Electronic Supplementary Material (ESI) for Dalton Transactions.

Temperature-driven order-disorder structural transition in oxygen sub-lattice and the complex superstructure of high temperature polymorph of $CaSrZn_2Ga_2O_7$

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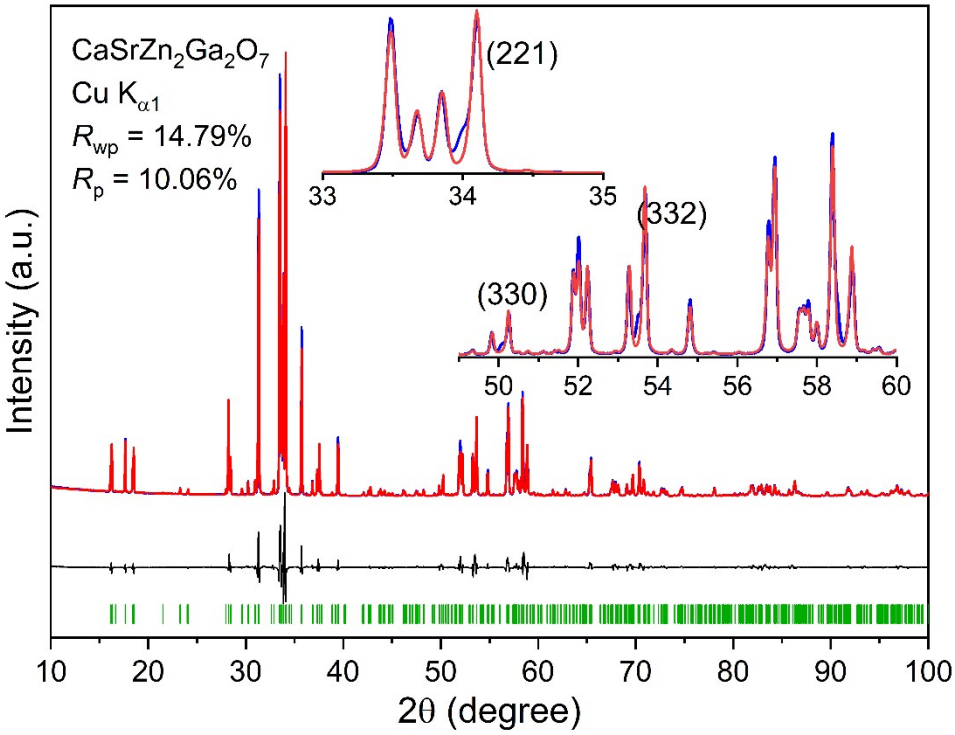
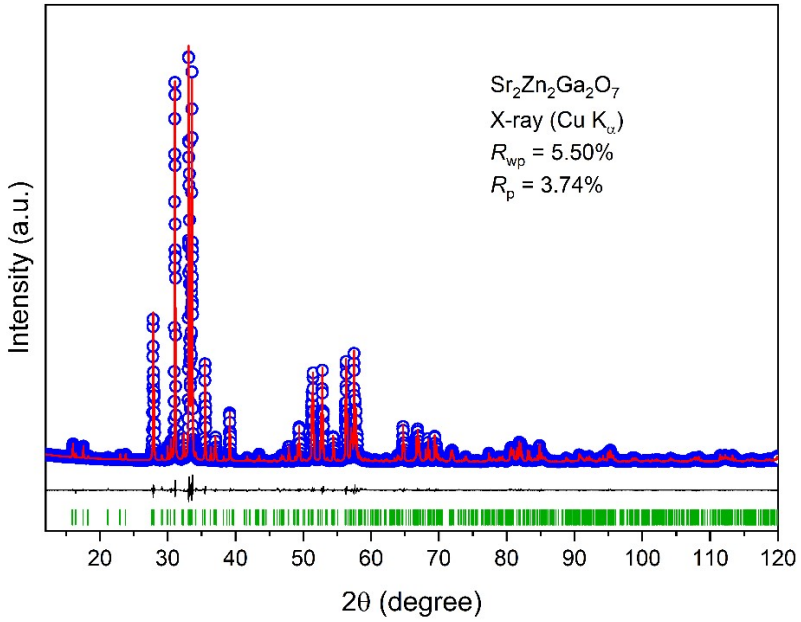
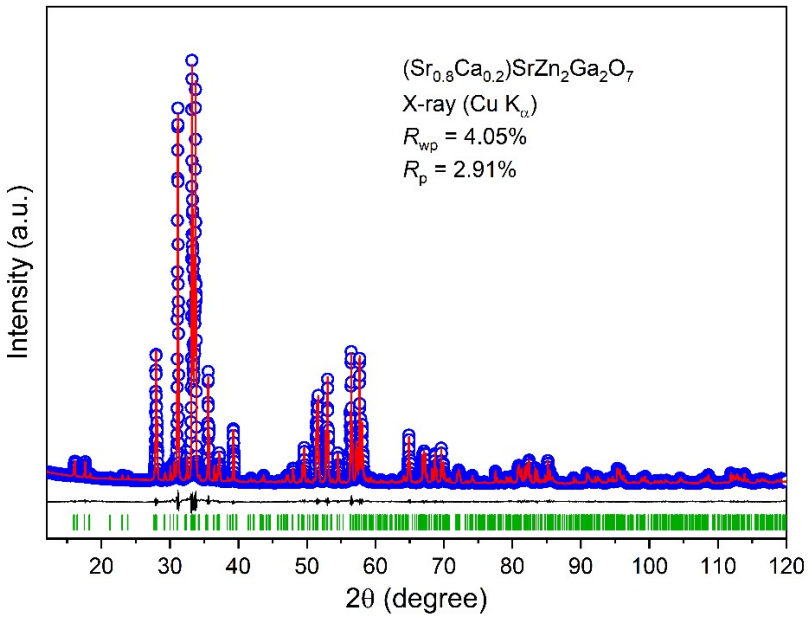
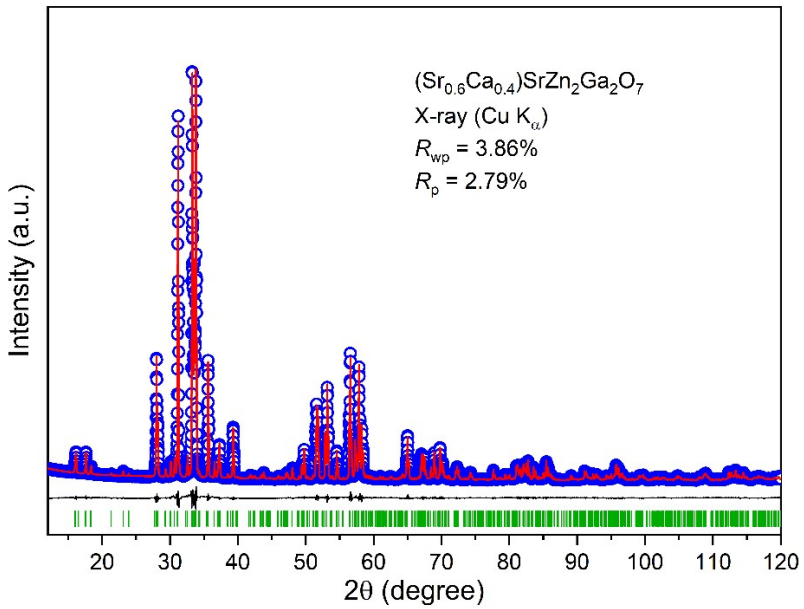
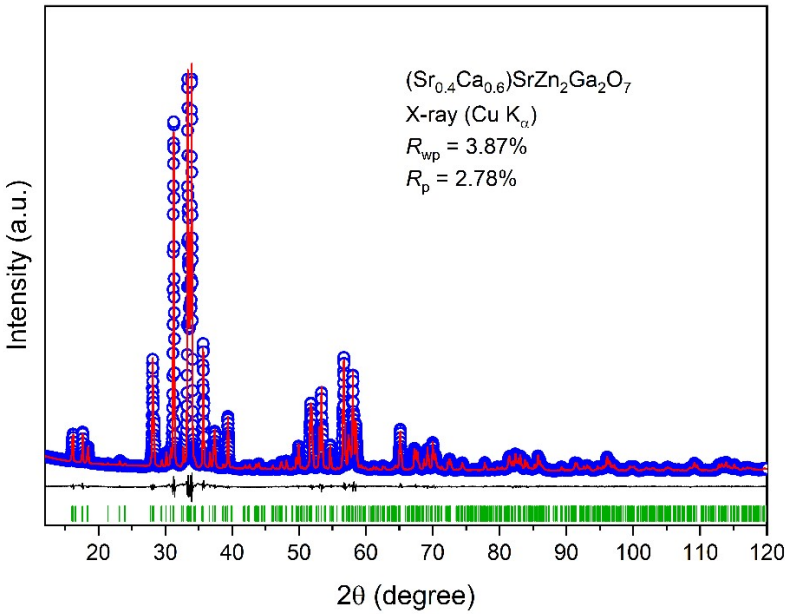


Fig. S1 Rietveld refinement plots of Cu $K_{\alpha 1}$ PXRD data for LT-$CaSrZn_2Ga_2O_7$. The inset shows a set of peaks that could not be fitted with the $Pna2_1$ model.




