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SUPPORTING INFORMATION FOR THE PAPER

The role of fluocerite in the genesis of bastnasite: mechanistic insights into the fluorite-fluocerite-bastnasite transformation.

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Fig. SI-1 Selected examples of Rietveld refinement containing (a) fluorite and fluocerite in the Nd experiment at 70 °C after 10 hours, (b) fluocerite and bastnäsite in the La experiment at 200 °C after 60 days, (c) fluocerite, bastnäsite and cerianite in the Ce experiment at 200 °C after 2 days.

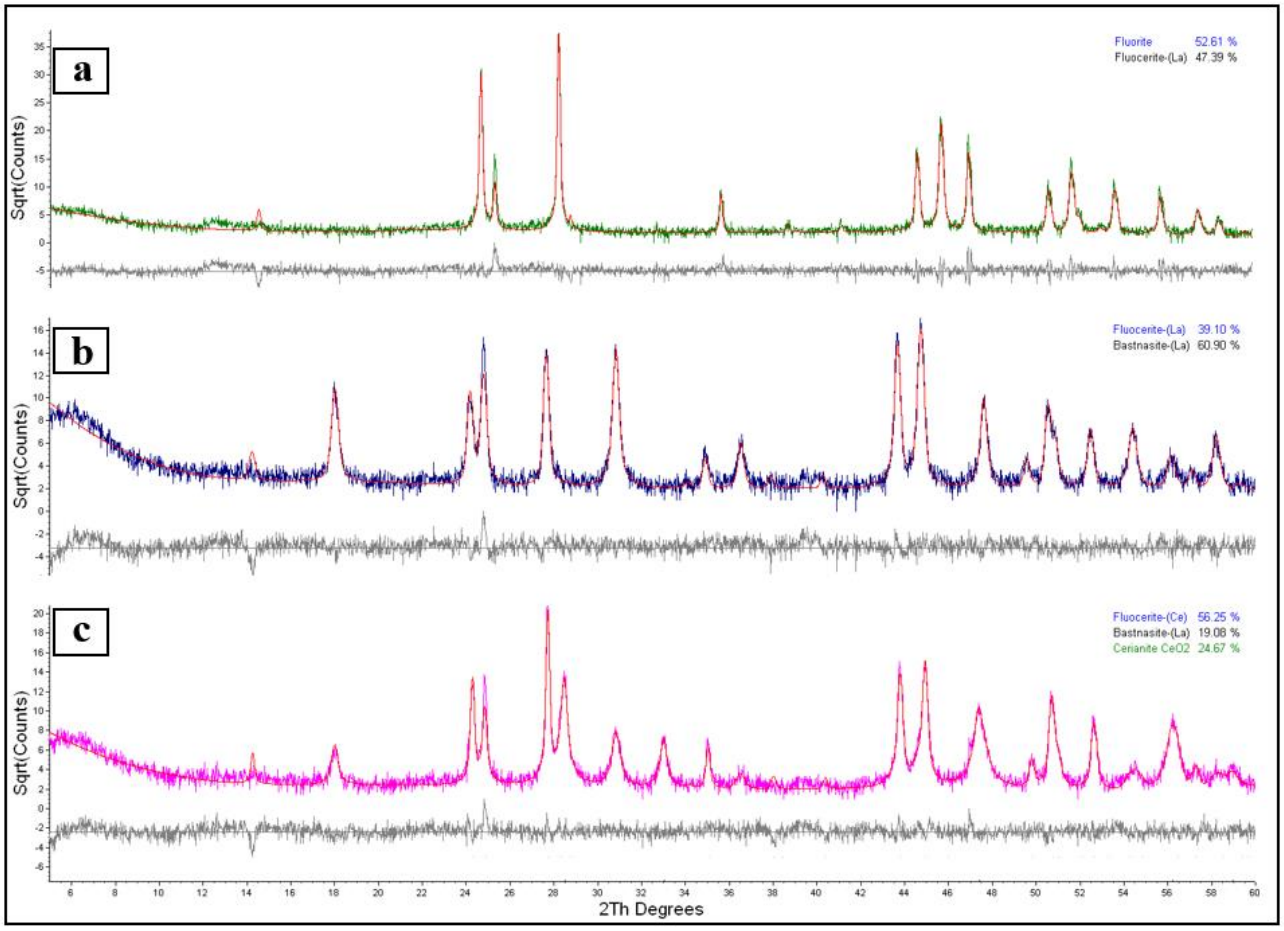

Fig. SI-2. Typical crystal morphologies of fluocerite obtained in our experiments.

