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

Supporting Information for

Reversible Thermochromic property of Cr, Mn, Fe, Co-doped $Ca_{14}Zn_6Ga_{10}O_{35}$

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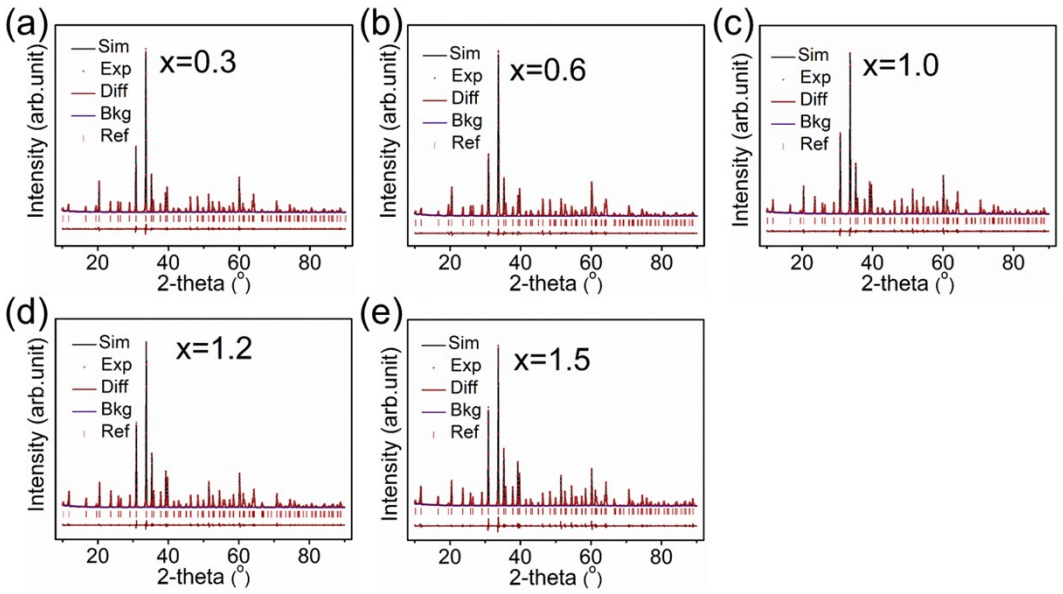

Fig. S1. Pawley refinement of powder of x-ray diffraction spectra of $Ca_{14}Zn_6Ga_{10-x}Cr_xO_{35}$ with (a) x=0.3, (b) x=0.6, (c) x=1.0, (d) x=1.2, and (e) x=1.5, respectively.

