Interstitial Oxide Ion Order and Conductivity in \( \text{La}_{1.64}\text{Ca}_{0.36}\text{Ga}_3\text{O}_{7.32} \)
Melilite**

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1. Experimental Section

The A2B3O7 melilite structure, where A is a large eight-coordinated cation (A = Ca, Sr, Na, Ba, La) and B is small cation (B = Mg, Zn, Al, Ga, Si, Ge, …) in tetrahedral coordination, consists of anionic layers of five-membered rings of totally (four neighbouring tetrahedra) and partially condensed (three neighbouring tetrahedral with a terminal oxygen) BO4 tetrahedra, separated by parallel sheets of A cations located over the five-ring centres along [001] (Figure S1.1).

La1+xCa1-xGa3O7+δ (0 ≤ x ≤ 0.7) (A = La/Ca, B = Ga) were prepared by solid state reaction using La2O3 (99.999%, Alfa Aesar), CaCO3 (99.997%, Alfa Aesar) and Ga2O3 (99.999%, Alfa Aesar) as starting materials, which were mixed in ethanol and calcined at 1200 °C for 12 h in alumina crucibles. After regrinding, the powders were uniaxially pressed into pellets and fired at 1400 °C for samples with x < 0.5 and 1350 °C for samples with x > 0.5 for 12 h at 5 °C/min heating and cooling rates. To compensate the Ga volatilization during the reaction which results in the form of the second phase Ca-doped LaGaO3, a slight excess of Ga2O3 (~0-1.7 mol% for x ≤ 0.6; ~2-3.3 mol% for 0.6 < x ≤ 0.65; ~5 mol% for x > 0.65) was added into the initial starting mixture. Attempts to obtain single phase materials at x = 0.65 by adding excess Ga2O3 (e.g. ~ 2 mol% and ~ 3.3 mol%) failed to remove the second phase Ca-doped LaGaO3. Slightly reducing the La/Ca ratio to x = 0.64 with ~ 2.3 mol% extra Ga2O3 (i.e. initial composition La1.64Ca0.36Ga3.07) produced a nearly single phase material La1.64Ca0.36Ga3O7.32 with a very small Ga2O3 impurity. To avoid reacting with the alumina, the pellets were put on platinum foil during the preparation. The phase purity was checked by powder X-ray diffraction data with a Panalytical X’pert Pro Multi-Purpose X-ray diffractometer (Co Kα1 radiation λ = 1.78901Å). Silicon was added as an internal standard during the laboratory XRD experiments in order to refine the variation of the cell parameter with composition. Time-of-flight (TOF) neutron powder diffraction (NPD) data of La1.64Ca0.36Ga3O7.32 sample were collected from ambient temperature to 800 °C on the HRPD diffractometer at ISIS. After the variable temperature diffraction, the sample
was offline cooled to ambient temperature and another ambient temperature TOF data was collected from comparison with that for the as-made sample. Rietveld refinement was carried out using the GSAS package\(^1\). Compositional analysis was carried out by using the EDAX analyzer on a JEOL 2000FX transmission electron microscope operated at 200 KV. Ac Impedance Spectroscopy (IS) measurements in air from 200 °C to 850 °C were performed with a Solartron 1255B Frequency 

Figure S1.1. Slab view of A\(_2\)B\(_3\)O\(_7\) melilite structure along (a) [001] and (b) [010] direction, showing the five membered BO\(_4\) rings and location of A cations. Four connected BO\(_4\) tetrahedron, yellow; three connected BO\(_4\), purple; A cation, blue; bridging oxygen, red; terminal oxygen, green.
Response Analyzer, a Solartron 1296 dielectric interface and a Solartron 1287 electrochemical interface over the $10^{-2}$-$10^6$ Hz frequency range. Prior to the measurement, platinum paste was painted on the opposite faces of the pellets and fired at 800 °C for 30 minutes in air.

2. XRD data for $\text{La}_{1+x}\text{Ca}_{1-x}\text{Ga}_3\text{O}_{7+0.5x}$

The parent material $\text{LaCaGa}_3\text{O}_7$ crystallizes in a tetragonal melilite structure in $P4_2_1m$ ($a = 7.9553(2)$ Å, $c = 5.2727(2)$ Å). With the substitution of $\text{Ca}^{2+}$ by $\text{La}^{3+}$, the tetragonal phase extends to $\text{La}_{1.5}\text{Ca}_{0.5}\text{Ga}_3\text{O}_{7.25}$. The cell parameters of $\text{La}_{1+x}\text{Ca}_{1-x}\text{Ga}_3\text{O}_{7+0.5x}$ obey Vegard’s law for $0 < x < 0.5$. The $\text{La}^{3+}$ substitution expanded the a-axis and shortened the c-axis. The volume increased with increasing $\text{La}^{3+}$ content. Each $(hkl)$ $(h$ and $k \neq 0)$ reflection is broadened at $x = 0.525$ and splits into two distinct peaks at $x > 0.525$, which could be explained by a lower symmetry with inequivalent a-axis and b-axis, i.e. an orthorhombic cell ($a$ and $b \sim \sqrt{2}a_{\text{tetra}}, c = c_{\text{tetra}}$) with a sub-group $Cmm2$ of $P4_2_1m$. The XRD patterns (Figure S2.1) suggested that the as-made samples $x > 0.5$ actually contained both tetragonal and orthorhombic phases and the orthorhombic phase dominates in the samples $x \geq 0.55$. The cell parameters for orthorhombic and tetragonal $\text{La}_{1+x}\text{Ca}_{1-x}\text{Ga}_3\text{O}_{7+0.5x}$, shown in Figure S2.2, become constant after $x = 0.65$ which suggests that the solid solution terminates at $x = 0.65$. The XRD pattern of the as-made $\text{La}_{1.64}\text{Ca}_{0.36}\text{Ga}_3\text{O}_{7.32}$ showed a pure orthorhombic phase with no apparent residual tetragonal phase in the sample. EDS (energy-dispersive spectroscopy) elemental analysis in the TEM investigation showed a homogenous cation ratio $\text{La}_{1.62}\text{Ca}_{0.36}\text{Ga}_3$ for $\text{La}_{1.64}\text{Ca}_{0.36}\text{Ga}_3\text{O}_{7.32}$ against $\text{La}_{1.01}\text{Ca}_{0.93}\text{Ga}_3$ from the EDS analysis for the parent material $\text{LaCaGa}_3\text{O}_7$. 

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Figure S2.1. XRD patterns of as-made $\text{La}_{1+x}\text{Ca}_{1-x}\text{Ga}_3\text{O}_{7+0.5x}$. (a) $x \leq 0.5$ adopting the tetragonal cell and (b) $x \geq 0.55$ indexed with the orthorhombic cell. The arrows mark reflections from the second phase Ca-doped $\text{LaGaO}_3$. 
**Figure S2.2.** Cell parameters versus compositions for the La$_{1+x}$Ca$_{1-x}$Ga$_3$O$_{7+x}$ solid solution. The orthorhombic cell parameters $a_{\text{ortho}}$ and $b_{\text{ortho}}$ were divided by $\sqrt{2}$ and volume by 2 for comparison with tetragonal cell. The tetragonal and orthorhombic cells are represented by using filled and open squares, respectively.
3. SAED and HRTEM analysis

SAED results showed that, although the main diffraction features were consistent with the crystal structure proposed by XRD (space group $Cmm2$, $a = 11.42\ \text{Å}$, $b = 11.23\ \text{Å}$ and $c = 5.25\ \text{Å}$), extra weak reflections were observed in the diffraction patterns along certain crystal axes. These extra spots can be indexed simply by doubling the $c$ axis of the proposed unit cell. The reciprocal lattice reconstruction indicates a $c$-axis doubled body-centered supercell based on the above $Cmm2$ cell with no other systematic absences observable, suggesting possible space groups $Imm2$, $Im11$, and even in triclinic cell $I1$. Figure S3.2 shows the simulated SAED patterns for $\text{La}_{1.64}\text{Ca}_{0.36}\text{Ga}_{3}\text{O}_{7.32}$ according the the triclinic cell (Space group of $P1$, $a = 9.5735\ \text{Å}$, $b = 9.5754\ \text{Å}$, $c = 9.5691\ \text{Å}$, $\alpha = 106.78^\circ$, $\beta = 108.17^\circ$, $\gamma = 113.51^\circ$, its relationship to the $I1$ cell is shown in Figure S3.1)

![Figure S3.1](image)

**Figure S3.1** The relationship between body-centred ($I$) and primitive ($P$) unit cells, where the $I$-cell edges are black, $P$-cell edges green, and the green spheres are the centres of $I$-cell.
Figure S3.2 SAED patterns for La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ along the (a) [001] axis where no extra reflections are observed, and the (b) [112] (c) [116] and (d) [106] axes where superlattice reflections (as marked by white arrows), which can be indexed as ($hk \frac{2n+1}{2}$), indicate the c-doubling. The axes and reflections are indexed according to the $P1$ cell.

HRTEM was applied to check possible microstructural crystal defects, such as twinning, in order to investigate any relationship with the weak diffraction features. Figure S3.3 is the HRTEM image along [112] (left) and [121] (right) simulated in the triclinic c-doubled supercell in $P1$ with the final refined structural model. The images simulated from different directions are quite similar, and it is thus clear that the extra weak reflections in SAED are intrinsic features, instead of arising from microscopic defects, and responsible for the doubled $c$-axis.
Figure S3.3 HRTEM of La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ along [112](left) and [121](right) in $Par{1}$ cell. Inset is the simulated image from the final refined model along this direction.
4. Phase transition (Variable temperature NPD)

![Graph showing phase transition](image)

**Figure S4.1** Variable temperature (VT) time-of-flight neutron diffraction (TOF ND) patterns for La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ upon heating show a phase transition between 600 and 700 °C. The phases present at each temperature are marked as orthorhombic (O) and tetragonal (T) phases. The O and T phases coexist as shown in the ambient temperature (AT) data after VT experiment, compared with the AT data for as-made sample (O phase only).
5. Structure refinement for La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ in average models

High resolution neutron HRPD (TOF) data from both backscattering (NPD168) and 90 degree (NPD90) detectors were used for crystal structure refinement in GSAS. Refinements were carried out in the following sequence (Figure S5.1), in order to explore the possible space groups suggested by SAED.

![Diagram](Tetra. (P421m) → Ortho. (Cmm2) → Ortho. (Imm2) → Mono. (Im11) → Tri. (P1))

**Tetra. (P421m)**

**Ortho. (Cmm2)** \(a, b \sim 2^{1/2}a_{\text{tetra}}; c \sim c_{\text{tetra}}\)

\[a, b, c = 11.416, 11.226, 5.248 \text{ Å}\]

**Ortho. (Imm2)** \(a, b \sim 2^{1/2}a_{\text{tetra}}; c \sim 2^*c_{\text{tetra}}\)

\[a, b, c = 11.416, 11.228, 10.497 \text{ Å}\]

**Mono. (Im11)** \(a, b, c \sim a_{\text{ortho}}, b_{\text{ortho}}, c_{\text{ortho}}\)

\[a, b, c = 11.416, 11.228, 10.497 \text{ Å}\]

\[\alpha = 90.02^\circ\]

**Tri. (P1)** \(a, b, c \sim a_{\text{ortho}}, b_{\text{ortho}}, c_{\text{ortho}}^{\text{-I1}}\)

\[a, b, c = 9.573, 9.576, 9.569\]

\[\alpha, \beta, \gamma = 106.78, 108.17, 113.51^\circ\]

*Figure S5.1* Schematic diagram for structure refinement

The general parameters, including histogram scale factors, background coefficients, unit cell parameters, zero error and peak shape coefficients, were varied for all refinements. Framework atoms of the starting model were derived from tetragonal melilite phase and the extra oxygen sites were
established using Fourier synthesis techniques and refined in accordance with nominal composition and charge balance. The atomic positional and displacement parameters of mixed site atoms were constrained to be the same. In the split-site model, the atomic displacement parameters (ADPs) for split sites were refined isotropically for convergence, and the related values for bulk and defect structure were simultaneously refined to be the same value. The final refined results were shown in Table S5.1.

