Deep hydration of an Li$_{7-3x}$La$_3$Zr$_2$$M^{III}$$_x$O$_{12}$ solid-state electrolyte material: a case study on Al- and Ga-stabilized LLZO

Günther J. Redhammer, Gerold Tippelt and Daniel Rettenwander

Abstract: Single crystals of an Li-stuffed, Al- and Ga-stabilized garnet-type solid-state electrolyte material, Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO), have been analysed using single-crystal X-ray diffraction to determine the pristine structural state immediately after synthesis via ceramic sintering techniques. Hydrothermal treatment at 150 °C for 28 d induces a phase transition in the Al-stabilized compound from the commonly observed cubic $Ia\overline{3}d$ structure to the acentric $I43d$ subtype. Li$^+$ ions at the interstitial octahedrally (4 + 2-fold) coordinated 48e site are most easily extracted and Al$^{III}$ ions order onto the tetrahedral 12a site. Deep hydration induces a distinct depletion of Li$^+$ at this site, while the second tetrahedral site, 12b, suffers only minor Li$^+$ loss. Charge balance is maintained by the incorporation of H$^+$, which is bonded to an O atom. Hydration of Ga-stabilized LLZO induces similar effects, with complete depletion of Li$^+$ at the 48e site. The Li$^+$/H$^+$ exchange not only leads to a distinct increase in the unit-cell size, but also alters some bonding topology, which is discussed here.

1. Introduction

The garnet family, $X_3Y_2Z_3O_{12}$, has been well described mineralogically and crystallographically in recent decades (Novak & Gibbs, 1971), and is of interest to a range of scientists from the fields of geoscience and technology, due to its thermodynamic stability in a variety of geological environments and its flexible structure, which can host ~60 different chemical elements as major and minor components (Geiger, 2013; Baxter et al., 2013). Furthermore, the so-called Li-stuffed garnets, e.g. Li$_4$La$_3$Zr$_3$Li$_3$O$_{12}$, or as sum formula, Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO), have raised particular interest as promising materials for use as solid-state electrolytes in all solid-state Li batteries due to their superior Li-ion conductivity (Cussen, 2010; Wang et al., 2020; Murugan et al., 2007; Samson et al., 2019). Pure end-member LLZO is tetragonal, has the space group $I4_1/acd$ (Awaka et al., 2009) and has distinctly lower Li-ion conductivities. The high Li-ion conductivity is associated with the ‘standard’ cubic garnet structure with $Ia\overline{3}d$ symmetry. The latter can be stabilized by various aliovalent substitutions, e.g. by small amounts of Al$^{III}$, which – in the first experiments – entered the structure as a contaminant from the corundum crucibles during synthesis (Geiger et al., 2011; Buschmann et al., 2011). The incorporation of Ga$^{III}$ into LLZO also increases the Li-ion conductivity, but induces a reduction of the symmetry to $I43d$ (Rettenwander et al., 2016; Wagner et al., 2016a; Robben et al., 2016), i.e. the space group of hydrogarnet Ca$_3$Al$_2$(O$_4$H$_4$)$_3$ (Lager et al., 1987). A stabilization of the cubic structure for nominally
pure LLZO is also possible by the uptake of $\text{H}^+$, which raises a question about LLZO stability in hydrous environments (Larraz et al., 2013). Several studies have investigated the role of Li$^+$/H$^+$ exchange under different environmental conditions and found that LLZO-type materials are distinctly unstable in the presence of moisture (Ma et al., 2015; Galven et al., 2011, 2012, 2013; Larraz et al., 2015; Orera et al., 2016; Liu et al., 2019). Surfaces quickly degrade with the formation of LiOH and Li$_2$CO$_3$, and an increase in unit-cell parameters is observed as Li$^+$/H$^+$ exchange progresses. Until now, only a few studies have systematically investigated the mechanisms behind this structural degradation. In recent studies, we have shown, using diffraction methods, that significant Li$^+$ is especially lost from the interstitial sites of the structure in Al$^{III}$-, Ga$^{III}$- and Ta$^{VII}$-substituted LLZOs during aging at room temperature under high humidity (Hiebl et al., 2019; Redhammer et al., 2021a,b). In this article, we report on the deep hydration of Al- and Ga-substituted LLZO using hydrothermal treatment of single-crystalline material.

2. Experimental methodology

2.1. Synthesis and aging of material

Single crystals of Al- and Ga-stabilized LLZO were obtained using a solid-state ceramic sintering method, which has been described in detail elsewhere (Rettenwander et al., 2016; Wagner et al., 2016a). In brief, Li$_2$CO$_3$ (with an excess of 10%), La$_2$O$_3$, ZrO$_2$, and Al$_2$O$_3$ or Ga$_2$O$_3$ were carefully mixed in the required stoichiometric proportions for the nominal compositions Li$_{6.55}$La$_3$Zr$_2$Al$_{0.15}$O$_{12}$ (Al$_{15}$-LLZO) and Li$_{6.8}$La$_3$Zr$_2$Ga$_{0.3}$O$_{12}$ (Ga$_{40}$-LLZO). The mixtures were pressed into pellets and preheated at 850 °C for 4 h for decarbonization. The samples were subsequently milled in a high-energy ball mill under alcohol using ZrO$_2$ balls, then dried, pelletized and sintered at 1230 °C for a period of 28 d. The pH value of the liquid, in which the crystals were submerged, was measured after the experiment; the pH value was ~13 for both compositions. The hydrated single LLZO crystallites were then filtered off and the remaining liquid was left to evaporate. The resulting precipitate was identified as Li$_2$CO$_3$ using powder diffraction (PXRD), i.e., proving that Li$^+$ was extracted from the LLZO material.

2.2. Refinement

Information on data collection and refinement results is given in Table 1. Indexing the diffraction data for pristine Al-LLZO yields the space-group symmetry $Ia\overline{5}d$. Refining the structure with framework cations and O atoms results in only two strong residual electron-density peaks at the 24d and 96h positions. Assuming that Li atoms occupy only these two positions, then there must be a distinct overpopulation at the 24d site. Thus, Al$^{III}$ is assigned to the 24d site and its content was fixed using the chemical composition calculated from energy dispersive X-ray (EDX) analysis on a similar material synthesized using an identical experimental setup (Rettenwander et al., 2016). The Li content was allowed to refine freely.