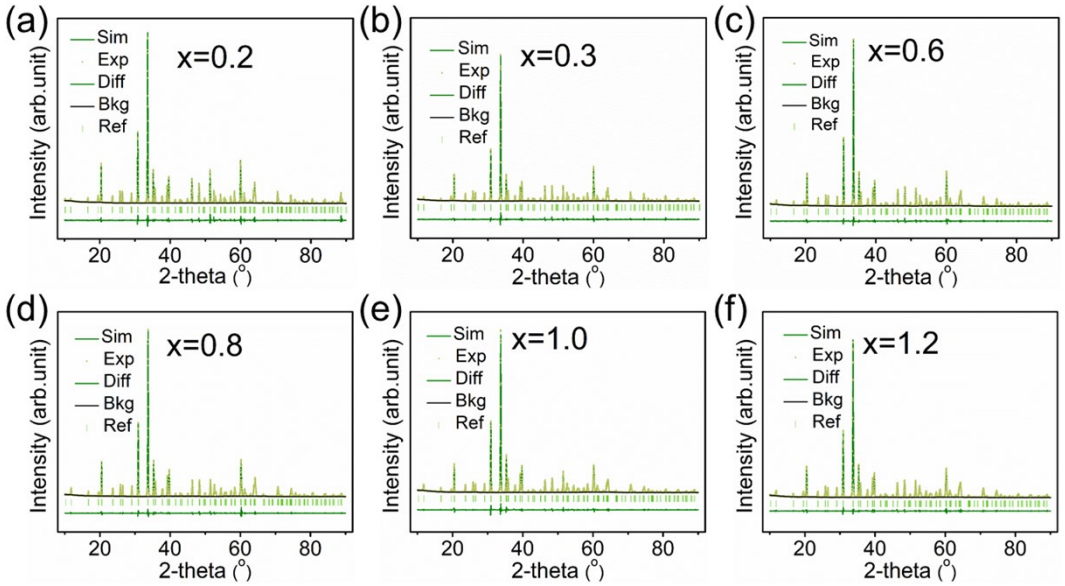

Fig. S2. Pawley refinement of powder of x-ray diffraction spectra of $Ca_{14}Zn_6Ga_{10-x}Mn_xO_{35}$ with (a) x=0.2, (b) x=0.3, (c) x=0.6, (d) x=0.8, (e) x=1.0, and (f) x=1.2, respectively.

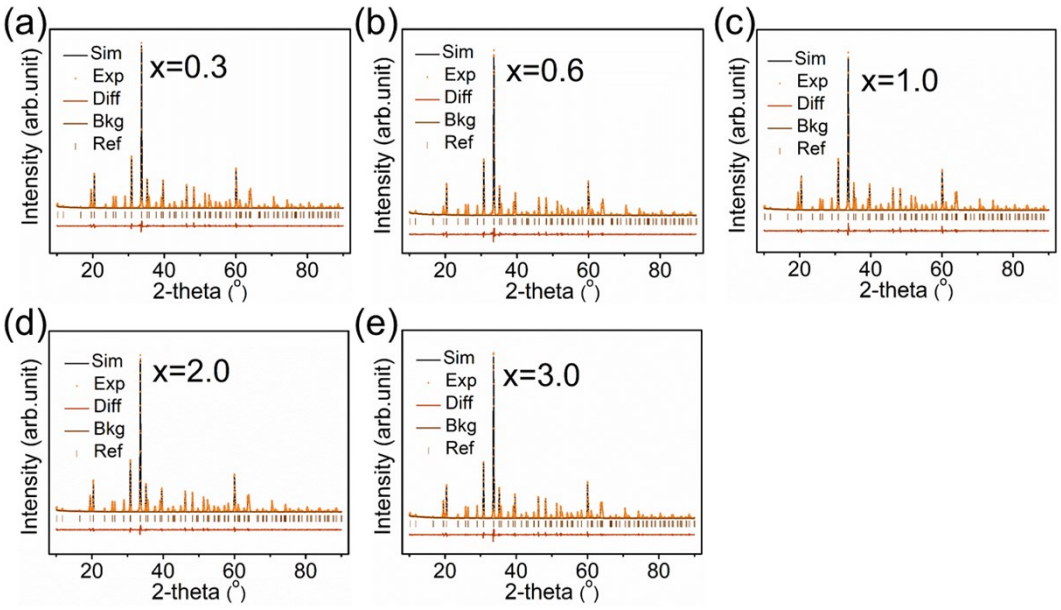

Fig. S3. Pawley refinement of powder of x-ray diffraction spectra of $Ca_{14}Zn_6Ga_{10-x}Fe_xO_{35}$ with (a) x=0.3, (b) x=0.6, (c) x=1.0, (d) x=2.0, and (e) x=3.0, respectively.