Table S5.1 The cell parameters, refined variables (RV), and fitted parameters from the final refinement in S.G. Cmm2, Imm2, Im11, P1 (average model (PI-average) and split model (PI-split)) for comparing.

| S.G.   | Cmm2       | Imm2       | Im11       | P1-average | P1-split |
|--------|------------|------------|------------|------------|----------|
|        | a (Å)      | b (Å)      | c (Å)      | α (°)      | β (°)    | γ (°) |
| a (Å)  | 11.41253(6)| 11.41582(3)| 11.41608(3)| 90         | 90       | 90 |
| b (Å)  | 11.22407(6)| 11.22801(3)| 11.22797(3)| 90         | 90       | 90 |
| c (Å)  | 5.24802(9) | 10.49733(3)| 10.49736(2)| 90         | 90       | 90 |
| α (°)  | 90         | 90         | 90         | 106.781(1) | 106.779(1)| 113.510(1)|
| β (°)  | 90         | 90         | 90         | 108.173(1) | 108.176(1)| 113.501(1)|
| γ (°)  | 90         | 90         | 90         | 113.510(1) | 113.501(1)| 113.501(1)|
| V (Å³) | 672.24(2)  | 1345.516(6)| 1345.547(5)| 672.846(4) | 672.726(4)| 672.726(4)|
| RV     | 122        | 201        | 320        | 536        | 507      |
| Rwp/Rp %| 4.81/5.47  | 4.12/5.37  | 3.37/4.96  | 3.21/4.60  | 3.30/4.42| 4.81 |
| χ²     | 9.31       | 6.84       | 4.69       | 4.28       | 4.81     |

5.1 Orthorhombic cell, Cmm2 space group

The Rietveld refinement plots of data in the Cmm2 cell (see Section 3 and Figure S5.1) are shown in Figure S5.2 ($R_{wp}/R_p = 4.81/5.47\%$, $\chi^2 = 9.31$). As can be seen in Figure S5.2, the fit is poor, especially in the high d-spacing range (~ 2.4 Å). No significant improvement on the fitting was achieved by adding a tetragonal phase in the refinement, indicating that there is no minor quenched tetragonal phase. Excess weak reflections could be examined as shown in the inset of Figure S5.2a, which requires a larger supercell. Thus, the following refinements were carried out considering the c-axis doubled supercell as discussed above (Section 3 and Figure S5.1).
Figure S5.2 Rietveld refinement of RT HRPD ND data in S.G. *Cmm2* from (a) backscattering (b) 90 degree banks. Three rows of vertical tick mark the reflections from La$_{1.64}$Ca$_{0.36}$Ga$_{3}$O$_{7.32}$, the vanadium container, and Ga$_2$O$_3$ from bottom to top, respectively. The enlarged inset of (a) between 2.15-2.56Å to show two set of weak reflections, which cannot be accounted for by the *Cmm2* cell, requiring a *c*-doubling cell. The impurity Ga$_2$O$_3$ has contribution to the weak reflections around 2.35 Å marked as 2.
5.2 Orthorhombic cell, \textit{Imm2} space group

The followed Rietveld refinement in the c-doubled supercell in \textit{Imm2} still gave poor fitting (Figure S5.3; $R_{wp}/R_p = 4.12/5.37\%$, $\chi^2 = 6.84$). The fit cannot be improved by switching to the Stephen’s anisotropic broadening function\(^2\) or by adding the tetragonal phase into the refinement, which suggested the investigation of lower symmetry for La\(_{1.64}\)Ca\(_{0.36}\)Ga\(_3\)O\(_{7.32}\).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure.png}
\caption{Rietveld refinement of RT HRPD ND data in S.G. \textit{Imm2} from (a) backscattering (b) 90 degree banks. Three rows of vertical tick mark the reflections from La\(_{1.64}\)Ca\(_{0.36}\)Ga\(_3\)O\(_{7.32}\), the vanadium container, and Ga\(_2\)O\(_3\) from bottom to top, respectively.}
\end{figure}


5.3 Monoclinic cell, $Im\overline{1}$ space group

Figure S5.4 Rietveld refinement of RT HRPD ND data based on the average model in S.G. $Im\overline{1}$ from (a) backscattering (b) 90 degree banks. Three rows of vertical tick mark the reflections from La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$, the vanadium container, and Ga$_2$O$_3$ from bottom to top, respectively.

The Rietveld refinement in the lower symmetry monoclinic space group $Im\overline{1}$ is significantly improved as shown in Figure S5.4 compared with Figure S5.3 and converged to $R_{wp}/R_p = 3.37/4.96\%$, and $\chi^2 = 4.69$. Three distinct interstitial sites were revealed and the total population was constrained to be 2.56 for charge balance as listed in Table S5.2 and Figure S5.5. However, a slight misfit in the high d-spacing range (~2.0 Å) could be observed (Figure S5.4), implying lower symmetry and/or more
ordered extra oxide distribution. Therefore, further refinement was performed in a triclinic cell \((P1)\) by removing the mirror symmetry element in Figure S5.5.

**Table S5.2** Refined structural parameters for \(\text{La}_{1.64}\text{Ca}_{0.36}\text{Ga}_{3}\text{O}_{7.32}\) at room temperature for the average structure in monoclinic \(\text{Im}1\).1

| Atom      | Site | x     | y     | z     | Occupancy       |
|-----------|------|-------|-------|-------|-----------------|
| La/Ca1    | 4b   | 0.3367(1) | 0.4926(2) | 0.7498(1) | 0.780(1)/0.220(1) |
| La/Ca2    | 4b   | 0.3371(1) | 0.4904 (3) | 0.2496(1) | 0.984(1)/0.016(1) |
| La/Ca3a   | 2a   | 0.5    | 0.8309(2) | 0.7538(3) | 0.915(1)/0.085(1) |
| La/Ca3b   | 2a   | 0.5    | 0.1529(2) | 0.7589(2) | 0.620(1)/0.380(1) |
| La/Ca4a   | 2a   | 0.5    | 0.8250(2) | 0.2621(2) | 0.651(1)/0.349(1) |
| La/Ca4b   | 2a   | 0.5    | 0.1534(2) | 0.2464(2) | 0.846(1)/0.154(1) |
| Ga1a      | 4b   | 0.2520(3) | 0.7432(3) | 0.4961(2) | 1                |
| Ga1b      | 4b   | 0.7491(3) | 0.2423(3) | 0.4969(2) | 1                |
| Ga2a      | 4b   | 0.1351(1) | 0.4858(3) | 0.5165(1) | 1                |
| Ga2b      | 4b   | 0.1371(1) | 0.4851(2) | 0.0170(1) | 1                |
| Ga3a1     | 2a   | 0.5    | 0.6368(2) | 0.9818(2) | 1                |
| Ga3a2     | 2a   | 0.5    | 0.3360(2) | 0.9805(2) | 1                |
| Ga3b1     | 2a   | 0.5    | 0.6378(2) | 0.4867(2) | 1                |
| Ga3b2     | 2a   | 0.5    | 0.3438(2) | 0.4823(2) | 1                |
| O1        | 2a   | 0.5    | 0.4871(4) | 0.9088(2) | 1                |
| O2        | 2a   | 0.5    | 0.4926(4) | 0.4044(2) | 1                |
| O3a       | 2a   | 0.5    | 0.0236(2) | 0.5978(3) | 0.704(8)         |
| O3b       | 2a   | 0.5    | 0.9884(11) | 0.6074(6) | 0.296(8)         |
| O4a       | 2a   | 0.5    | -0.0047(11) | 0.0952(5) | 0.444(6)         |
| O4b       | 2a   | 0.5    | 0.9377(4) | 0.0815(6) | 0.556(6)         |
| O5        | 4b   | 0.1376(1) | 0.4923(4) | 0.8454(1) | 1                |
| O6        | 4b   | 0.1376(1) | 0.4931(3) | 0.3441(1) | 1                |
| O7a       | 2a   | 0.5    | 0.6286(2) | 0.6580(3) | 1                |
| O7b       | 2a   | 0.5    | 0.3502(2) | 0.6548(2) | 1                |
| O8a       | 2a   | 0.5    | 0.6238(3) | 0.1540 (3) | 1                |
| O8b       | 2a   | 0.5    | 0.3538(2) | 0.1501(2) | 1                |
| O9a       | 4b   | 0.2384(2) | 0.5998(2) | 0.0802(2) | 1                |
| O9b       | 4b   | 0.7897(2) | 0.36108(2) | 0.1053(2) | 1                |
| O10a      | 4b   | 0.2151(2) | 0.6140(2) | 0.6006(2) | 1                |
| O10b      | 4b   | 0.7895(2) | 0.3630(2) | 0.6020(2) | 1                |
| O11a      | 4b   | 0.8739(2) | 0.2075(2) | 0.3936(2) | 1                |
| O11b      | 4b   | 0.1383(2) | 0.8017(2) | 0.3938(2) | 1                |
| O12a      | 4b   | 0.8722(2) | 0.1959(2) | 0.8932(2) | 1                |
| O12b      | 4b   | 0.1235(1) | 0.7790(1) | 0.8923(2) | 1                |
| O13       | 4b   | 0.490(2)  | 0.1459(4) | 0.0152(7) | 0.155(2)         |
| O14a      | 2a   | 0.5    | 0.8271(3) | 0.4961(4) | 0.673(1)         |
| O14b      | 2a   | 0.5    | 0.1550(6) | 0.484(3)  | 0.294(2)         |
Space group: \textit{Im}11; \( Z = 8; a = 11.4161(1) \text{ Å}, b = 11.2280(1) \text{ Å}, c = 10.4974(1), \alpha = 90.02(1)^\circ, V = 1345.55(1) \text{ Å}^3; \)
\( R_{wp}/R_p(\text{NPD168}) = 6.41/6.30\%; \)
\( R_{wp}/R_p(\text{NPD90}) = 2.90/3.60\%; \)
\( R_{wp}/R_p \) (Total) = 3.37/4.97\%; and \( \chi^2 = 4.72. \)

\(^a\) Occupancies of mixed La/Ca site were constrained to be unity and the total La/Ca = 6.56/1.44

\(^b,c\) Occupancy (Occ.) sum of O3a and O3b was constrained to be unity (Occ.O3a + Occ. O3b = 1), as for O4a and O4b (Occ.O4a + Occ. O4b = 1).

\(^d\) The interstitial oxide content was constrained according to the charge-balanced nominal composition at 2.56 in the unit cell.

| Atom          | \( U_{11} (\text{Å}^2) \) | \( U_{22} (\text{Å}^2) \) | \( U_{33} (\text{Å}^2) \) | \( U_{12} (\text{Å}^2) \) | \( U_{13} (\text{Å}^2) \) | \( U_{23} (\text{Å}^2) \) |
|---------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| La/Ca1\(^a\)  | 0.0055 (5)               | 0.0058 (4)               | 0.0060 (4)               | 0.001 (2)                | 0.0001 (6)               | 0.0015 (13)              |
| La/Ca2\(^a\)  | 0.0207 (5)               | 0.0295 (5)               | 0.0369 (6)               | -0.008 (2)               | -0.0039 (7)              | 0.001 (2)                |
| La/Ca3a\(^a\) | 0.053 (2)                | 0.053 (1)                | 0.056 (1)                | 0                       | 0                        | -0.002 (2)               |
| La/Ca3b\(^a\) | 0.0065 (10)              | 0.0060 (9)               | 0.0066 (10)              | 0                       | 0                        | 0.001 (1)                |
| La/Ca4a\(^a\) | 0.0134 (11)              | 0.0132 (10)              | 0.0205 (11)              | 0                       | 0                        | -0.004 (1)               |
| La/Ca4b\(^a\) | 0.0256 (11)              | 0.0122 (10)              | 0.0348 (10)              | 0                       | 0                        | 0.005 (1)                |
| Ga1a          | 0.0092 (5)               | 0.0093 (5)               | 0.0103 (4)               | -0.0004 (5)              | 0.003 (2)                | 0.004 (2)                |
| Ga1b          | 0.0099 (5)               | 0.0090 (5)               | 0.0175 (5)               | 0.0034 (5)               | 0.007 (2)                | -0.005 (2)               |
| Ga2a          | 0.0237 (6)               | 0.0361 (7)               | 0.0260 (7)               | 0.001 (2)                | -0.002 (1)               | -0.014 (2)               |
| Ga2b          | 0.0056 (5)               | 0.0136 (5)               | 0.0079 (3)               | 0.001 (1)                | -0.0020 (5)              | -0.007 (1)               |
| Ga3a1         | 0.0069 (9)               | 0.0114 (10)              | 0.0118 (10)              | 0                       | 0                        | -0.0004 (1)              |
| Ga3a2         | 0.0084 (10)              | 0.0027 (9)               | 0.0059 (9)               | 0                       | 0                        | -0.0039 (9)              |
| Ga3b1         | 0.087 (11)               | 0.0228 (11)              | 0.0225 (12)              | 0                       | 0                        | -0.003 (1)               |
| Ga3b2         | 0.0149 (10)              | 0.0206 (11)              | 0.0141 (11)              | 0                       | 0                        | -0.004 (1)               |
| O1            | 0.034 (1)                | 0.034 (1)                | 0.024 (1)                | 0                       | 0                        | -0.016 (4)               |
| O2            | 0.0113 (10)              | 0.0146 (10)              | 0.001 (1)                | 0                       | 0                        | 0.001 (3)                |
| O3a/O3b\(^a\) | 0.0021 (11)              | 0.026 (2)                | 0.009 (1)                | 0                       | 0                        | 0.009 (2)                |
| O4a/O4b\(^a\) | 0.048 (2)                | 0.071 (4)                | 0.037 (2)                | 0                       | 0                        | -0.010 (3)               |
| O5            | 0.0243 (9)               | 0.029 (9)                | 0.0255 (8)               | -0.006 (3)               | -0.0030 (9)              | 0.001 (2)                |
| O6            | 0.0052 (7)               | 0.0055 (6)               | 0.0052 (6)               | 0.001 (1)                | 0.0003 (7)               | 0.002 (2)                |
| O7a           | 0.019 (1)                | 0.013 (11)               | 0.0016 (11)              | 0                       | 0                        | 0.001 (1)                |
| O7b           | 0.0018 (11)              | 0.0019 (1)               | 0.0018 (1)               | 0                       | 0                        | 0.0002 (5)               |
| O8a           | 0.052 (2)                | 0.034 (2)                | 0.036 (2)                | 0                       | 0                        | -0.015 (2)               |
| O8b           | 0.0016 (11)              | 0.0018 (11)              | 0.0021 (11)              | 0                       | 0                        | 0.0002 (1)               |
| O9a           | 0.0222 (11)              | 0.050 (1)                | 0.043 (1)                | 0.0012 (11)              | -0.011 (1)               | 0.002 (1)                |
| O9b           | 0.0245 (9)               | 0.0103 (8)               | 0.0124 (9)               | -0.0029 (8)              | 0.0049 (10)              | -0.002 (1)               |
| O10a          | 0.0280 (11)              | 0.0279 (11)              | 0.0201 (11)              | -0.0066 (9)              | -0.009 (1)               | 0.0154 (10)              |
| O10b          | 0.0364 (11)              | 0.0214 (10)              | 0.0203 (11)              | -0.009 (1)               | 0.006 (1)                | 0.001 (1)                |
| O11a          | 0.045 (1)                | 0.057 (1)                | 0.027 (1)                | 0.014 (1)                | -0.004 (1)               | 0.006 (1)                |
| O11b          | 0.0171 (10)              | 0.0354 (11)              | 0.0114 (9)               | 0.0014 (9)               | -0.004 (1)               | -0.003 (1)               |
| O12a          | 0.0290 (11)              | 0.047 (1)                | 0.0249 (11)              | 0.0114 (10)              | -0.004 (1)               | 0.007 (1)                |
| O12b          | 0.0037 (8)               | 0.0056 (8)               | 0.0045 (7)               | 0.0015 (7)               | -0.003 (1)               | -0.001 (1)               |
| O13           | 0.006 (5)                | 0.008 (4)                | 0.008 (4)                | 0.004 (11)               | -0.005 (1)               | -0.005 (4)               |
Table S5.3 Selected inter-atomic distances and BVS calculations for $La_{1.64}Ca_{0.36}Ga_3O_{7.32}$ at room temperature from the average model in monoclinic cell (S.G. $Im\bar{1}$)