(Sr0.8Ca0.2)SrZn2Ga2O7
X-ray (Cu Kα)
Rwp = 4.05%
Rp = 2.91%
Intensity (a.u.)
20 30 40 50 60 70 80 90 100 110 120
2θ (degree)


(Sr0.6Ca0.4)SrZn2Ga2O7
X-ray (Cu Kα)
Rwp = 3.86%
Rp = 2.79%
Intensity (a.u.)
20 30 40 50 60 70 80 90 100 110 120
2θ (degree)


(Sr0.4Ca0.6)SrZn2Ga2O7
X-ray (Cu Kα)
Rwp = 3.87%
Rp = 2.78%
Intensity (a.u.)
20 30 40 50 60 70 80 90 100 110 120
2θ (degree)

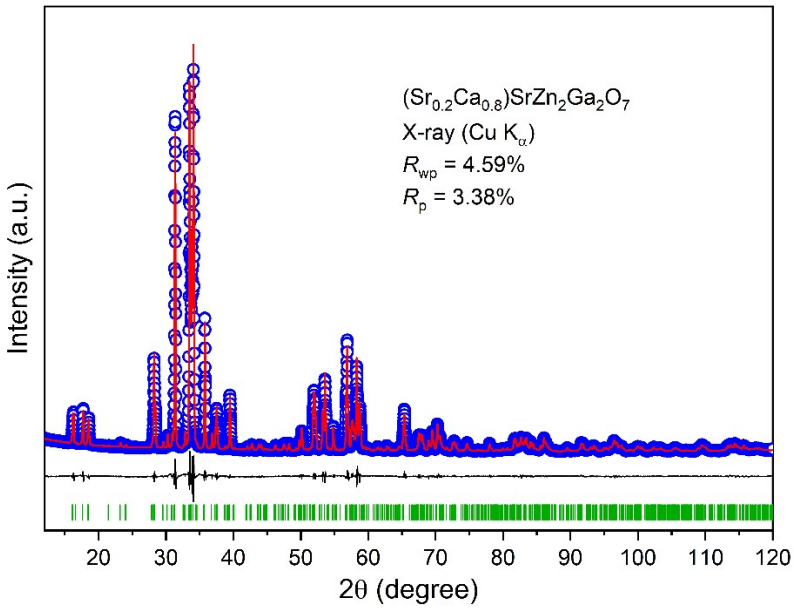


Fig. S2 Rietveld refinement patterns for orthorhombic LT-$(Sr_{1-x}Ca_x)SrZn_2Ga_2O_7$ (x = 0, 0.2, 0.4, 0.6, and 0.8).

