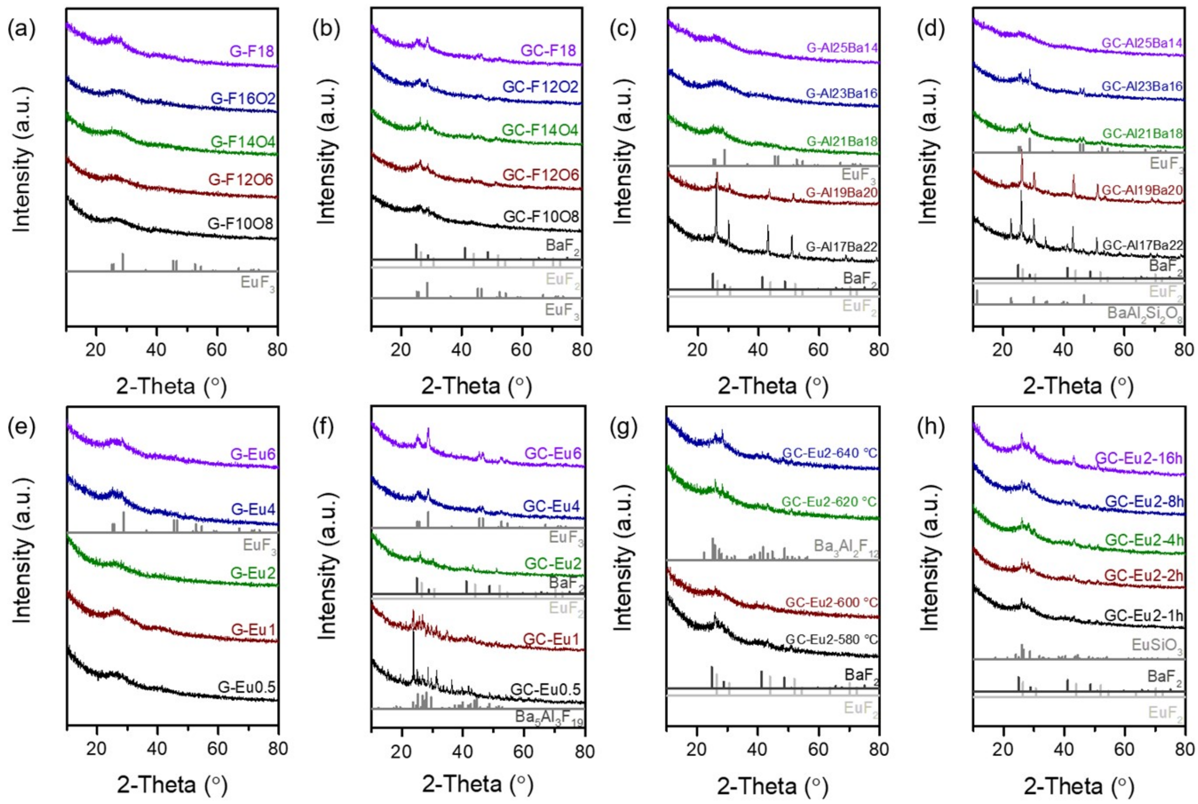

Figure S2 XRD curves of all the investigated samples list in Table 1~5.