| Bond       | Length(Å) | Bond       | Length(Å) |
|------------|-----------|------------|-----------|
| La/Ca1     |           | Ga1a       |           |
| O5         | 2.485(2)  | O11b       | 1.807(4)  |
| O10a       | 2.498(3)  | O9b        | 1.803(3)  |
| O1         | 2.507(2)  | O12a       | 1.825(4)  |
| O10b       | 2.569(3)  | O10a       | 1.867(3)  |
| O7a        | 2.595(3)  | BVS for Ga1a | 3.10    |
| O11b       | 2.639(3)  |           |           |
| O7b        | 2.650(2)  | Ga1b       | 1.808(4)  |
| O11a       | 2.877(3)  | O9a        | 1.827(4)  |
| BVS for La/Ca1 | 2.62/1.50 | O11a       | 1.833(4)  |
|            |           | O12b       | 1.853(4)  |
| La/Ca2     |           | Ga2a       |           |
| O9a        | 2.437(3)  | O4a        | 1.753(3)  |
| O2         | 2.470(2)  | O4b        | 1.771(3)  |
| O6         | 2.484(2)  | O6         | 1.813(2)  |
| O9b        | 2.550(3)  | O10b       | 1.857(3)  |
| O8a        | 2.590(3)  | O10a       | 1.919(3)  |
| O8b        | 2.627(3)  | BVS for Ga2a | 3.02    |
| O12a       | 2.785(4)  |           |           |
| O12b       | 2.842(3)  |           |           |
| BVS for La/Ca2 | 2.70/1.55 | Ga2b       | 1.804(2)  |
|            |           | O5         |           |
| La/Ca3a    |           | Ga3a1      |           |
| O3b        | 2.343(11) | O3b        | 1.831(3)  |
| O11a       | 2.479(3)  | O9b        | 1.870(3)  |
| O7a        | 2.483(4)  | O9a        | 1.854(3)  |
| O6         | 2.585(3)  | BVS for Ga2b | 2.98    |
| O14a       | 2.705(5)  |           |           |
| O3a        | 2.714(4)  | Ga3a1      | 1.814(4)  |
| O9b        | 2.882(2)  | O1         | 1.845(5)  |
| BVS for La/Ca3a | 2.84/1.63 | O11a       | 1.887(3)  |
|            |           |           |           |
| La/Ca3b    |           | Ga3b1      |           |
| O3a        | 2.228(4)  | O8b        | 1.791(3)  |
| O3b        | 2.437(10) | O1         | 1.853(5)  |
| O7b        | 2.471(3)  | O11b       | 1.863(2)  |
| O6         | 2.547(3)  | O13        | 2.169(5)  |
| O11b       | 2.701(3)  | BVS for Ga3a2 | 3.57    |
| O13        | 2.694(8)  |           |           |
| O14b       | 2.89(3)   | Ga3b1      | 1.802(3)  |

*a ADPs of mixed La/Ca and disordered O3a/O3b, O4a/O4b pairs were constrained to be the same value.*
| BVS for La/Ca3b | 3.03/1.74 | O2 | 1.845(5) (x1) |
|------------------|----------|----|----------------|
|                  |          | O12a | 1.875(3) (x2) |
| La/Ca4a         | O4b | 2.279(6) (x1) | O14a | 2.127(4) (x1) |
| O14a            | 2.457(6) (x1) | BVS for Ga3b1 | 3.25 |
| O12a            | 2.475(3) (x2) |
| O8a             | 2.528(4) (x1) | Ga3b2 | O7b | 1.813(3) (x1) |
| O4a             | 2.594(10) (x1) | O12b | 1.846(2) (x2) |
| O5              | 2.600(4) (x2) | O2 | 1.860(5) (x1) |
| O10b            | 2.963(2) (x2) | O14b | 2.120(7) (x1) |
| BVS for La/Ca4a | 3.15/1.81 | BVS for Ga3b2 | 3.31 |
| La/Ca4b         | O4a | 2.381(10) (x1) | O3a | O3b | 0.408(12) (x1) |
| O13             | 2.431(8) (x2) | O14b | 1.90(2) (x1) |
| O14b            | 2.49(3) (x1) | O14a | 2.452(5) (x1) |
| O8b             | 2.468(3) (x1) | O3b | O14a | 2.155(12) (x1) |
| O12b            | 2.515(3) (x2) | O14b | 2.28(2) (x1) |
| O5              | 2.611(4) (x2) | O4a | O4b | 0.663(13) (x1) |
| O10a            | 2.927(2) (x2) | O13 | 1.891(12) (x2) |
| O4b             | 2.976(6) (x1) | O4b | O13 | 2.442(7) (x2) |
| BVS for La/Ca4b | 3.35/1.92 |

**Figure S5.5** Projection view of the crystal structure along the c-axis in $Im\bar{1}l$ symmetry. The dashed line shows the ‘mirror plane’. The A-site cations and oxygens overlapped with galliums were omitted for clarity.

**Figure S5.5** shows a view of the crystal structure along the c-axis. In the crystal structure, Ga1aO4 and Ga1bO4 tetrahedra are 4-connected with no terminal oxygens, the other GaO4 polyhedra are 3-
connected with one non-bridging oxygen. Two interstitial sites O14a and O14b are located on the “mirror” plane, O13 is disordered on either side of this plane. As in to La\(_{1.54}\)Sr\(_{0.46}\)Ga\(_3\)O\(_{7.25}\), all the interstitial oxides are closest to tetrahedra with terminal oxygen, namely Ga\(_3\)a\(_2\)O\(_4\), Ga\(_3\)b\(_1\)O\(_4\), and Ga\(_3\)b\(_2\)O\(_4\). Ga2a and Ga2b are also 3-connected with disordered bridging oxygen pairs of O4a/O4b and O3a/O3b, respectively. There is no interstitial oxide connected to Ga2a and Ga2b, leaving the candidate interstitial sites empty inside the channels neighbouring the occupied interstitials.

5.4 Triclinic cell with space group of \(P1\)

The optimized refinement in triclinic \(P1\) (\(R_{wp}/R_p = 3.21/4.60\%\), and \(\chi^2 = 4.28\), Figure S5.6) exhibited four distinct interstitial sites with total population of 1.28 as listed in Table S5.4. Compared with the crystal structure in monoclinic symmetry \(Im1\) (Section 5.2), all the interstitial oxides are incorporated into GaO\(_4\) tetrahedra with terminal oxygens. Four of the A-sites show cation ordering and are occupied by La only - the occupancy of La was set to be one if it refined to be greater than 0.98. The other four A-sites are disordered and the occupancies were refined to yield a total La/Ca ratio of 6.54/1.44 (Table S5.4). Refinement of a random A-site distribution (La/Ca = 0.82/0.18 for each site) led to a poorer fit (\(R_{wp}/R_p = 3.49/4.84\%\), \(\chi^2 = 4.96\)), which recovered to the previous A-site cation order after the occupancies were refined.
Figure S5.6 Rietveld refinement of RT HRPD ND data for the average model in P1 from (a) backscattering (b) 90 degree bank. Three rows of vertical ticks mark the reflections from La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$, the vanadium container, and Ga$_2$O$_3$ from bottom to top, respectively.

Table S5.4 Refined structural parameters for La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ at room temperature for the average structure model in P1.

| Atom   | Site | x     | y     | z     | Occupancy |
|--------|------|-------|-------|-------|-----------|
| La1a   | la   | 0.2395(2) | 0.0877(2) | 0.8281(2) | 1         |
| La/Ca1b| la   | 0.2390(2) | 0.4077(3) | 0.1503(2) | 0.814(1)/0.186(1)$^3$ |
| La2a   | la   | 0.7411(3) | 0.5894(3) | 0.8235(3) | 1         |
| La2b   | la   | 0.7325(2) | 0.9107(3) | 0.1506(2) | 1         |
| Atom   | Site | $x$  | $y$  | $z$  | $U_{eq}$ |
|--------|------|------|------|------|---------|
| La3a   | 1a   | 0.5777(3) | 0.2456(4) | 0.3282(3) | 1       |
| La/Ca3b| 1a   | 0.9118(3) | 0.2640(3) | 0.6550(3) | 0.312(1)/0.688(1) |
| La/Ca4a| 1a   | 0.0860(2) | 0.7608(3) | 0.3237(3) | 0.623(1)/0.377(1) |
| La/Ca4b| 1a   | 0.4022(3) | 0.7509(2) | 0.6536(2) | 0.811(1)/0.189(1) |
| Ga1a   | 1a   | 0.2323(4) | 0.7434(4) | 0.9860(4) | 1       |
| Ga1b   | 1a   | 0.2346(4) | 0.2472(5) | 0.4888(5) | 1       |
| Ga1c   | 1a   | 0.7319(5) | 0.2385(4) | 0.9810(4) | 1       |
| Ga1d   | 1a   | 0.7409(4) | 0.7462(4) | 0.4935(4) | 1       |
| Ga2a   | 1a   | 0.0023(2) | 0.6555(3) | 0.6233(2) | 1       |
| Ga2b   | 1a   | 0.0086(3) | 0.3778(3) | 0.3556(3) | 1       |
| Ga2c   | 1a   | 0.5084(2) | 0.1534(2) | 0.6255(2) | 1       |
| Ga2d   | 1a   | 0.5042(2) | 0.8835(3) | 0.3487(2) | 1       |
| Ga3a1  | 1a   | 0.6189(2) | 0.4804(2) | 0.1354(2) | 1       |
| Ga3a2  | 1a   | 0.3202(2) | 0.4781(3) | 0.8359(3) | 1       |
| Ga3b1  | 1a   | 0.1240(3) | 0.9855(3) | 0.1354(3) | 1       |
| Ga3b2  | 1a   | 0.8247(2) | 0.9825(3) | 0.8407(3) | 1       |
| O1     | 1a   | 0.3942(4) | 0.4074(4) | 0.9853(4) | 1       |
| O2     | 1a   | 0.8924(3) | 0.9002(3) | 0.9812(3) | 1       |
| O3a    | 1a   | 0.6267(4) | 0.0856(4) | 0.5294(4) | 0.618(5) |
| O3b    | 1a   | 0.5758(6) | 0.0985(6) | 0.4753(6) | 0.382(5) |
| O4a    | 1a   | 0.0958(9) | 0.5927(8) | 0.5029(8) | 0.272(12) |
| O4b    | 1a   | 0.0530(4) | 0.5911(5) | 0.4562(4) | 0.728(12) |
| O5a    | 1a   | 0.3367(3) | 0.9809(3) | 0.6249(3) | 1       |
| O5b    | 1a   | 0.3393(3) | 0.7092(3) | 0.3542(3) | 1       |
| O6a    | 1a   | 0.8382(3) | 0.48417(29) | 0.6314(3) | 1       |
| O6b    | 1a   | 0.8303(3) | 0.2048(4) | 0.3478(3) | 1       |
| O7a    | 1a   | 0.2877(3) | 0.1566(3) | 0.1268(3) | 1       |
| O7b    | 1a   | 0.0056(3) | 0.1541(3) | 0.8493(3) | 1       |
| O8a    | 1a   | 0.7779(3) | 0.6501(3) | 0.1216(3) | 1       |
| O8b    | 1a   | 0.5053(3) | 0.6530(3) | 0.8541(3) | 1       |
| O9a    | 1a   | 0.6767(4) | 0.3178(5) | 0.8344(5) | 1       |
| O9b    | 1a   | 0.6998(4) | 0.8656(4) | 0.3870(5) | 1       |
| O9c    | 1a   | 0.4697(4) | 0.8887(4) | 0.1435(4) | 1       |
| O9d    | 1a   | 0.4675(3) | 0.3194(3) | 0.5831(3) | 1       |
| O10a   | 1a   | 0.2110(4) | 0.8137(4) | 0.8281(4) | 1       |
| O10b   | 1a   | 0.2304(4) | 0.4080(4) | 0.4271(4) | 1       |
| O10c   | 1a   | 0.9664(4) | 0.3801(4) | 0.1482(4) | 1       |
| O10d   | 1a   | 0.9690(3) | 0.8159(3) | 0.5840(3) | 1       |
| O11a   | 1a   | 0.6277(5) | 0.2858(5) | 0.1047(5) | 1       |
| O11b   | 1a   | 0.5937(4) | 0.5188(4) | 0.3266(4) | 1       |
| O11c   | 1a   | 0.1844(3) | 0.5249(3) | 0.9256(3) | 1       |
| O11d   | 1a   | 0.1962(4) | 0.2512(4) | 0.6644(4) | 1       |
| O12a   | 1a   | 0.1043(4) | 0.7740(4) | 0.0825(4) | 1       |
Space group: P1; Z = 4; a = 9.5735(1) Å, b = 9.5748(1) Å, c = 9.5691(1) Å, α = 106.78(1)°, β = 108.17(1)°, γ = 113.51(1)°, V = 672.85(1) Å³. \(R_wp/R_p\% (ND168) = 6.08/5.84, R_wp/R_p\% (ND90) = 2.77/3.33, R_wp/R_p\% (Total) = 3.21/4.60, \chi^2 = 4.28.