For pristine Ga-stabilized LLZO, indexing of the diffraction data yields the space-group symmetry $I\overline{4}3d$. Three different sites are identified from residual electron-density maps for the Li$^+$ ions: at Wyckoff positions 12a, 12b and 48e. It is evident that Ga$^{III}$ must be located at the 12a position, as the 12a site becomes distinctly overpopulated when refined with only Li$^+$. In subsequent refinements, both the Li1 and Li2 sites are assumed to be fully occupied and the electron density is modelled with Li + Ga = 1. The result is that Ga$^{III}$ almost exclusively resides at the 12a position. Refinement of the anisotropic atomic displacement parameters (adps) is possible for all atoms using the same strategy as that applied by Wagner et al. (2016a,b). The data of the hydrothermally treated Ga-LLZO sample can also be indexed using $I\overline{4}3d$ symmetry when the model for untreated material is used as the starting point. The Li1 site is again assumed to be fully occupied and its electron density was modelled with Li + Ga = 1. This approach is considered valid as the resultant Ga$^{III}$ content is similar (albeit slightly higher) to that obtained for the untreated sample. The Li2 and, in particular, the Li3 sites are distinctly depleted in Li and no anisotropic atomic displacement refinement is possible. Thus, the isotropic adps are adjusted and fixed to the $U_{eq}$ value refined for the Li1 site; anisotropic adps could be obtained for Li1. Protons are located close to the O1 atom using residual electron-density maps. Fixing the $U_{eq}$ value of hydrogen yields reliable occupation factors for this site and an almost charge-balanced chemical formula (with a slight surplus of 0.35 negative charges).

For deeply hydrated Al-LLZO, indexing of data yields a change in symmetry from $Ia\overline{5}d$ to acentric $I\overline{4}3d$. The structure of this compound is refined using the model of the Ga-stabilized LLZO, as described above for the La-, Zr- and the two O-atom positions. The electron densities at Li1 and Li2 were modelled first with only Li$^+$ ions. In this case, the Li1 position is distinctly overpopulated, while the occupation of the Li2 position is low, and there is no indication that the Li3 position is occupied at all. Consequently, all Al$^{III}$ is assigned to the Li1 site and its occupation is fixed to the value used in the unaltered sample, consistent with the assumption that no Al left the structure during hydration. Refinement of the anisotropic adps is not possible for the Li1 site, and the isotropic adp is very small, so the isotropic adp of Li1 was adjusted in such a way that it has a similar value to the $U_{eq}$ value of the Li2 site (where anisotropic adp refinements were possible) and fixed as such in subsequent refinements. Two distinct residual electron-density peaks are identified in residual electron-density maps: one high (2.5 e Å$^{-3}$), very close to the Zr-atom position, and another at ~0.8 Å from the O1 atom. This latter (x, y, z) position is close to the proposed H-atom positions.
Table 1
Experimental details.

For all structures: Z = 8. Experiments were carried out at 298 K with Mo Kα radiation using a Bruker SMART APEX diffractometer. Absorption was corrected for by multi-scan methods (APEX2; Bruker, 2012). LLZO-Al15-pristine = fresh sample of Al-doped LLZO, measured directly after the end of the synthesis. LLZO-Al15-hydro-150°C = Al-doped LLZO aged hydrothermally at 150 °C. LLZO-Ga40-pristine = fresh sample of Ga-doped LLZO, measured directly after the end of the synthesis and LLZO-Ga40-hydro-150°C = Ga-doped LLZO aged hydrothermally at 150 °C.

| Crystal data | LLZO-Al15-pristine | LLZO-Al15-hydro-150°C | LLZO-Ga40-pristine | LLZO-Ga40-hydro-150°C |
|--------------|---------------------|------------------------|---------------------|------------------------|
| Chemical formula | Al0.15La2.95Li5.73O12Zr2 Al0.15H5.52La2.88-O12Zr2 | Ga0.28La1.20Li1.20O12Zr2 Ga0.28H0.82La1.20Zr2 | Li1.99O12Zr2 | Li1.99O12Zr2 |
| M, g mol⁻¹ | 827.89 | 847.67 | 821.46 | 821.46 |
| Crystal system, space group | Cubic, Ia̅3d | Cubic, Ia̅3d | Cubic, Ia̅3d | Cubic, Ia̅3d |
| a (Å) | 12.9637 (2) | 12.9669 (2) | 13.88 | 13.57 |
| b (Å) | 2178.65 (10) | 2234.63 (10) | 2180.26 (10) | 2231.25 (6) |
| c (Å) | 2180.26 (10) | 2231.25 (6) | | |
| μ (mm⁻¹) | 12.61 | 12.61 | 13.88 | 13.88 |
| Crystal size (mm) | 0.12 × 0.11 × 0.07 | 0.13 × 0.12 × 0.08 | 0.13 × 0.13 × 0.10 | 0.12 × 0.11 × 0.09 |

Data collection

| Tmin, °C | 0.22, 0.39 | 0.21, 0.36 | 0.19, 0.25 | 0.21, 0.36 |
| No. of measured, independent and observed reflections | 33130, 455, 441 | 34201, 819, 819 | 35033, 1054, 1045 | 35657, 918, 915 |
| R(ω), (sin θ/λ)max (Å⁻¹) | 0.029 | 0.026 | 0.038 | 0.028 |
| 0.840 | 0.804 | 0.884 | 0.838 |