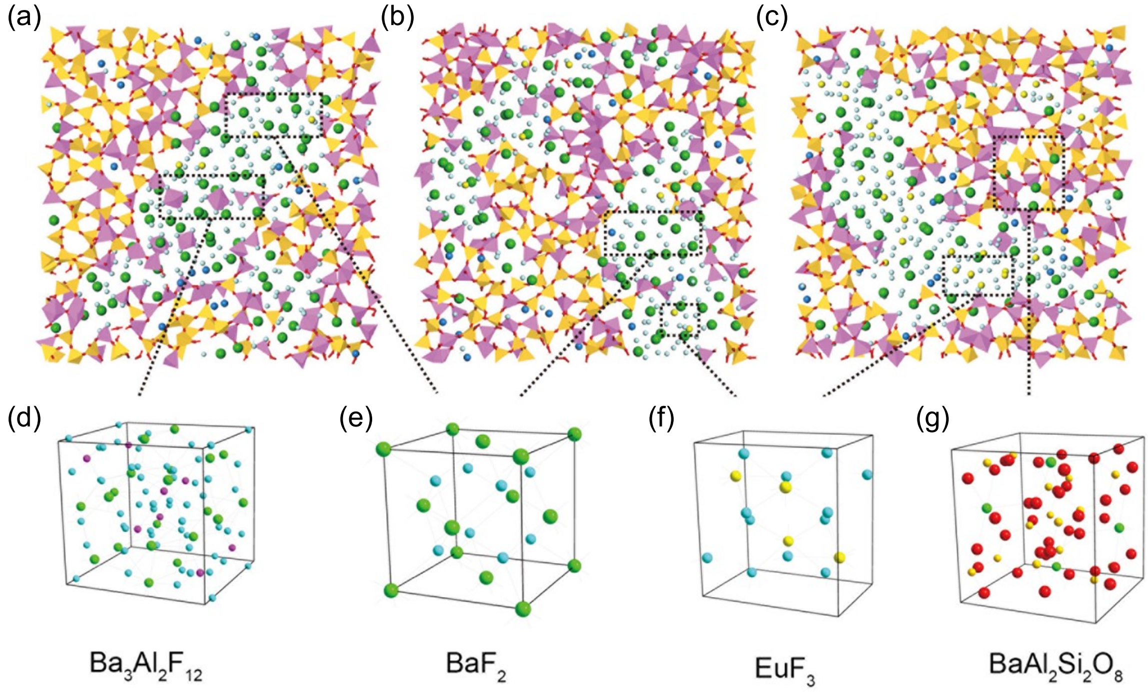

Figure S3 Snapshots from MD simulations to show the phase separation in the glasses Eu0.5 (a), Eu2(b) and Eu6 (c). Orange: Si, pink: Al, yellow: La, blue: Na, cyan: F, red: O. It can predict the precipitation of $Ba_3Al_2F_{12}$ (d) /BaF_2 (e) /EuF_3 (f) /$Ba_3Al_2F_{12}$ (g) crystallites from the separated fluoride phases as well as the precipitation of BaAl2Si2O8 feldspar phases from the separated oxide phases.

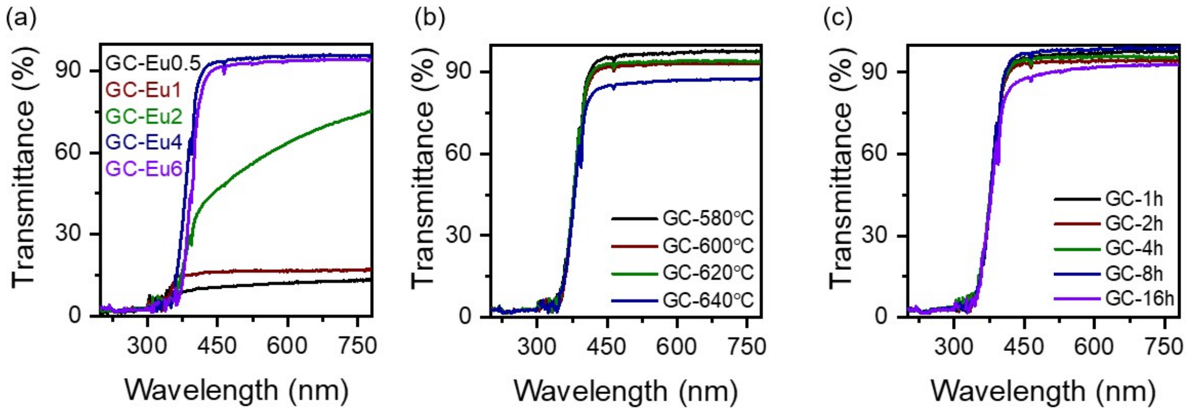

Figure S4 Optical absorption spectra of the glass-ceramics list in Table 3-5 (a-c) .