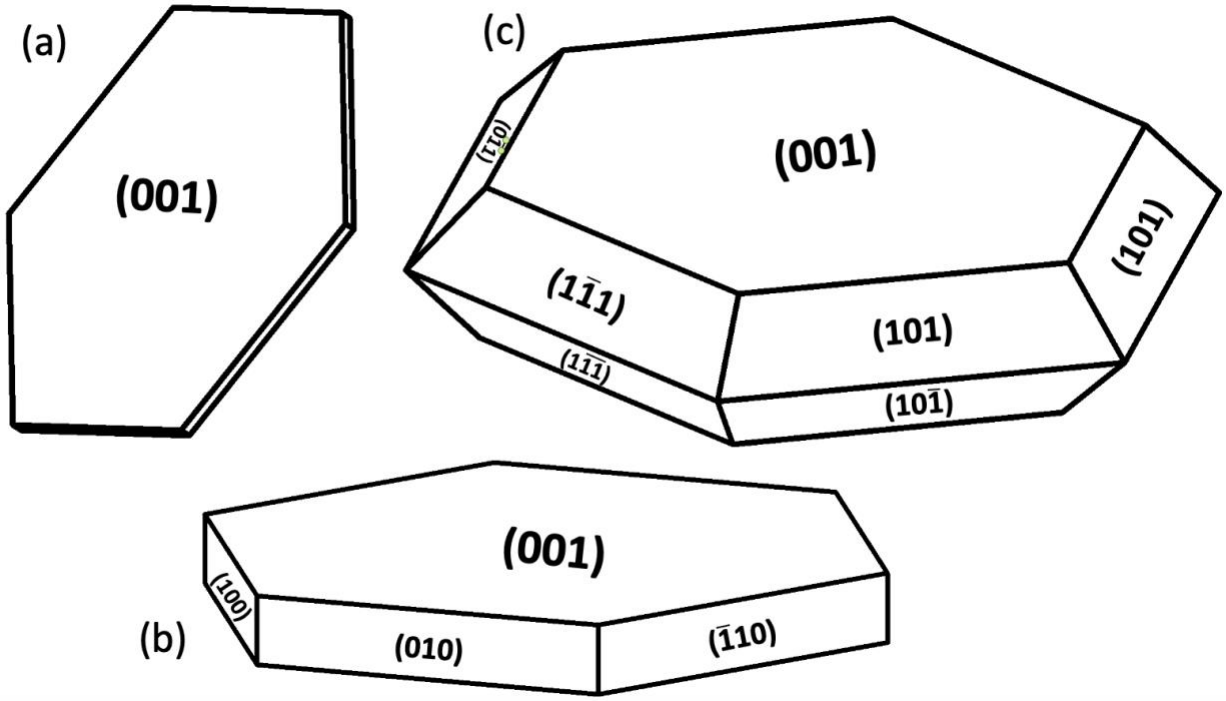

Fig. SI-3. Fluocerite crystals showing (a) rounded morphologies at early stage of reaction at 50 ºC in the La system, (b) pseudohexagonal morphologies after 9.5 hr of reaction at 70 ºC in the Ce system and (c) well-developed hexagonal shape at 90 ºC in the Nd system after 24 hr of reaction.