Refinement

| R[F² > 2σ(F²)], wR(F²), S | 0.016, 0.032, 1.51 | 0.013, 0.029, 1.27 | 0.013, 0.026, 1.29 | 0.018, 0.037, 1.12 |
| 0.016, 0.032, 1.51 | 0.013, 0.029, 1.27 | 0.013, 0.026, 1.29 | 0.018, 0.037, 1.12 |
| No. of reflections | 455 | 819 | 1054 | 918 |
| No. of parameters | 25 | 44 | 48 | 43 |
| No. of restraints | 2 | 2 | 2 | 2 |
| H-atom treatment | Only H-atom coordinates refined | Only H-atom coordinates refined | Only H-atom coordinates refined | Only H-atom coordinates refined |
| Δρmax, Δρmin (e Å⁻³) | 0.71, −0.44 | 0.58, −0.51 | 0.53, −0.65 | 0.54, −0.52 |
| Absolute structure | Refined as an inversion twin | Refined as an inversion twin | Refined as an inversion twin | Refined as an inversion twin |
| Absolute structure parameter | 0.50 (3) | 0.50 (4) | 0.99944 (15) | |

Computer programs: APEX2 (Bruker, 2012), SIR2014 (Burla et al., 2012), SHELX2014 (Sheeldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012) and WinGX (Farrugia, 2012).

given by Larraz et al. (2013) and Orera et al. (2016). Hence, this residual density is assigned to the H atom, which is bonded to the O1 atom. Independent refinement of the x, y and z positions, and the occupation of the H atom is possible, whereas the isotropic adp had to be fixed. A residual density close to Zr can be explained by positional disorder at this site, similar to that reported for deeply hydrated Ta-substituted LLZO, which also transformed to the Ia̅3d structure. However, there is a marked decrease in the reliability factors associated with the refinements when Zr IV disorder is applied, e.g. there is no sign of another site close to O2 that would allow for another H atom to be bonded to the O2 atom. Furthermore, no reliable residual electron-density peaks can be detected.

Two additional crystals were hydrated in the same way and both were then analysed; the results are consistent with those reported in the tables and below.

3. Results and discussion

In the pristine state, Al-LLZO shows the typical garnet structure with Ia̅3d symmetry. LaIII occupies the eightfold-coordinated 24c site with two symmetrically independent La—O bond lengths (see Table 2). A slight deficit in the La—O bond length occupation is observed, which is in line with previous studies (Hiebl et al., 2019; Rettenwander et al., 2016; Wagner et al., 2016a, b). The Zr IV ions are located at the 16a position with a regular sixfold oxygen coordination and a bond length of...
2.076 (16) Å. As depicted in Fig. 1, the garnet structure comprises an integrated framework constructed of edge-sharing octahedral and dodecahedral sites, in which the Li atoms are located at both the regular 24d tetrahedral site (Li1) and at the interstitial 96d position (Li2), often denoted to have a distorted octahedral coordination [Li2—O distances range between 1.854 (15) and 2.646 (14) Å, with the average of the four smaller bond lengths being 2.085 Å]. AlIII substitutes into the 24d position and the four equivalent Li—O lengths are 1.9044 (17) Å; both the 24d and the 96d positions show distinct vacancies.

The hydrothermally altered sample of Al-LLZO shows additional Bragg peaks of type \( k = \text{odd} \) and \( l = \text{odd} \) that obey \( Ia\overline{3}d \) symmetry. Calculated precession images of the \( hk0 \) plane for unaltered and altered Al-LLZO are compared in Fig. 2, where some Bragg peaks that obey \( Ia\overline{3}d \) symmetry are marked. Indexing of the observed data definitively yield the space-group symmetry \( Ia\overline{3}d \), in accordance with the findings of Larraz et al. (2013) and Orera et al. (2016) for Li/H-

**Figure 2**
Reconstructed precession images of the \( hk0 \) plane of (a) a single crystal of Al-stabilized LLZO directly after synthesis with some selected Bragg reflections indexed and (b) a single crystal after hydrothermal alteration at 150 °C for 28 d. Note the presence of sharp superstructure reflections, which obey \( Ia\overline{3}d \) symmetry. In part (b), the yellow encircled Bragg reflections are the same as in part (a), while the blue encircled reflections in the rectangular box correspond (from left to right) to the 370, 370, 170, . . . Bragg reflections.

---

**Table 2**
Selected geometric parameters (Å).

| Set | LlZO-Al15-pristine | LlZO-Al15-hydro-150C | LlZO-Ga40-pristine | LlZO-Ga40-hydro-150C |
|-----|-------------------|----------------------|-------------------|---------------------|
| Ll1—O1      | 2.510 (17)        | Zr1—O2vi         | Ll1—O1         | 1.854 (15)          |
| Ll1—O2      | 2.595 (17)        | Ll2—O1xiii        | Ll1—O1         | 2.085 (14)          |
| Zr1—O1      | 2.1078 (16)       | Zr1—O1xv         | Zr1—O1        | 2.159 (15)          |
| Ll1—Zr1     | 1.616 (14)        | Ll1—O1xv         | Ll1—O1        | 2.242 (14)          |
| Ll1—Zr2     | 1.9044 (17)       | Ll1—O1xv         | Ll2—O1        | 2.159 (15)          |
| Ll2—O2      | 2.367 (14)        | Ll2—O1xv         | Ll2—O1        | 2.242 (14)          |
| Ll2—Zr2     | 0.79 (3)          | Ll2—O1xv         | Ll2—O1        | 2.159 (15)          |

Symmetry codes: (i) \( z, x, y \); (ii) \( x - \frac{1}{4}, z - \frac{1}{4}, y - \frac{1}{4} \); (iii) \( z + \frac{1}{2}, y - \frac{1}{2}, x - \frac{1}{2} \); (iv) \( z, -x + \frac{1}{2}, y + \frac{1}{2} \); (v) \( x, y, z \); (vi) \( x - \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2} \); (vii) \( y - \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{2} \); (viii) \( y + \frac{1}{2}, x - \frac{1}{2}, z - \frac{1}{2} \); (ix) \( -z + \frac{1}{2}, x + \frac{1}{2}, y + \frac{1}{2} \); (x) \( -z + \frac{1}{2}, y - \frac{1}{2}, x - \frac{1}{2} \); (xi) \( z - \frac{1}{2}, -y + \frac{1}{2}, -x + \frac{1}{2} \); (xii) \( z + \frac{1}{2}, y - \frac{1}{2}, x - \frac{1}{2} \); (xiii) \( -x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2} \); (xiv) \( -x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2} \).
a symmetry reduction to $I\bar{A}3d$. A disorder at the $ZrI\text{a}Ta$ site is also observed in hydrated LLZTO similar to that in hydrated Al-stabilized LLZO in this study. It would appear that the symmetry reduction, induced by LiI/H\text{I}\text{I} exchange, causes a large distortion of the O-atom environment around the 16\text{c} position and induces some positional disorder.