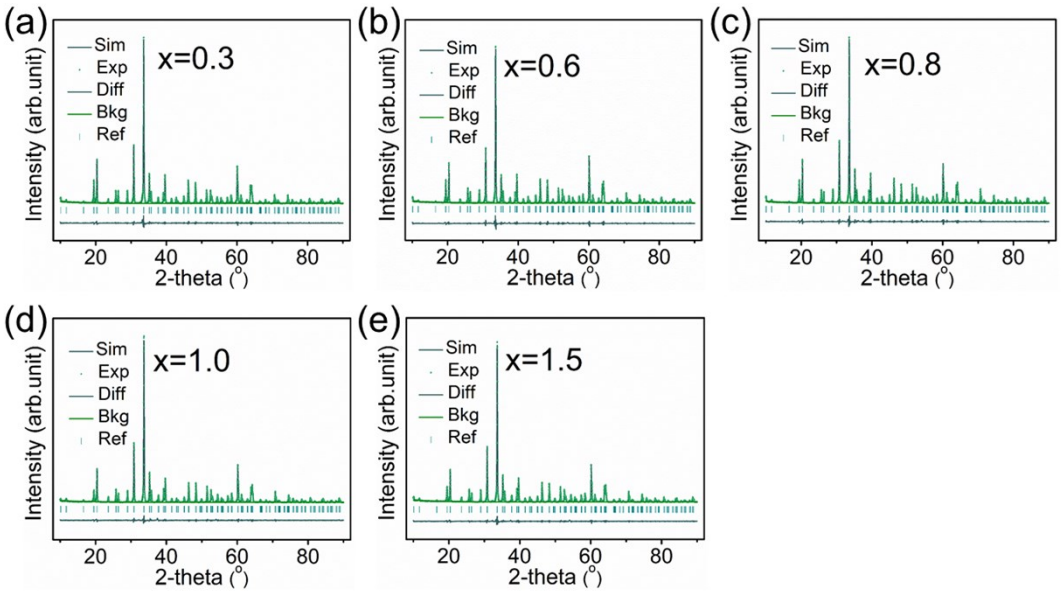

Fig. S4. Pawley refinement of powder of x-ray diffraction spectra of $Ca_{14}Zn_6Ga_{10-x}Co_xO_{35}$ with (a) x=0.3, (b) x=0.6, (c) x=0.8, (d) x=1.0, and (e) x=1.5, respectively.

Table S1 XRD refinement results of $Ca_{14}Zn_6Ga_{10-x}M_xO_{35}$ (M=Cr, Mn, Fe, Co) thermochromic pigments

$Ca_{14}Zn_6Ga_{10-x}Cr_xO_{35}$						
x	Lattice Type	Space Group	Lattice (Å)	α (°)	R_{wp} (%)	R_p (%)
0.3	Cubic	F23	15.1096(4)	90	7.42	5.36
0.6	Cubic	F23	15.0957(6)	90	7.83	5.52
1.0	Cubic	F23	15.0958(3)	90	7.67	5.45
1.2	Cubic	F23	15.0744(3)	90	6.91	4.98
1.5	Cubic	F23	15.0602(3)	90	9.50	6.94
$Ca_{14}Zn_6Ga_{10-x}Mn_xO_{35}$						
x	Lattice Type	Space Group	Lattice (Å)	α (°)	R_{wp} (%)	R_p (%)
0.2	Cubic	F23	15.1092 (7)	90	8.66	6.20
0.3	Cubic	F23	15.1085 (4)	90	8.33	6.15
0.6	Cubic	F23	15.0928 (6)	90	7.82	5.40
0.8	Cubic	F23	15.0796 (5)	90	6.73	4.89
1.0	Cubic	F23	15.0693 (6)	90	7.63	5.52
1.2	Cubic	F23	15.0651 (8)	90	6.82	4.91
$Ca_{14}Zn_6Ga_{10-x}Fe_xO_{35}$						
x	Lattice Type	Space Group	Lattice (Å)	α (°)	R_{wp} (%)	R_p (%)
0.3	Cubic	F23	15.1041(5)	90	8.13	5.44
0.6	Cubic	F23	15.0992(4)	90	9.64	6.74
1.0	Cubic	F23	15.0782(5)	90	7.70	5.15
2.0	Cubic	F23	15.1049(4)	90	6.87	5.01
3.0	Cubic	F23	15.1182(5)	90	8.43	5.99
$Ca_{14}Zn_6Ga_{10-x}Co_xO_{35}$						
x	Lattice Type	Space Group	Lattice (Å)	α (°)	R_{wp} (%)	R_p (%)
0.3	Cubic	F23	15.0671(6)	90	9.21	6.14
0.6	Cubic	F23	15.0600(4)	90	10.09	6.92
0.8	Cubic	F23	15.0532(5)	90	10.29	6.86
1.0	Cubic	F23	15.0594(5)	90	9.03	5.68
1.5	Cubic	F23	15.0530(6)	90	9.34	6.04