\(^a\) Occupancies of the mixed La/Ca site were constrained to be unity and the total La/Ca ratio 6.56/1.44

\(^b,c\) Occupancy sum of O3a and O3b was constrained to be unity (Occ.O3a + Occ. O3b = 1); the same to O4a and O4b (Occ.O4a + Occ. O4b = 1).

\(^d\) The interstitial oxide content was fixed according to the charge-balanced nominal composition of 1.28 in the unit cell.

| Atom       | \(U_{11}\) (Å²) | \(U_{22}\) (Å²) | \(U_{33}\) (Å²) | \(U_{12}\) (Å²) | \(U_{13}\) (Å²) | \(U_{23}\) (Å²) |
|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| La1a       | 0.0037(5)       | 0.0036(5)       | 0.0041(5)       | 0.0033(4)       | 0.0010(4)       | 0.0013(5)       |
| La/Ca1b\(^b\) | 0.0087(6)       | 0.0098(6)       | 0.0054(7)       | 0.0081(5)       | 0.0019(5)       | 0.0037(6)       |
| La2a       | 0.0399(8)       | 0.0441(11)      | 0.0471(11)      | 0.0291(7)       | 0.0209(7)       | 0.0078(9)       |
| La2b       | 0.0263(7)       | 0.0344(9)       | 0.0289(9)       | 0.0188(6)       | 0.0172(6)       | 0.0112(7)       |
| La3a       | 0.0441(9)       | 0.0463(11)      | 0.0474(12)      | 0.0279(7)       | 0.0207(9)       | 0.0172(8)       |
| La/Ca3b\(^b\) | 0.0169(9)       | 0.0168(9)       | 0.0141(10)      | 0.0142(7)       | 0.0118(8)       | 0.0124(7)       |
| La/Ca4a\(^b\) | 0.0104(7)       | 0.0144(9)       | 0.0136(9)       | 0.0101(6)       | 0.0034(7)       | 0.0040(7)       |
| La/Ca4b\(^b\) | 0.0164(7)       | 0.0137(7)       | 0.0133(8)       | 0.0112(5)       | 0.0028(6)       | 0.0091(5)       |
| Ga1a       | 0.0134(7)       | 0.0111(7)       | 0.0124(8)       | 0.0071(5)       | 0.0044(7)       | 0.0071(7)       |
| Ga1b       | 0.0127(7)       | 0.0139(7)       | 0.0111(7)       | 0.0071(5)       | 0.0075(6)       | 0.0057(7)       |
| Ga1c       | 0.0109(7)       | 0.0142(8)       | 0.0132(8)       | 0.0054(5)       | 0.0037(7)       | 0.0063(7)       |
| Ga1d       | 0.0103(7)       | 0.0093(7)       | 0.0082(7)       | 0.0053(5)       | 0.0031(6)       | 0.0046(7)       |
| Ga2a       | 0.0173(8)       | 0.0202(9)       | 0.0197(8)       | 0.0061(7)       | 0.0135(6)       | 0.0072(8)       |
| Ga2b       | 0.0339(9)       | 0.0435(12)      | 0.040(1)        | 0.0119(9)       | 0.0267(7)       | 0.0117(11)      |
| Ga2c       | 0.0018(6)       | 0.0016(6)       | 0.0017(6)       | 0.0009(5)       | 0.0007(5)       | 0.0015(6)       |
| Ga2d       | 0.0146(7)       | 0.0212(9)       | 0.0163(8)       | 0.0051(7)       | 0.0142(5)       | 0.0070(8)       |
| Ga3a1      | 0.0057(6)       | 0.0024(6)       | 0.0035(7)       | 0.0022(5)       | 0.0028(6)       | 0.0005(5)       |
| Ga3a2      | 0.0099(7)       | 0.0190(9)       | 0.0216(9)       | 0.0091(6)       | 0.0052(7)       | 0.0030(7)       |
| Ga3b1      | 0.0182(7)       | 0.0227(9)       | 0.0194(9)       | 0.0116(7)       | 0.0117(7)       | 0.0080(7)       |
| Ga3b2      | 0.0145(8)       | 0.0206(9)       | 0.0231(9)       | 0.0090(7)       | 0.0105(7)       | 0.0057(7)       |
| O1         | 0.0267(10)      | 0.0352(11)      | 0.0265(11)      | 0.0129(8)       | 0.0140(9)       | 0.0162(9)       |
| O2         | 0.0114(8)       | 0.0171(9)       | 0.0121(9)       | 0.0051(7)       | 0.0083(7)       | 0.0103(7)       |
|    | Bond         | Length (Å) | Bond         | Length (Å) |
|----|--------------|------------|--------------|------------|
| O3a/3b | O3a/O3b     | 0.0031(11) | O4a/4b       | 0.0049(15) |
|     | O5a          | 0.0107(10) | O5b          | 0.0262(12) |
|     | O6a          | 0.0040(9)  | O6b          | 0.0245(12) |
|     | O7a          | 0.0043(8)  | O7b          | 0.0203(12) |
|     | O8a          | 0.0089(9)  | O8b          | 0.0209(11) |
|     | O9a          | 0.0547(16)| O9b          | 0.0489(17) |
|     | O10a         | 0.0533(17)| O10b         | 0.0265(14) |
|     | O10c         | 0.0156(11)| O10d         | 0.0602(9)  |
|     | O11a         | 0.0456(16)| O11b         | 0.0312(15) |
|     | O11c         | 0.0057(9)  | O11d         | 0.0164(12) |
|     | O12a         | 0.0252(11)| O12b         | 0.0475(16) |
|     | O12c         | 0.0046(9)  | O12d         | 0.0140(11) |
|     | O13a/O3b     | 0.025(3)   | O13a/O3b     | 0.025(3)   |
|     | O14a         | 0.035(2)   | O14b         | 0.37(2)    |

* ADPs for La/Ca on all sites and for O3a/O3b, O4a/O4b, O13a and O13b were constrained to be the same value.

Table S5.5 Selected inter-atomic distances and BVS calculations for La\textsubscript{1.64}Ca\textsubscript{0.36}Ga\textsubscript{3}O\textsubscript{7.32} at room temperature from the average model in P\textsubscript{1}.

| Bond  | Length (Å) |
|-------|------------|
| La1a  | -O1 (x1)  | 2.482(4) |
|       | -O10d (x1)| 2.505(2) |
|       | -O10a (x1)| 2.527(5) |
|       | -O5a (x1) | 2.536(4) |
|       | -O11d (x1)| 2.570(5) |
| Ga1a  | -O12a (x1)| 1.810(6) |
|       | -O10a (x1)| 1.812(6) |
|       | -O11c (x1)| 1.815(5) |
|       | -O9c (x1) | 1.871(4) |
|       | BVS for Ga1a| 3.08 |

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| Bond | Distance (Å) | Bond | Distance (Å) |
|------|-------------|------|-------------|
| La1a -O7a | 2.581(3) | Ga1b -O10b | 1.811(7) |
| La1a -O7b | 2.608(4) | -O11d | 1.822(7) |
| La1a -O5b | 2.536(4) | -O12b | 1.827(4) |
| La1a -O7a | 2.587(4) | -O12c | 1.814(5) |
| La1a -O7b | 2.608(3) | -O9a | 1.816(7) |
| La1a -O10b | 2.675(5) | -O11a | 1.841(7) |
| La1a -O11c | 2.704(4) | -O10c | 1.875(4) |
| La1a -O11b | 2.832(4) | BVS for Ga1b | 3.08 |
| La/Ca1b -O1 | 2.483(5) | -O9d | 1.849(5) |
| La/Ca1b -O5b | 2.536(4) | -O10d | 1.803(5) |
| La/Ca1b -O7a | 2.587(4) | -O6a | 1.805(4) |
| La/Ca1b -O7b | 2.608(3) | -O10a | 1.886(3) |
| La/Ca1b -O10b | 2.675(5) | BVS for La/Ca1b | 2.50/1.44 |
| La/Ca1b -O11c | 2.704(4) | BVS for Ga1c | 3.01 |
| La2a -O2 | 2.415(4) | -O10d | 1.814(5) |
| La2a -O6a | 2.450(5) | -O12d | 1.826(6) |
| La2a -O9a | 2.464(6) | -O11b | 1.849(4) |
| La2a -O9d | 2.498(3) | BVS for Ga1d | 3.09 |
| La2a -O8a | 2.618(4) | Ga2a -O4a | 1.778(10) |
| La2a -O8b | 2.638(5) | -O10d | 1.803(5) |
| La2a -O12d | 2.766(5) | -O6a | 1.805(4) |
| La2a -O12a | 2.924(4) | -O4b | 1.824(5) |
| BVS for La2a | 2.77 | BVS for Ga2a | 3.10 |
| La2b -O9c | 2.417(5) | Ga2b -O4a | 1.772(7) |
| La2b -O6b | 2.468(4) | -O4b | 1.788(5) |
| La2b -O9b | 2.510(6) | -O6b | 1.805(4) |
| La2b -O2 | 2.561(4) | -O10b | 1.884(5) |
| La2b -O8b | 2.588(3) | -O10c | 1.907(5) |
| La2b -O8a | 2.652(5) | BVS for Ga2b | 2.96 |
| La2b -O12b | 2.706(4) | BVS for La2b | 2.76 |
| La/Ca3a -O3b | 2.260(8) | Ga2c -O3b | 1.781(7) |
| La/Ca3a -O11a | 2.433(6) | -O9a | 1.794(3) |
| La/Ca3a -O7a | 2.444(4) | -O5a | 1.803(3) |
| La/Ca3a -O14a | 2.552(6) | -O3a | 1.885(5) |
| La/Ca3a -O6b | 2.555(5) | -O9d | 1.902(5) |
| La/Ca3a -O11b | 2.563(6) | BVS for Ga2c | 3.06 |
| La/Ca3a -O13b | 2.621(9) | BVS for La2b | 2.76 |
| La/Ca3a -O6a | 2.640(3) | Ga2d -O3b | 1.758(6) |