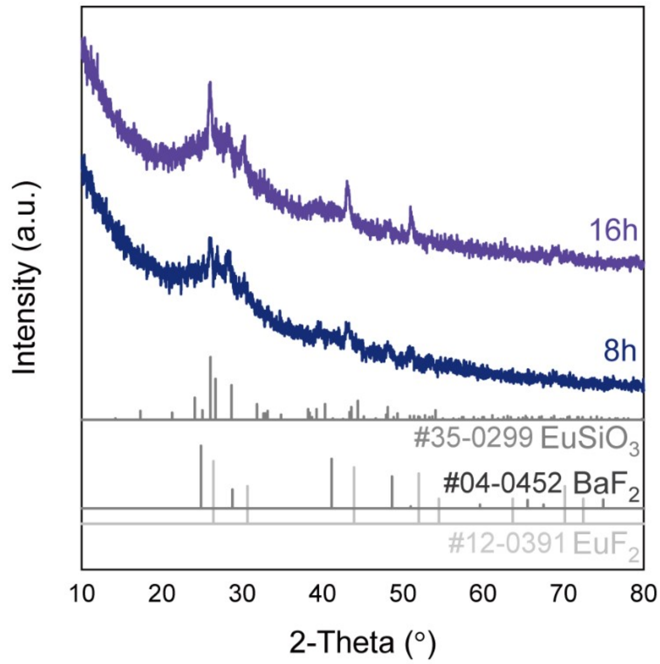

Figure S5 XRD curves of glass-ceramic samples obtained by heat treating glass sample E2 at 580 °C for 8 or 16 hours.