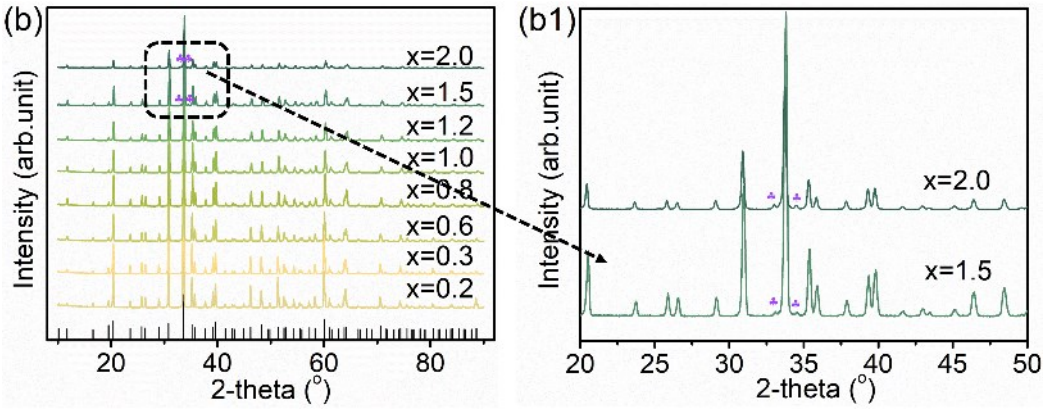

Fig. S5. Powder of x-ray diffraction spectra of (b) $Ca_{14}Zn_6Ga_{10-x}Mn_xO_{35}$ (b1) The enlargement of the X-ray diffraction spectra of $Ca_{14}Zn_6Ga_{10-x}Mn_xO_{35}$ (x=1.5, x=2.0).

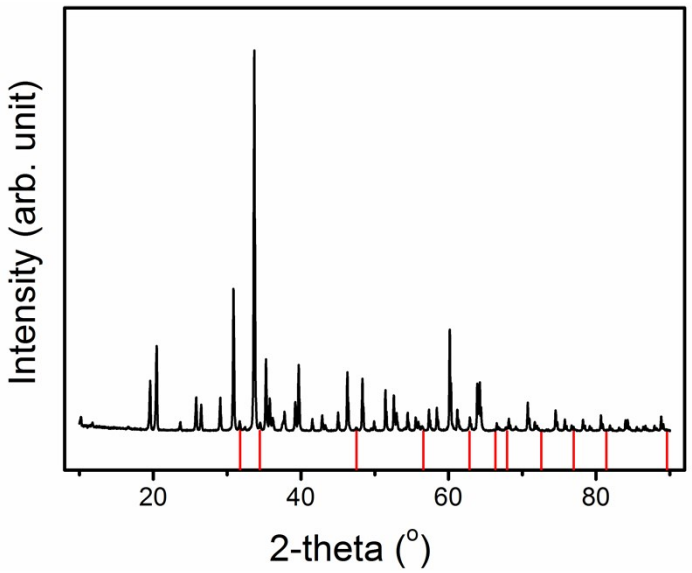

Fig. S6. Powder of x-ray diffraction of $Ca_{14}Zn_6Ga_8Co_2O_{35}$ sample, red bars indicate the diffraction peak positions of an impurity phase of ZnO due to the overdose doping of Co.