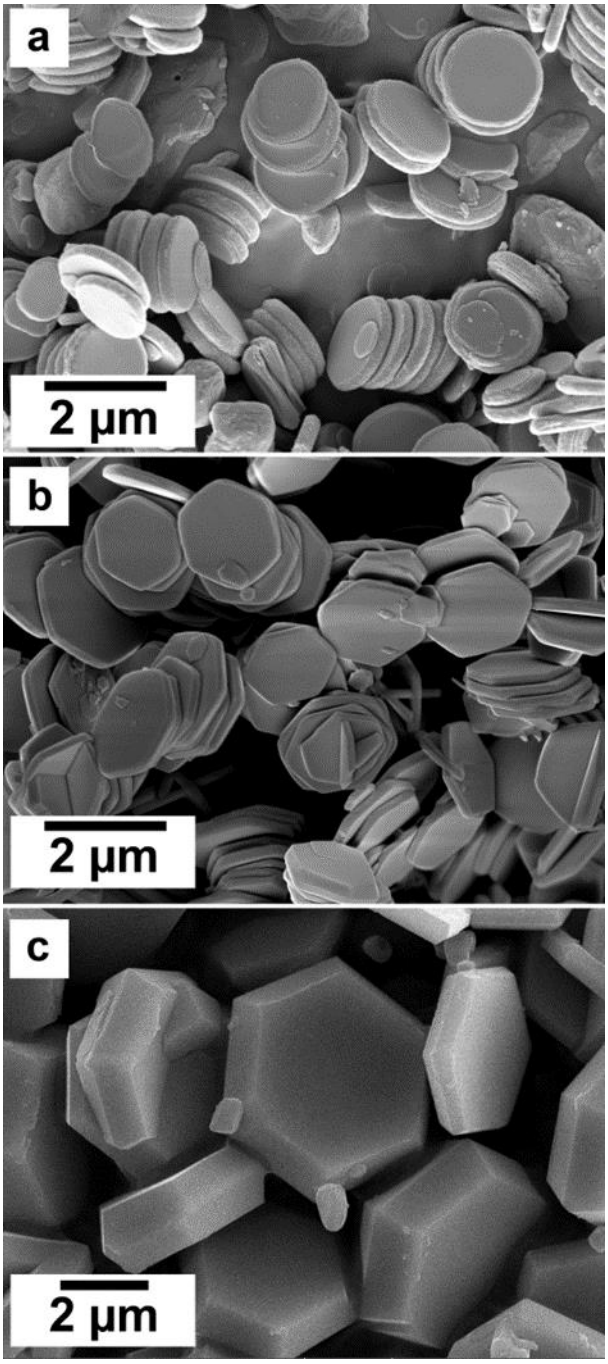

Fig. SI-4. Avrami plots for the fluorite to fluocerite transformation experiments in the presence of (a) La, (b) Ce and (c) Nd.

