

“Stabilization of the trigonal langasite structure in $\text{Ca}_3\text{Ga}_{2-2x}\text{Zn}_x\text{Ge}_{4+x}\text{O}_{14}$ ($0 \leq x \leq 1$) with partial ordering of three isoelectronic cations characterized by a multi-technique approach”

Haytem Bazzouai^a, Cécile Genevois^a, Dominique Massiot^a, Vincent Sarou-Kanian^a, Emmanuel Veron^a, Sébastien Chenu^b, Přemysl Beran^{c,d}, Michael J. Pitcher^{a*} and Mathieu Allix^{a*}

^a CEMHTI, CNRS UPR 3079, 1d Avenue de la Recherche Scientifique, 45071 Orléans, France.

^b Rennes Institute of Chemical Sciences, UMR CNRS 6226, Beaulieu Campus, 263 Av. Général Leclerc, 35042 Rennes, France

^c Nuclear Physics Institute of the CAS, Hlavní 130, 250 68 Řež, Czech Republic

^d European Spallation Source, ESS ERIC, Box 176, SE-22100 Lund, Sweden

E-mail: mathieu.allix@cnrs-orleans.fr michael.pitcher@cnrs-orleans.fr

Contents

I. Solid-state synthesis of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$	3
II. ^{71}Ga NMR study of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$	5
III. Tables S1 – S11	6
IV. Figures S1 – S16	11

I. Solid-state synthesis of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$:

The feasibility of classic solid-state methods for the synthesis of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ($x=0$) was evaluated by in-situ PXRD. A reaction mixture was prepared from high purity reagents CaCO_3 , Ga_2O_3 and GeO_2 which were ground in an agate mortar under ethanol. Once dried, the mixture was loaded into a platinum-lined corundum sample holder for variable temperature powder X-ray diffraction measurements (VT-PXRD). The reaction products at 1200 °C were a langasite type compound “ $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ” as the main phase, with a substantial amount of CaGeO_3 and Ga_2O_3 as secondary phases (see Figure I.1, below), indicating an incomplete reaction. The melting point of the mixture at ~1250°C precludes the use of higher temperatures, implying that several cycles of grinding and refiring at ~1200°C would be required to obtain a phase pure $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ceramic in this system.

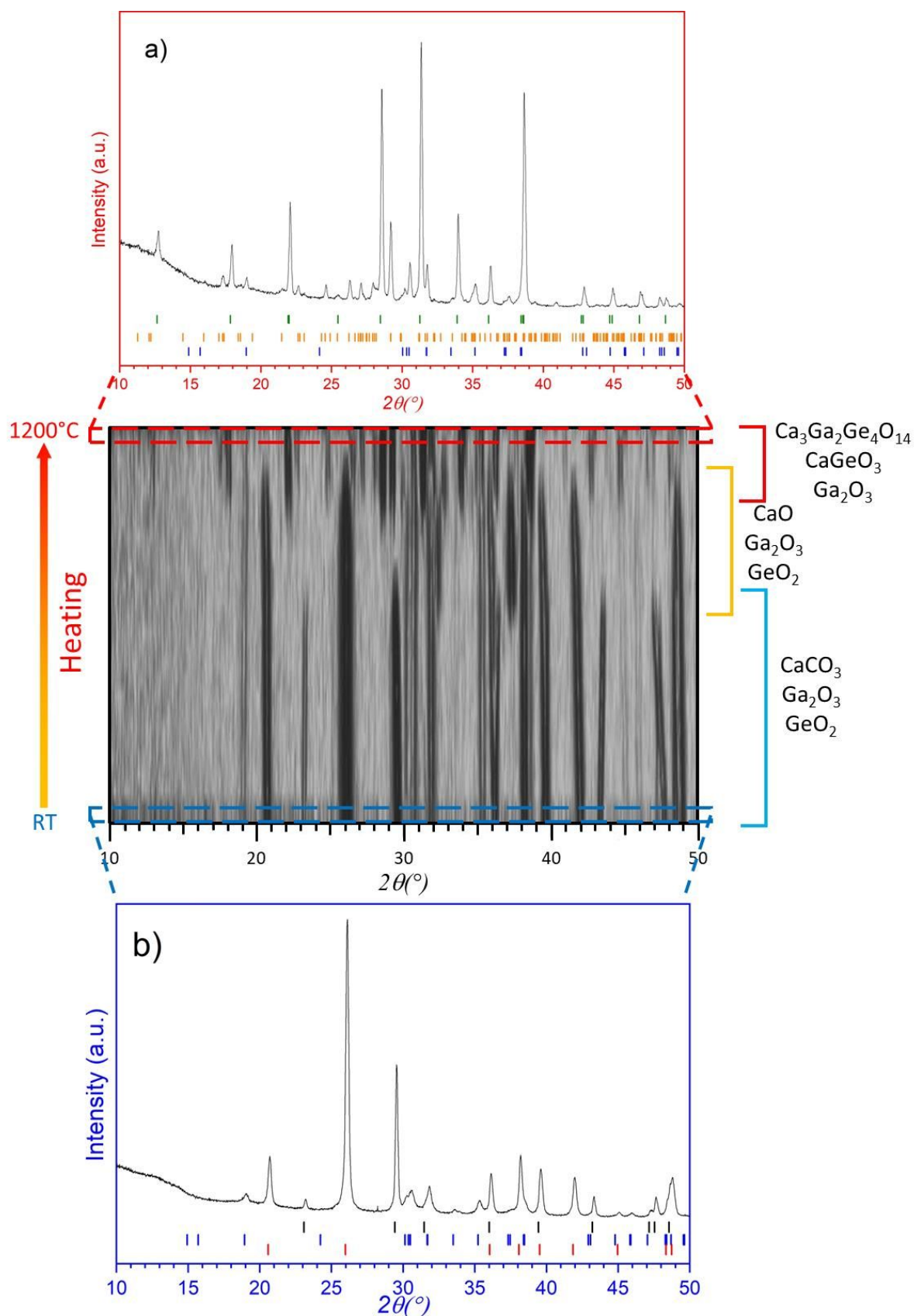


Figure I.1. In-situ powder X-ray diffraction (VT-PXRD) data of a $\text{CaCO}_3\text{-Ga}_2\text{O}_3\text{-GeO}_2$ mixture, with respect of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ nominal composition, between room temperature and 1200°C . a) and b) inserts show the indexed diffraction patterns at room temperature and 1200°C , with the different color tickmarks corresponding to, CaCO_3 (black), Ga_2O_3 (blue), GeO_2 (red), $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ (green) and CaGeO_3 (orange).

II. ^{71}Ga NMR study of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$.

^{71}Ga NMR is a powerful tool to probe the Ga local structure in terms of coordination and also to provide a quantification of its different environments ^{1,2}. ^{71}Ga solid-state NMR spectroscopy was performed on the $x = 0$ member only ($\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$) at 20 T with a Bruker Avance Neo spectrometer equipped with a 0.7 mm magic angle spinning (MAS) double resonance Bruker probe-head. The powdered sample was spun at a MAS frequency of 100 kHz. Given the wide spectral broadening of the ^{71}Ga NMR environments, a radiofrequency field of 125 kHz was used, which corresponds to 90° and 180° central-transition selective pulses of 1 μs and 2 μs , respectively. A spin-echo experiment was recorded using a full echo acquisition (interpulse delay of 150 μs), a recycling delay of 2 s, and with 26,000 scans. Furthermore, a two-dimensional QPASS (Quadrupolar Phase-Adjusted Spinning Sidebands)³ experiment was performed in order to improve the spectral resolution of the Ga environments by separating the overlapping spinning sidebands. Eight sets of timings (constant full duration of seven rotor periods) were needed for a proper separation, with a recycling delay of 2 s, and 8,000 scans per set of timings. The spectra were referenced to a 1 mol gallium nitrate solution.

As shown in Figure II.1 (below), the spectrum obtained from the spin-echo experiment lacks resolution because of overlapping spinning sidebands, even at ultra-high MAS frequency (100 kHz). The “spinning sidebands-free” QPASS spectrum allows to achieve ultimate spectral resolution and clearly identifies two contributions located at ca. 0 ppm and 100 ppm corresponding to 6-coordinated and 4-coordinated Ga respectively. However, the complexity of the QPASS experiment does not allow a precise quantification of the two Ga environments. The observed ^{71}Ga lineshapes have smoothed profiles as opposed to singularities expected for fully ordered crystalline phases, indicative of geometrical and chemical disorder of both Ga environments in the second coordination sphere.

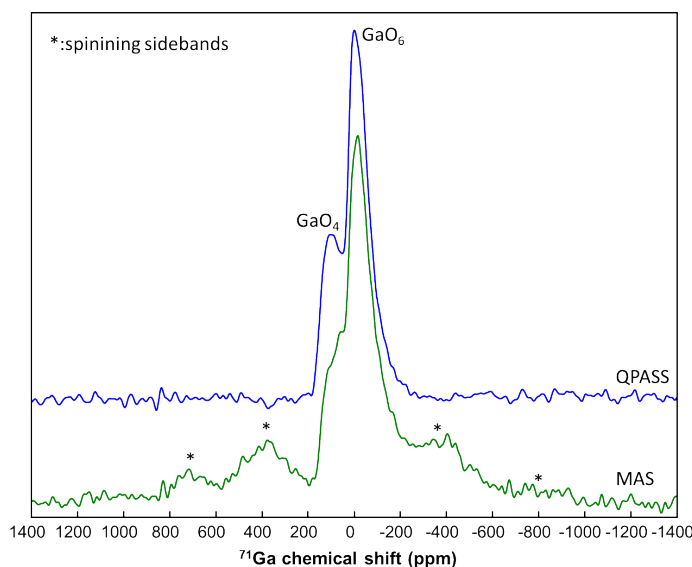


Figure II.1. ^{71}Ga NMR spectra acquired on sample of composition $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ($x=0$) by a MAS spin echo (green) and a QPASS (blue) experiments, showing the two coordination types of Ga in the sample.

