

UV-C Emitting Phosphor of Pr³⁺-Doped Fluoroborate Nano-Glass Composites for Disinfection and Fast Scintillator

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Thermal treatment condition optimization:

To determine the optimal annealing and thermal treatment temperatures, differential scanning calorimetry (DSC) tests were performed on the PG sample (**Fig. S1**). According to the DSC results, the heating process was initially carried out within the temperature range of 580-600°C for crystallization. Subsequently, thermal treatments were performed within this range to explore the impact on the material's properties.

As shown in **Fig. S2(b)**, X-ray diffraction (XRD) analysis revealed the various degrees of crystallization in the glass at different temperatures and durations. Specifically, the nanocrystals (NCs) precipitated within the glass matrix were identified as Li(Al₇B₄O₁₇). To achieve an optimal balance between high UV band transmittance and strong XEL intensity, a thermal treatment at 590°C for 10 hours was found to be the most favorable condition, as demonstrated in **Fig. S2(c)** and **S2(d)**.

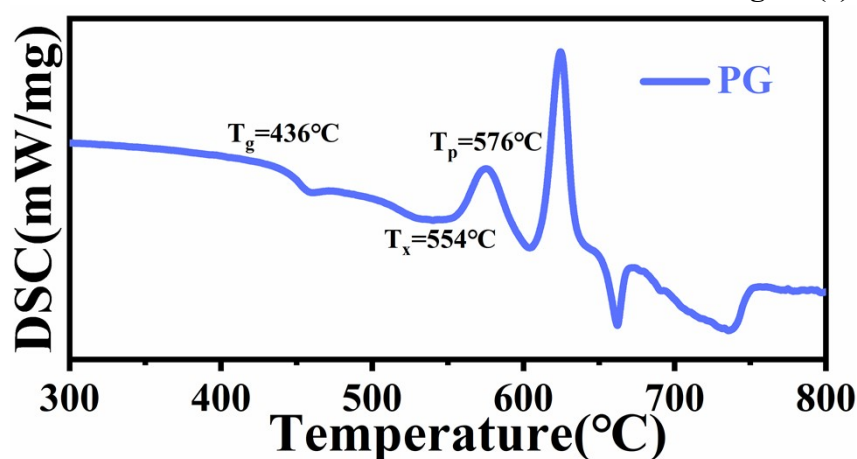


Fig. S1 DSC curve of the PG sample.