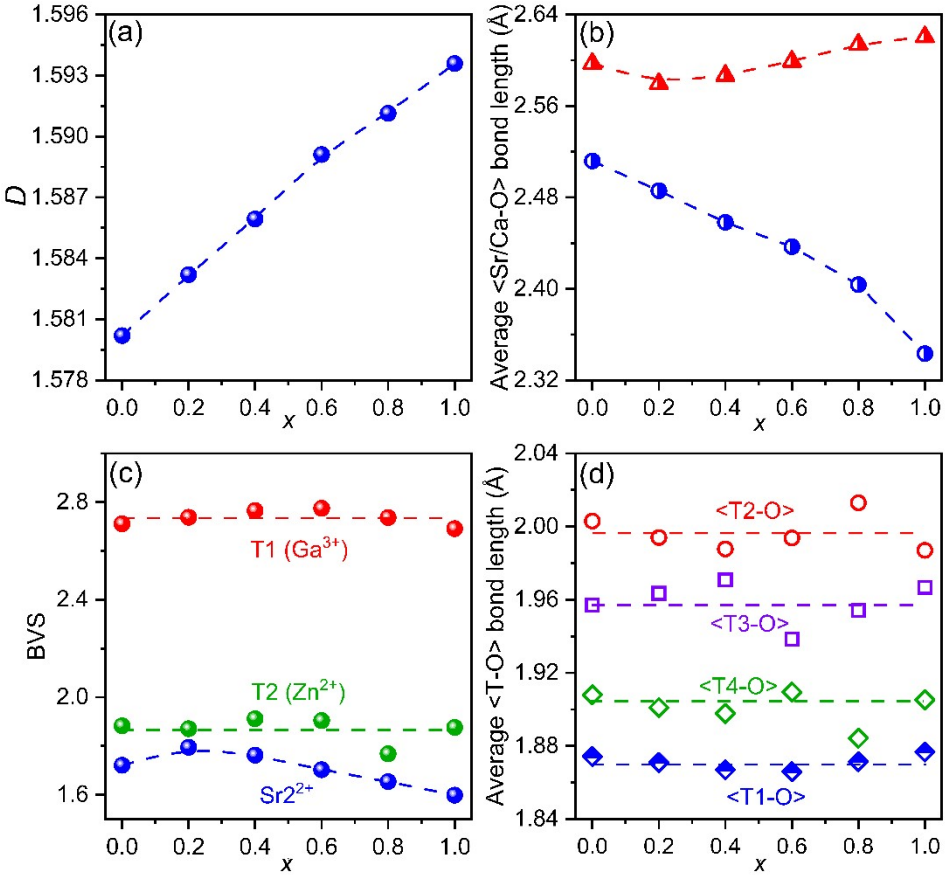
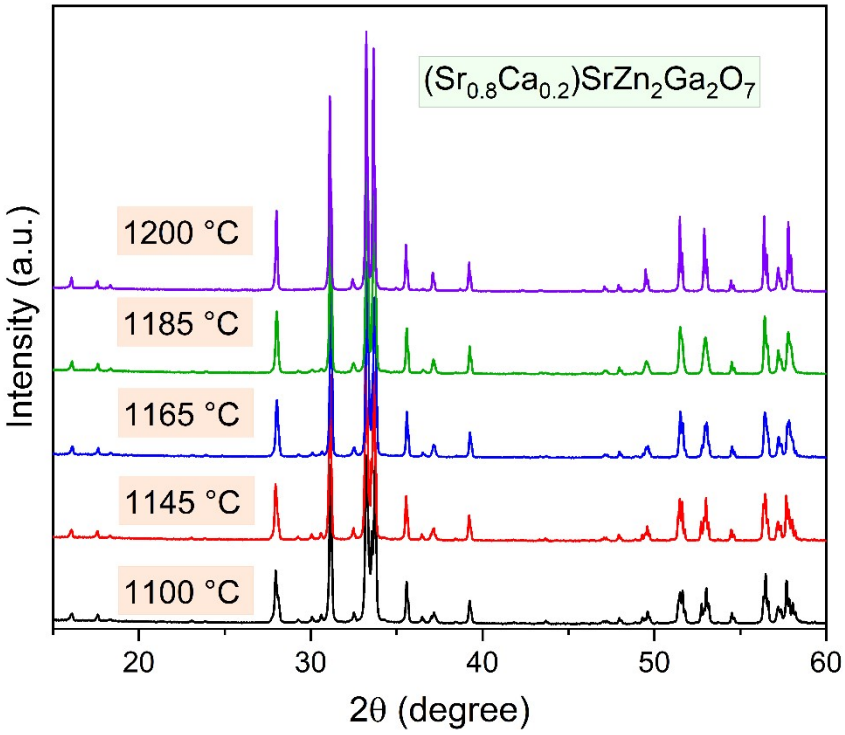
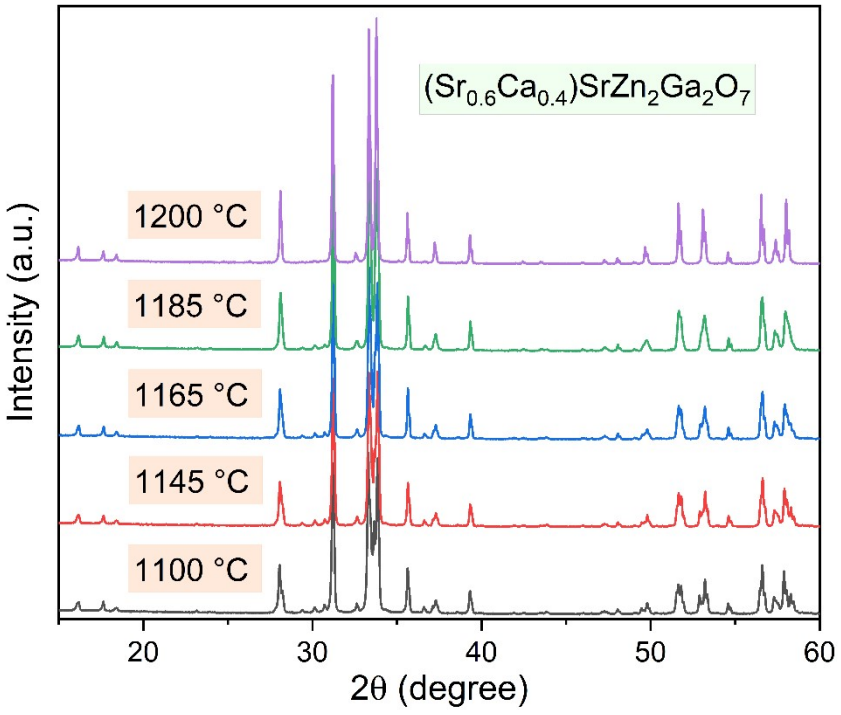
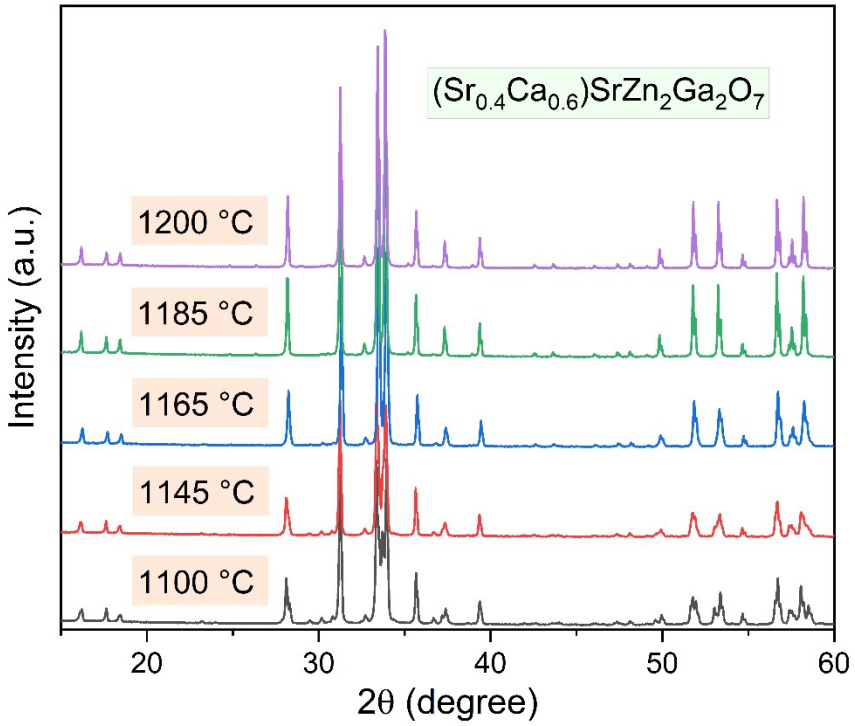
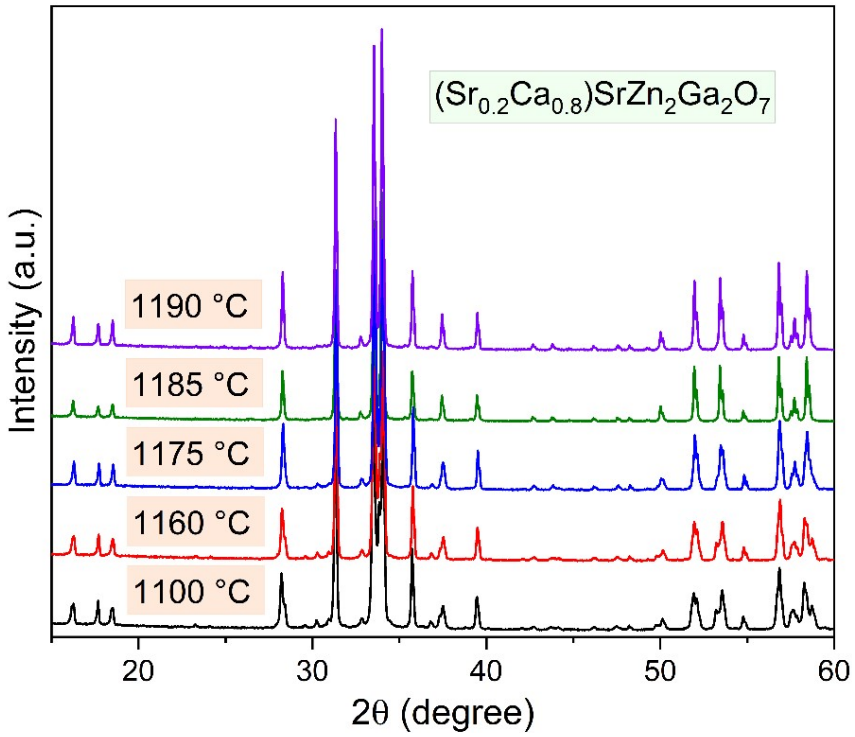


Fig. S3 Plots of distortion factor D (a), the average Sr1/Ca1-O and Sr2-O bond lengths (b), BVS values for Ga^{3+}, Zn^{2+}, and $Sr2^{2+}$ cations, and average T-O bond lengths versus Ca^{2+}-content (x) in $(Sr_{1-x}Ca_x)SrZn_2Ga_2O_7$ (x = 0-1).


(Sr0.8Ca0.2)SrZn2Ga2O7
1200 °C
1185 °C
1165 °C
1145 °C
1100 °C
Intensity (a.u.)
20
30
40
50
60
2θ (degree)


(Sr0.6Ca0.4)SrZn2Ga2O7
1200 °C
1185 °C
1165 °C
1145 °C
1100 °C
Intensity (a.u.)
20
30
40
50
60
2θ (degree)


(Sr0.4Ca0.6)SrZn2Ga2O7
1200 °C
1185 °C
1165 °C
1145 °C
1100 °C
Intensity (a.u.)
20
30
40
50
60
2θ (degree)


(Sr0.2Ca0.8)SrZn2Ga2O7
1190 °C
1185 °C
1175 °C
1160 °C
1100 °C
Intensity (a.u.)
20
30
40
50
60
2θ (degree)