Table S1. Glass transition and crystallisation temperatures extracted from DSC measurements (data presented in Figure 2 of the main text).

	Glass transition temperature $T_g(^{\circ}\text{C})$	Exothermal peak onset point (crystallisation temperature $T(^{\circ}\text{C})$)
$\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ($x=0$)	688 $^{\circ}\text{C}$	830 $^{\circ}\text{C}$
$\text{Ca}_3\text{Ga}_{1.5}\text{Zn}_{0.25}\text{Ge}_{4.25}\text{O}_{14}$ ($x=0.25$)	674 $^{\circ}\text{C}$	832 $^{\circ}\text{C}$
$\text{Ca}_3\text{GaZn}_{0.5}\text{Ge}_{4.5}\text{O}_{14}$ ($x=0.5$)	665 $^{\circ}\text{C}$	812 $^{\circ}\text{C}$
$\text{Ca}_3\text{Ga}_{0.5}\text{Zn}_{0.75}\text{Ge}_{4.75}\text{O}_{14}$ ($x=0.75$)	648 $^{\circ}\text{C}$	770 $^{\circ}\text{C}$
$\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ ($x=1$)	642 $^{\circ}\text{C}$	747 $^{\circ}\text{C}$

Table S2. Refined structural parameters obtained from SPD data collected at room temperature on $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ($x=0$) ($P321$ space group, $a= 8.072032(6)$ Å and $c= 4.966435(5)$ Å) sample.

Atom	Position	x	y	z	Occ	B_{iso}
Ca	3e	0.42012(7)	0	0	1	0.96(1)
Ga1/Ge1	1a	0	0	0	0.4/0.6*	0.608(7)
Ga2/Ge2	3f	0.76255(3)	0	0.5	0.47/0.53*	0.679(5)
Ge3	2d	1/3	2/3	0.53090(8)	1	0.593(6)
O1	2d	1/3	2/3	0.1914(4)	1	1.21(2) ^a
O2	6g	0.4652(2)	0.3154(2)	0.3180(2)	1	1.21(2) ^a
O3	6g	0.2144(2)	0.0795(2)	0.7626(3)	1	1.21(2) ^a

*Fixed occupancy from ⁴

^a: constrained to refine to the same B_{iso} values.

Table S3. Refined structural parameters obtained from SPD data collected at room temperature on $\text{Ca}_3\text{Ga}_{1.5}\text{Zn}_{0.25}\text{Ge}_{4.25}\text{O}_{14}$ ($x=0.25$) ($P321$ space group, $a= 8.05847(2)$ Å and $c= 4.986577(14)$ Å) sample.

Atom	Position	x	y	z	Occ	B_{iso}
Ca	3e	0.41970(8)	0	0	1	1.02(1)
Ga1/Ge1/Zn1	1a	0	0	0	1*	1.04(1)
Ga2/Ge2/Zn2	3f	0.76349(4)	0	0.5	1*	0.90(1)
Ge3	2d	1/3	2/3	0.53149(10)	1	0.76(1)
O1	2d	1/3	2/3	0.1913(5)	1	1.40(3) ^a
O2	6g	0.4649(2)	0.3170(2)	0.3183(3)	1	1.40(3) ^a
O3	6g	0.2165(2)	0.0759(2)	0.7588(3)	1	1.40(3) ^a

*Site was set to be fully occupied without refining each atom occupancy

^a: constrained to refine to the same B_{iso} values.

Table S4. Refined structural parameters obtained from SPD data collected at room temperature on $\text{Ca}_3\text{GaZn}_{0.5}\text{Ge}_{4.5}\text{O}_{14}$ ($x=0.5$) ($P321$ space group, $a= 8.041920(12)$ Å and $c= 4.999015(8)$ Å) sample.

Atom	Position	x	y	z	Occ	B_{iso}
Ca	3e	0.41956(8)	0	0	1	1.00(1)
Ga1/Ge1/Zn1	1a	0	0	0	1*	1.15(1)
Ga2/Ge2/Zn2	3f	0.76427(4)	0	0.5	1*	1.006(6)
Ge3	2d	1/3	2/3	0.52968(9)	1	0.844(7)
O1	2d	1/3	2/3	0.1867(5)	1	1.72(2) ^a
O2	6g	0.4650(2)	0.3164(2)	0.3208(3)	1	1.72(2) ^a
O3	6g	0.21624(19)	0.0756(2)	0.7547(3)	1	1.72(2) ^a

*Site was set to be fully occupied without refining each atom occupancy

^a: constrained to refine to the same B_{iso} values.

Table S5. Refined structural parameters obtained from SPD data collected at room temperature on $\text{Ca}_3\text{Ga}_{0.5}\text{Zn}_{0.75}\text{Ge}_{4.75}\text{O}_{14}$ ($x=0.75$) ($P321$ space group, $a= 8.03574(2)$ Å and $c= 5.009068(17)$ Å) sample.

Atom	Position	x	y	z	Occ	B _{iso}
Ca	3e	0.41827(11)	0	0	1	0.92(2)
Ga1/Ge1/Zn1	1a	0	0	0	1*	1.26(2)
Ga2/Ge2/Zn2	3f	0.76488(6)	0	0.5	1*	0.971(1)
Ge3	2d	1/3	2/3	0.52939(14)	1	0.79(1)
O1	2d	1/3	2/3	0.1880(7)	1	1.26(4) ^a
O2	6g	0.4676(3)	0.3187(3)	0.3224(4)	1	1.26(4) ^a
O3	6g	0.2203(2)	0.0763(3)	0.7527(4)	1	1.26(4) ^a

*Site was set to be fully occupied without refining each atom occupancy

^a: constrained to refine to the same B_{iso} values.

Table S6. Refined structural parameters obtained from SPD data collected at room temperature on $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ ($x=1$) ($P321$ space group, $a= 8.02913(3)$ Å and $c= 5.014309(19)$ Å) sample. No strain modelled.

Atom	Position	x	y	z	Occ	B _{iso}
Ca	3e	0.41841(8)	0	0	1	1.16(1)
Zn1/Ge1	1a	0	0	0	1*	1.48(1)
Zn2/Ge2	3f	0.76499(4)	0	0.5	1*	1.154(7)
Ge3	2d	1/3	2/3	0.52849(11)	1	1.009(9)
O1	2d	1/3	2/3	0.1919(6)	1	1.95(3) ^a
O2	6g	0.4671(2)	0.3189(2)	0.3233(3)	1	1.95(3) ^a
O3	6g	0.22055(19)	0.0773(2)	0.7504(3)	1	1.95(3) ^a

*Site was put to be fully occupied without refining each atom occupancy

^a: constrained to refine to the same B_{iso} values.

Table S7. Refined structural parameters obtained from SPD data collected at room temperature on $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ ($x=1$) ($P321$ space group, $a= 8.02916(2)$ Å and $c= 5.014362(17)$ Å) sample. Modelled strain.

Atom	Position	x	y	z	Occ	B _{iso}
Ca	3e	0.41846(8)	0	0	1	1.15(1)
Zn1/Ge1	1a	0	0	0	1*	1.47 (1)
Zn2/Ge2	3f	0.76506(4)	0	0.5	1*	1.126(7)
Ge3	2d	1/3	2/3	0.52816(11)	1	0.999(8)
O1	2d	1/3	2/3	0.1926(5)	1	1.91(3) ^a
O2	6g	0.4676(2)	0.3195(2)	0.3230(3)	1	1.91(3) ^a
O3	6g	0.22065(19)	0.0772(2)	0.7502(3)	1	1.91(3) ^a

*Site was put to be fully occupied without refining each atom occupancy

^a: constrained to refine to the same B_{iso} values.

Table S8. Refined structural parameters obtained from SPD data collected at room temperature on $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ (C2 space group, $a= 13.91669(9)$ Å, $b= 8.02315(5)$ Å, $c= 5.01415(2)$ Å and $\beta= 90.0759(4)$ °) sample. No strain modelled.

Atom	Position	x	y	z	Occ	B _{iso}
Ca1	2a	0.5	0.7623(5)	0	1	1.44(8)
Ca2	4c	0.2917(2)	0.3948(4)	0.0006(7)	1	1.02(4)
Zn1	1a	0.11841(10)	0.56943(16)	0.4969(4)	1	1.39(3)
Ge1	4c	0.33313(10)	0.6860(2)	0.47222(13)	1	0.96(1)
Ge2	2b	0.5	0.41986(18)	0.5	1	0.92(4)
Ge3	4c	0.5	0.1858(3)	0	1	1.00(1)
O1	4c	0.1177(4)	0.6953(9)	0.7829(10)	1	1.21(4) ^a
O2	4c	0.1611(6)	0.3732(11)	0.680(2)	1	1.21(4) ^a
O3	4c	0.4249(5)	0.5748(11)	0.3031(15)	1	1.21(4) ^a
O4	4c	0.4317(5)	0.3296(9)	0.7441(13)	1	1.21(4) ^a
O5	4c	0.3341(6)	0.6729(11)	0.8088(6)	1	1.21(4) ^a
O6	4c	0.0234(4)	0.4947(8)	0.2834(13)	1	1.21(4) ^a
O7	4c	0.2304(5)	0.5907(10)	0.3407(17)	1	1.21(4) ^a

^a: constrained to refine to the same B_{iso} values.

Table S9. Refined structural parameters obtained from SPD data collected at room temperature on $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ ($C2$ space group, $a=13.90286(11)$ Å, $b=8.03170(7)$ Å, $c=5.014276(16)$ Å and $\beta=89.9544(10)^\circ$) sample. Modelled strain.

