Fluorophosphate Upconversion Luminescent Glass-Ceramics Containing $Ba_2LaF_7:Er^{3+}$ Nanocrystals: An Advanced Solid-State Nuclear Magnetic Resonance Study

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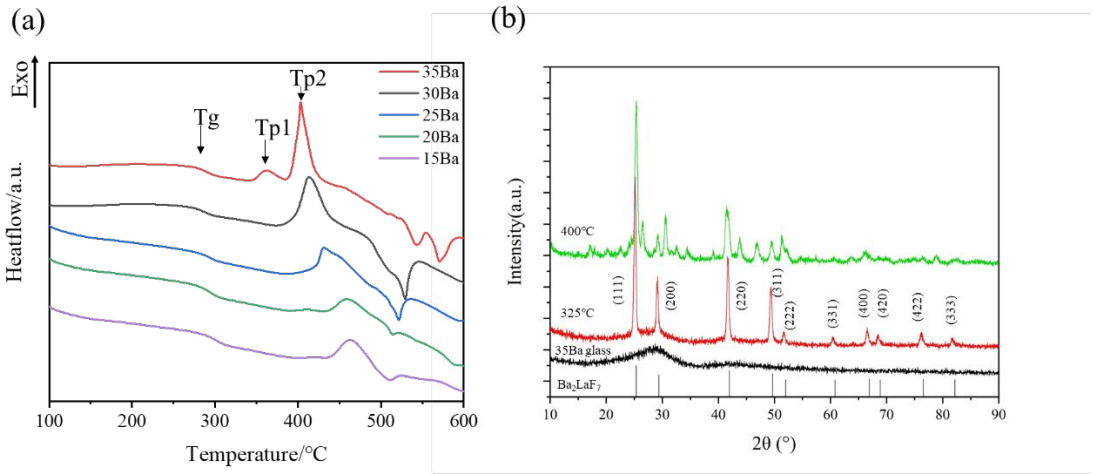

Fig. S1 (a) The measured DSC curves of $xBaF_2$-(90-x) $NaPO_3$-$10LaF_3$ (x=15, 20, 25, 30, 35 glass samples; (b) The measured XRD patterns of x=35 glass and glass ceramics with heating temperature of 325℃ and 400℃, respectively.

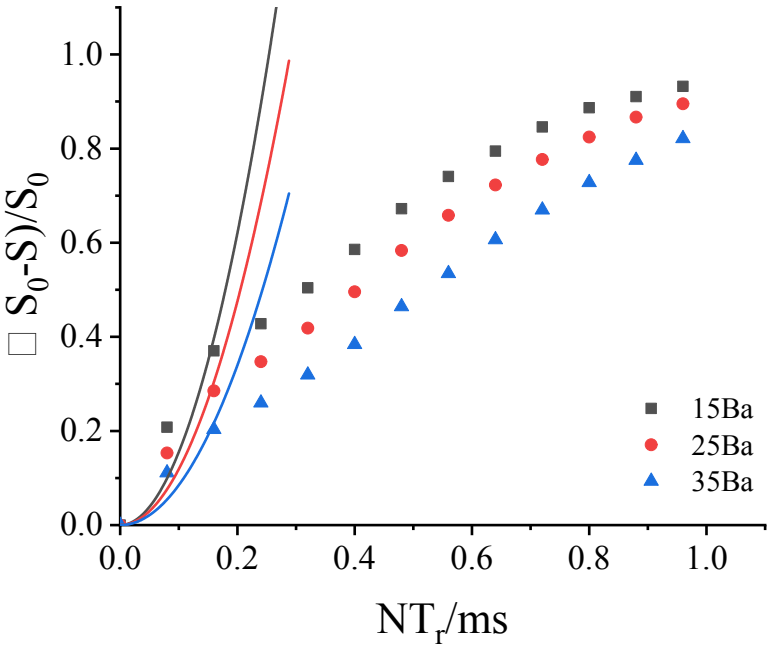

Fig. S2 $^{19}F\{^{31}P\}$ REDOR dephasing curves of x = 15, 25, and 35 glasses. The REDOR dephasing curves were acquired by integrating the whole spectra.