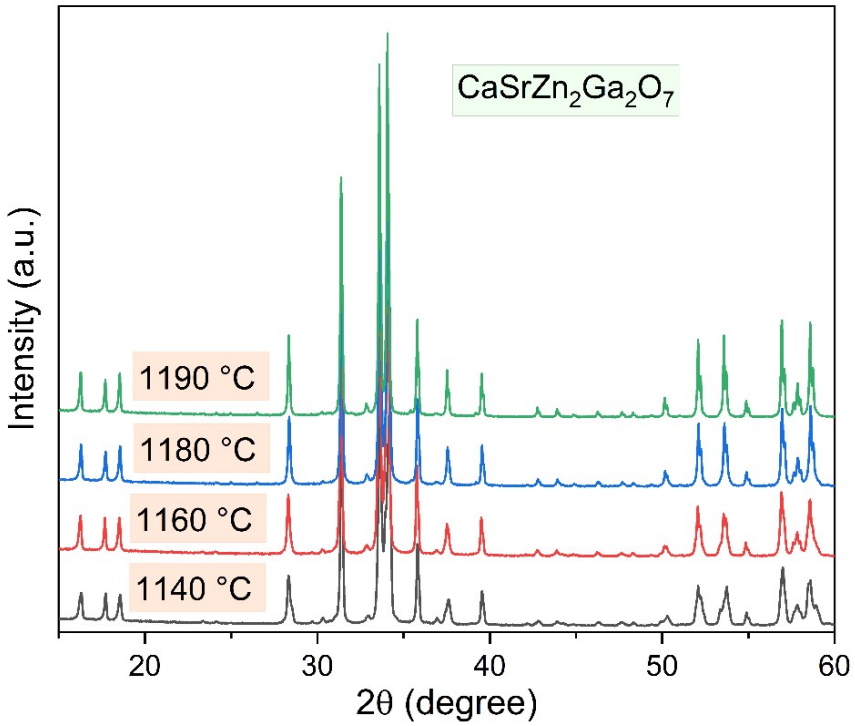


Fig. S4 The XRD patterns for $(Sr_{1-x}Ca_x)SrZn_2Ga_2O_7$ (x = 0.2, 0.4, 0.6, 0.8, and 1) after being calcinated at different temperatures.

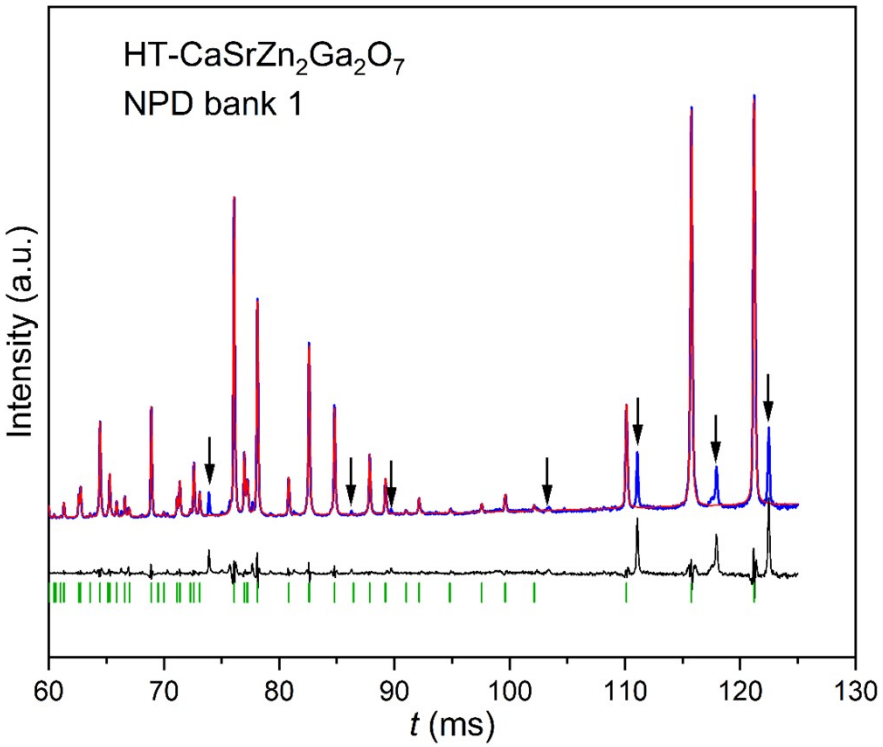


Fig. S5 Rietveld refinement plots of NPD data from bank 1 for HT $CaSrZn_2Ga_2O_7$ using the $P31c$ model. The black arrows represent the unindexed peaks.

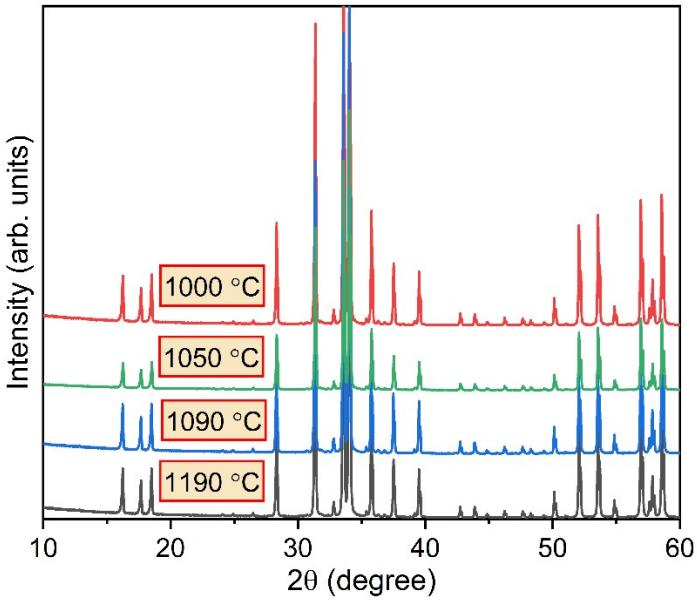


Fig. S6 PXRD patterns for $P6_3$-$CaSrZn_2Ga_2O_7$ after being annealed at 1090, 1050, and 1000 °C for 15 h.

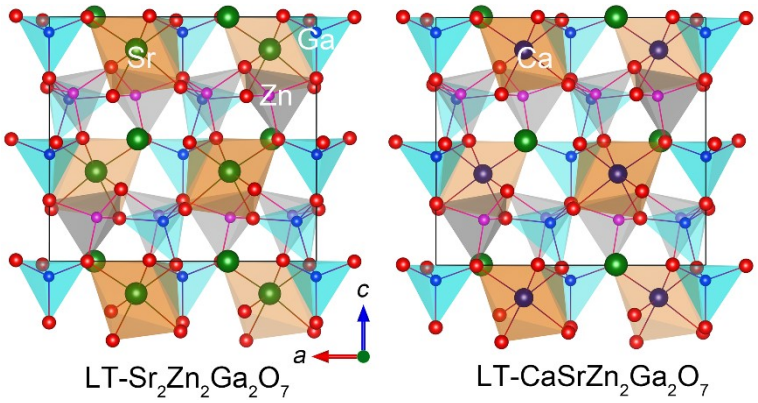


Fig. S7 Optimized LT structures for $CaSrZn_2Ga_2O_7$ and $Sr_2Zn_2Ga_2O_7$.

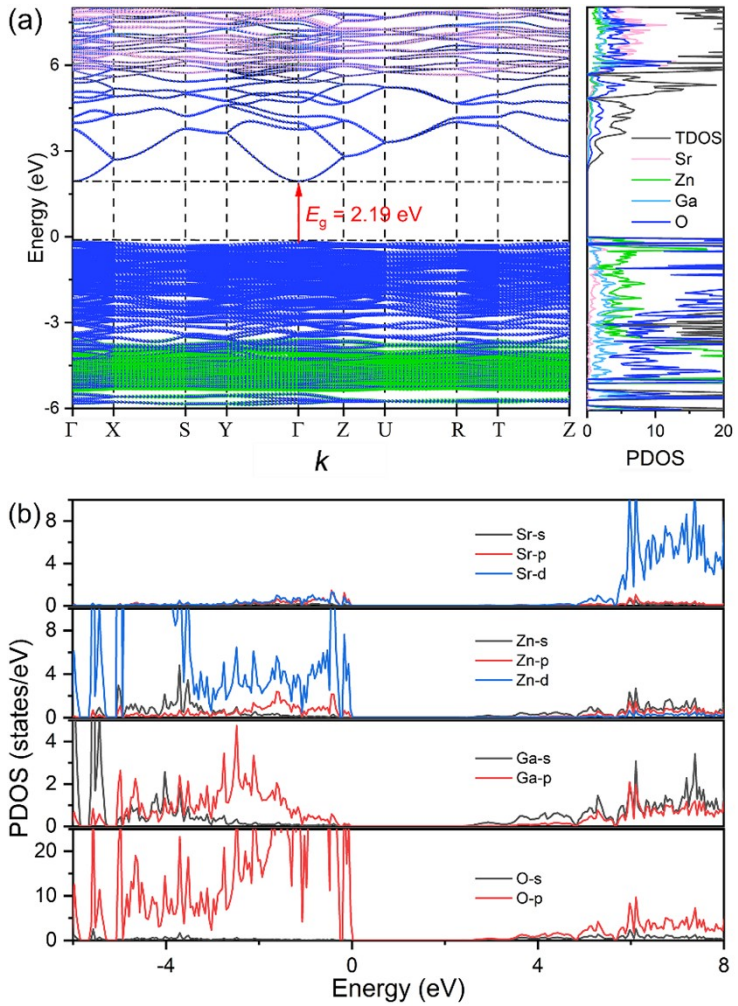


Fig. S8 (a) The electronic band structure and total DOS of LT orthorhombic $Sr_2Zn_2Ga_2O_7$. (b) The partial DOS of Sr, Zn, Ga, and O.