Atom	Position	x	y	z	Occ	B _{iso}
Ca1	2a	0.5	0.7601(4)	0	1	0.45(6)
Ca2	4c	0.2903(2)	0.3895(5)	0.0005(8)	1	1.55(4)
Zn1	1a	0.11569(10)	0.55532(16)	0.5034(4)	1	1.25(3)
Ge1	4c	0.33367(13)	0.6757(3)	0.47220(10)	1	0.980(7)
Ge2	2b	0.5	0.4145(2)	0.5	1	1.07(5)
Ge3	4c	0.5	0.1800(4)	0	1	0.97(1)
O1	4c	0.1017(4)	0.7363(7)	0.7201(10)	1	1.46(3) ^a
O2	4c	0.1562(6)	0.3734(13)	0.674(2)	1	1.46(3) ^a
O3	4c	0.4298(6)	0.5696(13)	0.3262(18)	1	1.46(3) ^a
O4	4c	0.4377(4)	0.3391(9)	0.7873(9)	1	1.46(3) ^a
O5	4c	0.3344(7)	0.679(2)	0.8071(4)	1	1.46(3) ^a
O6	4c	0.0451(5)	0.4900(9)	0.2636(13)	1	1.46(3) ^a
O7	4c	0.2364(6)	0.5876(13)	0.3066(17)	1	1.46(3) ^a

^a: constrained to refine to the same B_{iso} values.

Table S10. Atom Wyckoff positions in the hexagonal $P321$ structure and their equivalents in the monoclinic $C2$ cell.

Origin in $P321$		Analogue in $C2$	
Atom	Wyk. Pos.	Atom	Wyk. Pos.
Ca1	3f	Ca1	2a
		Ca2	4c
Ge1/Zn1	1a	Zn1	2a
Ge2/Zn2	3f	Ge1	4c
		Ge3	4c
Ge3	2d	Ge2	2b
O1	2d	O5	4c
O2	6g	O2	4c
		O3	4c
		O7	4c
O3	6g	O1	4c
		O4	4c
		O6	4c

Table S11. Extracted (refined) occupancies from the 2D EDS maps refinements in both zone1 and zone2, for the $\text{Ca}_3\text{GaZn}_{0.5}\text{Ge}_{4.5}\text{O}_{14}$ ($x=0.5$) composition.

		Site Atom	1a	3f	2d
Zone1	Zn		0.19(6)	0.10(6)	0
	Ga		0.22(3)	0.26(3)	0
	Ge		0.59(3)	0.64(3)	1
Zone2	Zn		0.16(6) ^a	0.11(6) ^a	0
	Ga		0.25(3) ^a	0.25(3) ^a	0
	Ge		0.59(3) ^a	0.64(3) ^a	1

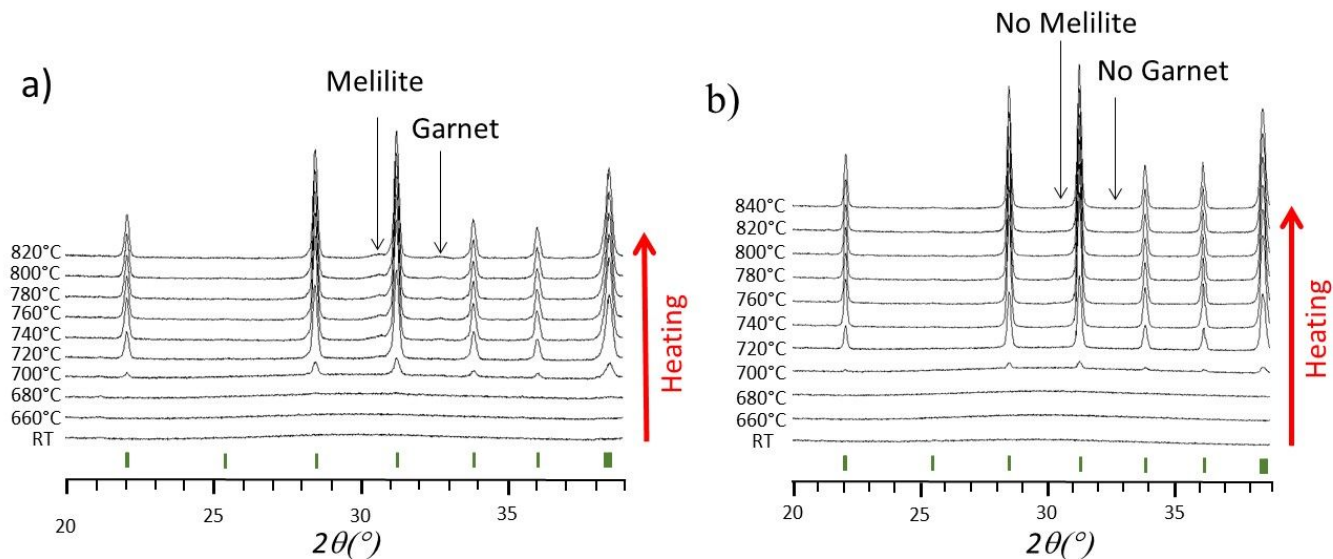


Figure S1. Variable temperature powder X-ray diffraction (VT-PXRD) measurements of, a) glass of composition $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ($x=0$), b) glass of a slightly deviated composition from $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ($x=0$) with an excess of 2.17% (%wt) of GeO_2 added in the nominal composition. Green tickmarks represent the $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ indexation.

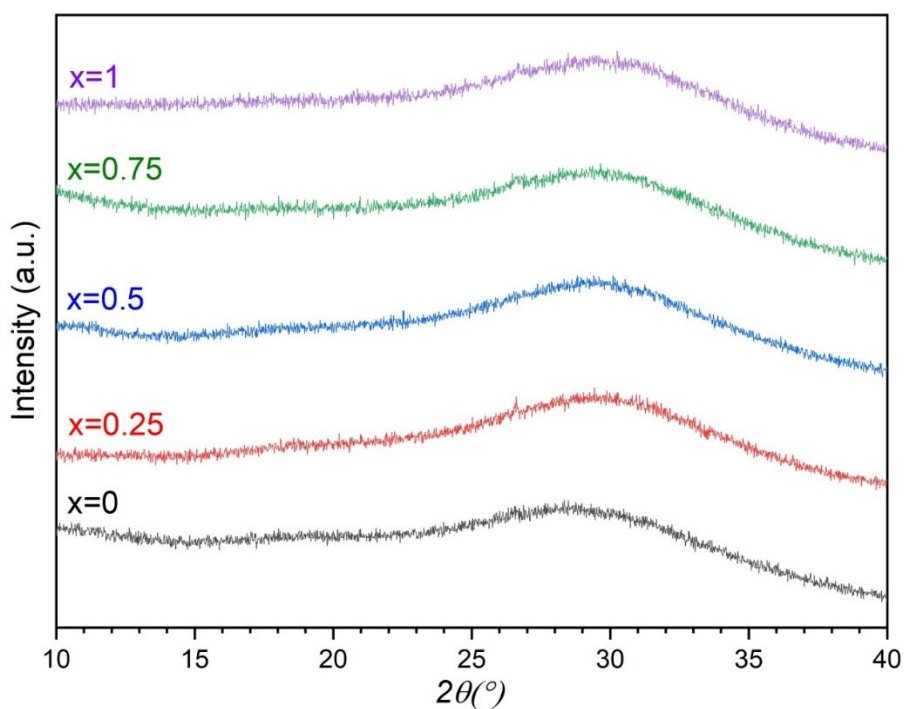


Figure S2. Laboratory X-ray powder diffraction data of $\text{Ca}_3\text{Ga}_{2-x}\text{Zn}_x\text{Ge}_{4+x}\text{O}_{14}$ ($x=0, 0.25, 0.5, 0.75, 1$) glass samples synthesized by aerodynamic levitation coupled to laser heating (ADL).

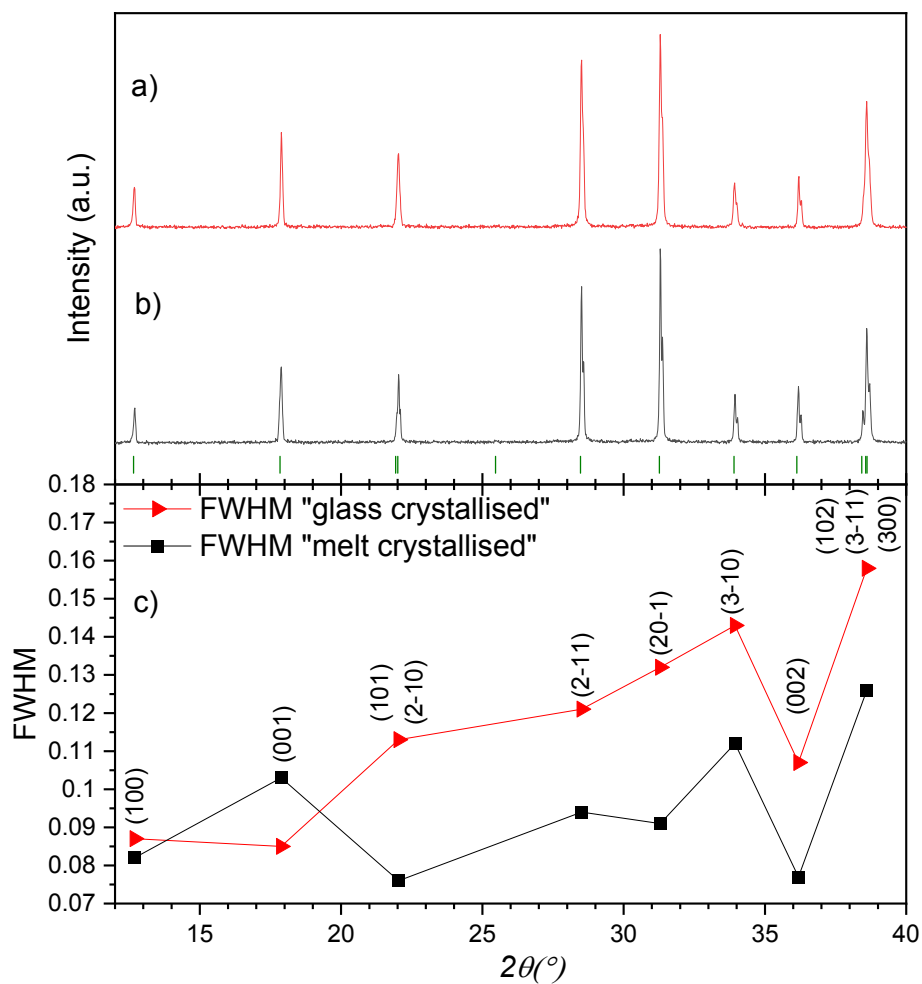


Figure S3. Crystallized $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ($x=0$) sample from a) glass at 820°C in an open atmosphere furnace, b) molten liquid on the ADL montage, by turning the lasers off while the droplet is touching the nozzle. Green tick marks represent $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ indexing. c) the extracted FWHM's for each peak from a) and b).