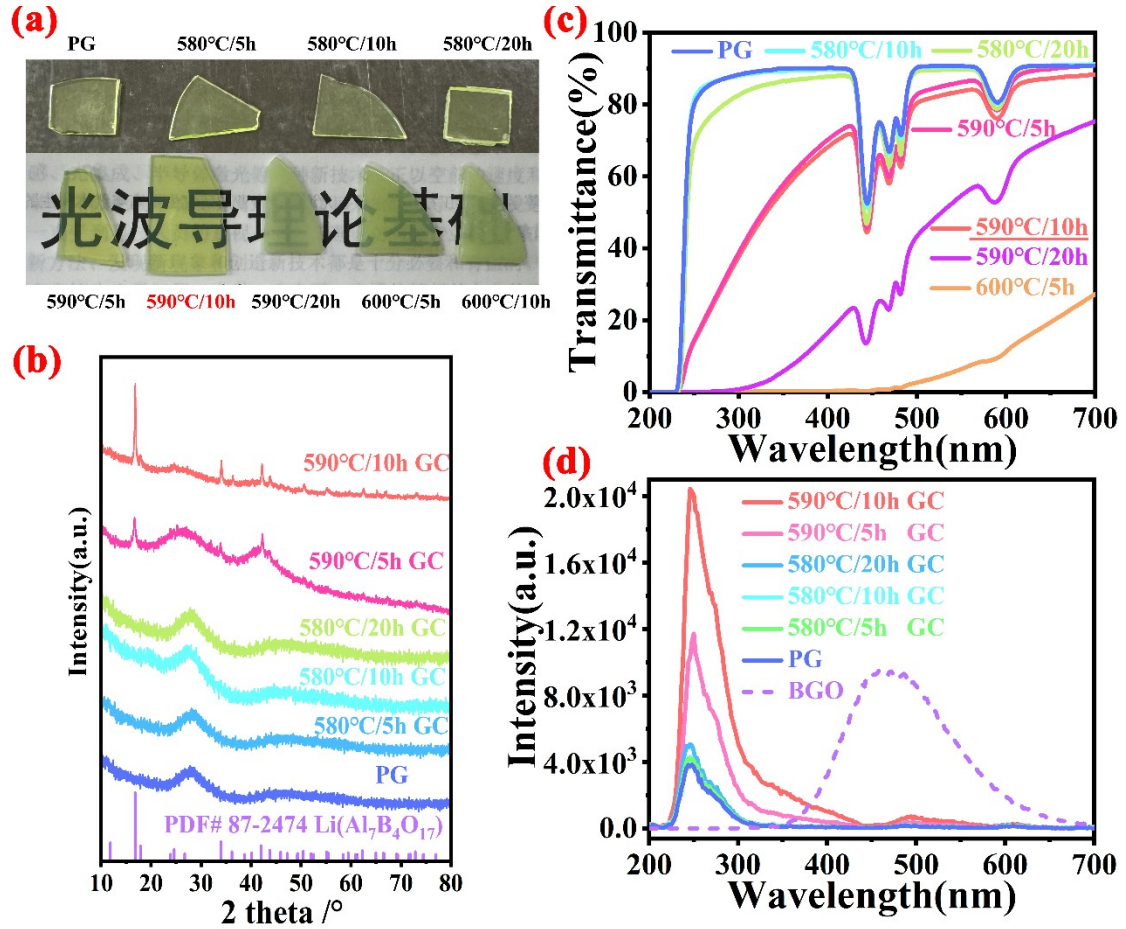


Fig. S2 (a) Photos of the Pr^{3+} -doped samples under various thermal treatment conditions; (b) XRD patterns of PG and GC samples; (c) Transmission spectra of PG and GC samples; (d) XEL spectra of PG and GC samples.

Composition optimization:

We have prepared a series of samples with the compositions of $40\text{B}_2\text{O}_3 - x\text{BaF}_2 - (40-x)\text{LiF} - 20\text{Al}_2\text{O}_3$ ($x = 0, 5, 10, 15, 20, 25, 30, 35, 40$ in mol.%) abbreviated as $x\text{Ba}-(40-x)\text{Li}$. The optimization of Pr^{3+} ions doping concentration was also investigated in $10\text{Ba}-30\text{Li}$ system which mentioned in main text (Fig. S3 (b)).

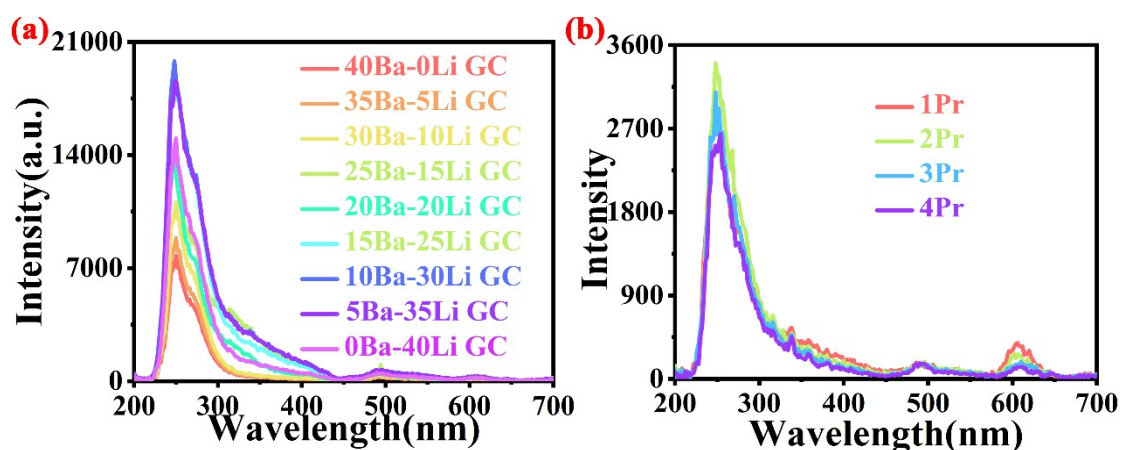


Fig. S3 (a) XEL spectra of Pr^{3+} -doped fluoroborate GC samples; (b) XEL spectra of different Pr^{3+} ions doping concentration in $40\text{B}_2\text{O}_3 - 10\text{BaF}_2 - 30\text{LiF} - 20\text{Al}_2\text{O}_3$ glass.