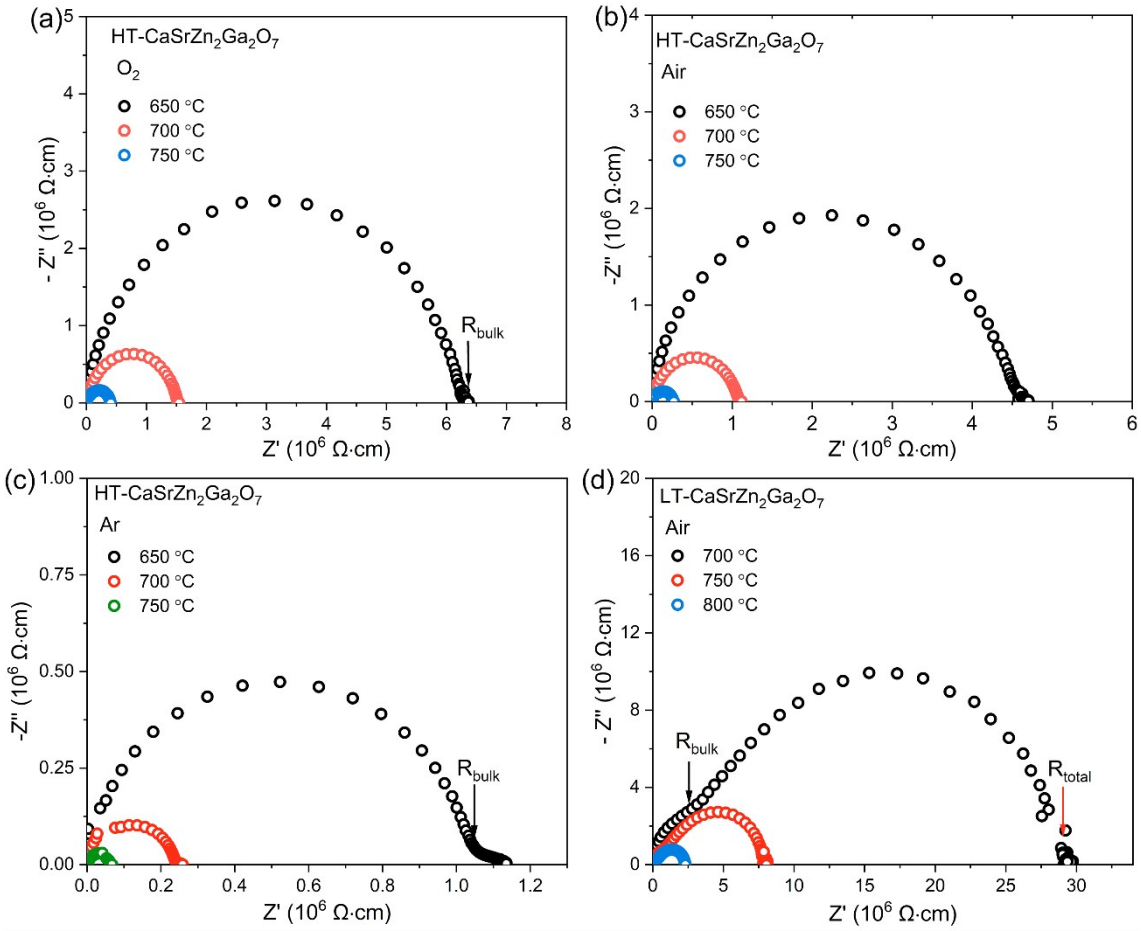


Fig. S9 Complex impedance spectra for HT-$CaSrZn_2Ga_2O_7$ measured in O2 (a), air (b), and Ar (c) at different temperatures. (d) Complex impedance spectra for LT-$CaSrZn_2Ga_2O_7$ measured in air.

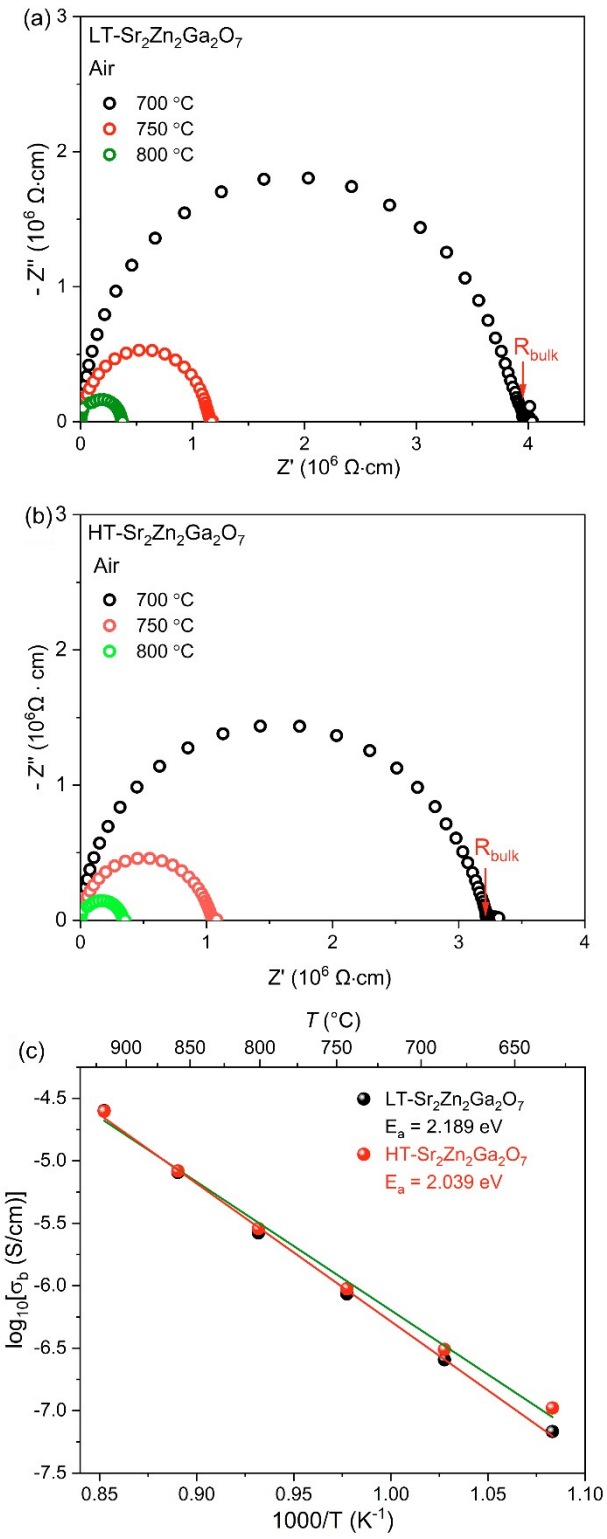


Fig. S10 Complex impedance spectra for LT-$Sr_2Zn_2Ga_2O_7$ (a) and HT-$Sr_2Zn_2Ga_2O_7$ (b) measured in air. (c) Arrhenius plots of bulk conductivities for LT- and HT-$Sr_2Zn_2Ga_2O_7$.