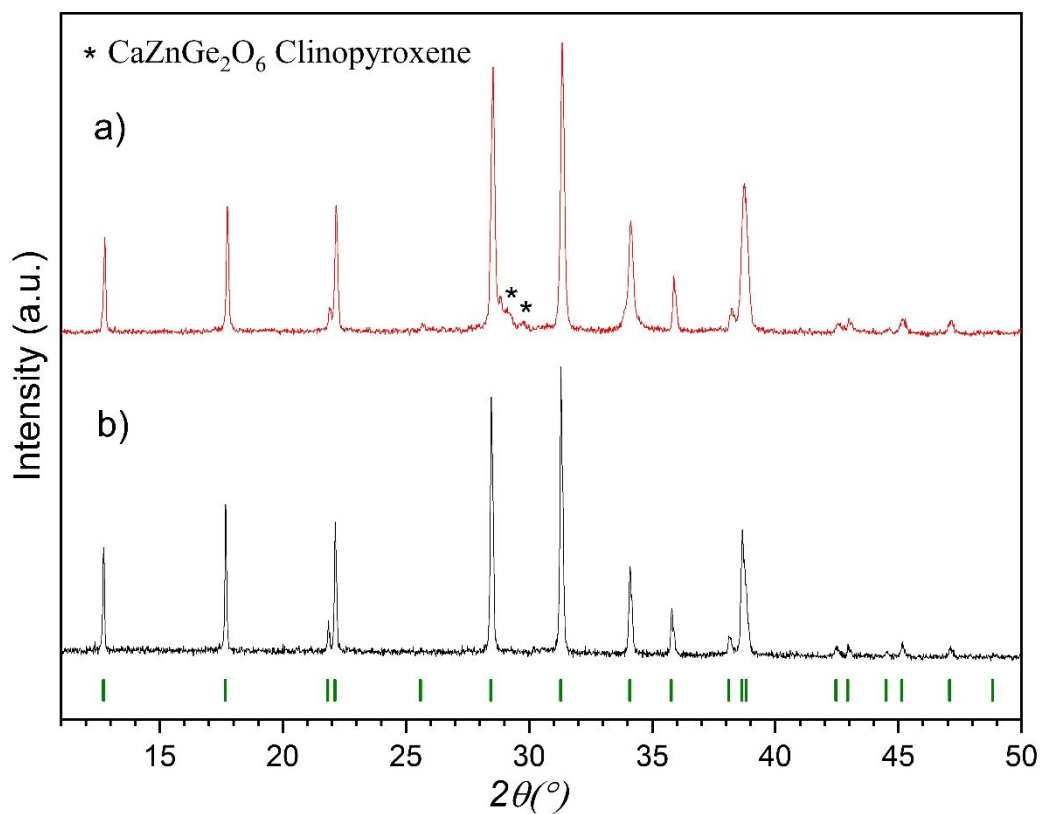


Figure S4. Lab powder X-ray diffraction data of two crystallized $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ samples at 800°C under (a) powder form, (b) bulk form. Green tick marks represent $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ indexation.

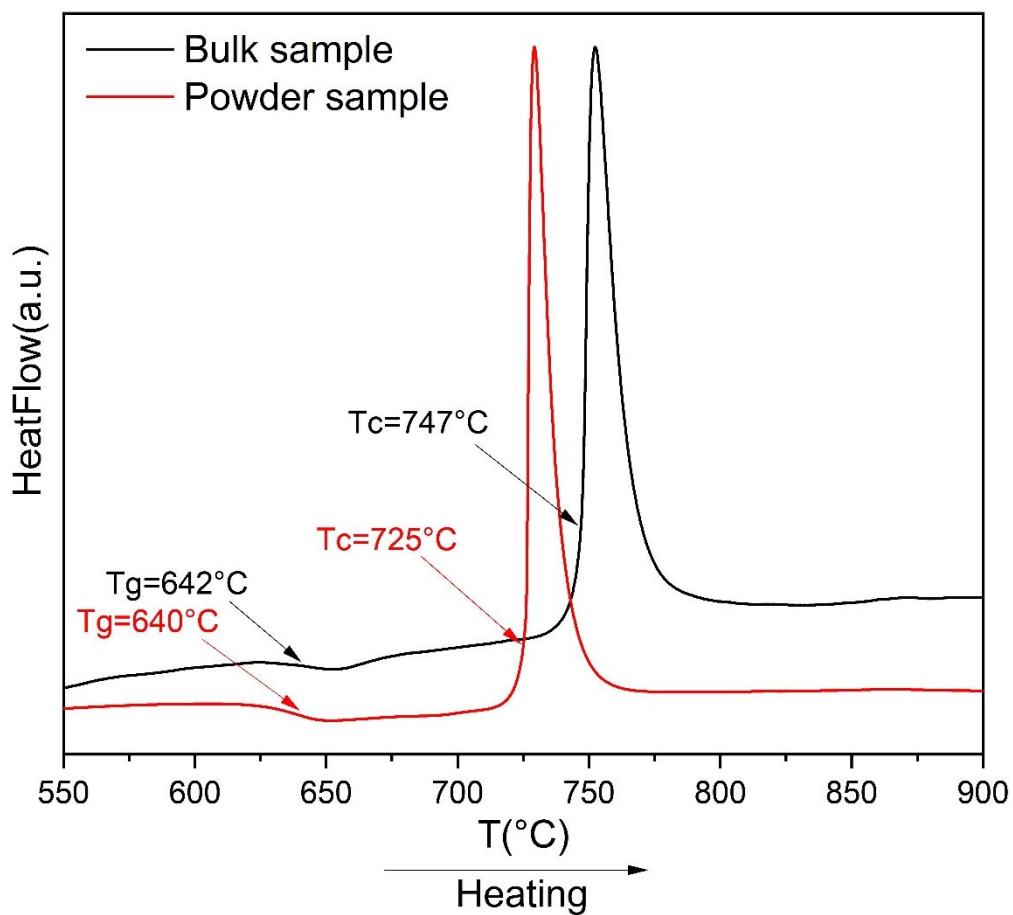


Figure S5. Comparison between a bulk and powder measured samples of the same composition $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ ($x=1$) on the DSC.

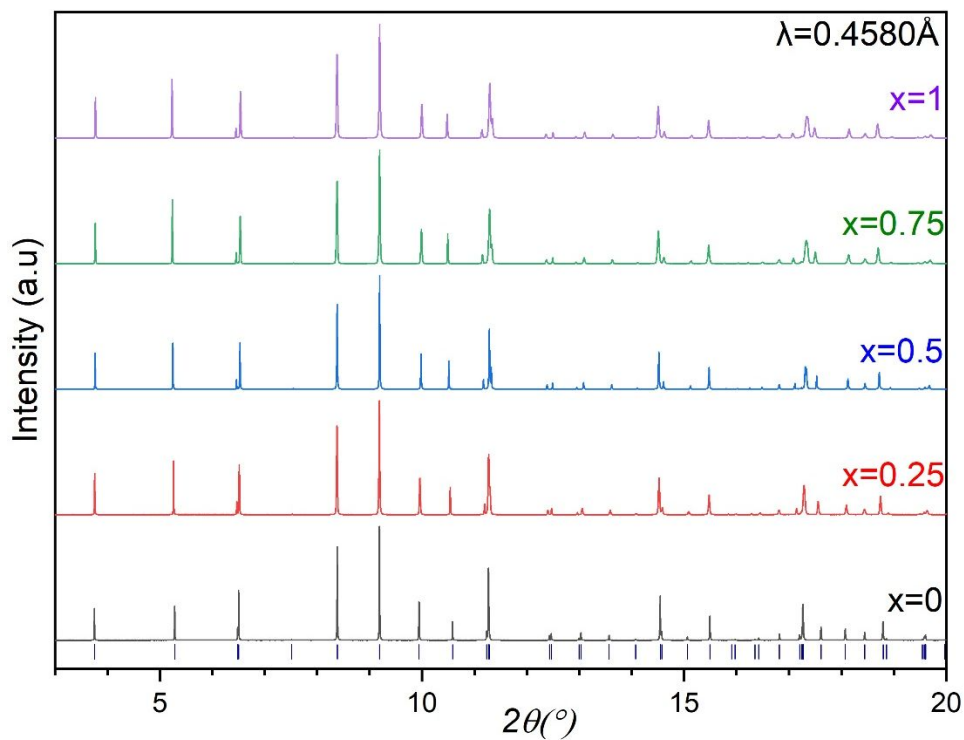


Figure S6. SPD data of $\text{Ca}_3\text{Ga}_{2-2x}\text{Zn}_x\text{Ge}_{4+x}\text{O}_{14}$ $x=0$ (black), 0.25 (red), 0.5 (blue), 0.75 (green) and 1 (purple) compositions, with dark blue tickmarks corresponding to $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ indexation.