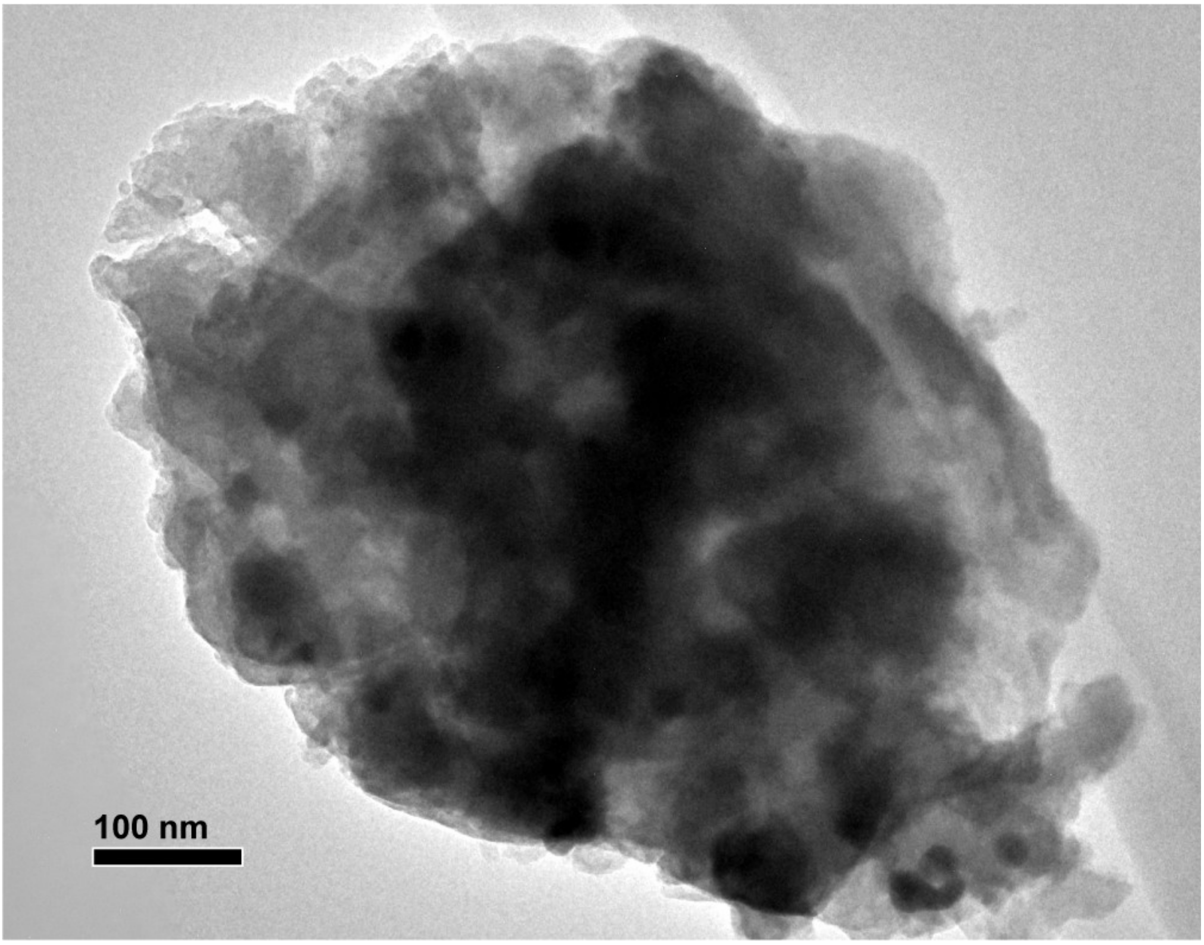

Figure S6 TEM image of glass-ceramic samples with irregular shape crystallites

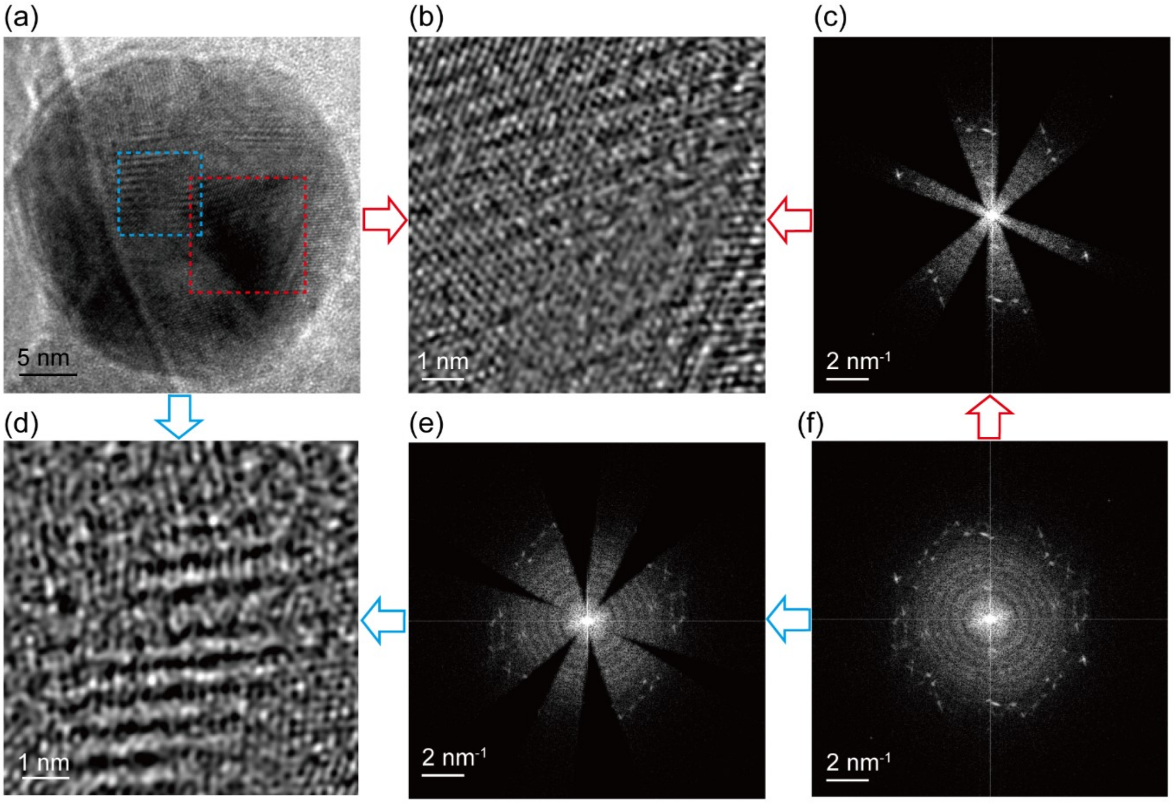

Figure S7 images of the glass-ceramic samples obtained by heat treating glass sample Eu2 at 580 °C for 4 hours (a) the inverse FFT image of two region of BaF2 and EuSiO3 (b, d) respectively, the FFT pattern for BaF2 and EuSiO3 (c, e) respectively, and FFT image of whole crystal (f).