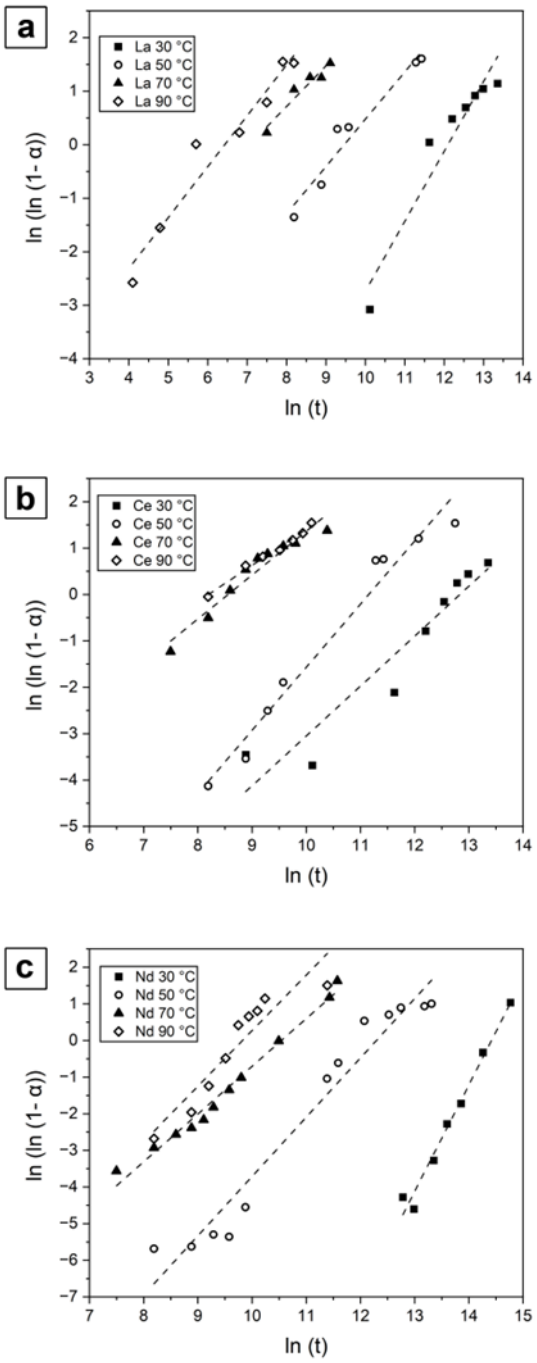

Table SI-1. Unit cell parameters of fluorite and of the solid phases obtained during the fluorite to fluocerite transformation experiments and fluocerite carbonation experiments in the La system.

Fluorite	T (°C)	Unit-cell parameters		RWP	GOF
		a (Å)	Cell Vol (Å^3)		
	90	5.460(33)	162.8(23)	19.02	2.11
La	**Fluocerite**				
	T (°C)	**Unit-cell parameters**		**RWP**	**GOF**
		a (Å)	**c (Å)**	**Cell Vol (Å^3)**	
	30	7.156(11)	7.336(11)	325.4(11)	19.45	1.57
	50	7.158(71)	7.331(75)	325.4(72)	18.32	1.49
	70	7.165(65)	7.334(69)	326.1(67)	18.81	1.71
	90	7.180(24)	7.355(26)	328.4(25)	16.27	1.42
	Bastnäsite				
	T (°C)	**Unit-cell parameters**		**RWP**	**GOF**
		a (Å)	**c (Å)**	**Cell Vol (Å^3)**	
	50	7.199(61)	9.856(47)	221.2(43)	20.82	1.32
	90	7.213(33)	9.864(26)	222.19(24)	22.86	1.47
	200	7.173(55)	9.828(40)	218.9(38)	26.60	1.19

Table SI-2. Unit cell parameters of the solid phases obtained during the fluorite to fluocerite transformation experiments and fluocerite carbonation experiments in the Ce system.

Ce	**Fluocerite**					
	T (°C)	**Unit-cell parameters**			**RWP**	**GOF**
		a (Å)	**c (Å)**	**Cell Vol (Å^3)**		
	30	7.1091(28)	7.270(31)	318.2(29)	18.88	1.49
	50	7.117(30)	7.277(30)	319.2(30)	14.4	1.70
	70	7.108(18)	7.277(17)	318.4(18)	18.78	1.43
	90	7.104(13)	7.277(13)	318.1(13)	17.85	1.42
	Bastnäsite					
	T (°C)	**Unit-cell parameters**			**RWP**	**GOF**
		a (Å)	**c (Å)**	**Cell Vol (Å^3)**		
	50	7.115(40)	9.788(41)	214.6(30)	19.16	1.28
	90	7.119(36)	9.808(20)	215.3(23)	20.95	1.41
	200	7.165(50)	9.828(39)	218.4(35)	24.78	1.15
	Cerianite					
	T (°C)	**Unit-cell parameters**			**RWP**	**GOF**
		a (Å)		**Cell Vol (Å^3)**		
	50	5.422(20)		159.4(23)	19.16	1.28
	90	5.415(34)		158.8(30)	20.95	1.41
	200	5.421(36)		159.3(32)	24.78	1.15

Table SI-3. Unit cell parameters of the solid phases obtained during the fluorite to fluocerite transformation experiments and fluocerite carbonation experiments in the Nd system.