Table S1 Assignment of main Raman scattering bands of samples

Wavenumber (cm^{-1})	Raman assignments	Reference
550	Transverse motion of bridging oxygen within $\text{Al}^{\text{IV}}\text{-O-}\text{Al}^{\text{IV}}$ linkages/loose diborate group	1,2
677	B-O-B stretching in metaborate rings	3
780	Al-O stretch vibrations of AlO_4 tetrahedral structural units with different numbers of non-bridging oxygen (NBO)/symmetric breathing vibration of six-membered rings with one or two $[\text{BO}_4]$ /borate superstructures such as ditriborates, and penta-, tetra- or tri-borate species	4-7
840	Pyroborate vibrations	8
920	Vibration of orthoborate $[\text{BO}_3]$ structural units	4,9,10
1013	$[\text{BO}_4]^-$ units linked to borate groups containing NBO	11
1238	Trigonal boron groups, stretching of terminal B-O bonds in metaborate units, pyro-borate groups	8
1298	High frequency Raman bands to the B-O bonds linked to large borate groups	10
1406	Vibration of $[\text{BO}_3]$ triangle units	12
1505	Longitudinal B-O metaborate rings, $[\text{BO}_2\text{O}]^-$ triangles connected to other borate triangular units	10
1784	$\text{Li}(\text{Al}_7\text{B}_4\text{O}_{17})$ crystal phase	13

Table S2 The Judd-Ofelt intensity parameters ($\Omega_\lambda, \times 10^{-20} \text{ cm}^2$) of glass system containing Pr^{3+} ions

Sample	Ω_2	Ω_4	Ω_6	References
Germanate	6.93	19.68	8.95	14
Silicate	5.40	3.88	7.41	15

Tellurite	3.84	7.64	5.90	16
Borate	1.33	6.81	8.62	17
Fluoroborate	0.98	4.67	4.96	18
Borovanadate	1.704	2.689	4.937	19
Phosphate	1.51	18.03	19.81	20
ZBLAN	2.44	4.41	5.52	21
PbB ₄ O ₇ PG	5.917	4.77	21.35	22
PbB ₄ O ₇ GC	2.476	4.638	20.727	22
CaF ₂ PG	5.49	2.66	5.03	23
CaF ₂ GC	2.10	2.88	2.01	23
SrF ₂ PG	1.83	18.82	6.25	24
SrF ₂ GC	0.18	3.83	1.24	24
PG	0.242	1.793	8.972	This work
GC	0.161	1.356	14.042	This work

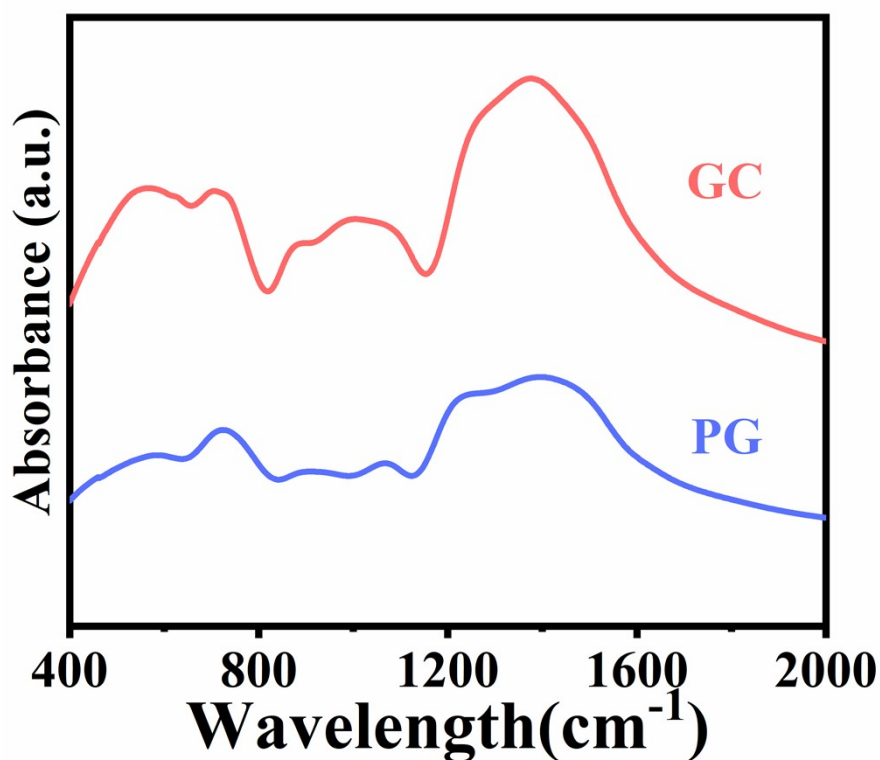


Fig. S4 FTIR spectra of PG and GC.