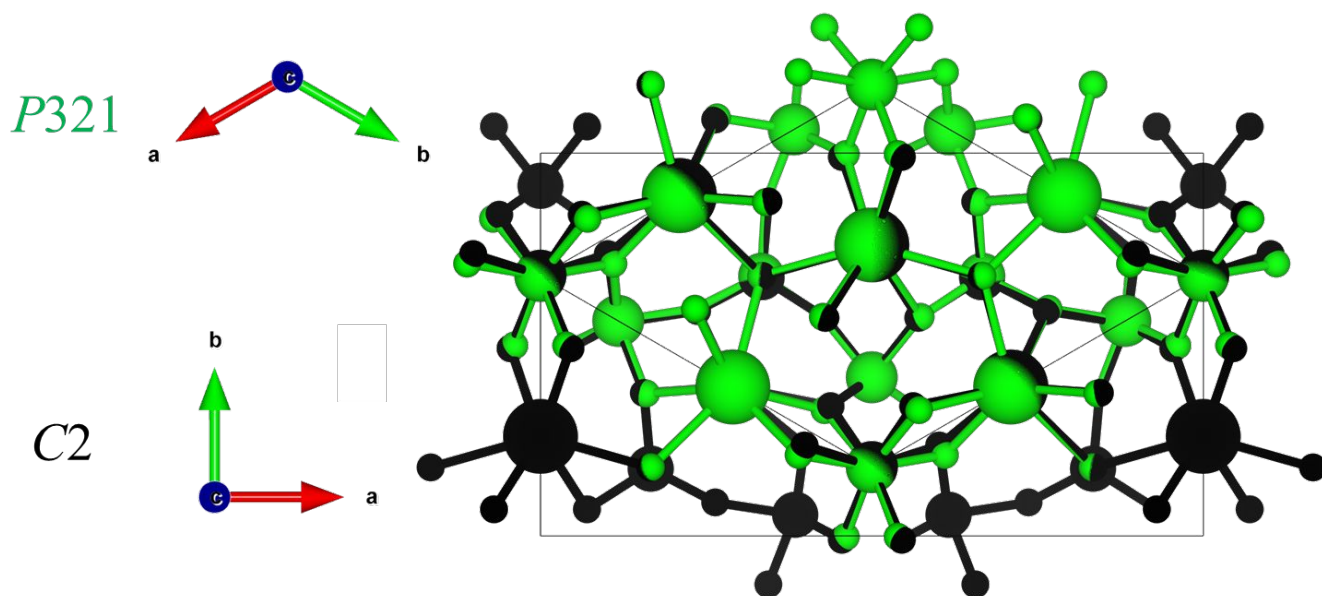


Figure S7. Overlay between Rietveld refined $C2$ (black atoms) and $P321$ (green atoms) structures for the $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ ($x=1$) composition against SPD data, along the c -axis.

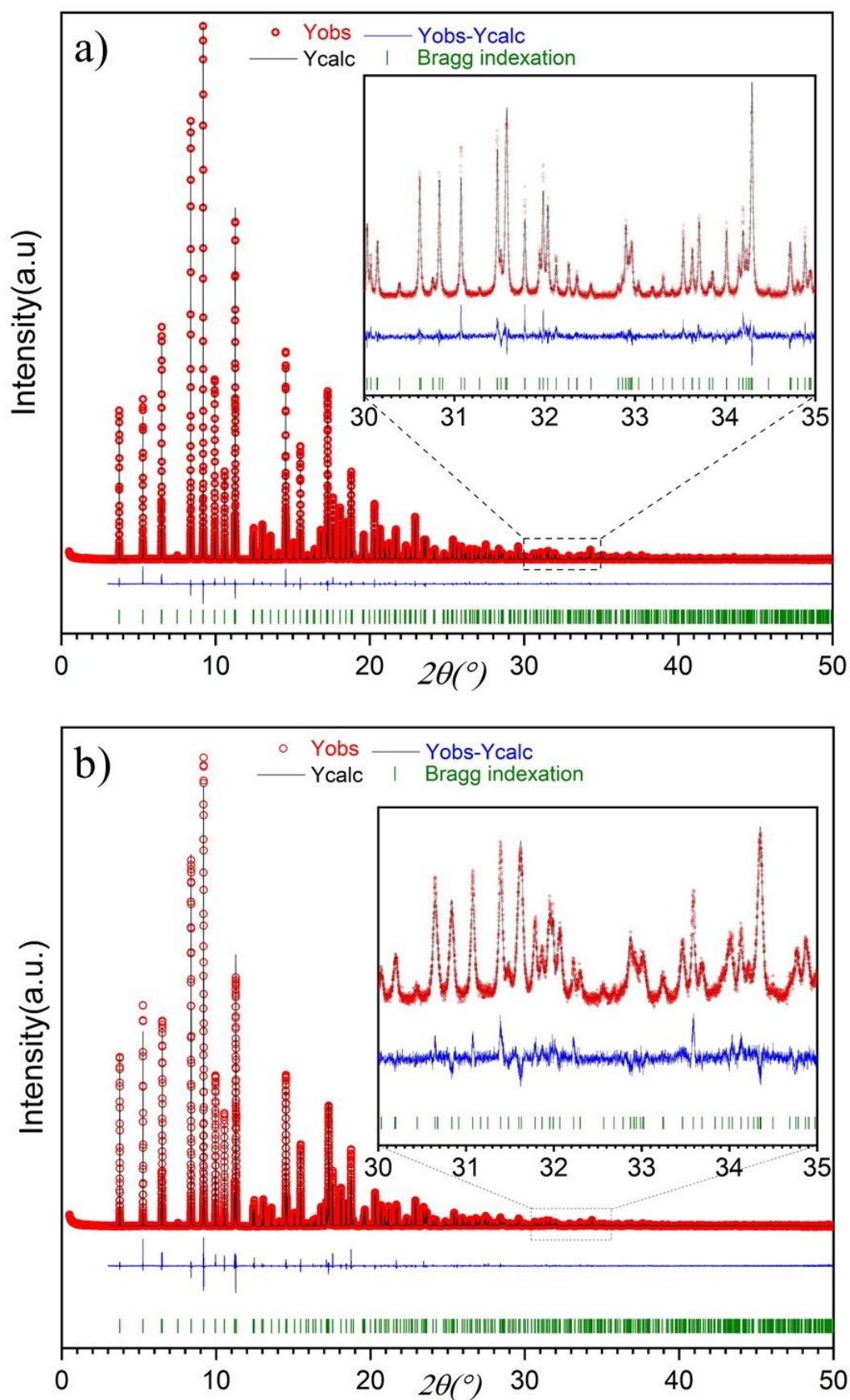


Figure S8. Rietveld refinement of a) $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ($x=0$) (SPD data, $R_p = 7.617\%$, $R_{wp} = 9.506\%$) and b) $\text{Ca}_3\text{Ga}_{1.5}\text{Zn}_{0.25}\text{Ge}_{4.25}\text{O}_{14}$ ($x=0.25$) (SPD data, $R_p = 8.465\%$, $R_{wp} = 10.907\%$). Observed (red dot), calculated (black line), and difference (blue line) profiles are shown. The set of green vertical lines corresponds to reflection positions.