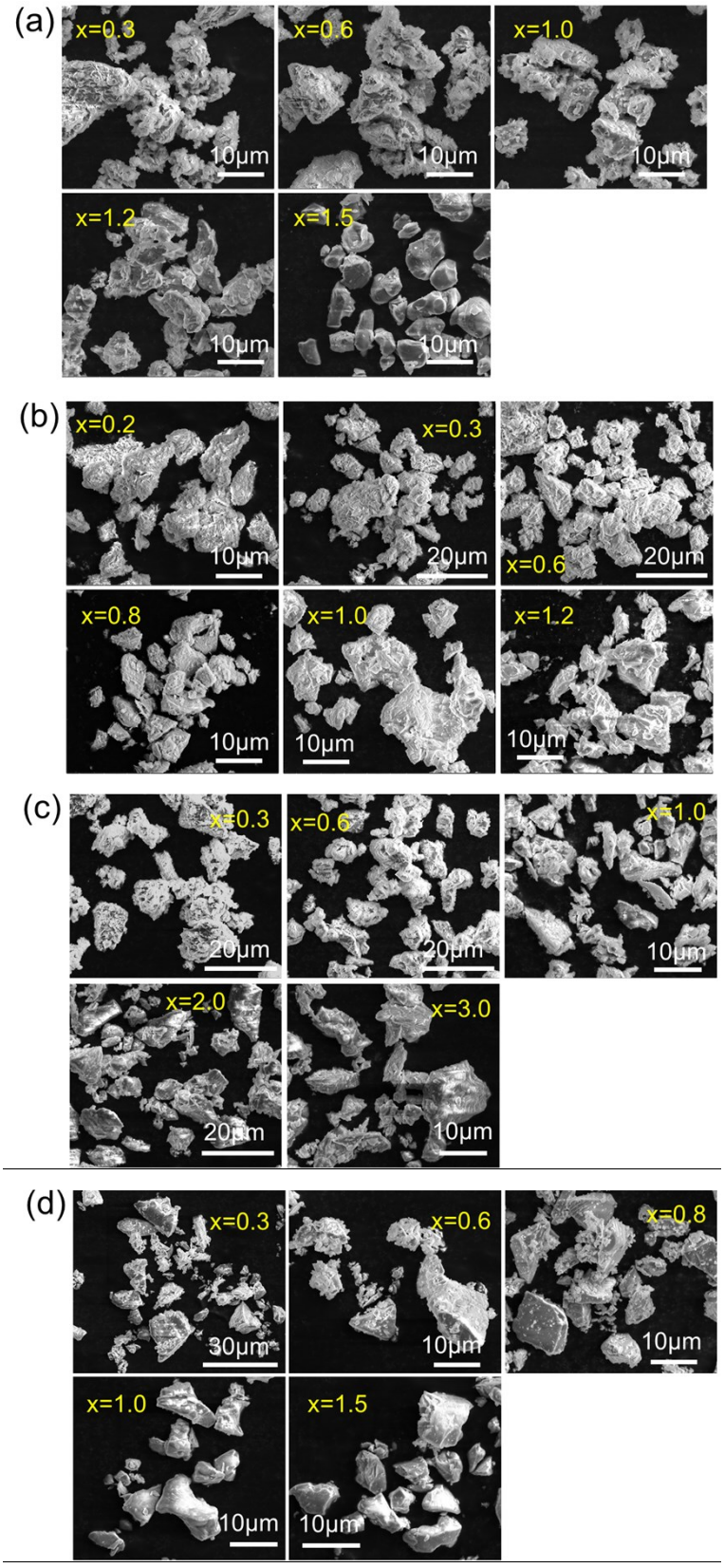

Fig. S7 SEM graphs of as-synthesized $Ca_{14}Zn_6Ga_{10-x}M_xO_{35}$ samples: (a) Cr, (b) Mn, (c) Fe, and (d) Co, respectively.