25
|                  | BVS for Ga2d  3.01 | BVS for Ga3a1  3.30 | BVS for Ga3a2  3.29 | BVS for Ga3b1  3.28 | BVS for Ga3b2  3.28 |
|------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| -O3a (x1) 2.826(6) |                     |                     |                     |                     |                     |
| -O9e (x1) 2.903(5)  |                     |                     |                     |                     |                     |
| -O9d (x1) 2.960(5)  |                     |                     |                     |                     |                     |
| BVS for La/Ca3a  2.88/1.66 |                 |                     |                     |                     |                     |
| Ga3a1 -O8a (x1) 1.803(4) |                 |                     |                     |                     |                     |
| La/Ca3b -O3a (x1) 2.205(4) |                 |                     |                     |                     |                     |
| -O7b (x1) 2.492(5)  |                     |                     |                     |                     |                     |
| -O6a (x1) 2.521(5)  |                     |                     |                     |                     |                     |
| -O11c (x1) 2.570(3) |                     |                     |                     |                     |                     |
| -O13a (x1) 2.587(8) |                     |                     |                     |                     |                     |
| -O3b (x1) 2.593(5)  |                     |                     |                     |                     |                     |
| -O6b (x1) 2.613(4)  |                     |                     |                     |                     |                     |
| -O11d (x1) 2.748(5) |                     |                     |                     |                     |                     |
| BVS for La/Ca3b  2.44/1.40 |                 |                     |                     |                     |                     |
| Ga3a2 -O8b (x1) 1.802(4) |                 |                     |                     |                     |                     |
| La/Ca4a -O4b (x1) 2.319(6) |                 |                     |                     |                     |                     |
| -O12a (x1) 2.403(5) |                     |                     |                     |                     |                     |
| -O8a (x1) 2.516(3)  |                     |                     |                     |                     |                     |
| -O14a (x1) 2.551(5) |                     |                     |                     |                     |                     |
| -O5a (x1) 2.579(3)  |                     |                     |                     |                     |                     |
| -O5b (x1) 2.609(4)  |                     |                     |                     |                     |                     |
| -O12b (x1) 2.657(6) |                     |                     |                     |                     |                     |
| -O4a (x1) 2.675(9)  |                     |                     |                     |                     |                     |
| -O13b (x1) 2.777(8) |                     |                     |                     |                     |                     |
| -O10d (x1) 3.032(4) |                     |                     |                     |                     |                     |
| -O10c (x1) 3.059(4) |                     |                     |                     |                     |                     |
| BVS for La/Ca4a  2.85/1.64 |                 |                     |                     |                     |                     |
| Ga3b2 -O7b (x1) 1.809(4) |                 |                     |                     |                     |                     |
| La/Ca4b -O14b (x1) 2.276(11) |                |                     |                     |                     |                     |
| -O4a (x1) 2.352(7)  |                     |                     |                     |                     |                     |
| -O8b (x1) 2.476(4)  |                     |                     |                     |                     |                     |
| -O12c (x1) 2.519(2) |                     |                     |                     |                     |                     |
| -O12d (x1) 2.551(5) |                     |                     |                     |                     |                     |
| -O13a (x1) 2.554(8) |                     |                     |                     |                     |                     |
| -O5a (x1) 2.581(4)  |                     |                     |                     |                     |                     |
| -O5b (x1) 2.608(4)  |                     |                     |                     |                     |                     |
| -O4b (x1) 2.720(4)  |                     |                     |                     |                     |                     |
| -O10b (x1) 2.746(4) |                     |                     |                     |                     |                     |
| -O10a (x1) 2.951(5) |                     |                     |                     |                     |                     |
| BVS for La/Ca4b  2.78/1.60 |                 |                     |                     |                     |                     |
Figure S5.7 (a) Parallel polyhedral view and (b) projection view along the [110] direction of La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ ($P1$, average model) to show the A site cation location and ordering. The A site cations fill the Ga$_3$O$_7$ interlayer space and sandwich the interstitial sites in the 5-rings. (c) Parallel view of the highlighted part in (b) to show ordered cations and their distances to interstitial oxide, where the Ga and framework oxygens were omitted for clarity. Paired interstitials O13a/O14b and O13b/O14a are shown as red and green spheres in (b) and (c), respectively. La-sites, yellow; La/Ca-sites, blue; La/Ca1b = 0.814(1)/0.186(1), La/Ca3b = 0.312(1)/0.688(1), La/Ca4a = 0.623(1)/0.377(1), La/Ca4b = 0.811(1)/0.189(1).
Figure S5.8 Projection view of La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ in $P1$ along [110] direction to show (a) the location of interstitial oxides and atomic displacement parameters (ADPs, 80% probability shown) within the rings and (b) the environment of O14a within 3Å in the average structure. The numbers denote the distances from each atom to O14a. Local atomic displacements of La3a, La/Ca4a, O3b, O12a, and O12b towards La3al, La/Ca4al, O3a, O12al, and O12bl due to the O14a incorporation are marked by arrows.
6. Simulated annealing (SA) approach

To validate the structure model \( (P1) \) from the least-squares Rietveld refinement, simulated annealing (SA) analysis was performed. Peak shape and background parameters were obtained by Le Bail refinement of the NPD data from the 90° and backscattering banks of detectors of the HRPD instrument using TOPAS\(^3\), with a single main melilitite phase. The standard simulated annealing macro implemented within TOPAS was run using a fixed framework model from the GSAS Rietveld refinement, with eight possible interstitial oxygen sites specified. The occupancies of these sites were allowed to vary during the minimization, along with the La and Ca occupancies of the split A sites. Penalty functions were specified to bias the total interstitial oxygen and La/Ca occupancies towards previously obtained values constrained by the chemical composition. The SA result \( (R_{wp} = 6.78 \%, R_p = 7.72 \%, \chi^2 = 4.32, \text{Figure S5.2}) \) is in good agreement with refined structure (Figure S5.1 and Table S5.2) and confirmed the reliability of the proposed structural model regarding the interstitial occupancies and A site cation ordering.

**Figure S6.1** Interstitial oxide location and population from the simulated annealing analysis with TOPAS
**Figure S6.2** SA plots for neutron data from backscattering (left) and 90° bank (right), respectively.

**Table S6.1** A-site La/Ca cation ordering extracted from the crystal structure from different approaches (1% error of occupancy), a) GSAS Rietveld refinement (La/Ca = 6.56/1.44); b) TOPAS simulated annealing (La/Ca = 6.61/1.39).

|        | La/Ca1a | La/Ca1b | La/Ca2a | La/Ca2b | La/Ca3a | La/Ca3b | La/Ca4a | La/Ca4b |
|--------|---------|---------|---------|---------|---------|---------|---------|---------|
| a      | 1.00/000| 0.81/0.19| 1.00/0.00| 1.00/0.00| 1.00/0.00| 0.31/0.69| 0.62/0.38| 0.81/0.19|
| b      | 0.99/0.01| 0.91/0.09| 1.00/0.00| 0.94/0.06| 1.00/0.00| 0.35/0.65| 0.60/0.40| 0.82/0.18|

7. **Structure refinement for La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ in split model (triclinic $P1$)**

In this split-site model, the relaxations around interstitials were modelled by introducing atomic displacements as shown in **Table S7.1-3**. Ga3a1, O11a, O11b, and La3a were displaced to Ga3a1L, O11aL, O11bL, and La3aS around O13b, including O4a in the local defect structure. Similarly, Ga3a2L, O11cL, O11dL, La/Ca3bL, La/Ca4bL, and O4b are involved in the local defect structure around O13a, Ga3b1L, O12aL, O12bL, La/Ca3aL, La/Ca4aL, and O3a around O14a, Ga3b2L, O12cL, O12dL, La/Ca4bS, and O3b around O14b, respectively. This models the cases where an interstitial defect is present and where it is absent.
Figure S7.1 Rietveld refinement of RT HRPD ND data for the split-site model for La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ in $P\bar{1}$ from (a) backscattering bank and (b) 90 degree bank. Three rows of vertical tick mark the reflections from La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$, the vanadium container, and Ga$_2$O$_3$ from bottom to top, respectively.

Table S7.1 Refined structural parameters for La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ at room temperature for the split-site model in the triclinic cell ($P\bar{1}$)

| Atom     | $x$     | $y$     | $z$     | $U_{iso}$ (Å$^2$) | Occupancy  |
|----------|---------|---------|---------|------------------|------------|
| La1a     | 0.2389(3)| 0.0887(2)| 0.8285(3)| -                | 1          |
| La/Ca1b  | 0.2381(2)| 0.4102(3)| 0.1501(2)| -                | 0.825(1)/0.175(1)$^b$ |
| La2a     | 0.7381(4)| 0.5852(3)| 0.8259(4)| -                | 1          |
| La2b     | 0.7343(2)| 0.9124(3)| 0.1514(2)| -                | 1          |
| La3a     | 0.5747(11)| 0.2569(8)| 0.3257(10)| 0.0411(6)       | 0.241(1)$^b$ |
| La3a$_L$ | 0.5747(5)| 0.2394(5)| 0.3306(5)| 0.0411(6)       | 0.582(1)$^{b,3}$ |
| La3a$_S$ | 0.5896(13)| 0.2644(14)| 0.3227(14)| 0.0411(6)       | 0.177(1)$^{b,2}$ |
| La/Ca3b  | 0.9059(4)| 0.2661(4)| 0.6588(4)| 0.0027(5)       | 0.227(1)/0.501(1)$^b$ |
| La3/Ca3b | 0.9158(10)| 0.2669(10)| 0.6426(10)| 0.0027(5)       | 0.085(1)/0.187(1)$^{b,1}$ |
|     | La/Ca4a | La/Ca4aL | La/Ca4b | La/Ca4bL | La/Ca4bS |
|-----|---------|----------|---------|----------|---------|
|     | 0.0758(7) | 0.7556(7) | 0.3202(7) | 0.0118(5) | 0.260(1)/0.157(1) |
|     | 0.0886(4) | 0.7659(5) | 0.3173(5) | 0.0118(5) | 0.363(1)/0.220(1) |
|     | 0.4020(1) | 0.7539(1) | 0.6549(1) | 0.0127(5) | 0.375(1)/0.100(1) |
|     | 0.3808(9) | 0.7289(10) | 0.649(1)  | 0.0127(5) | 0.220(1)/0.051(1) |
|     | 0.4121(1) | 0.7643(1) | 0.6548(1) | 0.0127(5) | 0.199(1)/0.046(1) |

|     | Ga1a | Ga1b | Ga1c | Ga1d | Ga2a |
|-----|------|------|------|------|------|
|     | 0.2302(4) | 0.2353(4) | 0.7337(4) | 0.7373(4) | 0.0023(3) |
|     | 0.2495(5) | 0.2434(3) | 0.7481(4) | 0.9831(4) | 0.6538(3) |
|     | 0.4926(4) | 0.9842(4) | 0.4931(4) | 0.6262(3) | 0.3810(3) |
|     | -     | -     | -     | -     | -     |

|     | Ga2b | Ga2c | Ga2d | Ga3a1 | Ga3a1L |
|-----|------|------|------|-------|--------|
|     | 0.0053(3) | 0.5013(2) | 0.5006(2) | 0.6144(2) | 0.6366(4) |
|     | 0.3494(3) | 0.1549(2) | 0.8853(3) | 0.4834(3) | 0.4876(3) |
|     | -     | -     | -     | -     | -     |

|     | Ga3a2 | Ga3b1 | Ga3b1L | Ga3b2 | Ga3b2L |
|-----|------|------|--------|------|--------|
|     | 0.3073(4) | 0.1140(4) | 0.1314(3) | 0.8262(3) | 0.8116(4) |
|     | 0.4826(4) | 0.9782(3) | 0.9838(3) | 0.9852(3) | 0.9844(4) |
|     | 0.8215(5) | 0.1257(4) | 0.1438(2) | 0.8482(3) | 0.8281(4) |
|     | 0.0135(5) | 0.0105(4) | 0.0105(4) | 0.0238(5) | 0.0238(5) |
|     | 0.271(1) | 0.418(1)  | 0.582(1)  | 0.755(1)  | 0.245(1)  |
|     | -     | -     | -     | -     | -     |

|     | O1    | O2    | O3a   | O3b   | O4a   |
|-----|------|------|------|------|------|
|     | 0.3945(3) | 0.8923(3) | 0.6158(4) | 0.5634(6) | 0.0860(12) |
|     | 0.4098(3) | 0.8988(3) | 0.0934(4) | 0.1024(6) | 0.5971(12) |
|     | 0.9902(3) | 0.9824(3) | 0.5246(4) | 0.4654(6) | 0.4910(12) |
|     | -     | -     | -     | -     | -     |

|     | O4b   | O5a   | O5b   | O6a   | O6b   |
|-----|------|------|------|------|------|
|     | 0.0396(4) | 0.3384(3) | 0.3343(3) | 0.8374(3) | 0.8429(3) |
|     | 0.5909(4) | 0.9802(3) | 0.7086(3) | 0.4824(3) | 0.2076(3) |
|     | 0.4463(4) | 0.6286(3) | 0.3516(3) | 0.6339(3) | 0.3571(3) |
|     | -     | -     | -     | -     | -     |

|     | O7a   | O7b   | O8a   | O8b   | O9a   |
|-----|------|------|------|------|------|
|     | 0.2889(3) | 0.0052(3) | 0.7797(3) | 0.5078(3) | 0.6688(4) |
|     | 0.1587(2) | 0.1542(3) | 0.6522(3) | 0.6625(3) | 0.3144(5) |
|     | 0.1307(2) | 0.8507(3) | 0.1232(3) | 0.8650(3) | 0.8340(4) |
|     | -     | -     | -     | -     | -     |