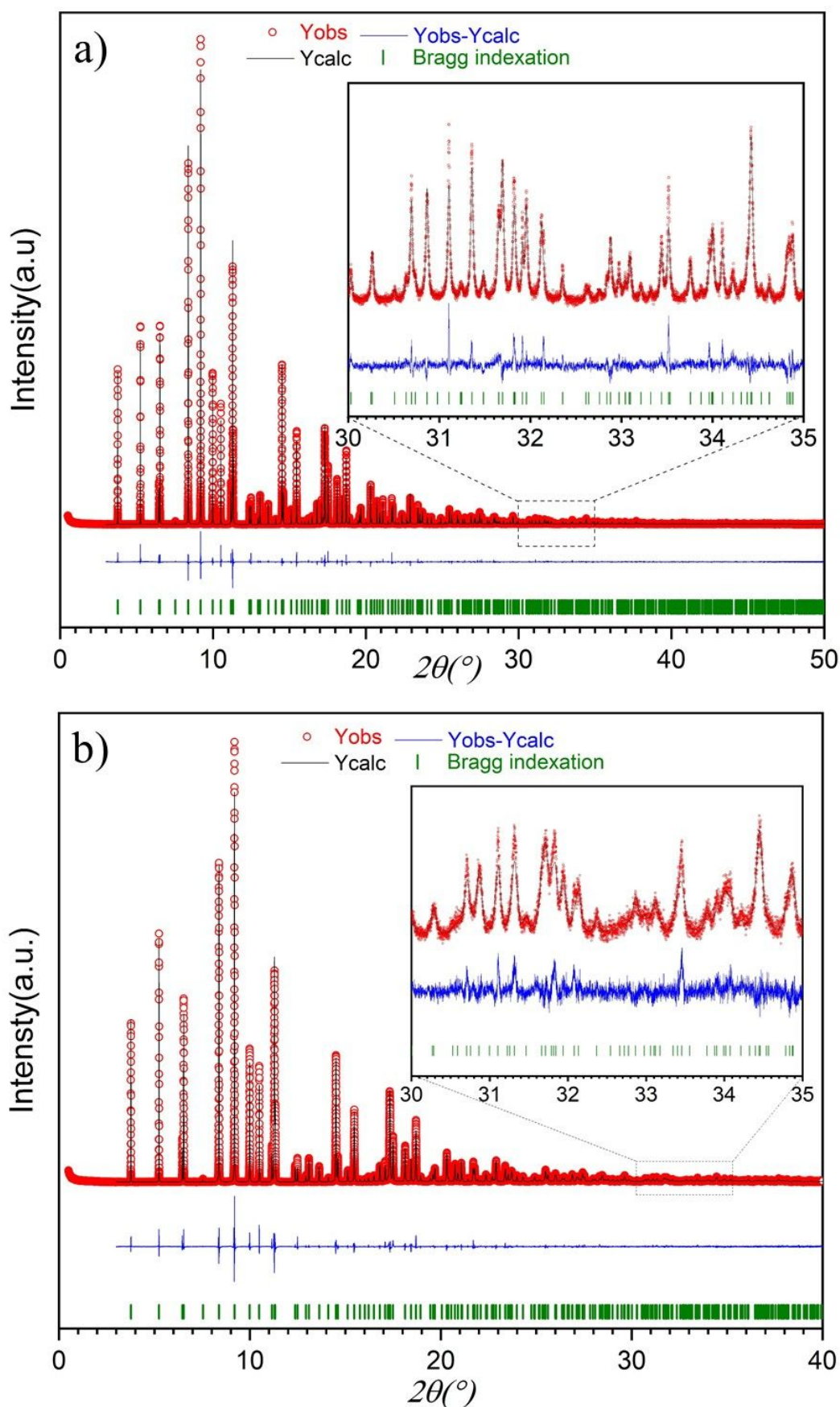


Figure S9. Rietveld refinement of a) $\text{Ca}_3\text{GaZn}_{0.5}\text{Ge}_{4.5}\text{O}_{14}$ ($x=0.5$) (SPD data, $R_p=7.617\%$ $R_{wp}=9.506\%$) and b) $\text{Ca}_3\text{Ga}_{0.5}\text{Zn}_{0.75}\text{Ge}_{4.75}\text{O}_{14}$ ($x=0.75$) (SPD data, $R_p=8.465\%$ $R_{wp}=10.907\%$). Observed (red dot), calculated (black line), and difference (blue line) profiles are shown. The set of green vertical lines corresponds to reflection positions.

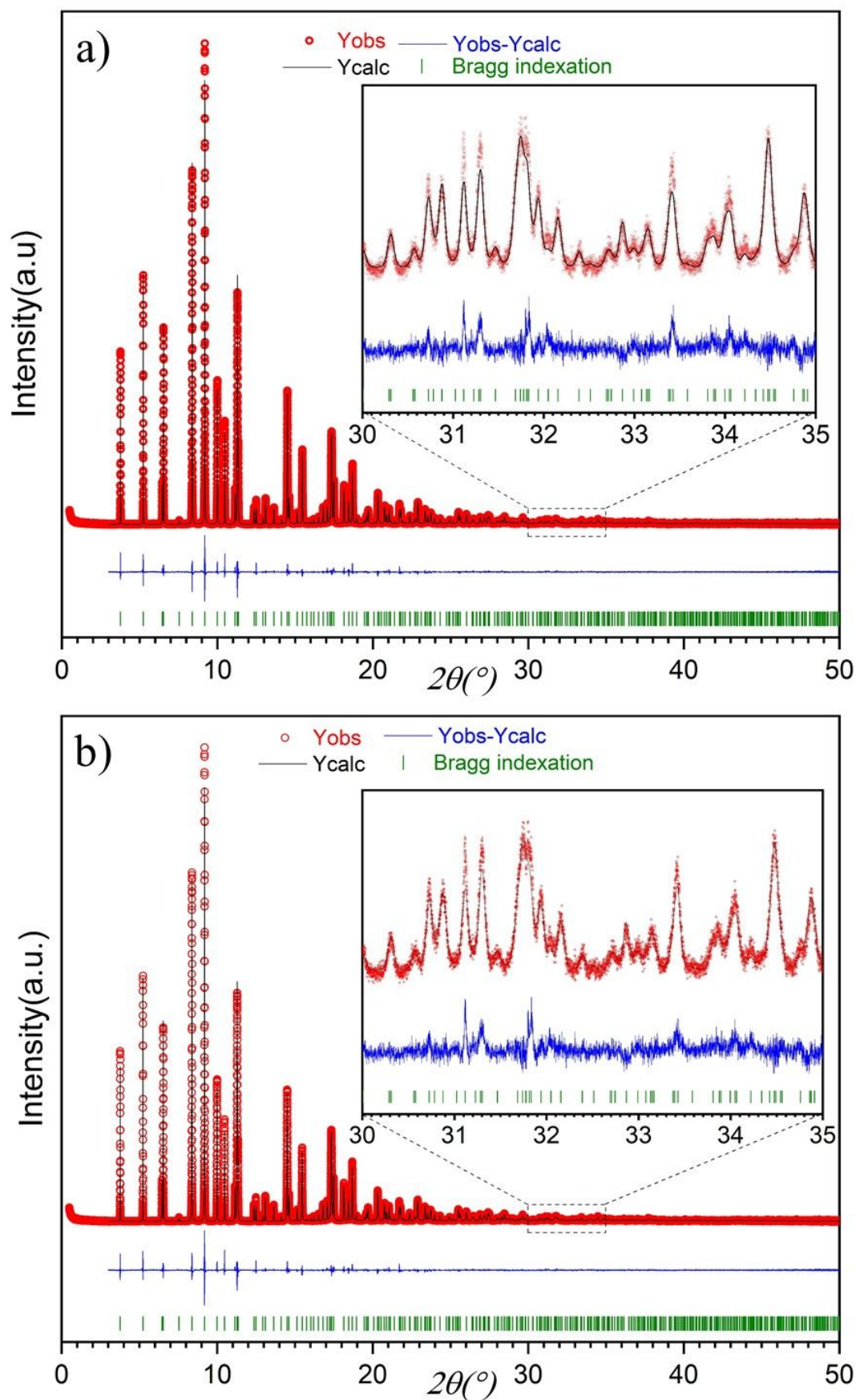


Figure S10 Rietveld refinement of $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}(x=1)$ SPD data against the hexagonal $P321$ cell, a) without strain ($R_p = 7.18\%$ $R_{wp} = 8.93\%$), b) modelled strain ($R_p = 7.02\%$ $R_{wp} = 8.75\%$). Observed (red dot), calculated (black line), and difference (blue line) profiles are shown. The set of green vertical lines corresponds to reflection positions.

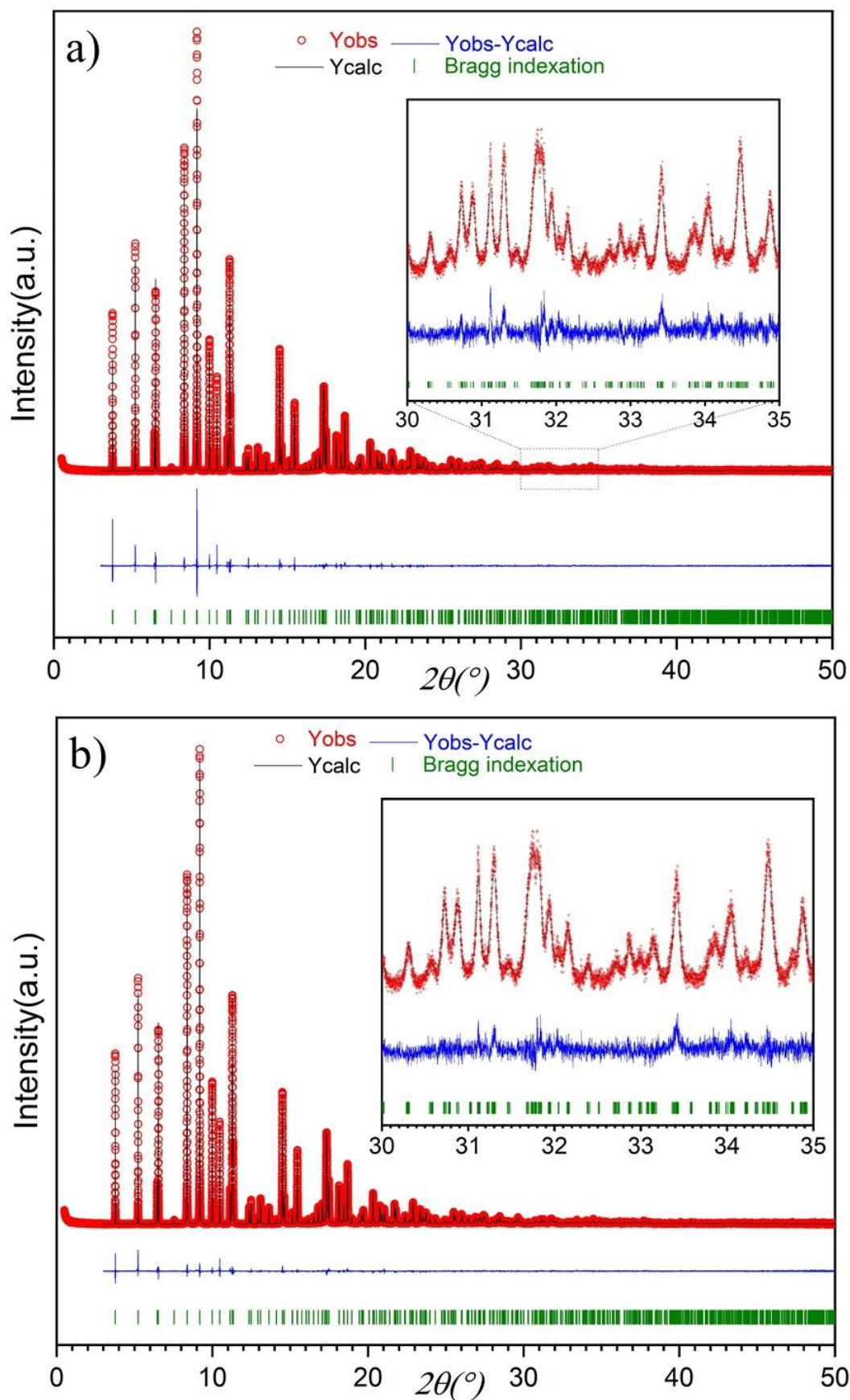


Figure S11. Rietveld refinement of $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ (x=1) SPD data against the monoclinic $C2$ structure, a) without strain ($R_p = 7.20\%$ $R_{wp} = 8.93\%$), b) modelled strain ($R_p = 5.14\%$ $R_{wp} = 6.68\%$). Observed (red dot), calculated (black line), and difference (blue line) profiles are shown. The set of green vertical lines corresponds to reflection positions.