Table S3 Assignment of FT-IR spectrum distribution of samples

Wavenumber (cm ⁻¹)	FT-IR assignments	Ref.
560	Specific vibrations of Ba-O bonds	25
710	Stretching vibrations of Al-O bonds in AlO ₆ groups; Bending vibrations of B-O-B; Vibration of [BO ₃] bending vibration; BO ₃ -O-BO ₃ bond bending vibrations	26–29

883	Asymmetric stretching of B-O in [BO ₄]	30
910	Stretching vibration of BO ₄ units in various structural groups; Vibration of Al-O bonds in AlO ₄ group	6,29
990	B-O-B bond stretching vibrations in [BO ₄]	11,31
1066	B-O stretching vibrations of BO ₄ units from tri, tetra, and pentaborate groups; Symmetric stretching of B-O in [BO ₄]	29,32
1238	Asymmetric stretching vibrations of B-O bonds from orthoborate groups; B-O stretching vibrations of trigonal [BO ₃] units in meta-, pyro and ortho-borate groups	28,29,33
1366	Symmetric stretching vibrations of [BO ₃] groups; B-O bond stretching vibration of BO ₃ of various borate rings	29,34
1480	Asymmetric stretching modes of borate triangles BO ₃ units; B-O ⁻ bond stretching in BO ₃	28,29

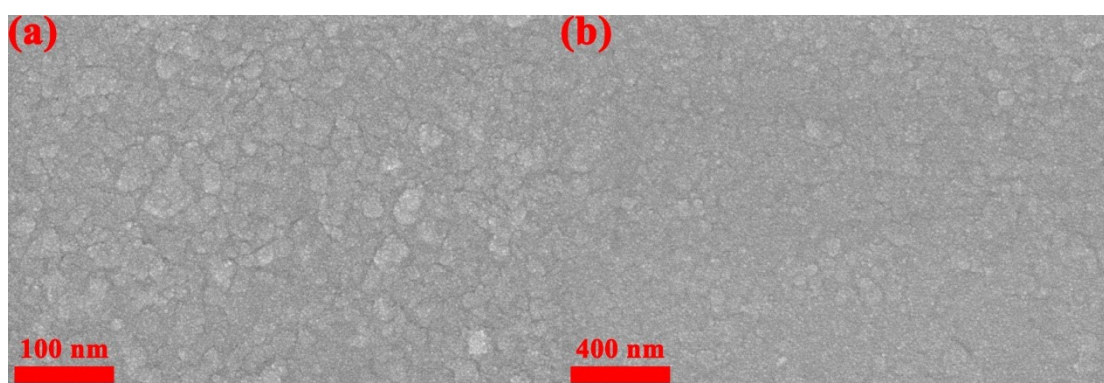


Fig. S5 SEM images of GC.

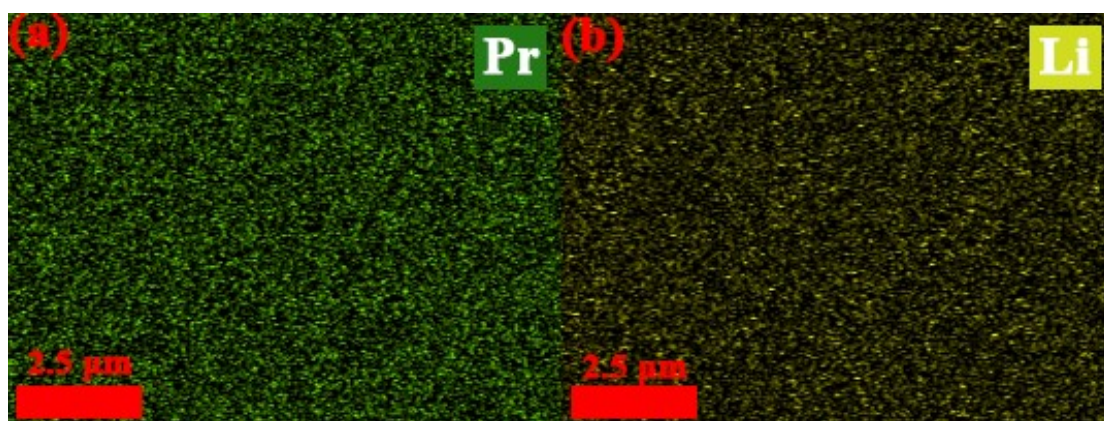


Fig. S6 Elemental mappings of (a) Pr, (b) Li, with the concentrations reflected by the brightness in color.