Table S2. CIE-Lab parameters of $Ca_{14}Zn_6Ga_{10-x}Cr_xO_{35}$ (x=0.3, 0.6, 1.0, 1.2, 1.5) at different temperature.

T(°C)	x=0.3			x=0.6			x=1.0			x=1.2			x=1.5		
	L*	a	b	L*	a	b	L*	a	b	L*	a	b	L*	a	b
20	53	23	12	47	26	13	38	26	17	34	24	15	31	7	9
80	53	20	10	47	24	12	38	22	17	31	20	15	30	5	10
110	53	19	11	45	20	11	34	18	14	33	18	14	28	5	8
140	55	19	11	48	20	11	35	19	14	30	17	12	28	3	8
170	57	16	10	51	19	11	36	19	13	32	17	12	31	3	8
200	54	15	11	48	18	12	34	17	13	28	14	12	25	0	8
230	53	15	11	48	17	11	33	13	13	26	10	12	24	-1	8
260	52	13	10	47	14	10	30	11	13	25	8	11	23	-3	8
290	52	12	10	41	12	10	34	8	13	28	8	12	24	-3	10
320	53	11	10	45	11	10	35	9	12	26	7	12	25	-4	10
350	55	10	12	48	12	13	34	10	13	28	8	12	25	-4	10
380	52	10	13	45	11	13	34	7	12	25	5	12	24	-4	9
400	53	8	11	42	8	11	31	8	13	25	5	12	21	-4	10
420	56	8	16	51	10	15	32	8	12	25	5	12	23	-4	11
440	56	9	16	45	12	15	31	8	13	26	6	13	26	-4	11
460	56	9	15	49	9	16	34	7	13	27	5	14	25	-4	12

Table S3. CIE-Lab parameters of $Ca_{14}Zn_6Ga_{10-x}Mn_xO_{35}$ (x=0.2, 0.3, 0.6, 0.8, 1.0, 1.2, 1.5, 2.0) at different temperature.

T(°C)	x=0.2			x=0.3			x=0.6			x=0.8		
	L*	a	b	L*	a	b	L*	a	b	L*	a	b
20	77	-2	39	80	-7	39	78	-9	48	74	-18	53
80	79	2	35	82	-3	38	77	-3	46	72	-11	51
110	78	3	32	80	-1	34	77	-1	43	74	-9	47
140	78	3	32	81	1	34	76	2	42	73	-5	45
170	76	7	30	78	6	33	73	6	41	70	0	44
200	75	7	30	79	7	34	69	9	42	67	2	42
230	75	7	26	77	8	30	71	10	37	64	7	40
260	71	9	28	74	12	31	71	12	35	64	13	41
290	75	9	25	78	11	27	68	14	32	63	13	33
320	70	9	23	72	13	25	67	16	30	61	15	31
350	74	10	22	77	14	25	65	18	28	61	16	30
380	74	12	24	77	14	26	66	19	28	59	19	29
400	69	10	21	70	14	23	65	19	26	59	19	27
420	70	10	21	73	15	23	67	19	28	62	21	28
440	68	10	20	69	16	22	63	20	26	57	20	25
460	71	11	21	70	14	22	62	19	24	58	20	23
T(°C)	x=1.0			x=1.2			x=1.5			x=2.0		
	L*	a	b	L*	a	b	L*	a	b	L*	a	b
20	71	-24	46	64	-29	29	53	-25	12	50	-23	4
80	72	-20	46	63	-25	28	48	-20	10	45	-19	3
110	70	-17	44	62	-24	27	48	-20	10	46	-18	2
140	69	-14	41	62	-20	26	48	-18	8	46	-17	1
170	69	-12	41	62	-19	25	48	-18	7	46	-17	1
200	67	-9	38	60	-17	22	48	-16	5	45	-16	0
230	67	-5	37	60	-15	22	47	-14	5	45	-15	-1
260	66	-1	35	60	-12	22	46	-13	4	44	-13	-1
290	65	2	33	59	-9	20	46	-11	4	43	-12	-2
320	63	5	32	57	-7	19	45	-10	3	43	-11	-2
350	63	7	28	58	-5	17	46	-7	3	45	-10	-3
380	62	9	26	56	-3	17	43	-7	3	42	-9	-2
400	60	10	24	55	-2	16	42	-6	3	41	-9	-2
420	60	10	24	54	-1	17	42	-4	3	42	-8	-1
440	56	12	21	52	1	15	44	-4	3	44	-8	-2
460	57	12	21	53	2	15	42	-3	2	43	-8	-3