Table S1. Crystallographic data for LT $Sr_{2-x}Ca_xZn_2Ga_2O_7$ (x = 0, 0.2, 0.4, 0.6, and 0.8).

Source	Laboratory X-ray	Laboratory X-ray	Laboratory X-ray	Laboratory X-ray	Laboratory X-ray
Chemical formula	$Sr_2Zn_2Ga_2O_7$	$Sr_{1.8}Ca_{0.2}Zn_2Ga_2O_7$	$Sr_{1.6}Ca_{0.4}Zn_2Ga_2O_7$	$Sr_{1.4}Ca_{0.6}Zn_2Ga_2O_7$	$Sr_{1.2}Ca_{0.8}Zn_2Ga_2O_7$
Formula weight (g/mol)	557.50	547.99	538.48	528.97	519.47
Temperature (K)	300	300	300	300	300
Wavelength (Å)	Cu K_α, λ = 1.54060	Cu K_α, λ = 1.54060	Cu K_α, λ = 1.54060	Cu K_α, λ = 1.54060	Cu K_α, λ = 1.54060
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group (No.)	$Pna2_1$ (33)	$Pna2_1$ (33)	$Pna2_1$ (33)	$Pna2_1$ (33)	$Pna2_1$ (33)
Unit cell dimensions (Å)	a = 11.12385(4) b = 6.38024(3) c = 10.11548(4) $\alpha = \beta = \gamma = 90°$	a = 11.09618(5) b = 6.35839(3) c = 10.10473(5) $\alpha = \beta = \gamma = 90°$	a = 11.06463(5) b = 6.33441(3) c = 10.08874(5) $\alpha = \beta = \gamma = 90°$	a = 11.0321(1) b = 6.31190(7) c = 10.0761(1) $\alpha = \beta = \gamma = 90°$	a = 10.9968(1) b = 6.29129(6) c = 10.0564(1) $\alpha = \beta = \gamma = 90°$
V (Å^3)	717.824(5)	712.927(6)	707.099(6)	701.34(1)	695.74(1)
Z	4	4	4	4	4
d-space range (Å)	0.85-8.83	0.85-8.83	0.85-8.83	0.85-8.83	0.85-8.83
χ^2	2.67	3.78	3.58	4.52	4.18
R_p (%)	3.74	2.91	2.79	2.78	3.38
R_{wp} (%)	5.50	4.05	3.86	3.87	4.59
R_{exp} (%)	2.06	1.07	1.08	0.855	1.10

Table S2. Crystallographic data for LT and HT $CaSrZn_2Ga_2O_7$.

Source	Laboratory X-ray	Neutron
Chemical formula	$CaSrZn_2Ga_2O_7$	$CaSrZn_2Ga_2O_7$
Formula weight (g/mol)	509.96	509.96
Temperature (K)	300	300
Wavelength (Å)	Cu $K_{\alpha 1}$ (λ = 1.54060)	—
Crystal system	Orthorhombic	Hexagonal
Space group (No.)	$Pna2_1$ (33)	$P6_3$ (173)
Unit cell dimensions (Å)	a = 10.9664(4) b = 6.2664(2) c = 10.0380(3) $\alpha = \beta = \gamma = 90°$	a = 10.92134(4) b = 10.92134(4) c = 10.04737(6) $\alpha = \beta = 90°$, $\gamma = 120°$
V (Å^3)	689.80(4)	1034.90(1)
Z	4	6
d-space range (Å)	1.00-10.00	0.72-3.74
χ^2	3.67	3.18
R_p (%)	4.89	3.22
R_{wp} (%)	6.66	3.80
R_{exp} (%)	1.81	1.19

Table S3. The Atomic Coordinates, Occupancies, Isotropic Thermal Displacement Factors for LT $Sr_{2-x}Ca_xZn_2Ga_2O_7$ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) Obtained from Rietveld Refinements against X-ray Diffraction Data.

x = 0	Site	x	y	z	Occ.	$B_{eq.}$ (Å)
Sr1	4a	0.6731(1)	1.0002(1)	0.8687(1)	1	1.48(5)
Sr2	4a	0.6659(2)	0.0062(2)	0.5	1	1.42(5)
Ga1(T1)	4a	0.0017(3)	0.0141(3)	0.9377(3)	1	1.02(4)
Zn1(T2)	4a	0.1755(1)	0.9802(3)	0.6805(4)	1	0.93(4)
T3	4a	0.0873(2)	0.2497(3)	0.1902(2)	1	1.11(5)
T4	4a	0.9245(1)	0.2638(3)	0.6639(3)	1	0.91(6)
O1	4a	0.9971(9)	0.978(1)	0.2482(7)	1	0.64(6)
O2	4a	0.4901(7)	0.122(1)	0.2147(7)	1	0.64(6)
O3	4a	0.2700(7)	0.797(1)	0.7909(7)	1	0.64(6)
O4	4a	0.7410(7)	0.737(1)	0.1780(9)	1	0.64(6)
O5	4a	0.1475(7)	0.880(1)	0.500(1)	1	0.64(6)
O6	4a	0.1231(7)	0.169(1)	0.008(1)	1	0.64(6)
O7	4a	0.9738(7)	0.263(1)	0.4903(7)	1	0.64(6)
x = 0.2	Site	x	y	z	Occ.	$B_{eq.}$ (Å)
Sr1/Ca1	4a	0.6732(2)	0.0164(3)	0.8691(1)	0.8/0.2	0.27(7)
Sr2	4a	0.6660(2)	0.0088(3)	0.5	1	0.87(7)
Ga1(T1)	4a	0.0025(5)	0.0115(4)	0.9386(5)	1	1.02(4)
Zn1(T2)	4a	0.1755(2)	0.9890(4)	0.6805(5)	1	0.58(5)

T3	4a	0.0885(2)	0.2461(3)	0.1915(4)	1	0.30(6)
T4	4a	0.9242(2)	0.2675(4)	0.6662(4)	1	0.79(7)
O1	4a	0.002(1)	0.973(2)	0.2503(7)	1	0.51(9)
O2	4a	0.4870(8)	0.012(2)	0.2195(9)	1	0.51(9)
O3	4a	0.2701(9)	0.808(2)	0.7971(8)	1	0.51(9)
O4	4a	0.7466(9)	0.747(1)	0.174(1)	1	0.51(9)
O5	4a	0.1436(8)	0.882(1)	0.495(1)	1	0.51(9)
O6	4a	0.1224(8)	0.179(1)	0.010(1)	1	0.51(9)
O7	4a	0.9732(8)	0.268(1)	0.491(1)	1	0.51(9)

$x = 0.4$	Site	x	y	z	Occ.	$B_{eq.}$ (Å)
Sr1/Ca1	4a	0.6732(2)	0.0164(3)	0.8691(1)	0.6/0.4	0.27(7)
Sr2	4a	0.6660(2)	0.0088(3)	0.5	1	0.87(7)
Ga1(T1)	4a	0.0025(5)	0.0115(4)	0.9386(5)	1	1.02(4)
Zn1(T2)	4a	0.1755(2)	0.9890(4)	0.6805(5)	1	0.58(5)
T3	4a	0.0885(2)	0.2461(3)	0.1915(4)	1	0.30(6)
T4	4a	0.9242(2)	0.2675(4)	0.6662(4)	1	0.79(7)
O1	4a	0.002(1)	0.973(2)	0.2503(7)	1	0.51(9)
O2	4a	0.4870(8)	0.012(2)	0.2195(9)	1	0.51(9)
O3	4a	0.2701(9)	0.808(2)	0.7971(8)	1	0.51(9)
O4	4a	0.7466(9)	0.747(1)	0.174(1)	1	0.51(9)
O5	4a	0.1436(8)	0.882(1)	0.495(1)	1	0.51(9)
O6	4a	0.1224(8)	0.179(1)	0.010(1)	1	0.51(9)