The regular 24\text{d} tetrahedral site of the $Ia\bar{3}d$ garnet structure splits into two different sites, 12\text{a} (Li1) and 12\text{b} (Li2), upon symmetry reduction to $I\bar{A}3d$. Al\text{II} is ordered onto the 12\text{a} (Li1) site but a distinct number of vacancies are observed on both sites. While $\sim 4.5$ apfu LiI occupy the interstitial 96\text{h} position in the pristine state, this position (Li3 at 48\text{e}) is completely unoccupied in the deeply hydrated form, i.e. all the LiI ions have vacated the interstitial octahedral site.

Recently, Redhammer et al. (2021b) observed a progressive increase of the tetrahedral site (24\text{d} and 12\text{a}) occupation in Al-stabilized LLZO during continuous LiI/H\text{I}\text{I} exchange in a humid atmosphere and under mild hydrothermal conditions. The shift and ordering of LiI from the interstitial site to the regular tetrahedral site, and the preference of LiI and Al\text{II} for the 12\text{a} position, are described as triggers for the symmetry reduction from $Ia\bar{3}d$ to $I\bar{A}3d$ (Redhammer et al., 2021b). A study of the structure of the deeply hydrated samples here shows that, after complete recovery of LiI from the interstitial site, the tetrahedral 12\text{a} and 12\text{b} sites also take part in the LiI/H\text{I}\text{I} exchange. When compared to the data of Redhammer et al. (2021b), it is obvious that, in this study, more LiI is extracted from the 12\text{a} site ($\sim 1.4$ to 0.64 (2) apfu), but there is only a moderate change in site occupation at 12\text{b} ($\sim 1.1$ to 0.82 (2) apfu). As LiI is extracted from the structure, H\text{I} is incorporated and bonds with the O1 atom. The LiI ions in the 12\text{a} tetrahedron are thus coordinated by four OH groups, with the O–H vector pointing towards the empty Li3 site (compare with Fig. 3). The proposed position of H\text{I} is in line with that found by Orera et al. (2016) for pure undoped LLZO based on neutron diffraction on polycrystalline powders. Refinements indicate that the deeply hydrated Al-LLZO has a composition of La2.88Zr1.95Al0.15Li1.64H5.52O12. It is also worth noting that a significantly lower number of La\text{II} ions are found at the 24\text{d} site, so it would appear that La\text{II} also leaves the structure under hydrothermal conditions. This is in line with the observations of Redhammer et al. (2021a,b), who observed an instability of LLZO powders in highly humid air, with decomposition of LLZO, leading to the formation of lanthanite La2(CO3)3•8H2O within $\sim 30$ d of exposure.

The LiI/H\text{I}\text{I} exchange is accompanied by a large increase in the $a$ unit-cell parameter from 12.9637 (2) to 13.0738 (2) Å, which is among the largest values yet recorded for hydrated LLZO, cf. 13.06245 (4) Å at 77 K for hydrated LLZO with an Li2.88H9.85La1.43Zr2.58O12 composition (Orera et al., 2016) or 13.0530 (8) Å for Li3.08H3.52La3Zr2O12Ta0.4 (Yow et al., 2016). A replacement of stronger Li–O bonds by weaker O–H bonds and the creation of a large number of vacant sites, especially around the empty 48\text{e} (Li3) site, both require more space and are considered responsible for the lattice expansion.

Pristine unaltered Ga-stabilized LLZO shows $I\bar{A}3d$ symmetry. A section of this crystal structure is illustrated in Fig. 3, together with that of the hydrothermally treated sample. Both the tetrahedrally coordinated 12\text{a} and 12\text{b} positions appear to be fully occupied, with the Ga\text{II} ions ordered onto the 12\text{a} position. In contrast to the Li-stuffed garnets with $Ia\bar{3}d$ symmetry, the decreased number of vacancies at the regular tetrahedral sites are considered to be a characteristic feature of the $I\bar{A}3d$ garnet structure. The 48\text{e} interstitial site [Li3 in Fig. 3(a)] is occupied by 3.71 LiI apfu, equivalent to being $\sim 62\%$ full. All of the tetrahedral faces of the fourfold oxygen coordination around the Li1 and Li2 sites are shared with neighbouring Li3 sites, with interatomic contacts of 1.645 (8) Å (Li1–Li3) and 2.340 (9) Å (Li2–Li3), thereby forming a three-dimensional network that is responsible for the good Li+ conductivity in this compound. The dodecahedral site has a small number of vacancies, while the regular octahedral positions are fully occupied with Zr\text{IV}, resulting in a complex structural pattern.
position of $\text{La}_{2.94}\text{Zr}_{2.00}\text{Ga}_{0.28}\text{Li}_{6.43}\text{O}_{12}$ for the unaltered Ga-stabilized LLZO material. A smaller and larger set of La—O1/O2 bonds are observed at the dodecahedral site [2.4935 (19)—2.5264 (19) and 2.587 (2)—2.5975 (19) Å] and the octahedron is regular with two independent Zr—O bonds ranging between 2.0823 (18) and 2.1346 (18) Å. Therefore, the octahedra are much less distorted than those in the altered Al-LLZO with the same symmetry (Table 2). The Li1 (12a) site, which hosts GaIII, is slightly smaller than the Li2 (12b) site, whereas the Li3 site, as in Al-LLZO, shows a very distorted 4 + 2-fold coordination, with bond lengths between 1.878 (4) and 2.639 (8) Å; the average of the four shorter bonds is 2.073 Å, i.e. slightly smaller than in the pristine Al-LLZO [see Fig. 3(a)].