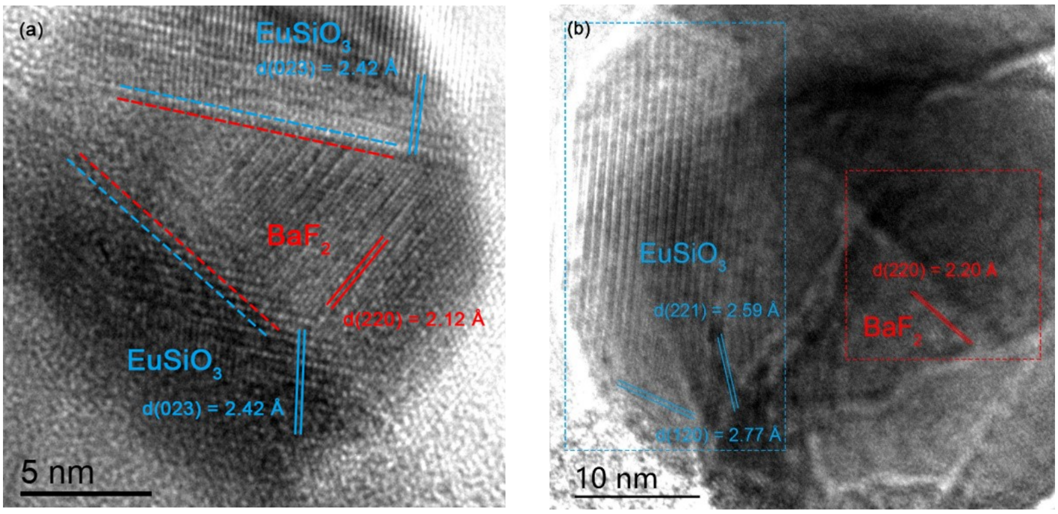

Figure S8 Two or even more HRTEM evidences can be got to confirm the $EuSiO_3$ constrained BaF_2 nanocrystals structures.