O7	4a	0.9732(8)	0.268(1)	0.491(1)	1	0.51(9)
$x = 0.6$	Site	x	y	z	Occ.	$B_{eq.}$ (Å)
Sr1/Ca1	4a	0.6728(3)	0.0160(5)	0.8700(2)	0.4/0.6	0.22(8)
Sr2	4a	0.6663(3)	0.0065(3)	0.9377(5)	1	1.29(7)
Ga1(T1)	4a	0.0014(5)	0.0104(4)	0.9377(5)	1	0.67(4)
Zn1(T2)	4a	0.1747(2)	0.9910(5)	0.6809(5)	1	0.60(5)
T3	4a	0.0897(2)	0.2461(4)	0.1899(4)	1	0.22(7)
T4	4a	0.9239(2)	0.2673(3)	0.6674(4)	1	0.78(8)
O1	4a	0.006(1)	0.974(2)	0.2500(7)	1	0.22(9)
O2	4a	0.4849(8)	0.025(2)	0.2225(9)	1	0.22(9)
O3	4a	0.2667(9)	0.805(1)	0.7949(8)	1	0.22(9)
O4	4a	0.7463(9)	0.749(2)	0.176(1)	1	0.22(9)
O5	4a	0.1467(9)	0.887(1)	0.490(1)	1	0.22(9)
O6	4a	0.1187(8)	0.189(1)	0.008(1)	1	0.22(9)
O7	4a	0.9694(9)	0.271(1)	0.489(1)	1	0.22(9)
$x = 0.8$	Site	x	y	z	Occ.	$B_{eq.}$ (Å)
Sr1/Ca1	4a	0.6728(3)	0.0160(5)	0.8697(2)	0.2/0.8	0.22(8)
Sr2	4a	0.6663(3)	0.0065(3)	0.5	1	1.29(7)
Ga1(T1)	4a	0.0014(5)	0.0104(4)	0.9377(5)	1	0.67(4)
Zn1(T2)	4a	0.1747(2)	0.9910(5)	0.6809(5)	1	0.60(5)
T3	4a	0.0897(2)	0.2461(4)	0.1899(4)	1	0.22(7)
T4	4a	0.9239(2)	0.2673(4)	0.6674(4)	1	0.78(8)

O1	4a	0.006(1)	0.974(2)	0.2500(7)	1	0.22(9)
O2	4a	0.4849(8)	0.025(1)	0.2225(9)	1	0.22(9)
O3	4a	0.2667(9)	0.805(1)	0.7949(8)	1	0.22(9)
O4	4a	0.7462(9)	0.749(2)	0.176(1)	1	0.22(9)
O5	4a	0.1467(9)	0.887(1)	0.490(1)	1	0.22(9)
O6	4a	0.1187(8)	0.189(1)	0.008(1)	1	0.22(9)
O7	4a	0.9694(9)	0.270(1)	0.489(1)	1	0.22(9)

$x = 1$	Site	x	y	z	Occ.	$B_{eq.}$ (Å)
Ca1	4a	0.6711(4)	0.0130(6)	0.8694(4)	1	0.20(8)
Sr2	4a	0.6668(2)	0.0039(3)	0.5	1	1.14(5)
Ga1(T1)	4a	0.0006(4)	0.0086(4)	0.9383(4)	1	0.44(1)
Zn1(T2)	4a	0.1755(2)	0.9890(4)	0.6823(4)	1	0.44(1)
T3	4a	0.0900(2)	0.2508(3)	1915(4)	1	0.44(1)
T4	4a	0.9219(2)	0.2633(3)	6705(4)	1	0.44(1)
O1	4a	0.001(1)	0.982(2)	0.251(1)	1	0.19(8)
O2	4a	0.4869(8)	0.008(2)	0.2273(9)	1	0.19(8)
O3	4a	0.2609(8)	0.785(1)	0.7984(9)	1	0.19(8)
O4	4a	0.7471(9)	0.727(1)	0.190(1)	1	0.19(8)
O5	4a	0.1513(8)	0.901(1)	0.499(1)	1	0.19(8)
O6	4a	0.1204(7)	0.196(1)	0.004(1)	1	0.19(8)
O7	4a	0.9658(8)	0.276(1)	0.488(1)	1	0.19(8)

Table S4. Selected interatomic distances (Å) in LT $(Sr_{1-x}Ca_x)SrZn_2Ga_2O_7$ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1.0) obtained from Rietveld refinements against high-quality PXRD data.

			x = 0		
Sr1-O3	2.316(9)	Sr2-O5	2.472(7)	T1-O6	1.819(8)
Sr1-O2	2.394(8)	Sr2-O4	2.540(8)	T1-O7	1.866(7)
Sr1-O5	2.515(8)	Sr2-O3	2.562(7)	T1-O5	1.899(8)
Sr1-O7	2.543(7)	Sr2-O7	2.597(7)	T1-O1	1.918(7)
Sr1-O6	2.600(8)	Sr2-O6	2.601(7)	T2-O3	1.929(9)
Sr1-O4	2.626(8)	Sr2-O2	2.782(8)	T2-O5	1.96(1)
T3-O2	1.881(9)	T4-O7	1.840(8)	T2-O4	2.026(8)
T3-O3	1.911(8)	T4-O4	1.865(8)	T2-O1	2.06(1)
T3-O6	1.95(1)	T4-O2	1.918(9)		
T3-O1	2.089(9)	T4-O1	1.965(9)		
			x = 0.2		
Sr1/Ca-O2	2.340(9)	Sr2-O3	2.463(9)	T1-O5	1.846(11)
Sr1/Ca-O3	2.44(1)	Sr2-O5	2.499(8)	T1-O6	1.85(1)
Sr1/Ca-O6	2.47(1)	Sr2-O4	2.52(1)	T1-O7	1.878(9)
Sr1/Ca-O5	2.49(1)	Sr2-O7	2.567(9)	T1-O1	1.906(9)
Sr1/Ca-O7	2.57(1)	Sr2-O6	2.637(9)	T2-O4	1.89(1)
Sr1/Ca-O4	2.61(1)	Sr2-O2	2.796(9)	T2-O3	1.95(1)
T3-O6	1.92(1)	T4-O7	1.86(1)	T2-O5	2.03(1)
T3-O2	1.93(1)	T4-O4	1.90(1)	T2-O1	2.11(1)
T3-O3	1.94(1)	T4-O2	1.92(1)		
T3-O1	2.07(1)	T4-O1	1.93(1)		
			x = 0.4		
Sr1/Ca-O2	2.319(9)	Sr2-O3	2.470(8)	T1-O5	1.84(1)
Sr1/Ca-O3	2.418(9)	Sr2-O4	2.510(7)	T1-O6	1.86(1)
Sr1/Ca-O6	2.427(9)	Sr2-O5	2.51(1)	T1-O7	1.880(8)
Sr1/Ca-O5	2.436(9)	Sr2-O7	2.584(9)	T1-O1	1.886(8)
Sr1/Ca-O7	2.538(9)	Sr2-O6	2.641(8)	T2-O4	1.871(9)

Sr1/Ca-O4	2.61(1)	Sr2-O2	2.804(9)	T2-O3	1.942(9)
T3-O6	1.92(1)	T4-O7	1.86(1)	T2-O5	2.03(1)
T3-O2	1.94(1)	T4-O4	1.90(1)	T2-O1	2.11(1)
T3-O3	1.950(9)	T4-O2	1.92(1)		
T3-O1	2.07(1)	T4-O1	1.92(1)		
		$x = 0.6$			
Sr1/Ca-O2	2.301(9)	Sr2-O5	2.492(7)	T1-O5	1.84(1)
Sr1/Ca-O3	2.40(1)	Sr2-O3	2.497(9)	T1-O6	1.86(1)
Sr1/Ca-O6	2.40(1)	Sr2-O4	2.54(1)	T1-O7	1.875(9)
Sr1/Ca-O5	2.41(1)	Sr2-O7	2.59(1)	T1-O1	1.896(8)
Sr1/Ca-O7	2.51(1)	Sr2-O6	2.68(1)	T2-O4	1.86(1)
Sr1/Ca-O4	2.60(1)	Sr2-O2	2.801(9)	T2-O3	1.93(1)
T3-O2	1.88(1)	T4-O7	1.87(1)	T2-O5	2.06(1)
T3-O6	1.89(1)	T4-O4	1.88(1)	T2-O1	2.13(1)
T3-O3	1.94(1)	T4-O1	1.90(1)		
T3-O1	2.04(1)	T4-O2	1.99(1)		
		$x = 0.8$			
Sr1/Ca-O2	2.28(1)	Sr2-O3	2.51(1)	T1-O5	1.83(1)
Sr1/Ca-O3	2.33(1)	Sr2-O5	2.515(8)	T1-O6	1.87(1)
Sr1/Ca-O6	2.34(1)	Sr2-O4	2.54(1)	T1-O7	1.89(1)
Sr1/Ca-O5	2.38(1)	Sr2-O7	2.57(1)	T1-O1	1.904(9)
Sr1/Ca-O7	2.50(1)	Sr2-O6	2.70(1)	T2-O4	1.93(1)
Sr1/Ca-O4	2.52(1)	Sr2-O2	2.84(1)	T2-O3	1.96(1)
T3-O2	1.87(1)	T4-O4	1.84(1)	T2-O5	2.05(1)
T3-O6	1.93(1)	T4-O7	1.85(1)	T2-O1	2.11(1)
T3-O3	1.95(1)	T4-O1	1.88(1)		
T3-O1	2.06(1)	T4-O2	1.97(1)		
		$x = 1$			
Ca-O3	2.23(1)	Sr2-O3	2.544(9)	T1-O5	1.86(1)
Ca-O2	2.25(1)	Sr2-O5	2.544(7)	T1-O6	1.88(1)