As in Al-LLZO, hydrothermal treatment of Ga-LLZO induces LiI/HI exchange. Again, a large increase of the lattice parameter to 13.06720 (12) Å is close to the value in hydrated Al-LLZO, suggesting that values around 13.07 Å represent an upper limit for lattice-parameter increase due to hydration. From site-occupation refinements, very minor LiI ions are found at the interstitial 48f site where the amount of LiI is reduced from 1.49 apfu in the altered sample. Protons are completely depleted. One key difference with Al-LLZO is that no LiI is lost from the 12a position. It seems that GaIII ions pin LiI at this site. However, LiI ions are extracted from the 12b site where the amount of LiI is reduced from 1.49 apfu in the pristine to 0.50 apfu in the altered sample. Protons are again located close to the O1 atom [Fig. 3(b)], giving rise to a fully hydrated Li1(OH)4 coordination around the 12a site. Some differences to Al-LLZO are, however, evident: there is no indication of disorder at the 16d position, i.e. there is no significant reduction in the La-site occupation and no residual electron density is observed close to the ZrIV ions, i.e. there is no indication of disorder at the 16c position in altered Ga-LLZO. Nevertheless, the ZrO6 octahedron is much more distorted in the altered sample, with Zr—O bond lengths ranging between 2.03 (3) and 2.187 (4) Å; the difference between the two independent Zr—O bonds increases with prolonged LiI/HI exchange. This was outlined by Redhammer et al. (2021b) and the data of this study fit the extrapolated trends observed there. A distinct alteration is also observed within the coordination sphere of the 24d site due to H⁺ incorporation. The most prominent effects include the reduction of the longer La1—O1iv distance by ~0.073 Å, as well as changes in the three other La—O bond lengths. In addition, Li1—I1iv and Li2—O2vi are extended in the altered sample (see Table 2).

References
Awaka, J., Kijjima, N., Hayakawa, H. & Akimoto, J. (2009). J. Solid State Chem. 182, 2046–2052.
Baxter, E. F., Caddick, M. J. & Ague, J. J. (2013). Elements, 9, 415–419.
Bruker (2012). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzi, B., Cascarano, G. L., Giacovazzo, C., Mallomo, M., Mazzeo, A., Polidori, G. & Spagna, R. (2012). J. Appl. Cryst. 45, 357–361.
Buschmann, H., Döllé, J., Berendts, S., Kuhn, A., Bottek, P., Wilkening, M., Heitjans, P., Senyshyn, A., Ehrenberg, H., Lotnyk, A., Duppl, V., Kienle, L. & Janek, J. (2011). Phys. Chem. Chem. Phys. 13, 19378–19392.
Cussen, E. (2010). Functional Oxides, edited by D. W. Bruce, D. O’Hare & R. I. Walton, pp. 119–202: London: John Wiley & Sons Ltd.
Farrugia, L. J. (2012). J. Appl. Cryst. 45, 849–854.
Galven, C., Dittmer, J., Suard, E., Le Berre, F. & Crosnier-Lopez, M.-P. (2012). Chem. Mater. 24, 3335–3345.
Galven, C., Fourquet, J.-L., Crosnier-Lopez, M.-P. & Le Berre, F. (2011). Chem. Mater. 23, 1892–1900.
Galven, C., Suard, E., Mounier, D., Crosnier-Lopez, M.-P. & Le Berre, F. (2013). J. Mater. Res. 28, 2147–2153.
Geiger, C. A. (2013). Elements, 9, 447–452.
Geiger, C. A., Alexseev, E., Lazic, B., Fisch, M., Armbruster, T., Langner, R., Fechtelkord, M., Kim, N., Pettek, T. & Weppner, W. (2011). Inorg. Chem. 50, 1089–1097.
Hieber, C., Young, D., Wagner, R., Wilkening, H. M. R., Redhammer, G. J. & Rettenwander, D. (2019). J. Phys. Chem. C, 123, 1094–1098.
Lager, G. A., Armbruster, T. & Faber, J. (1987). Am. Mineral. 72, 756–765.
Larraz, G., Orera, A. & Sanjuan, M. L. (2013). J. Mater. Chem. A, 1, 11419–11428.
Larraz, G., Orera, A., Sanz, J., Sobrados, I., Díez-Gómez, V. & Sanjuan, M. L. (2015). J. Mater. Chem. A, 3, 5693–5691.
Liu, X., Chen, Y., Hood, Z. D., Ma, C., Yu, S., Sharafi, A., Wang, H., An, K., Sakamoto, J., Siegel, D. J., Cheng, Y., Jalarvo, N. H. & Chi, M. (2019). Energy Environ. Sci. 12, 945–951.
Ma, C., Rangasamy, E., Liang, C., Sakamoto, J., More, K. L. & Chi, M. (2015). Angew. Chem. Int. Ed. 54, 129–133.
Murugan, R., Thangadurai, V. & Weppner, W. (2007). Angew. Chem. Int. Ed. 46, 7778–7781.
Novak, G. A. & Gibbs, G. V. (1971). Am. Mineral. 56, 791–825.
Orera, A., Larraz, G., Rodriguez-Velamazán, J. A., Campo, J. & Sanjuan, M. L. (2016). Inorg. Chem. 55, 1324–1332.
Redhammer, G. J., Badami, P., Meven, M., Ganschow, S., Berendts, S., Tippelt, G. & Rettenwander, D. (2021a). Appl. Mater. Interfaces, 13, 350–359.
Redhammer, G. J., Tippelt, G., Portenkirchner, A. & Rettenwander, D. (2021b). Crystals, 11, 721.
Rettenwander, D., Redhammer, G., Preishuber-Pflugl, F., Cheng, L., Miara, L., Wagner, R., Welzel, A., Suard, E., Doeff, M. M., Wilkening, M., Fleig, J. & Amthauer, G. (2016). Chem. Mater. 28, 2384–2392.
Robben, L., Merzylikova, E., Heitjans, P. & Gesing, T. M. (2016). Acta Cryst. E72, 287–289.
Samson, A. J., Hofstetter, K., Bag, S. & Thangadurai, V. (2019). Energy Environ. Sci. 12, 2957–2975.
Sheldrick, G. M. (2015). Acta Cryst. C71, 3–8.
Wagner, R., Redhammer, G. J., Rettenwander, D., Senyshyn, A., Schmidt, W., Wilkening, M. & Amthauer, G. (2016a). Chem. Mater. 28, 1861–1871.
Wagner, R., Redhammer, G. J., Rettenwander, D., Tippelt, G., Welzel, A., Taibl, S., Fleig, J., Franz, A., Lottermoser, W. & Amthauer, G. (2016b). Chem. Mater. 28, 5943–5951.
Wang, C., Fu, K., Kammampata, S. P., McOwen, D. W., Samson, A. J., Zhang, L., Hitz, G. T., Nolan, A. M., Wachsman, E. D., Mo, Y., Thangadurai, V. & Hu, L. (2020). Chem. Rev. 120, 4257–4300.
Yow, Z. F., Oh, Y. L., Gu, W. Y., Rao, R. P. & Adams, S. (2016). Solid State Ionics, 292, 122–129.
Deep hydration of an Li$_{7-3x}$La$_{3}$Zr$_2$M$_{III,x}$O$_{12}$ solid-state electrolyte material: a case study on Al- and Ga-stabilized LLZO