|     | O9b   | O9c   | O9d   | O10a  | O10b  |
|-----|------|------|------|------|------|
|     | 0.7051(5) | 0.4649(4) | 0.4659(3) | 0.2092(4) | 0.2237(4) |
|     | 0.8742(5) | 0.8869(4) | 0.3170(4) | 0.8201(3) | 0.4015(4) |
|     | 0.3911(5) | 0.1437(4) | 0.5778(4) | 0.8299(3) | 0.4210(4) |
|     | -     | -     | -     | -     | -     |

|     | O10c  | O10d  |
|-----|------|------|
|     | 0.9655(4) | 0.9667(3) |
|     | 0.3805(5) | 0.8159(3) |
|     | 0.1486(4) | 0.5881(4) |
|     | -     | -     |
O11a 0.6190(4) 0.2813(3) 0.0961(5) 0.0453(13) 0.823(1) b
O11aL 0.5777(6) 0.2560(5) 0.0496(9) 0.0453(13) 0.177(1) b,2
O11b 0.5872(3) 0.5166(5) 0.3255(3) 0.0155(9) 0.823(1) b
O11bL 0.5580(5) 0.5326(13) 0.3135(4) 0.0155(9) 0.177(1) b,2
O11c 0.1701(4) 0.5185(4) 0.9060(4) 0.0087(7) 0.729(1) b
O11cL 0.2004(5) 0.5327(6) 0.9464(6) 0.0087(7) 0.271(1) b,1
O11d 0.1791(5) 0.2578(4) 0.6579(4) 0.0136(8) 0.729(1) b
O11dL 0.1995(12) 0.2440(8) 0.6682(8) 0.0136(8) 0.271(1) b
O12a 0.1210(6) 0.7819(4) 0.1003(7) 0.0243(12) 0.418(1) b,1
O12aL 0.0653(4) 0.7473(4) 0.0355(5) 0.0243(12) 0.582(1) b,3
O12b 0.1112(6) 0.0199(8) 0.3305(4) 0.0148(10) 0.418(1) b
O12bL 0.0678(4) 0.0352(5) 0.3128(4) 0.0148(10) 0.582(1) b,3
O12c 0.6620(3) 0.0147(3) 0.8920(4) 0.0037(7) 0.755(1) b
O12cL 0.6854(5) 0.0286(6) 0.9398(5) 0.0037(7) 0.245(1) b,4
O12d 0.6683(4) 0.7692(4) 0.6517(4) 0.0095(9) 0.755(1) b
O12dL 0.7090(7) 0.7465(4) 0.6809(5) 0.0095(9) 0.245(1) b,4
O13a 0.1511(7) 0.4990(7) 0.6405(7) - 0.271(1) d,1
O13b 0.8136(4) 0.5007(6) 0.3454(6) - 0.177(1) d,2
O14a 0.3330(4) 1.0134(4) 0.3316(4) - 0.582(1) d,3
O14b 0.6262(6) 0.9658(5) 0.6346(4) - 0.245(1) d,4

\[ R_{wp}/R_p\% (\text{ND168}) = 6.32/5.99, \quad R_{wp}/R_p\% (\text{ND90}) = 2.83/3.41, \quad R_{wp}/R_p\% (\text{Total})= 3.30/4.72, \quad \chi^2 = 4.81. \]

\(^a\) Occupancies of mixed La/Ca sited were constrained to be unity, the ADPs were refined to have the same values.

\(^b\) ADPs for related bulk- and defect- structure atoms were constrained to be the same, and the total occupancy was constrained to be unity, e.g. Occ.(La3a) + Occ.(La3aL) + Occ.(La3as) = 1.

\(^c\) Occupancies of O3a/O3b, and O4a/O4b pairs were constrained to be unity, and the ADPs were refined to have the same values, respectively.

\(^d\) The interstitial oxide content was fixed according to the charge-balanced nominal composition of 1.28 in the unit cell.

\(^{1,2,3,4}\) Occupancies were constrained to have the same values as the defect interstitials with which they are associated.

| Atom     | U11 (Å\(^2\)) | U22 (Å\(^2\)) | U33 (Å\(^2\)) | U12 (Å\(^2\)) | U13 (Å\(^2\)) | U23 (Å\(^2\)) |
|----------|---------------|---------------|---------------|---------------|---------------|---------------|
| La1a     | 0.0094(6)     | 0.0083(6)     | 0.0101(7)     | 0.0085(5)     | 0.0033(5)     | 0.0025(6)     |
| La/Ca1b  | 0.0067(7)     | 0.0073(7)     | 0.0058(7)     | 0.0047(6)     | 0.0018(6)     | 0.0042(6)     |
| La2a     | 0.0406(9)     | 0.0485(12)    | 0.0465(12)    | 0.0287(8)     | 0.0213(7)     | 0.0109(10)    |
| La2b     | 0.0160(7)     | 0.0254(8)     | 0.0195(9)     | 0.0126(6)     | 0.0110(6)     | 0.0089(7)     |
### Table S7.2

| Bulk Structure | Defect Structure | Bond Length (Å) | Bond | Defect Length (Å) |
|----------------|-----------------|----------------|------|------------------|
| La1a -O10a (x1) | La1a -O11dL (x1) | 2.476(4) | -O11dL (x1) | 2.471(9) |
| La1b -O10a (x1) | La1b -O11dL (x1) | 2.495(4) | -O11dL (x1) | 2.679(5) |

- ADPs for La/Ca on all sites and for O3a/O3b, O4a/O4b, O13a and O13b were constrained to be the same value.

Table S7.2 Selected inter-atomic distances and BVS calculations for La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$ at room temperature from the split-site model in $P1$. 

- O3a/3b$^a$
- O4a/4b$^a$
|     |     | Value |     |     | Value |
|-----|-----|-------|-----|-----|-------|
| -O10d | (x1) | 2.503(3) | -O11b | (x1) | 2.507(5) |
| -O5a | (x1) | 2.534(4) | -O11c_L | (x1) | 2.554(7) |
| -O7b | (x1) | 2.605(4) | -O10c | (x1) | 2.505(5) |
| -O7a | (x1) | 2.608(3) | -O5b | (x1) | 2.518(4) |
| -O11d | (x1) | 2.701(5) | -O7b | (x1) | 2.605(3) |
| -O11a | (x1) | 3.051(4) | -O7a | (x1) | 2.607(4) |
|     |     | 2.59   | La1b  | -O1 | 2.452(5) |
|     |     |     | -O10c | (x1) | 2.505(5) |
|     |     |     | -O5b | (x1) | 2.518(4) |
|     |     |     | -O7b | (x1) | 2.605(3) |
|     |     |     | -O10b | (x1) | 2.662(5) |
|     |     |     | -O11b | (x1) | 2.797(4) |
|     |     |     | -O11c | (x1) | 2.818(5) |
|     |     | 2.51   | La2a  | -O2 | 2.434(4) |
|     |     |     | -O9a | (x1) | 2.438(6) |
|     |     |     | -O6a | (x1) | 2.459(5) |
|     |     |     | -O9d | (x1) | 2.511(3) |
|     |     |     | -O8a | (x1) | 2.589(5) |
|     |     |     | -O8b | (x1) | 2.684(5) |
|     |     |     | -O12d | (x1) | 2.875(6) |
|     |     |     | -O12a | (x1) | 3.084(5) |
|     |     | 2.65   | La2b  | -O9c | 2.467(5) |
|     |     |     | -O6b | (x1) | 2.472(4) |
|     |     |     | -O9b | (x1) | 2.505(6) |
|     |     |     | -O8b | (x1) | 2.511(3) |
|     |     |     | -O2  | (x1) | 2.546(4) |
|     |     |     | -O8a | (x1) | 2.649(5) |
|     |     |     | -O12c | (x1) | 2.911(5) |
|     |     |     | -O12b | (x1) | 3.029(6) |
|     |     | 2.58   | La3a  | -O3b | 2.256(12) |
|     |     |     | -O7a | (x1) | 2.367(9) |
|     |     |     | -O11a | (x1) | 2.421(12) |
|     |     |     | -O11b | (x1) | 2.441(10) |
|     |     |     | -O6a | (x1) | 2.655(7) |
|     |     | 2.436(10) | -O13b | (x1) | 2.436(10) |
|     |     |     | -O14a | (x1) | 2.578(10) |
|     |     |     | -O11a_L | (x1) | 2.649(14) |
|     |     |     | -O11b_L | (x1) | 2.740(16) |
|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| -O6b  | (x1)  | 2.733(12) | La3a<sub>L</sub> | -O7a  | (x1)  | 2.437(5)    |
| -O3a  | (x1)  | 2.823(11) |                  | -O14a | (x1)  | 2.463(6)    |
| -O9d  | (x1)  | 2.912(12) |                  | -O6b  | (x1)  | 2.647(6)    |
| -O9c  | (x1)  | 3.002(8)  |                  | -O3a  | (x1)  | 2.653(7)    |
| BVS for La3a |       | 2.71   |                  | -O6a  | (x1)  | 2.654(4)    |
|       |       |       |                  | -O11a<sub>L</sub> | (x1)  | 2.747(10)   |
|       |       |       |                  | -O9c  | (x1)  | 2.864(6)    |
|       |       |       |                  | -O9d  | (x1)  | 2.893(7)    |
|       |       |       |                  | -O11b<sub>L</sub> | (x1)  | 2.922(14)   |
| BVS for La3a<sub>L</sub> |       | 2.31/1.33 |                  |       |       |       |
| La3a<sub>S</sub> |       |       | -O13b | (x1)  | 2.306(13) |
|       |       |       | -O3b  | (x1)  | 2.336(16) |
|       |       |       | -O7a  | (x1)  | 2.447(11) |
|       |       |       | -O11a<sub>L</sub> | (x1)  | 2.556(17) |
|       |       |       | -O6a  | (x1)  | 2.628(9)  |
|       |       |       | -O6b  | (x1)  | 2.634(15) |
|       |       |       | -O14a | (x1)  | 2.712(13) |
|       |       |       | -O11b<sub>L</sub> | (x1)  | 2.725(20) |
|       |       |       | -O3a  | (x1)  | 2.886(16) |
|       |       |       | -O9d  | (x1)  | 3.030(15) |
| BVS for La3a<sub>S</sub> |       | 2.85/1.64 |                  |       |       |       |
| La/Ca3b | -O3a | (x1)  | 2.232(4) | La/Ca3b | -O13a | (x1)  | 2.611(8)    |
|       | (x1)  | 2.434(3) |                  | -O11a<sub>L</sub> | (x1)  | 2.721(4)    |
|       |       | 2.458(5) |                  | -O11d<sub>L</sub> | (x1)  | 2.877(13)   |
|       |       | 2.507(5) |                  | -O14b | (x1)  | 2.929(6)    |
|       |       | 2.593(5) |                  |       |       |       |
|       |       | 2.650(7) |                  |       |       |       |
| -O3b  | (x1)  | 2.659(6) |                  | -O3a  | (x1)  | 2.317(8)    |
| BVS for La/Ca3b |       | 2.60/1.50 |                  | -O6b  | (x1)  | 2.423(10)   |
|       |       |       |                  | -O13a | (x1)  | 2.464(11)   |
|       |       |       |                  | -O6a  | (x1)  | 2.473(12)   |
|       |       |       |                  | -O7b  | (x1)  | 2.603(11)   |
|       |       |       |                  | -O3b  | (x1)  | 2.718(9)    |
|       |       |       |                  | -O11d<sub>L</sub> | (x1)  | 2.752(16)   |
|       |       |       |                  | -O11a<sub>L</sub> | (x1)  | 2.758(7)    |
| BVS for La/Ca3b<sub>L</sub> |       | 2.65/1.52 |                  |       |       |       |
| La/Ca4a | -O4b | (x1)  | 2.233(9) | La/Ca4a | -O14a | (x1)  | 2.645(7)    |
|       | (x1)  | 2.338(10) |                  | -O12a | (x1)  | 2.672(9)    |
|       | (x1)  | 2.383(11) |                  | -O12b | (x1)  | 2.728(9)    |
| Bond  | Type | D (Å)   | Bond  | Type | D (Å)   |
|-------|------|---------|-------|------|---------|
| -O8a  | (x1) | 2.432(6)| -O13b | (x1) | 2.854(8)|
| -O4a  | (x1) | 2.536(15)|       |       |         |
| -O5b  | (x1) | 2.630(8)| La/Ca4aL | -O4b | (x1) | 2.341(7)|
| -O5a  | (x1) | 2.655(5)|       | -O8a | (x1) | 2.493(4)|
| -O10c | (x1) | 3.032(8)| -O14b | (x1) | 2.510(5)|
| -O10d | (x1) | 3.049(9)| La/Ca4a | -O5b | (x1) | 2.567(6)|
|       |      |         | BVS for La/Ca4a | 3.23/1.82 |      |         |
|       |      |         | -O12aL | (x1) | 2.583(7)|
|       |      |         | -O5a  | (x1) | 2.630(4)|
|       |      |         | -O4a  | (x1) | 2.630(14)|
|       |      |         | -O12bL | (x1) | 2.675(7)|
|       |      |         | -O10c | (x1) | 3.084(6)|
|       |      |         | BVS for La/Ca4aL | 2.71/1.55 |      |         |
|       |      |         |       |       |         |
|       |      |         | La/Ca4b | -O12c | (x1) | 2.414(2)|
| -O4a  | (x1) | 2.433(9)| La/Ca4b | -O14b | (x1) | 2.403(5)|
| -O12d | (x1) | 2.505(4)|       | -O13a | (x1) | 2.582(6)|
| -O8b  | (x1) | 2.507(4)| -O12cL | (x1) | 2.695(3)|
| -O5a  | (x1) | 2.530(4)| -O12dL | (x1) | 2.903(7)|
| -O5b  | (x1) | 2.629(3)|       |       |         |
| -O10b | (x1) | 2.823(3)| La/Ca4bL | -O13a | (x1) | 2.369(11)|
| -O4b  | (x1) | 2.831(3)|       | -O8b | (x1) | 2.441(11)|
| -O10a | (x1) | 2.976(4)| -O5a  | (x1) | 2.644(11)|
|       |      |         | BVS for La/Ca4b | 2.51/1.44 |      |         |
|       |      |         | -O10b | (x1) | 2.663(8)|
|       |      |         | -O5b  | (x1) | 2.675(11)|
|       |      |         | -O4b  | (x1) | 2.702(8)|
|       |      |         | -O12cL | (x1) | 2.852(6)|
|       |      |         | -O10a | (x1) | 2.916(11)|
|       |      |         | -O12dL | (x1) | 2.990(12)|
|       |      |         | BVS for La/Ca4bL | 2.48/1.42 |      |         |
|       |      |         |       |       |         |
|       |      |         | La/Ca4bS | -O14b | (x1) | 2.295(5)|
| -O5a  | (x1) | 2.487(4)|       | -O5a | (x1) | 2.487(4)|
| -O4a  | (x1) | 2.505(9)|       | -O4a | (x1) | 2.505(9)|
| -O8b  | (x1) | 2.555(4)|       | -O8b | (x1) | 2.555(4)|
| -O5b  | (x1) | 2.589(3)|       | -O5b | (x1) | 2.589(3)|
| -O12cL | (x1) | 2.640(3)|       | -O12cL | (x1) | 2.640(3)|
| -O12dL | (x1) | 2.853(7)|       | -O12dL | (x1) | 2.853(7)|
| -O10b | (x1) | 2.885(3)|       | -O10b | (x1) | 2.885(3)|
| -O4b  | (x1) | 2.895(3)|       | -O4b | (x1) | 2.895(3)|
| -O10a | (x1) | 3.034(4)|       | -O10a | (x1) | 3.034(4)|
|       |      |         | BVS for La/Ca4bS | 2.69/1.55 |      |         |
|       |      |         |       |       |         |
|       |      |         | Ga1a | -O12a | (x1) | 1.806(8)|
|       |      |         | Ga1a | -O12aL | (x1) | 1.805(6)|