Table S4. CIE-Lab parameters of $Ca_{14}Zn_6Ga_{10-x}Fe_xO_{35}$ (x= 0.3, 0.6, 1.0, 2.0, 3.0) at different temperature.

T(°C)	x=0.3			x=0.6			x=1.0			x=2.0			x=3.0		
	L*	a	b	L*	a	b	L*	a	b	L*	a	b	L*	a	b
20	81	5	48	78	5	44	74	9	44	63	13	46	56	18	37
80	80	7	48	77	7	44	71	12	42	65	16	42	54	18	37
110	75	9	43	78	10	43	66	12	38	63	16	40	52	20	34
140	79	8	42	74	9	41	69	11	37	62	17	37	54	18	31
170	75	10	41	75	10	41	63	13	33	58	16	32	50	19	30
200	74	11	41	76	11	42	62	13	33	55	16	29	48	19	30
230	74	9	40	74	10	37	63	12	30	56	16	27	49	16	26
260	70	10	35	75	10	33	61	11	26	55	15	26	46	15	21
290	75	8	37	70	9	34	64	11	28	57	14	26	47	15	21
320	73	8	35	68	9	31	63	11	27	55	14	24	52	15	20
350	74	8	34	68	8	30	64	10	25	56	12	22	46	13	17
380	73	8	34	71	8	31	60	10	24	54	11	20	45	13	17
400	73	8	32	68	8	27	61	10	21	54	11	19	43	12	15
420	70	7	31	65	8	27	61	9	21	53	11	20	51	11	16
440	72	7	31	67	7	27	61	9	23	50	9	18	44	10	14
460	70	6	32	66	7	29	62	8	21	48	10	19	53	10	16

Table S5. CIE-Lab parameters of $Ca_{14}Zn_6Ga_{10-x}Co_xO_{35}$ (x= 0.3, 0.6, 0.8, 1.0, 1.5) at different temperature.

T(°C)	x=0.3			x=0.6			x=0.8			x=1.0			x=1.5		
	L*	a	b	L*	a	b	L*	a	b	L*	a	b	L*	a	b
20	72	-20	23	68	-21	30	66	-21	27	52	-19	16	41	-13	12
80	72	-18	24	67	-17	29	69	-22	29	50	-20	18	38	-12	10
110	71	-16	24	66	-17	28	67	-19	27	53	-17	16	42	-11	10
140	70	-15	23	66	-15	28	67	-18	28	52	-17	17	41	-12	12
170	69	-15	23	65	-15	27	69	-18	29	50	-14	14	42	-10	10
200	70	-13	22	64	-14	27	68	-16	27	52	-15	16	44	-10	10
230	70	-12	21	65	-12	26	66	-15	27	51	-14	18	43	-9	11
260	69	-11	20	63	-11	24	65	-14	26	50	-13	17	42	-6	8
290	70	-10	19	65	-11	23	64	-13	24	48	-12	14	41	-7	9
320	70	-9	18	63	-9	23	65	-13	26	47	-11	15	40	-6	10
350	69	-9	17	64	-9	21	64	-11	24	48	-11	15	40	-6	8
380	69	-8	17	64	-8	22	63	-10	25	50	-10	16	39	-5	8
400	71	-8	18	64	-8	21	64	-11	25	47	-9	15	38	-6	8
420	68	-7	17	63	-8	22	66	-10	26	49	-9	16	40	-4	8
440	69	-8	17	64	-8	24	64	-10	26	49	-9	15	39	-5	7
460	72	-8	22	63	-7	26	64	-9	26	48	-8	15	38	-4	8