Günther J. Redhammer, Gerold Tippelt and Daniel Rettenwander

Computing details

For all structures, data collection: APEX2 (Bruker, 2012); cell refinement: APEX2 (Bruker, 2012); data reduction: APEX2 (Bruker, 2012); program(s) used to solve structure: SIR2014 (Burla et al., 2012); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: WinGX (Farrugia, 2012).

(LLZO-Al15-pristine)

Crystal data

Al$_{0.15}$La$_{2.95}$Li$_{5.73}$O$_{12}$Zr$_2$  
$D_a = 5.048$ Mg m$^{-3}$  
Mo Kα radiation, $\lambda = 0.71073$ Å

Cubic, Ia$3d$  
Hall symbol: $-I 4bd 2c 3$

$\theta = 3.9$–$36.6^\circ$

$\mu = 13.24$ mm$^{-1}$

$T = 298$ K  
Cuboid, colorless

$0.12 \times 0.11 \times 0.07$ mm

Data collection

Bruker SMART APEX  
diffractometer

Graphite monochromator

rotation, $\omega$–scans at 4 different $\varphi$ positions  
Absorption correction: multi-scan

(APEx2; Bruker, 2012)

$\theta_{\text{min}} = 0.22, \theta_{\text{max}} = 0.39$

33130 measured reflections

455 independent reflections

441 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\text{max}} = 36.6^\circ, \theta_{\text{min}} = 3.9^\circ$

$h = -21 \rightarrow 21$

$k = -21 \rightarrow 21$

$l = -21 \rightarrow 21$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.016$

$wR(F^2) = 0.032$

$S = 1.51$

455 reflections

25 parameters

0 restraints

0 constraints

$w = 1/[\sigma^2(F_c^2) + (0.0044P)^2 + 13.2478P]$

where $P = (F_c^2 + 2F_s^2)/3$

$(\Delta \sigma)_{\text{max}} = 0.001$

$\Delta \rho_{\text{max}} = 0.71$ e Å$^{-3}$

$\Delta \rho_{\text{min}} = -0.44$ e Å$^{-3}$

Extinction correction: SHELXL2014  
(Sheldrick, 2015),  
$Fc^2 = kFc[1+0.001xFc^2/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00041 (3)
Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|        | x     | y     | z     | U(eq)/Ueq | Occ. (<1) |
|--------|-------|-------|-------|------------|-----------|
| La1    | 0.125 | 0     | 0.25  | 0.00857 (8)| 0.983 (3) |
| Zr1    | 0     | 0     | 0     | 0.00669 (12)|          |
| O1     | 0.09999 (13) | 0.19604 (13) | 0.28188 (13) | 0.0117 (3) |
| Li1    | 0.375 | 0     | 0.25  | 0.022 (6)  | 0.47 (6)  |
| Al1    | 0.0961 (10) | 0.1880 (11) | 0.4246 (11) | 0.023 (4)* |
| Li2    | 0.375 | 0     | 0.25  | 0.022 (5)  | 0.05      |

Atomic displacement parameters (Å²)

|        | U11   | U22   | U33   | U12   | U13   | U23   |
|--------|-------|-------|-------|-------|-------|-------|
| La1    | 0.01087 (11) | 0.00742 (9) | 0.00742 (9) | 0     | 0     | 0.00134 (7) |
| Zr1    | 0.00669 (12) | 0.00669 (12) | 0.00669 (12) | 0.00008 (8) | 0.00008 (8) | 0.00008 (8) |
| O1     | 0.0092 (6) | 0.0120 (7) | 0.0140 (7) | −0.0016 (5) | 0.0003 (5) | 0.0004 (5) |
| Li1    | 0.009 (9) | 0.029 (12) | 0.029 (12) | 0     | 0     | 0     |
| Al1    | 0.009 (15) | 0.029 (9) | 0.029 (9) | 0     | 0     | 0     |