Ca-O6	2.34(1)	Sr2-O4	2.55(1)	T1-O1	1.88(1)
Ca-O5	2.40(1)	Sr2-O7	2.604(9)	T1-O7	1.887(8)
Ca-O4	2.42(1)	Sr2-O6	2.648(8)	T2-O5	1.94(1)
Ca-O7	2.43(1)	Sr2-O2	2.838(9)	T2-O3	1.966(9)
T3-O2	1.92(1)	T4-O4	1.88(1)	T2-O4	1.97(1)
T3-O6	1.95(1)	T4-O7	1.89(1)	T2-O1	2.07(1)
T3-O3	1.968(9)	T4-O2	1.92(1)		
T3-O1	2.03(1)	T4-O1	1.93(1)		

Table S5. Selected interatomic distances (Å) in HT $CaSrZn_2Ga_2O_7$ obtained from Rietveld refinements against NPD data.

Ca-O1	2.11(3)	Sr-O8	2.46(2)	Ga1-O7 × 3	1.88(1)
Ca-O9′	2.26(4)	Sr-O9	2.54(2)	Ga1-O4	1.89(2)
Ca-O3	2.32(2)	Sr-O1′	2.59(2)	Ga1-O7′ × 3	1.90(9)
Ca-O7′	2.33(6)	Sr-O1	2.63(3)	Ga2-O8 × 3	1.81(2)
Ca-O2	2.33(3)	Sr-O2	2.68(2)	Ga2-O8′ × 3	1.86(3)
Ca-O8′	2.34(4)	Sr-O8′	2.70(3)	Ga2-O5	1.87(1)
Ca-O1′	2.38(2)	Sr-O7	2.71(1)	Ga3-O9 × 3	1.79(2)
Ca-O9	2.42(2)	Sr-O3	2.71(1)	Ga3-O9′ × 3	1.85(3)
Ca-O8	2.46(2)	Sr-O9′	2.71(3)	Ga6-O6	1.94(1)
Ca-O7	2.55(2)	Sr-O7′	2.80(8)		
Zn1-O7	1.73(1)	Zn2/Ga4-O1′	1.88(2)	Zn3/Ga5-O2	1.90(2)
Zn1-O7′	1.92(2)	Zn2/Ga4-O3	1.88(2)	Zn3/Ga5-O1′	1.92(3)
Zn1-O3	1.92(2)	Zn2/Ga4-O6	1.95(1)	Zn3/Ga5-O9′	1.98(4)
Zn1-O2	1.92(2)	Zn2/Ga4-O8′	1.98(3)	Zn3/Ga5-O5	1.99(1)
Zn1-O4	2.06(1)	Zn2/Ga4-O8	2.02(2)	Zn3/Ga5-O9	2.05(2)
		Zn2/Ga4-O1	2.00(3)	Zn3/Ga5-O1	2.02(4)

Definition of the tolerance factor in $(Sr_{1-x}Ca_x)SrZn_2Ga_2O_7$.

As described in the main text, the structure of $(Sr_{1-x}Ca_x)SrZn_2Ga_2O_7$ is isostructural to the archetype structure of $P6_3mc$-$YBaCo_4O_7$, which is built by alternatively mixed hexagonal closed packing BaO_3-layers [AO_3] and cubic closed packing O_4-layers. The octahedral (M) and tetrahedral (T) cavities are partially occupied by Y^{3+} and $Co^{2+/3+}$ ions. As shown in Fig. S11, the framework structure of MAT_4O_7 is composed of MO_6, AO_{12}, and TO_4 polyhedra. Assuming that all these polyhedra are undistorted, hence the cell dimensions (a and c) and the M-O ($d_{M\text{-}O}$) and A-O ($d_{A\text{-}O}$) bond distances can be expressed in terms of the T-O bond distance ($d_{T\text{-}O}$), as given below:

$$a_{ideal} = \frac{4\sqrt{6}}{3} d_{T-O} \quad \textbf{(1)}$$

$$c_{ideal} = \frac{16}{3} d_{T-O} \quad \textbf{(2)}$$

$$d_{M-O} = \frac{2}{\sqrt{3}} d_{T-O} \quad \textbf{(3)}$$

$$d_{A-O} = \frac{4}{\sqrt{6}} d_{T-O} \quad \textbf{(4)}$$

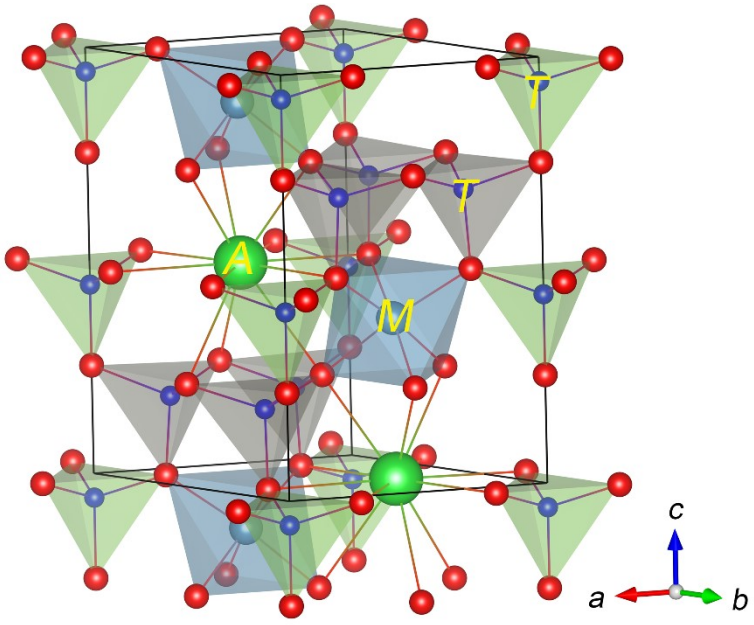


Fig. S11 Structural view of the $P6_3mc$-model for MAT_4O_7 oxides.

According to equations **3** and **4**, we can further obtain the following equations

$$\frac{d_{A-O}}{d_{M-O}} = \frac{2}{\sqrt{2}} = \sqrt{2} \quad \textbf{(5)}$$

$$\frac{R_A + R_O}{R_M + R_O} = \sqrt{2} \quad \textbf{(6)}$$

where R_A, R_M and R_O represent the radii of *A*, *M*, and O ions. Equations **5** and **6** share the same expression as the tolerance factor (τ) that defined by the radii of *A*, *B*, and O ions in ABO_3 perovskite. Furthermore, amongst the $Sr_{1-x}Ca_xSrZn_2Ga_2O_7$ series, the *T*-site Zn^{2+} and Ga^{3+} cations remained unchanged and we just adjusted the *M*-site cation size. Therefore, the structural flexibility or stability for the compounds with the general formula $MAZn_2Ga_2O_7$ can be assessed by the tolerance factor $\tau = (R_A + R_O)/\sqrt{2}(R_M + R_O)$.