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|        |       |       |        |       |       |       |       |       |       |
|--------|-------|-------|--------|-------|-------|-------|-------|-------|-------|
| -O11c  | (x1)  | 1.823(5) | -O11c_L | (x1)  | 1.822(7) |
| -O10a  | (x1)  | 1.824(5) | -O10a   | (x1)  | 1.824(5) |
| -O9c   | (x1)  | 1.858(4) | -O9c_L  | (x1)  | 1.858(4) |
| BVS for Ga1a | 3.08  | BVS for Ga1a | 3.08  |        |       |
| Ga1b   | -O10b | (x1)  | 1.804(7) | Ga1b   | -O10b | (x1)  | 1.804(7) |
| -O11d  | (x1)  | 1.814(6) | -O11d_L | (x1)  | 1.828(10) |
| -O9d   | (x1)  | 1.841(5) | -O12b_L | (x1)  | 1.832(4) |
| -O12b  | (x1)  | 1.857(6) | -O9d   | (x1)  | 1.841(5) |
| BVS for Ga1b | 3.07  | BVS for Ga1b | 3.09  |        |       |
| Ga1c   | -O9a  | (x1)  | 1.805(6) | Ga1c   | -O12c_L | (x1)  | 1.799(7) |
| -O11a  | (x1)  | 1.819(7) | -O9a   | (x1)  | 1.805(6) |
| -O12c  | (x1)  | 1.831(4) | -O11a_L | (x1)  | 1.822(9) |
| -O10c  | (x1)  | 1.852(4) | -O10c  | (x1)  | 1.852(4) |
| BVS for Ga1c | 3.08  | BVS for Ga1c | 3.14  |        |       |
| Ga1d   | -O9b  | (x1)  | 1.815(7) | Ga1d   | -O9b  | (x1)  | 1.815(7) |
| -O12d  | (x1)  | 1.826(6) | -O10d  | (x1)  | 1.829(5) |
| -O10d  | (x1)  | 1.829(5) | -O11b_L | (x1)  | 1.856(7) |
| -O11b  | (x1)  | 1.876(4) | -O12d_L | (x1)  | 1.903(7) |
| BVS for Ga1d | 3.01  | BVS for Ga1d | 2.90  |        |       |
| Ga2a   | -O4a  | (x1)  | 1.788(13) |        |       |       |       |
| -O6a   | (x1)  | 1.807(4) |        |       |       |       |
| -O10d  | (x1)  | 1.824(5) |        |       |       |       |
| -O4b   | (x1)  | 1.846(5) |        |       |       |       |
| -O10a  | (x1)  | 1.882(3) |        |       |       |       |
| -O3b   | (x1)  | 2.284(5) |        |       |       |       |
| BVS for Ga2a | 3.00  |        |       |       |       |       |
| Ga2b   | -O4a  | (x1)  | 1.779(10) |        |       |       |       |
| -O4b   | (x1)  | 1.792(5) |        |       |       |       |
| -O6b   | (x1)  | 1.806(4) |        |       |       |       |
| -O10c  | (x1)  | 1.836(5) |        |       |       |       |
| -O10b  | (x1)  | 1.892(5) |        |       |       |       |
| BVS for Ga2b | 3.06  |        |       |       |       |       |
| Ga2c   | -O3b  | (x1)  | 1.784(7) |        |       |       |       |
| -O3a   | (x1)  | 1.798(5) |        |       |       |       |
| -O9a   | (x1)  | 1.808(3) |        |       |       |       |
| -O5a   | (x1)  | 1.815(4) |        |       |       |       |
| -O9d   | (x1)  | 1.843(5) |        |       |       |       |

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| BVS for Ga2c      | 3.13 |
|------------------|------|
| Ga2d             |      |
| -O3a (x1)        | 1.775(3) |
| -O3b (x1)        | 1.779(6) |
| -O5b (x1)        | 1.810(4) |
| -O9c (x1)        | 1.902(5) |
| -O9b (x1)        | 1.926(6) |
| BVS for Ga2d     | 2.90 |
| Ga3a1            |      |
| -O1 (x1)         | 1.814(3) |
| -O8a (x1)        | 1.823(4) |
| -O11b (x1)       | 1.868(4) |
| -O11a (x1)       | 1.882(5) |
| BVS for Ga3a1    | 2.93 |
| -O3b (x1)        | 2.203(6) |
| BVS for Ga3a1    | 3.03 |
| Ga3a1L           |      |
| -O8a (x1)        | 1.806(4) |
| -O11aL (x1)      | 1.899(6) |
| -O11bL (x1)      | 1.911(6) |
| -O13b (x1)       | 1.996(6) |
| -O1 (x1)         | 2.019(4) |
| BVS for Ga3a1L   | 3.01 |
| Ga3a2            |      |
| -O8b (x1)        | 1.802(4) |
| -O1 (x1)         | 1.804(5) |
| -O11d (x1)       | 1.864(3) |
| -O11c (x1)       | 1.904(6) |
| BVS for Ga3a2    | 2.96 |
| -O13a (x1)       | 2.221(8) |
| BVS for Ga3a2    | 3.11 |
| Ga3a2L           |      |
| -O8b (x1)        | 1.810(4) |
| -O11cL (x1)      | 1.879(8) |
| -O11dL (x1)      | 1.917(7) |
| -O13a (x1)       | 1.997(8) |
| -O1 (x1)         | 2.015(6) |
| BVS for Ga3a2L   | 3.03 |
| Ga3b1            |      |
| -O2 (x1)         | 1.805(4) |
| -O7a (x1)        | 1.840(4) |
| -O12a (x1)       | 1.855(6) |
| -O12b (x1)       | 1.895(6) |
| BVS for Ga3b1    | 2.91 |
| -O14a (x1)       | 2.206(5) |
| BVS for Ga3b1    | 2.98 |
Table S7.3 Bond angles in the GaOn polyhedra of La1.64Ca0.36Ga3O7.32 from the split-model in P1.

| Bond          | Angle (°) | Bond          | Angle (°) |
|---------------|-----------|---------------|-----------|
| G1aO4 tetrahedron |           | G1aO4 tetrahedron |           |
| O12a -Ga1a- O11c | 109.8(3)  | O12aL -Ga1a- O11cL | 106.2(3)  |
| O12a -Ga1a- O10a | 113.4(2)  | O12aL -Ga1a- O10a | 102.1(2)  |
| O12a -Ga1a- O9c  | 103.5(3)  | O12aL -Ga1a- O9c  | 120.8(3)  |
| O11c -Ga1a- O10a | 115.6(2)  | O11cL -Ga1a- O10a | 125.0(3)  |
| O11c -Ga1a- O9c  | 109.2(2)  | O11cL -Ga1a- O9c  | 100.0(2)  |
| O10a -Ga1a- O9c  | 104.4(2)  | O10a -Ga1a- O9c  | 104.4(2)  |
| Average       | 109.3     | Average       | 109.8     |

| Bond          | Angle (°) | Bond          | Angle (°) |
|---------------|-----------|---------------|-----------|
| Ga1bO4 tetrahedron |           | Ga1bO4 tetrahedron |           |
| O10b -Ga1b- O11d | 113.4(3)  | O10b -Ga1b- O11dL | 121.5(3)  |
| Bond                        | Angle (°)   | Bond                        | Angle (°)   |
|-----------------------------|-------------|-----------------------------|-------------|
| O10b-Ga1b-O9d               | 104.5(3)    | O10b-Ga1b-O12bL             | 105.3(3)    |
| O10b-Ga1b-O12b              | 116.6(4)    | O10b-Ga1b-O9d               | 104.5(3)    |
| O11d-Ga1b-O9d               | 108.2(3)    | O11dL-Ga1b-O12b             | 109.0(3)    |
| O11d-Ga1b-O12b              | 108.3(2)    | O11dL-Ga1b-O9d              | 101.3(4)    |
| O9d-Ga1b-O12b               | 105.1(3)    | O12bL-Ga1b-O9d              | 119.3(3)    |
| Average                     | 109.4       | Average                     | 109.6       |

| Ga1cO4 tetrahedron          | Ga1cO4 tetrahedron |
|-----------------------------|---------------------|
| O9a-Ga1c-O11a               | 100.0(2)            | O12cL-Ga1c-O9a              | 126.8(3)    |
| O9a-Ga1c-O12c               | 114.4(3)            | O12cL-Ga1c-O11a             | 103.2(3)    |
| O9a-Ga1c-O10c               | 116.4(2)            | O12cL-Ga1c-O10c             | 102.4(3)    |
| O11a-Ga1c-O12c              | 110.2(2)            | O9a-Ga1c-O12c               | 91.3(3)     |
| O11a-Ga1c-O10c              | 103.6(3)            | O9a-Ga1c-O10c               | 116.4(3)    |
| O12c-Ga1c-O10c              | 110.9(2)            | O11aL-Ga1c-O10c             | 116.2(3)    |
| Average                     | 109.3              | Average                     | 109.4       |

| Ga1dO4 tetrahedron          | Ga1dO4 tetrahedron |
|-----------------------------|---------------------|
| O9b-Ga1d-O12d               | 111.6(3)            | O9b-Ga1d-O10d               | 110.0(3)    |
| O9b-Ga1d-O10d               | 110.0(3)            | O9b-Ga1d-O11b               | 96.5(3)     |
| O9b-Ga1d-O11b               | 105.4(3)            | O9b-Ga1d-O12dL              | 127.5(3)    |
| O12d-Ga1d-O10d              | 109.9(3)            | O10d-Ga1d-O11bL             | 123.9(3)    |
| O12d-Ga1d-O11b              | 106.7(2)            | O10d-Ga1d-O12dL             | 96.2(3)     |
| O10d-Ga1d-O11b              | 113.2(2)            | O11bL-Ga1d-O12dL            | 105.5(2)    |
| Average                     | 109.5              | Average                     | 109.9       |

| Ga2aO4 tetrahedron          | Ga2bO4 tetrahedron |
|-----------------------------|---------------------|
| O4a-Ga2a-O6a                | 118.5(4)            | O4a-Ga2b-O6b                | 117.8(4)    |
| O4a-Ga2a-O10d               | 103.1(4)            | O4a-Ga2b-O10c               | 104.5(4)    |
| O4a-Ga2a-O10a               | 101.4(3)            | O4a-Ga2b-O10b               | 96.3(4)     |
| O6a-Ga2a-O4b                | 116.8(2)            | O6b-Ga2b-O10a               | 117.0(2)    |
| O6a-Ga2a-O10a               | 116.0(2)            | O4b-Ga2b-O10a               | 93.3(2)     |
| Average                     | 108.4               | Average                     | 108.4       |
| O4b  | -Ga2b- | O10b | 109.1(2) |
|------|--------|------|---------|
| O6b  | -Ga2b- | O10c | 119.6(2) |
| O6b  | -Ga2b- | O10b | 114.4(2) |
| O10c | -Ga2b- | O10b | 100.5(2) |
| Average |        |      | 108.1   |