Nd	**Fluocerite**						
	T (°C)	**Unit-cell parameters**				**RWP**	**GOF**
		a (Å)		**c (Å)**	**Cell Vol (Å^3)**		
	30	7.018(30)		7.205(29)	307.4(29)	20.59	2.02
	50	7.015(17)		7.192(17)	306.6(17)	17.25	1.40
	70	7.018(25)		7.195(27)	306.9(25)	19.63	1.44
	90	7.012(18)		7.192(19)	306.3(18)	19.00	1.36
	Bastnäsite						
	T (°C)	**Unit-cell parameters**				**RWP**	**GOF**
		a (Å)		**c (Å)**	**Cell Vol (Å^3)**		
	50	7.080(47)		9.742(36)	211.5(32)	24.88	1.29
	90	7.029(38)		9.891(23)	211.6(25)	24.53	1.60
	200	7.082(11)		9.814(82)	213.2(78)	24.76	1.76
	Kozoite						
	T (°C)	**Unit-cell parameters**				**RWP**	**GOF**
		a (Å)	**b (Å)**	**c (Å)**	**Cell Vol (Å^3)**		
	50	7.155(39)	4.955(28)	8.443(50)	299.4(30)	24.88	1.29
	90	7.132(48)	4.953(32)	8.425(11)	297.7(37)	24.53	1.60
	200	7.211(13)	4.962(77)	8.357(18)	299.0(10)	24.76	1.76

Table SI-4. Quantification of crystalline phases during the fluorite to La-fluocerite transformation reactions.

La			
T (°C)	**Time (h)**	**Fluorite wt%**	**Fluocerite wt%**
30	0.00	100	0
	6.83	96	4
	31.00	35	65
	55.25	20	80
	77.75	13	87
	98.83	8	92
	121.16	6	94
	174.92	4	96
50	0.00	100	0
	1.00	77	23
	2.00	65	35
	2.00	62	38
	3.00	26	74
	4.00	25	75
	4.00	24	76
	22.00	2	98
	25.42	0	100
70	0.00	100	0
	0.50	29	71
	1.00	6	94
	1.50	3	97
	2.50	2	98
	4.00	0	100
90	0.00	100	0
	0.02	93	7
	0.03	81	19
	0.08	36	64
	0.25	28	72
	0.50	11	89
	0.75	1	99
	1.00	0	100

Table SI-5. Quantification of crystalline phases during the fluorite to Ce-fluocerite transformation reactions.

Ce			
T (°C)	**Time (h)**	**Fluorite wt%**	**Fluocerite wt%**
30	0.00	100	0
	6.83	98	2
	31.00	89	11
	55.25	63	37
	77.75	42	58
	98.83	27	73
	121.16	21	79
	174.92	14	86
50	0.00	100	0
	1.00	98	2
	2.00	97	3
	3.00	92	8
	4.00	86	14
	22.00	12	88
	48.50	4	96
	95.25	0	100
70	0.00	100	0
	0.50	75	25
	1.00	55	45
	1.50	34	66
	2.00	18	82
	2.50	11	89
	3.00	9	91
	4.00	6	94
	5.00	5	95
	9.00	2	98
90	0.00	100	0
	1.00	38	62
	2.00	15	85
	2.75	10	90
	3.75	7	93
	4.75	4	96
	5.75	2	98
	6.75	1	99
	7.75	0	100

Table SI-6. Quantification of crystalline phases during the fluorite to Nd-fluocerite transformation reactions.

Nd			
T (°C)	**Time (h)**	**Fluorite wt%**	**Fluocerite wt%**
30	0.00	100	0
	98.83	99	1
	121.16	99	1
	174.92	96	4
	223.67	90	10
	288.92	84	16
	433.00	49	51
	720.75	6	94
50	0.00	100	0
	4.00	99	1
	5.41	99	1
	24.42	70	30
	29.92	58	42
	48.50	18	82
	76.33	13	87
	95.25	9	91
	147.17	8	92
	167.75	7	93
70	0.00	100	0
	0.50	97	3
	1.00	95	5
	1.50	93	7
	2.00	91	9
	2.50	89	11
	3.00	85	15
	4.00	77	23
	5.00	69	31
	10.00	37	63
	25.50	4	96
	29.50	0	100
90	0.00	100	0
	1.00	93	7
	2.00	87	13
	2.75	75	25
	3.75	54	46
	4.75	22	78
	5.75	14	86
	6.75	11	89
	7.75	4	96
	24.50	0	100

Table SI-7. Point analysis obtained with SEM-EDS on La-, Ce- and Nd-fluocerite final samples obtained at 90 ° C.