Geometric parameters (Å, °)

| La1—O1i | 2.5110 (17) | O1—Zr1iv | 2.1076 (16) |
|--------|-------------|-----------|-------------|
| La1—O1ii| 2.5110 (17) | O1—Li2i  | 2.159 (15)  |
| La1—O1iii| 2.5110 (17) | O1—Li2iix| 2.242 (14)  |
| La1—O1iv| 2.5110 (17) | O1—La1ix| 2.5110 (17) |
| La1—O1v | 2.5951 (17) | O1—Li2i | 2.646 (14)  |
| La1—O1vi| 2.5952 (17) | Li1—Li2ii| 1.616 (14)  |
| La1—O1vi| 2.5952 (17) | Li1—Li2iii| 1.616 (14) |
| La1—O1v| 2.5952 (17) | Li1—Li2i | 1.616 (14)  |
| La1—O1vi| 2.5952 (17) | Li1—Li2xi| 1.616 (14)  |
| La1—O1v| 2.5952 (17) | Li1—Li2xii| 1.616 (14) |
| La1—O1vi| 2.5952 (17) | Li1—O1i | 1.9044 (17) |
| La1—O1vi| 2.5952 (17) | Li1—O1xi| 1.9044 (17) |
| Zr1—O1ii| 2.1076 (16) | Li1—O1i | 1.9044 (17) |
| Zr1—O1ii| 2.1076 (16) | Li1—Li2i | 2.367 (14)  |
| Zr1—O1ii| 2.1076 (16) | Li1—Li2xi| 2.367 (14)  |
| Zr1—O1ii| 2.1076 (16) | Li1—Li2v| 2.367 (14)  |
| Zr1—Li2iix| 2.1076 (16) | Li2—Li2v| 2.367 (14)  |
| Zr1—Li2iix| 2.1076 (16) | Li2—Li2v| 2.367 (14)  |
| Zr1—Li2iix| 2.1076 (16) | Li2—O1i | 1.9044 (17) |
| Zr1—Li2iix| 2.1076 (16) | Li2—O1xi| 1.9044 (17) |
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| Zr1—Li2xviii  | 2.906 (15)   | Li2—O1v      | 2.159 (15)   |
| Zr1—Li2xix    | 2.906 (15)   | Li2—O1xi     | 2.242 (14)   |
| Zr1—Li2xvi    | 2.906 (15)   | Li2—Al1xvii  | 2.367 (14)   |
| O1—Li2        | 1.854 (15)   | Li2—Li1xviii | 2.367 (14)   |
| O1—Al1xx      | 1.9044 (17)  | Li2—Li2xvii  | 2.46 (2)     |
| O1—Li1xx      | 1.9044 (17)  | Li2—Li2xvii  | 2.46 (2)     |
| O1—Li2xvi     | 2.085 (14)   | Li2—O1xviii  | 2.646 (14)   |
| O1i—La1—O1ii  | 111.62 (8)   | Li1x—O1—La1x | 93.43 (7)    |
| O1i—La1—O1ii  | 71.83 (8)    | Li2xii—O1—La1x | 80.6 (4) |
| O1i—La1—O1iv | 160.65 (7)   | Zr1xv—O1—La1x | 103.01 (7) |
| O1i—La1—O1iv | 160.65 (7)   | Li2xv—O1—La1x | 164.2 (4)   |
| O1i—La1—O1vi | 71.83 (8)    | Li2xii—O1—La1x | 77.8 (4)    |
| O1ii—La1—O1iv| 111.62 (8)   | Li2—O1—La1  | 96.1 (5)     |
| O1i—La1—O1   | 68.90 (7)    | Al1x—O1—La1 | 123.07 (7)   |
| O1i—La1—O1   | 73.03 (6)    | Li1x—O1—La1 | 123.07 (7)   |
| O1i—La1—O1   | 124.22 (3)   | Li2xii—O1—La1 | 170.6 (4)   |
| O1i—La1—O1   | 95.13 (5)    | Zr1xv—O1—La1 | 100.28 (6)  |
| O1i—La1—O1   | 95.13 (5)    | Li2xv—O1—La1 | 89.0 (4)     |
| O1i—La1—O1   | 124.22 (3)   | Li2xii—O1—La1 | 85.3 (4)    |
| O1i—La1—O1   | 73.03 (6)    | Li1x—O1—La1 | 102.03 (6)   |
| O1i—La1—O1   | 68.90 (7)    | Li2—O1—Li2x | 78.6 (7)     |
| O1i—La1—O1   | 72.77 (8)    | Al1x—O1—Li2x | 60.1 (3)    |
| O1i—La1—O1   | 124.22 (3)   | Li1x—O1—Li2x | 60.1 (3)    |
| O1i—La1—O1   | 95.13 (5)    | Li2xii—O1—Li2x | 102.4 (4)  |
| O1i—La1—O1   | 68.90 (7)    | Zr1xv—O1—Li2x | 169.9 (3)  |
| O1i—La1—O1   | 73.03 (6)    | Li2xv—O1—Li2x | 94.4 (3)    |
| O1—La1—O1v   | 165.64 (7)   | Li2xii—O1—Li2x | 16.0 (6)   |
| O1i—La1—O1v  | 109.12 (7)   | Li1x—O1—Li2x | 79.2 (3)     |
| O1i—La1—O1v  | 73.03 (6)    | La1—O1—Li2x | 69.6 (3)     |
| O1i—La1—O1v  | 68.90 (7)    | Li2xv—Li1—Li2viii | 133.1 (10) |
| O1i—La1—O1v  | 95.13 (5)    | Li2xv—Li1—Li2viii | 99.1 (4)   |
| O1i—La1—O1v  | 124.22 (3)   | Li1—Li1—Li2i | 99.1 (4)     |
| O1i—La1—O1v  | 109.12 (7)   | Li2xv—Li1—Li2i | 99.1 (4)   |
| O1i—La1—O1v  | 165.64 (7)   | Li1—Li1—Li2i | 99.1 (4)     |
| O1i—La1—O1v  | 72.77 (8)    | Li2xv—Li1—O1viii | 133.1 (10) |