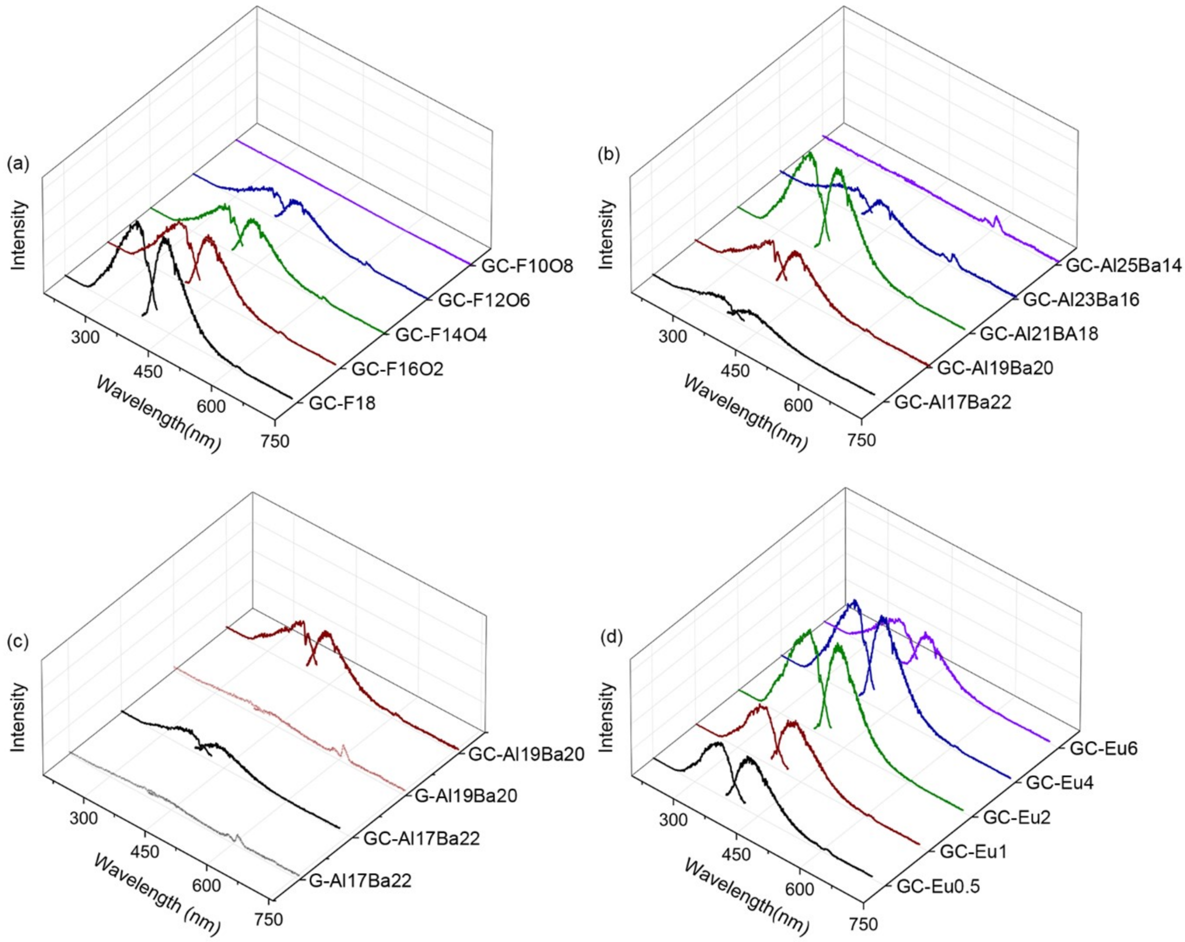

Figure S9 PL excitation and emission spectra of the glass samples list in Table 1 ~3 (a; b; d) and spectra comparison (c) between the glasses and the glass ceramics for the compositions Al17Ba22 and Al19Ba20, respectively.