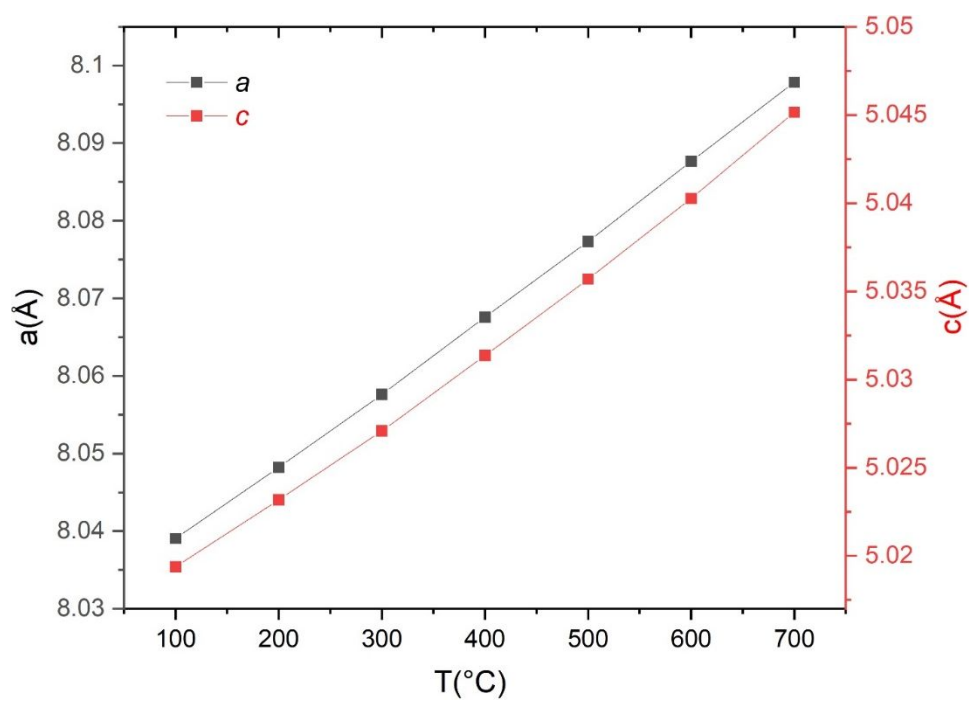


Figure S12. Cell parameters evolution of the $\text{Ca}_3\text{ZnGe}_5\text{O}_{14}$ sample vs temperature.

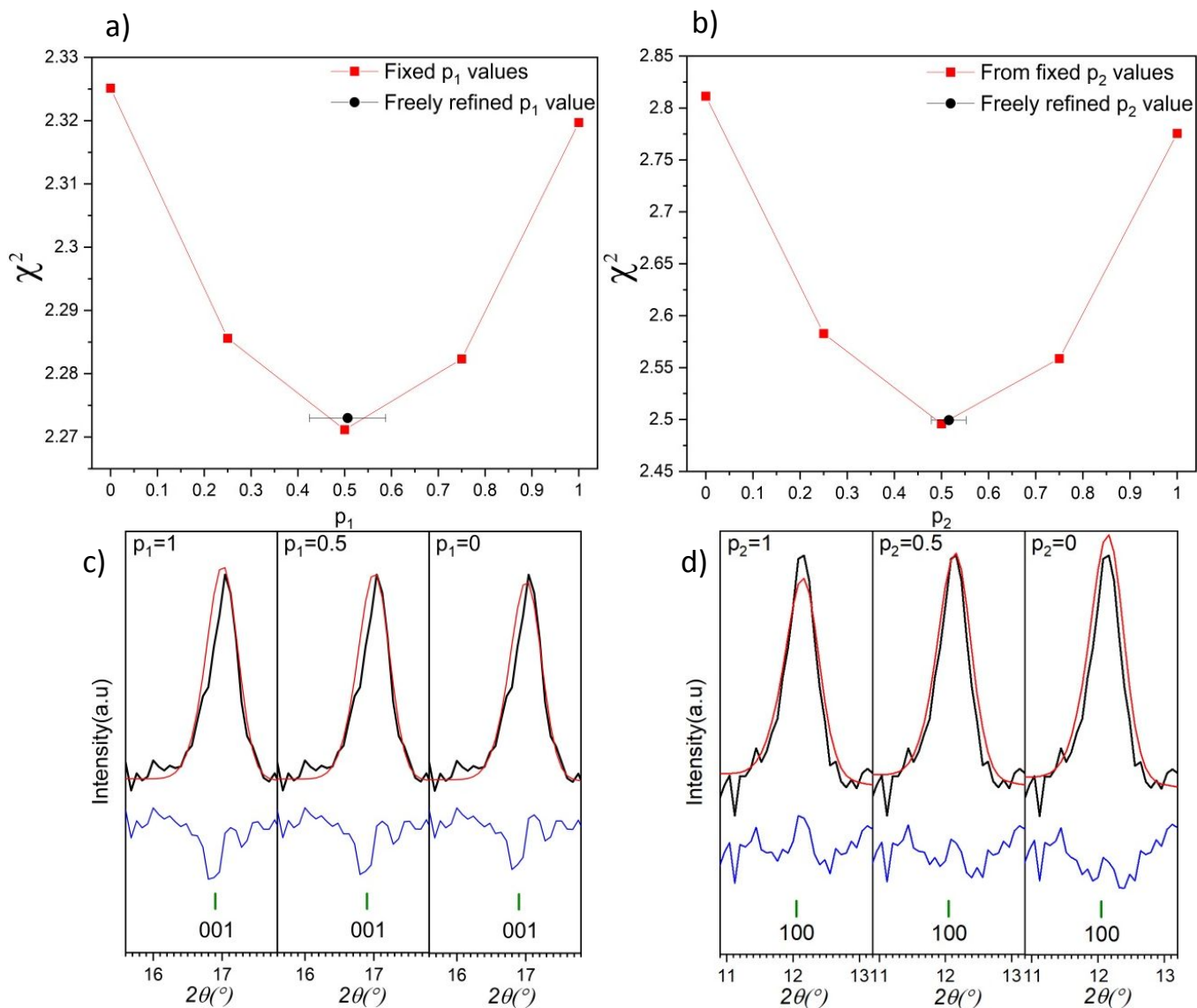


Figure S13. a), b) χ^2 evolution as a function of p_1 (Ga occupancy on the 1a site for $x=0$ compound), p_2 (Zn occupancy on the 1a site for $x=1$ compound). c), d) Rietveld fits (measured "black line", calculated "red line", difference "blue line" and indexation in green tick marks) zoomed view on the (001) and (100) for $x=0$ and $x=1$ compounds respectively for different fixed p_1 and p_2 values.

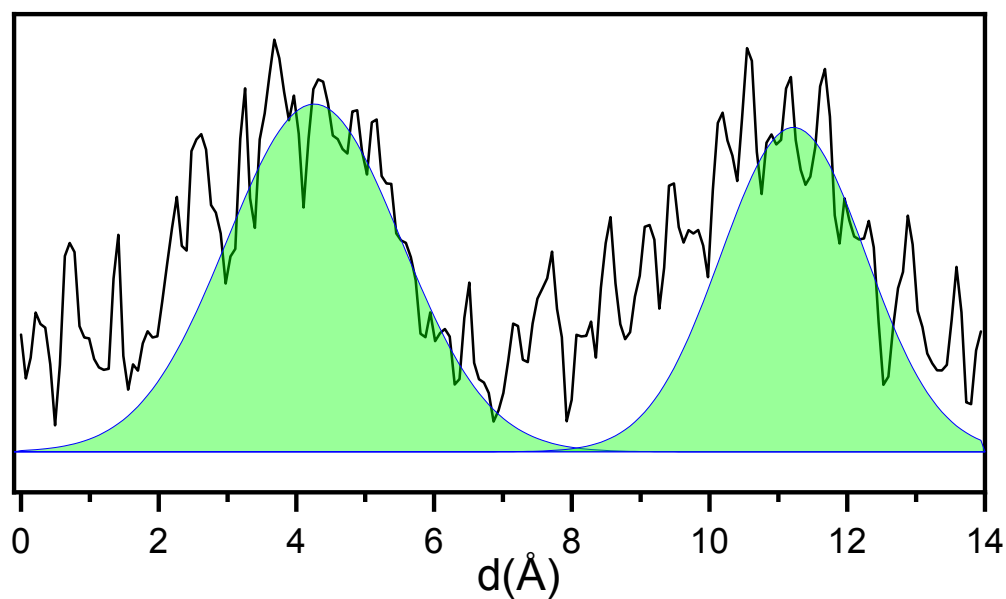


Figure S14. Refined signal of Zn from integrated area on the STEM-EDS raw maps with one Gaussian contribution from the 1a site position, where black curve, blue curve and green surface represents the raw integrated, calculated signals and the integrated area under the calculated curve.