**Ga2cO₄ tetrahedron**

| O3b  | -Ga2c- | O9a  | 119.1(2) |
|------|--------|------|---------|
| O3b  | -Ga2c- | O5a  | 118.7(2) |
| O3b  | -Ga2c- | O9d  | 94.8(2)  |
| O3a  | -Ga2c- | O9a  | 104.2(2) |
| O3a  | -Ga2c- | O5a  | 114.1(2) |
| O3a  | -Ga2c- | O9d  | 112.6(2) |
| O9a  | -Ga2c- | O5a  | 107.4(2) |
| O9a  | -Ga2c- | O9d  | 91.9(2)  |
| O5a  | -Ga2c- | O9d  | 122.2(2) |
| Average |        |      | 109.5   |

**Ga2dO₄ tetrahedron**

| O3a  | -Ga2d- | O5b  | 117.1(2) |
|------|--------|------|---------|
| O3a  | -Ga2d- | O9c  | 114.4(2) |
| O3a  | -Ga2d- | O9b  | 94.0(2)  |
| O3b  | -Ga2d- | O5b  | 121.0(3) |
| O3b  | -Ga2d- | O9c  | 96.9(2)  |
| O3b  | -Ga2d- | O9b  | 109.7(3) |
| O5b  | -Ga2d- | O9c  | 119.1(2) |
| O5b  | -Ga2d- | O9b  | 111.9(2) |
| O9c  | -Ga2d- | O9b  | 94.5(2)  |
| Average |        |      | 108.7   |

**Ga3a1O₄ tetrahedron**

| O1   | -Ga3a1- | O8a | 112.5(2) |
|------|---------|-----|---------|
| O1   | -Ga3a1- | O11b| 97.4(2) |
| O1   | -Ga3a1- | O11a| 105.2(2) |
| O8a  | -Ga3a1- | O11b| 123.7(2) |
| O8a  | -Ga3a1- | O11a| 116.2(2) |
| O11b | -Ga3a1- | O11a| 98.7(2)  |
| Average |       |      | 109.0   |

**Ga3a1O₃ tetrahedron**

| O1   | -Ga3a1- | O8a | 112.5(2) |
|------|---------|-----|---------|
| O1   | -Ga3a1- | O11aL| 94.0(3) |
| O1   | -Ga3a1- | O11bL| 88.5(2) |
| O8a  | -Ga3a1- | O11aL| 118.4(2) |
| O8a  | -Ga3a1- | O11bL| 122.4(2) |
| O11aL| -Ga3a1- | O11bL| 112.4(3) |
| Average |       |      | 108.0   |

**Ga3a1L₄O₄ trigonal bipyramid**

| O8a | -Ga3a1L- | O11aL| 120.8(2) |
|-----|---------|------|---------|
| O8a | -Ga3a1L- | O11bL| 124.3(3) |
| Ga3a2O4 tetrahedron | Ga3a2O4 tetrahedron |
|---------------------|---------------------|
| O8b -Ga3a2- O1      | O8b -Ga3a2- O1      |
| 111.3(2)            | 111.3(2)            |
| O8b -Ga3a2- O11d    | O8b -Ga3a2- O11c    |
| 127.3(2)            | 117.6(2)            |
| O8b -Ga3a2- O11c    | O8b -Ga3a2- O11dL   |
| 117.6(2)            | 126.4(3)            |
| O1 -Ga3a2- O11d     | O1 -Ga3a2- O11c     |
| 95.1(2)             | 95.5(2)             |
| O1 -Ga3a2- O11c     | O1 -Ga3a2- O11dL    |
| 95.5(2)             | 88.1(3)             |
| O11d -Ga3a2- O11c   | O11cL -Ga3a2- O11dL |
| 103.4(2)            | 114.8(3)            |
| Average              | Average             |
| 108.4               | 107.2               |

| Ga3a2L2O4 trigonal bipyramid |
|-----------------------------|
| Equatorial planar           |
| O8b -Ga3a2L- O11cL          |
| 117.2(3)                    |
| O8b -Ga3a2L- O11dL          |
| 105.2(3)                    |
| O11cL -Ga3a2L- O11dL        |
| 119.2(3)                    |
| Average                     |
| 111.4(3)                    |

| Ga3b1O4 tetrahedron | Ga3b1O4 tetrahedron |
|---------------------|---------------------|
| O2 -Ga3b1- O7a      | O2 -Ga3b1- O7a      |
| 117.2(2)            | 117.2(2)            |
| O2 -Ga3b1- O12a     | O2 -Ga3b1- O12aL    |
| 105.2(3)            | 89.9(2)             |
| O2 -Ga3b1- O12b     | O2 -Ga3b1- O12bL    |
| 102.3(2)            | 90.0(2)             |
| O7a -Ga3b1- O12a    | O7a -Ga3b1- O12aL   |
| 119.2(2)            | 123.1(2)            |
Ga3b1L\textsubscript{1}O\textsubscript{4} trigonal bipyramid

**Equatorial planar**

| Bond | Angle (°) |
|------|-----------|
| O7\textsubscript{a} -Ga3b1\textsubscript{L} - O12\textsubscript{bL} | 120.0(2) |
| O7\textsubscript{a} -Ga3b1\textsubscript{L} - O12\textsubscript{aL} | 123.8(2) |
| O12\textsubscript{bL} -Ga3b1\textsubscript{L} - O12\textsubscript{aL} | 114.3(2) |
| Average | 119.4 |

**Apex**

| Bond | Angle (°) |
|------|-----------|
| O2 -Ga3b1\textsubscript{L} - O14\textsubscript{aL} | 160.6(2) |

**Others**

| Bond | Angle (°) |
|------|-----------|
| O7\textsubscript{a} -Ga3b1\textsubscript{L} - O2 | 110.4(2) |
| O7\textsubscript{a} -Ga3b1\textsubscript{L} - O14\textsubscript{aL} | 89.9(2) |
| O12\textsubscript{bL} -Ga3b1\textsubscript{L} - O2 | 86.8(2) |
| O12\textsubscript{bL} -Ga3b1\textsubscript{L} - O14\textsubscript{aL} | 82.0(2) |
| O12\textsubscript{aL} -Ga3b1\textsubscript{L} - O2 | 85.1(2) |
| O12\textsubscript{aL} -Ga3b1\textsubscript{L} - O14\textsubscript{aL} | 85.2(2) |
| Average | 89.7 |

Ga3b2O\textsubscript{4} tetrahedron

| Bond | Angle (°) |
|------|-----------|
| O2 -Ga3b2\textsubscript{L} - O7\textsubscript{bL} | 114.4(2) |
| O2 -Ga3b2\textsubscript{L} - O12\textsubscript{cL} | 102.8(2) |
| O2 -Ga3b2\textsubscript{L} - O12\textsubscript{dL} | 95.8(2) |
| O7\textsubscript{b} -Ga3b2\textsubscript{L} - O12\textsubscript{cL} | 122.7(2) |
| O7\textsubscript{b} -Ga3b2\textsubscript{L} - O12\textsubscript{dL} | 119.3(2) |
| O12\textsubscript{cL} -Ga3b2\textsubscript{L} - O12\textsubscript{dL} | 97.3(2) |
| Average | 108.7 |

Ga3b2L\textsubscript{2}O\textsubscript{4} trigonal bipyramid

**Equatorial planar**

| Bond | Angle (°) |
|------|-----------|
| O7\textsubscript{b} -Ga3b2L\textsubscript{L} - O12\textsubscript{dL} | 121.9(3) |
| O7\textsubscript{b} -Ga3b2L\textsubscript{L} - O12\textsubscript{cL} | 123.2(3) |
| O12\textsubscript{dL} -Ga3b2L\textsubscript{L} - O12\textsubscript{cL} | 114.8(3) |
| Average | 120.0 |

**Apex**

| Bond | Angle (°) |
|------|-----------|
| O2 -Ga3b2L\textsubscript{L} - O14\textsubscript{bL} | 152.8(2) |

**Others**

| Bond | Angle (°) |
|------|-----------|
| O7\textsubscript{b} -Ga3b2L\textsubscript{L} - O2 | 106.6(2) |
| O7\textsubscript{b} -Ga3b2L\textsubscript{L} - O14\textsubscript{bL} | 99.8(2) |
| O12\textsubscript{dL} -Ga3b2L\textsubscript{L} - O2 | 77.2(2) |
| O12\textsubscript{dL} -Ga3b2L\textsubscript{L} - O14\textsubscript{bL} | 83.5(2) |
Figure S7.2 Environment of the C₁ ring centroid in (left) bulk and (right) defect structure in La₁.64Ca₀.₃₆Ga₃O₇.₃₂. The local displacement of La₃a, La/Ca₄a, Ga₃b₁, O₁₂a, and O₁₂b to accommodate the O₁₄a interstitials are marked with arrows in the bulk structure. The displacements (Å) calculated using the split-model for La₃a, La/Ca₄a, Ga₃b₁, O₁₂a, and O₁₂b are 0.19(1) (La₃a-La₃aₗ), 0.14(1) (La/Ca₄a-La/Ca₄aₗ), 0.17(1) (Ga₃b₁-Ga₃b₁ₗ), 0.56(1) (O₁₂a-O₁₂aₗ), and 0.49(1) (O₁₂b-O₁₂bₗ), respectively.
**Figure S7.3**  Structural relaxation around the interstitial oxide O13b in the split-model of La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$. Ga$_{3a1}$, O11$_a$, O11$_b$, O4$_b$, and La$_{3a}$ are involved in the local structural relaxation. (a) and (c) represent the refined structure in the absence of the interstitial O occupancy of this site with (b) and (d) showing the ring geometry and Ga trigonal bipyramidal structure formed when the interstitials (occupancy of 17.9(1)%) are present. O8$_a$ is the terminal oxygen in the polyhedron.
Figure S7.4 Structural relaxation around the interstitial oxide O13a in the split-model of La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$. Ga$_{3a2}$L, O$_{11c}$L, O$_{11d}$L, O$_{4b}$, La$_{3b}$L and La/Ca$_{4b}$L are involved in the local structural relaxation. (a) and (c) represent the refined structure in the absence of the interstitial O occupancy of this site with (b) and (d) showing the ring geometry and the Ga trigonal bipyramidal structure formed when the interstitials (occupancy of 28.0(1)% are present. O$_{8b}$ is the terminal oxygen in the polyhedron.
Figure S7.5 Structural relaxation around the interstitial oxide O14b in the split-model of La$_{1.64}$Ca$_{0.36}$Ga$_3$O$_{7.32}$. Ga$_{3b2}$ L, O$_{12c}$ L, O$_{12d}$ L, O$_{3b}$, and La/Ca$_{4b}$ S are involved in the local structural relaxation. (a) and (c) represent the refined structure in the absence of the interstitial O occupancy of this site with (b) and (d) showing the ring geometry and Ga trigonal bipyramidal structure formed when the interstitials (occupancy of 23.9(1)%) are present. O$_7$b is the terminal oxygen in the polyhedron.
Figure S7.6 Enlarged projection along [110] of (a) bulk and (b) defect structure to show the structural displacement to permit interstitial accommodation. The occupancy of two sets of centroids (C1/C7 and C3/C5) shares the same direction of displacement as marked by black and cyan arrows in (b), with the sense of the displacement being different in the two pairs.
8. Interstitial oxide and A-site cation ordering--composition and crystal structure

**Figure S8.1** Pentagons represent the interstitial sites in the five nearest edge-shared rings with a random tiling, corresponding to disordered interstitial occupancy of the 5-rings which are the centroids of the pentagons, with interstitial occupancy > 1/8 (left), and maximally doped structure of either randomly 2/3 occupied or partially ordered by dark grey, fully occupied and light grey 1/3 occupied (right, dark spheres represent two ring centroids sharing a common three-connected Ga$_2$O$_7$ edge). Ga(I)O$_4$, 4-connected; Ga(II)O$_4$, 3-connected; O(I), framework oxygens; O(II), interstitial sites.

**References**

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