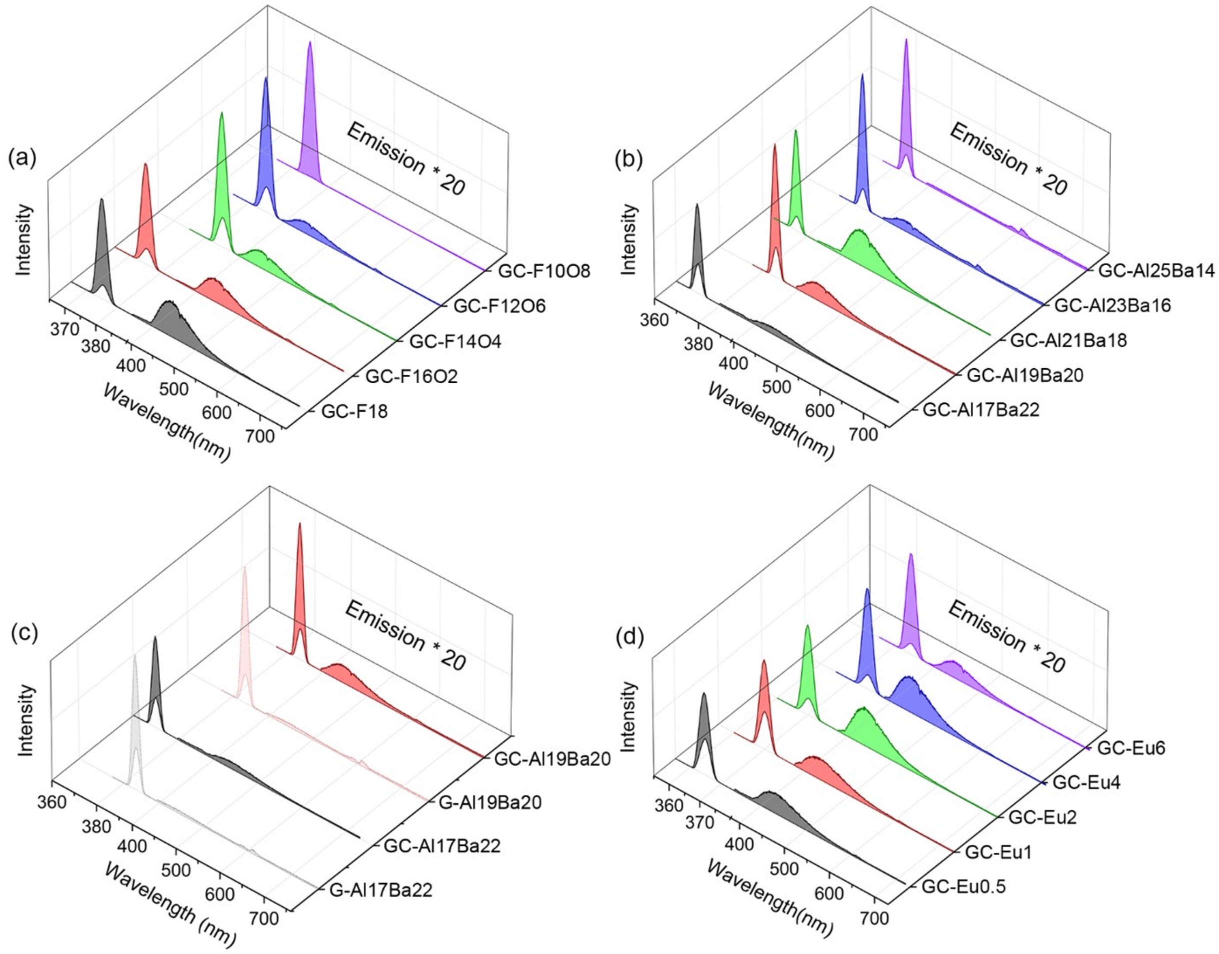

Figure S10 PL emission spectra collected by an integral sphere for the glass samples list in Table 1 ~3 (a; b; d) and spectra comparison (c) between the glasses and the glass ceramics for the compositions Al17Ba22 and Al19Ba20, respectively.

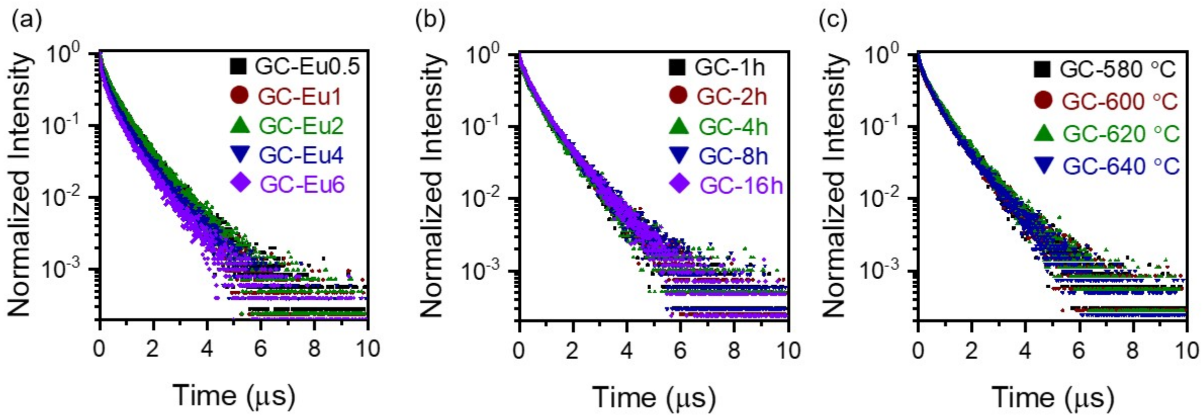

Figure S11 PL decay curves of the glass-ceramics list in Table 3-5 (a-c) .

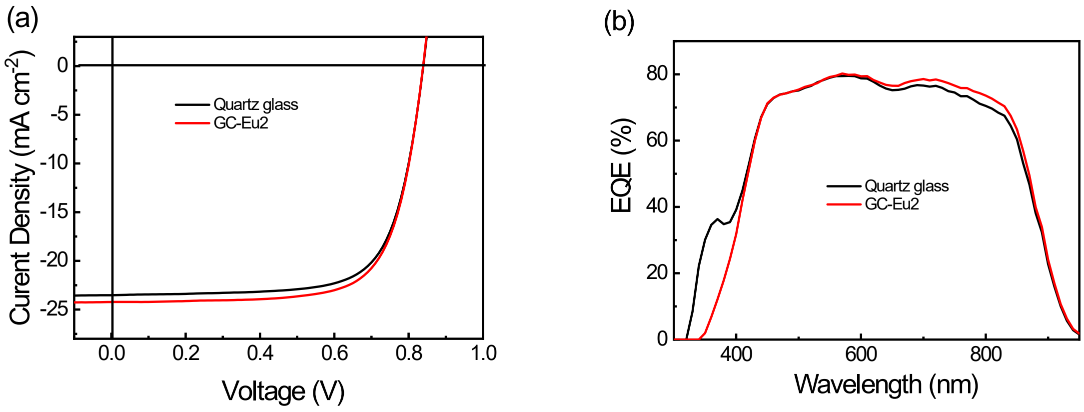

Figure S12 *J*-*V* curves (a) and EQE (b) of another OSCs with the spectral converting GCs and quartz glass.