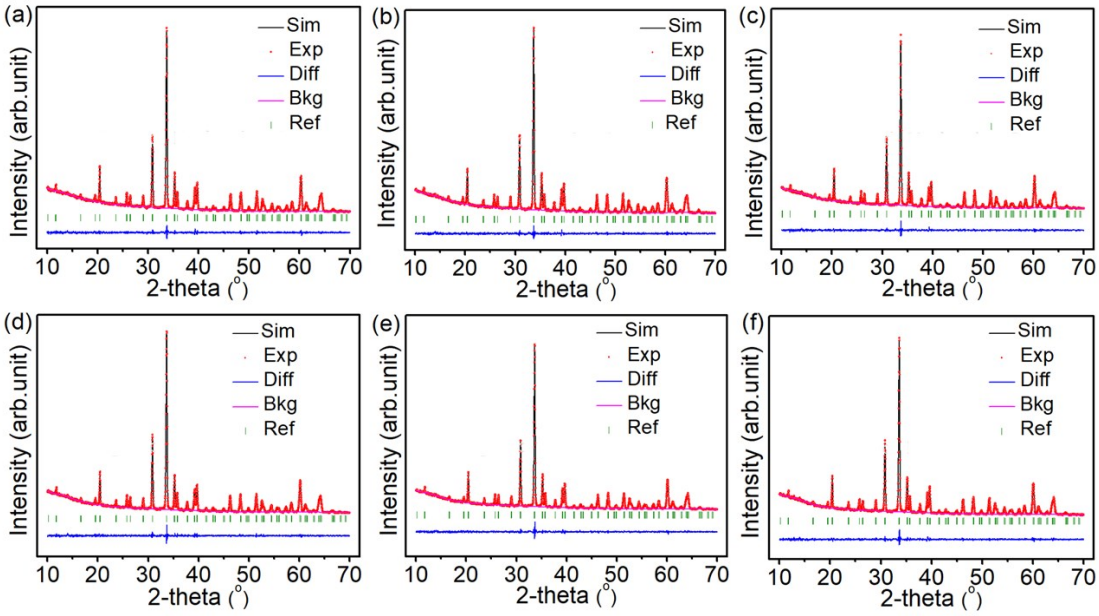

Figure S8. Pawley refinement of powder x-ray diffraction spectra (in heating process) of $Ca_{14}Zn_6Ga_{8.8}Mn_{1.2}O_{35}$ measured at (a) room temperature, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, and (f) 500 °C, respectively.

Table S6 Refinement results of powder x-ray diffraction spectra of $Ca_{14}Zn_6Ga_{8.8}Mn_{1.2}O_{35}$ at different temperature.

$Ca_{14}Zn_6Ga_{8.8}Mn_{1.2}O_{35}$						
T(°C)	Lattice Type	Space Group	Lattice (Å)	α (°)	R_{wp} (%)	R_p (%)
RT	Cubic	F23	15.0234(14)	90	3.60	2.71
100	Cubic	F23	15.0360(15)	90	3.68	2.80
200	Cubic	F23	15.0476(14)	90	3.64	2.81
300	Cubic	F23	15.0672(15)	90	3.68	2.81
400	Cubic	F23	15.0791(14)	90	3.87	3.04
500	Cubic	F23	15.0936(14)	90	3.66	2.82