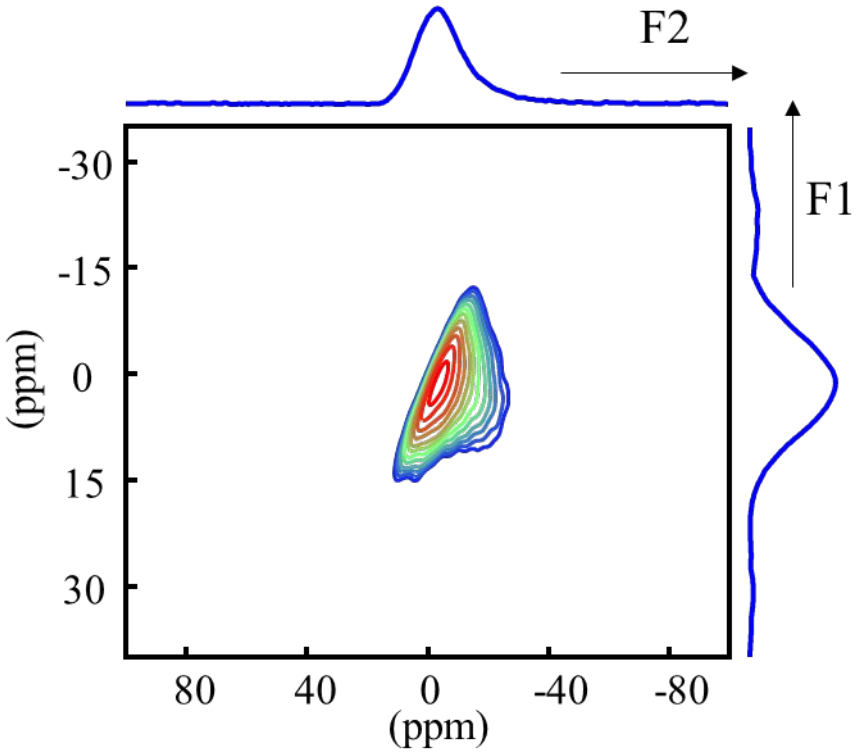

Fig. S3 ^{23}Na TQ MAS spectrum of x=25 glass.

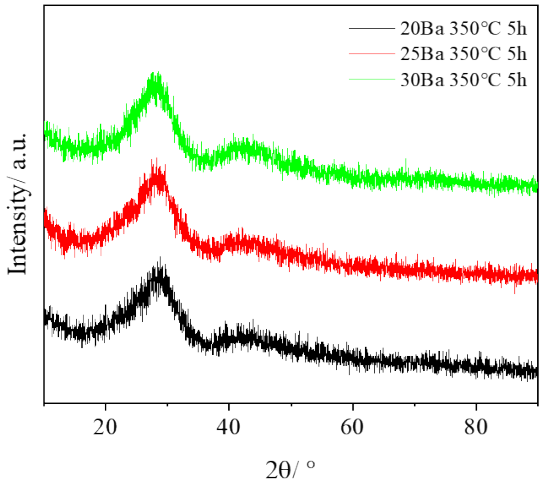

Fig. S4 The measured XRD patterns of the heated glasses with heating temperature of 350℃ for 5 hours.

Table S1. The parameters of ^{31}P and ^{19}F magic angle spinning (MAS) NMR experiments.

	90°pulse/μs	spinning rate/kHz	v_0/MHz	recycle delays/s	Reference compound [c]
^{31}P MAS	2.5	12	202.5	80 [a]/10 [b]	$NH_4H_2PO_4$
^{19}F MAS	2.1	25	470.5	40/5	AlF_3

[a] Relaxation time for glass samples.

[b] Relaxation time for the samples doped with Er^{3+}.

[c] The chemical shifts are 1.12ppm ($NH_4H_2PO_4$) and -172.5ppm (AlF_3).

Table S2. Experimental parameters used in the REDOR NMR experiments

REDOR	ν_0(S) [a] /MHz	ν_0(I) [b] /MHz	v [c]/kHz	T_1[d]/s	pulse length (S)/μs	pulse length (I) /μs
$^{19}F\{^{31}P\}$	470.5	202.5	25	20	4.2	4.2
$^{31}P\{^{19}F\}$	202.5	470.5	25	40	4.2	4.2
$^{31}P\{^{23}Na\}$	202.5	132.3	12	40	9.0	9.0
$^{23}Na\{^{31}P\}$	132.3	202.5	12	0.5	9.0	9.0
$^{19}F\{^{23}Na\}$	470.5	132.3	25	20	4.2	4.2
$^{23}Na\{^{19}F\}$	132.3	470.5	25	0.5	4.2	4.2

[a] S-spin resonance frequency.

[b] I-spin resonance frequency.

[c] Spinning rate.

[d] Relaxation time.

Table S3 . The glass transition temperature values of selected glass samples.