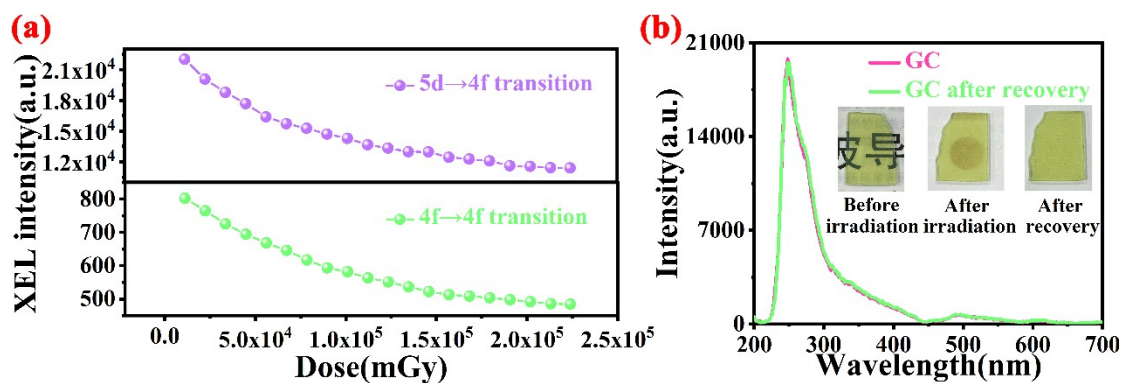


Fig. S7 (a) Various of XEL intensities of the 5d → 4f (250 nm) and 4f → 4f emissions (494 nm) in GC versus irradiation dose; (b) XEL spectra of GC and GC after thermal recovery; Inset: GC photos before and after X-ray irradiation; And GC photo after thermal recovery.

Table S4 Summary of cost of several luminescent materials.

Materials	Unit Price (\$/cm ³)	Ref.
LYSO: Ce ³⁺	150	35
LuAG: Ce ³⁺	150	35
CsI: Tl	50	36
LSO: Ce ³⁺	40	37
BGO	9	37
ZBLAN glass: Pr ³⁺	5.1	38
Fluoroborate glass: Pr ³⁺	2.6	This work

Table S5 Parameters of fast scintillators.

Sample	Light Yield (Photons/MeV)	Decay time	Ref.
BaF ₂	1,400	800 ps	39–41
LuAG: Pr ³⁺	19,000	20 ns	42,43
LuYAG: Pr ³⁺	33,000	20 ns	44
YAP: Pr ³⁺	12,000	10 ns	45
YAG: Ce ³⁺	28,000	90 ns	46–48
YAP: Ce ³⁺	17,000	26.7 ns	49
LuAG: Ce ³⁺	40,200	62.35 ns	50
LuYAP: Ce ³⁺	14,000	17 ns	51
GGAG: Ce ³⁺	50,000	90 ns	52,53

GYGAG: Ce ³⁺	50,000	-	54
GSO: Ce ³⁺	10,000	25 ns	55
Lu ₂ SiO ₅ : Ce ³⁺	30,000	42 ns	56,57
LuBr ₃ : Ce ³⁺	32,000	50 ns	58
LuCl ₃ : Ce ³⁺	13,000	4 μs	58
LuI ₃ : Ce ³⁺	42,000	35 ns	59,60
LaCl ₃ : Ce ³⁺	50,000	24 ns	56,58
LaBr ₃ : Ce ³⁺	78,000	15 ns	61
LaI ₃ : Ce ³⁺	95,000	24 ns	56
LGSO: Ce ³⁺	19,000	23 ns	55
LYSO: Ce ³⁺	30,000	30 ns	62
LSO: Ce ³⁺	20,000	28 ns	55
CeBr ₃	68,000	17 ns	63
BGO	10000	300 ns	64,65
KLaF ₄ GC: Ce ³⁺	17,000	53.6 ns	66
Na ₅ Lu _{9-x} Gd _x F ₃₂ GC: Ce ³⁺	8,000	52.7 ns	67
Fluorosilicate GC: Pr ³⁺	5,832	23 ns (UV)	68
Fluoroborate GC: Pr³⁺	8,567	21.53 ns (UV) 24.13 ns (γ-ray)	This work

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