Point of analysis	Atomic %					
	Fluorine	**Calcium**	**Lanthanum**	**Cerium**	**Neodymium**	**Total**
1	74.16	4.97	20.87	/	/	100
2	74.63	4.66	20.71	/	/	100
3	71.88	5.17	22.95	/	/	100
4	75.05	4.71	20.24	/	/	100
5	69.39	5.94	24.67	/	/	100
1	75.62	2.68	/	21.71	/	100
2	73.91	2.85	/	23.24	/	100
3	72.23	2.11	/	25.65	/	100
4	73.94	2.97	/	23.09	/	100
5	74.11	2.92	/	22.97	/	100
1	72.91	2.21	/	/	24.88	100
2	72.97	1.89	/	/	25.15	100
3	72.81	2.36	/	/	24.83	100
4	73.7	1.39	/	/	24.91	100
5	73.76	1.42	/	/	24.83	100

Table SI-8. Point analysis obtained with SEM-EDS on La-, Ce- and Nd-bastnasite final samples obtained at 90 ° C.

Point of analysis	Atomic %							
	Carbon	**Oxygen**	**Fluorine**	**Calcium**	**Lanthanum**	**Cerium**	**Neodymium**	**Total**
1	31.34	15.02	29.37	1.77	22.51	/	/	100
2	28.92	17.5	26.49	0.92	26.17	/	/	100
3	27.63	20	18.96	1.68	31.73	/	/	100
4	41.11	20.32	19.69	0.89	18	/	/	100
1	38.48	28.61	12.4	1.55	/	18.96	/	100
2	36.96	20.06	24.22	1.16	/	17.6	/	100
3	28.63	24.07	16.79	3.31	/	27.2	/	100
4	37.3	15.67	30.56	0.9	/	15.58	/	100
1	35.95	12.12	27.12	1.11	/	/	23.71	100
2	32.74	2.48	34.08	1.36	/	/	29.33	100
3	33.04	26.52	18.58	1.18	/	/	20.68	100
4	27.52	21.64	28.3	0.83	/	/	21.71	100

Table SI-9. Quantification of crystalline phases during the La-fluocerite to La-bastnasite transformation reactions.

La			
T (°C)	**Time (days)**	**Fluocerite wt%**	**Bastnasite wt%**
0	0	100	0
	1	95	5
	3	63	37
	5	48	52
	7	46	54
	14	26	74
	24	16	84
90	0	100	0
	1	83	17
	2	81	19
	5	81	19
	7	80	20
	16	83	17
	23	81	19
	33	79	21
200	0	100	0
	0.2	77	23
	1	65	35
	2	64	36
	6	65	35
	60	42	58

Table SI-10. Quantification of crystalline phases during the Ce-fluocerite to Ce-bastnasite and cerianite transformation reactions.

Ce				
T (°C)	**Time (days)**	**Fluocerite wt%**	**Bastnasite wt%**	**Cerianite wt%**
50	0	100	0	0
	1	98	<1	2
	3	77	10	13
	5	72	10	18
	7	65	11	24
	14	56	15	29
	24	50	12	38
90	0	100	0	0
	1	88	1	11
	3	77	0	23
	5	76	2	22
	7	58	2	40
	14	50	5	45
	24	27	8	65
200	0	100	0	0
	0.2	81	8	11
	1	57	20	23
	2	50	17	33
	6	63	29	8
	60	62	17	21

Table SI-11. Quantification of crystalline phases during the Nd-fluocerite to Nd-bastnasite and Nd-kozoite transformation reactions.

Nd				
T (°C)	**Time (days)**	**Fluocerite wt%**	**Bastnasite wt%**	**Kozoite wt%**
50	0	100	0	0
	1	99	1	0
	3	99	1	<1
	5	98	2	<1
	7	92	4	4
	14	80	11	9
	24	71	19	10
90	0	100	0	0
	1	96	<1	4
	2	91	<1	9
	5	94	<1	6
	7	96	<1	4
	16	97	<1	3
	23	96	1	3
	33	96	3	1
200	0	100	0	0
	0.2	86	11	3
	1	70	20	10
	2	66	22	12
	6	74	26	<1