Samples	*T*g/℃ (±5℃)
35Ba	291
30Ba	292
25Ba	296
20Ba	298
15Ba	304

Table S4. Deconvolution parameters of the ^{31}P MAS NMR spectra of the glasses and glass ceramics.

samples	P species	position/ppm (±0.5)	Width/ppm (±0.5)	fraction% (±10)
15Ba	Q^0_{0La}	4.6	7.7	3.0
	Q^1_{0La}	-0.4	7.6	9.9
	Q^1_{1La}	-4.4	8.8	48.6
	Q^2	-17.7	9.4	38.5
20Ba	Q^0_{0La}	4.6	7.1	4.5
	Q^1_{0La}	-0.4	7.7	13.6
	Q^1_{1La}	-4.4	8.5	49.8
	Q^2	-17.3	9.3	32.1
25Ba	Q^0_{0La}	4.6	6.6	5.3
	Q^1_{0La}	-0.4	7.5	15.3
	Q^1_{1La}	-4.4	8.2	54.0
	Q^2	-16.9	9.1	25.4
30Ba	Q^0_{0La}	4.6	6.6	7.5
	Q^1_{0La}	-0.4	7.7	18.8
	Q^1_{1La}	-4.4	8.2	53.4
	Q^2	-16.7	8.6	20.3
35Ba	Q^0_{0La}	4.6	6.2	6.5
	Q^1_{0La}	-0.4	8.0	18.8
	Q^1_{1La}	-4.4	8.0	58.3
	Q^2	-16.4	8.6	16.4
35Ba heated	Q^0_{0La}	4.6	6.9	6.8
	Q^1_{0La}	-1.5	7.3	40.2
	Q^1_{1La}	-4.4	8.7	28.4
	Q^2	-16.2	9.2	24.6

Table S5 Quantity of F bonding to P (N_{F-P}), number of the broken P-O-P bond (N^{F}_{P-O-P}) calculated according to N_{F-P} and the loss of F, and number of broken P-O-P bond (N^{P}_{P-O-P}) calculated according to the deconvolution of ^{31}P spectra.

composition	N^{P}_{P-O-P} [a] (±10%)	N_{F-P} [b] (±15%)	N_{loss} (±10%)	N^{F}_{P-O-P} [c] (±20%)	$N^{P}_{P-O-P}/N^{F}_{P-O-P}$
15Ba	24.2	14.1	38.1	33.1	0.73
20Ba	25.3	11.6	48.9	36.1	0.70
25Ba	26.0	15.1	46.6	38.6	0.68
30Ba	26.2	12.0	56.7	40.5	0.65
35Ba	24.7	12.3	60	42.3	0.58

[a] $N^{P}_{P-O-P} = N_P \times (Q^0 + 0.5Q^1)$, where N_P is nominal total mole content of P atoms, Q^n represents the fraction of the phosphorus species obtained by the deconvolution of ^{31}P spectra.

[b] $N_{F-P} = N_F \times F_{F-P}$, where N_F is residual mole content of F atoms; F_{F-P} is the fraction of P-F species obtained from the deconvolution of ^{19}F spectra.

[c] $N^{F}_{P-O-P} = 0.5N_{loss} + N_{F-P}$, where N_{loss} represents the mole quantity of the loss F.

Table S6. Deconvolution parameters of the ^{19}F MAS NMR spectra of all the glasses and the calculated R_F values.

19F MAS	F species	position/ppm (±0.5)	Width/ppm (±0.5)	CSA/ppm (±5)	η_{cs}(±0.01)	Fraction/% (±10)	R_F (±0.2)
	F-P	-73.8	10.9	-89	0.03	64.4	0.04
15Ba	La-F-Ba	-28.6	57.1	-65	0.03	22.8	0.08
	Ba-F…Na	-65.0	13.0	-76	0.09	12.8	0.09
	F-P	-73.6	10.5	-90	0.03	54.9	0.04
20Ba	La-F-Ba	-31.1	61.3	-60	0.03	33.7	0.10
	Ba-F…Na	-65.0	11.4	-74	0.09	11.4	0.06
	F-P	-73.5	11.1	-92	0.03	45.2	0.05
25Ba	La-F-Ba	-32.7	64.8	-67	0.03	44.0	0.18
	Ba-F…Na	-65.0	12.4	-75	0.09	10.8	0.07

	F-P	-73.2	10.9	-91	0.03	35.9	0.04
30Ba	La-F-Ba	-31.0	63.9	-58	0.03	50.1	0.19
	Ba-F…Na	-65.0	13.0	-73	0.09	14.0	0.08
	F-P	-72.7	11.4	-93	0.03	30.7	0.04
35Ba	La-F-Ba	-24.7	53.1	-50	0.03	47.8	0.19
	Ba-F…Na	-65.0	16.7	-76	0.09	21.5	0.12

Table S7. Dipolar second moment M_2(F-F) values of glasses

samples	$M_2/10^6$ rad^2/s^2(±10%)
35Ba	436.1
30Ba	364.2
25Ba	282.4
20Ba	214.9
15Ba	136.6