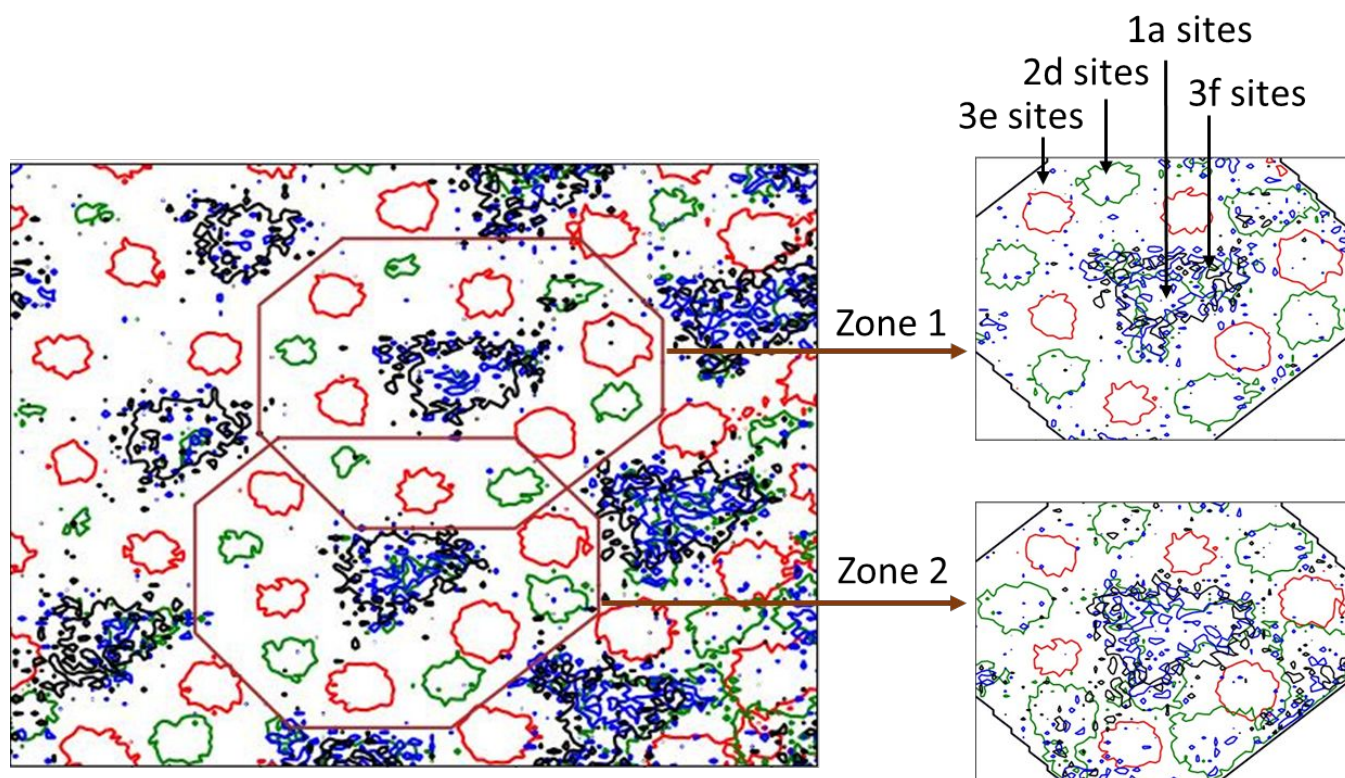


Figure S15. Overlay contour map of Ca (red), Ga (black), Ge (green) and Zn (blue) extracted from STEM-EDS raw data after the mask application.

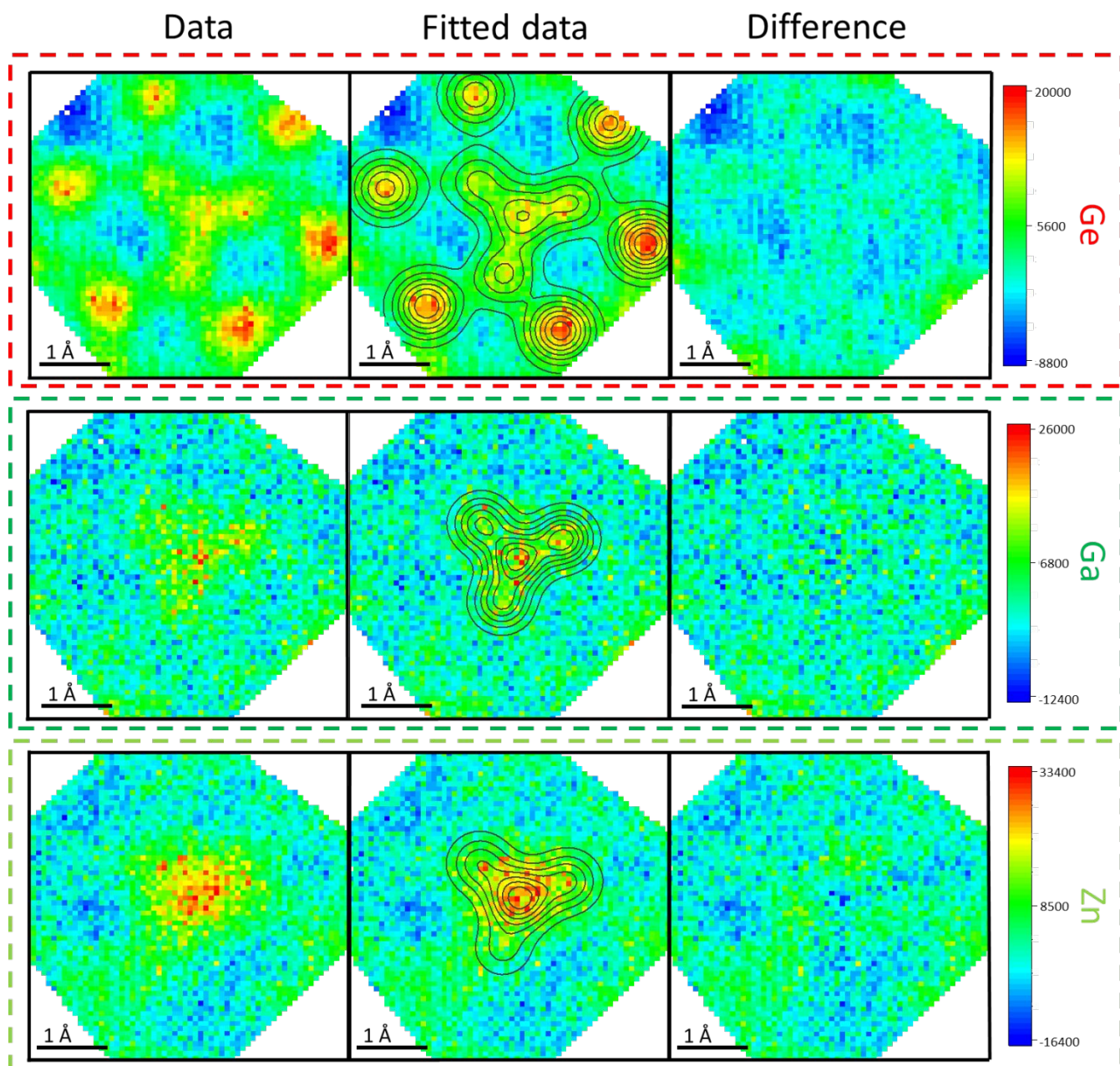


Figure S16. STEM-EDS 2D refinement plots of Ge, Ga and Zn from zone2 (zone 1 is shown in Figure 8 of the main text). The sample composition is $\text{Ca}_3\text{GaZn}_{0.5}\text{Ge}_{4.5}\text{O}_{14}$.

References:

- (1) Massiot, D.; Vosegaard, T.; Magneron, N.; Trumeau, D.; Montouillout, V.; Berthet, P.; Loiseau, T.; Bujoli, B. ^{71}Ga NMR of Reference Ga_{iv} , Ga_{v} , and Ga_{vi} Compounds by MAS and QPASS, Extension of Galliumaluminum NMR Parameter Correlation. **1999**, 11.
- (2) Fan, J.; Sarou-Kanian, V.; Yang, X.; Diaz-Lopez, M.; Fayon, F.; Kuang, X.; Pitcher, M. J.; Allix, M. $\text{La}_2\text{Ga}_3\text{O}_{7.5}$: A Metastable Ternary Melilite with a Super-Excess of Interstitial Oxide Ions Synthesized by Direct Crystallization of the Melt. *Chem. Mater.* **2020**, 32 (20), 9016–9025. <https://doi.org/10.1021/acs.chemmater.0c03441>.
- (3) Massiot, D.; Montouillout, V.; Fayon, F.; Florian, P.; Bessada, C. Order-Resolved Sideband Separation in Magic Angle Spinning NMR of Half Integer Quadrupolar Nuclei. *Chem. Phys. Lett.* **1997**, 272 (3–4), 295–300. [https://doi.org/10.1016/S0009-2614\(97\)88023-2](https://doi.org/10.1016/S0009-2614(97)88023-2).
- (4) Mill, B. V.; Klimenkova, A. A.; Maximov, B. A.; Molchanov, V. N.; Pushcharovsky, D. Yu. Enantiomorphism of the $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ Compound and Comparison of the $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ and $\text{Sr}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ Structures. *Crystallogr. Rep.* **2007**, 52 (5), 785–794. <https://doi.org/10.1134/S1063774507050069>.