| O1—La1—Li2viii| 43.4 (3)    | Li2xv—Li1—O1viii | 163.6 (5)  |
| O1i—La1—Li2viii| 147.5 (3)  | Li2xv—Li1—O1viii | 62.9 (5)   |
| O1i—La1—Li2viii| 47.1 (3)    | Li2xv—Li1—O1viii | 78.7 (5)   |
| O1i—La1—Li2viii| 47.1 (3)    | Li2xv—Li1—O1viii | 78.7 (5)   |
| O1i—La1—Li2viii| 77.2 (3)    | Li2xv—Li1—O1viii | 72.1 (5)   |
| O1i—La1—Li2viii| 56.0 (3)    | Li2xv—Li1—O1viii | 78.7 (5)   |
| O1i—La1—Li2viii| 166.0 (3)   | Li2xv—Li1—O1viii | 163.6 (5)  |
| O1i—La1—Li2viii| 110.0 (3)   | Li2xv—Li1—O1viii | 62.9 (5)   |
| O1v—La1—Li2viii| 124.3 (3)   | O1vii—Li1—Li1viii | 113.69 (5) |
| O1v—La1—Li2viii| 43.4 (3)    | Li2xv—Li1—Li1viii | 62.9 (5)   |
| O1v—La1—Li2viii| 124.3 (3)   | Li2xv—Li1—Li1viii | 163.6 (5)  |
| O1v—La1—Li2viii| 47.1 (3)    | Li2xv—Li1—Li1viii | 72.1 (5)   |
|           | Bond Length (Å) | Bond Angle (°) |
|-----------|----------------|---------------|
| O1—La1—Li2ix | 110.0 (3) | Li2ix—Li1—O1xi | 78.7 (5) |
| O1v—La1—Li2ix | 116.0 (3) | O1viii—Li1—O1xi | 101.32 (10) |
| O1vi—La1—Li2x | 56.0 (3) | O1iii—Li1—O1xi | 113.69 (5) |
| O1vii—La1—Li2x | 77.2 (3) | Li2x—Li1—O1i | 78.7 (5) |
| Li2viii—La1—Li2x | 168.0 (6) | Li2iviii—Li1—O1i | 72.1 (5) |
| O1i—La1—Li2c | 124.3 (3) | Li2iviii—Li1—Li2xxiii | 62.9 (5) |
| O1ii—La1—Li2c | 47.1 (3) | O1viii—Li1—O1i | 163.6 (5) |
| O1iii—La1—Li2c | 147.5 (3) | O1viii—Li1—O1i | 113.69 (6) |
| O1iv—La1—Li2c | 43.4 (3) | O1ii—Li1—O1i | 101.32 (10) |
| O1v—La1—Li2c | 56.0 (3) | O1v—Li1—O1i | 113.69 (5) |
| O1vi—La1—Li2c | 77.2 (3) | Li2viii—Li1—Li2xxiii | 7.0 (9) |
| O1vii—La1—Li2c | 116.0 (3) | O1vii—Li1—Li2xxiii | 135.9 (7) |
| O1viii—La1—Li2c | 116.0 (3) | Li2viii—Li1—Li2xxiii | 92.1 (7) |
| Li2viii—La1—Li2x | 122.0 (5) | Li2viii—Li1—Li2xxiii | 103.8 (7) |
| Li2vii—La1—Li2x | 59.4 (5) | O1v—Li1—Li2xxiv | 160.7 (4) |
| O1i—La1—Li2xi | 47.1 (3) | O1vii—Li1—Li2xxiv | 79.0 (4) |
| O1ii—La1—Li2xi | 124.3 (3) | O1vii—Li1—Li2xxiv | 59.6 (4) |
| O1iii—La1—Li2xi | 43.4 (3) | O1vii—Li1—Li2xxiv | 75.7 (3) |
| O1iv—La1—Li2xi | 147.5 (3) | Li2viii—Li1—Li2xxiv | 135.9 (7) |
| O1v—La1—Li2xi | 56.0 (3) | Li2viii—Li1—Li2xxiv | 7.0 (9) |
| O1vi—La1—Li2xi | 116.0 (3) | Li2viii—Li1—Li2xxiv | 103.8 (7) |
| O1vii—La1—Li2xi | 110.0 (3) | Li2viii—Li1—Li2xxiv | 92.1 (7) |
| O1viii—La1—Li2xi | 77.2 (3) | O1viii—Li1—Li2xxiv | 59.6 (4) |
| Li2viii—La1—Li2x | 59.4 (5) | O1iii—Li1—Li2xxiv | 75.7 (3) |
| Li2vii—La1—Li2x | 122.0 (5) | O1v—Li1—Li2xxiv | 160.7 (4) |
| Li2vii—La1—Li2x | 168.0 (6) | O1vii—Li1—Li2xxiv | 79.0 (4) |
| O1v—Zr1—O1vi | 180.00 (13) | Li2viii—Li1—Li2xxiv | 139.6 (7) |
| O1viii—Zr1—O1vi | 86.55 (7) | Li2viii—Li1—Li2xxiv | 103.8 (7) |
| O1vii—Zr1—O1vii | 93.45 (7) | Li2viii—Li1—Li2xxiv | 92.1 (7) |
| O1viii—Zr1—O1v | 93.45 (7) | Li2viii—Li1—Li2xxiv | 7.0 (9) |
| O1vii—Zr1—O1i | 86.55 (7) | Li2viii—Li1—Li2xxiv | 135.9 (7) |
| O1v—Zr1—O1i | 93.45 (7) | O1viii—Li1—Li2xxiv | 75.7 (4) |
| O1viii—Zr1—O1iv | 86.55 (7) | O1iii—Li1—Li2xxiv | 160.7 (4) |
| O1vii—Zr1—O1iv | 93.45 (7) | O1i—Li1—Li2xxv | 79.0 (4) |
| O1v—Zr1—O1iv | 93.45 (7) | Li2viii—Li1—Li2xxiv | 79.0 (4) |
| O1viii—Zr1—O1iv | 86.55 (7) | Li2viii—Li1—Li2xxiv | 96.8 (2) |
| O1vii—Zr1—O1iv | 93.45 (7) | Li2viii—Li1—Li2xxv | 96.8 (2) |
| O1v—Zr1—O1iv | 93.45 (7) | Li2viii—Li1—Li2xxv | 92.1 (7) |
| O1viii—Zr1—O1iv | 86.55 (7) | Li2viii—Li1—Li2xxv | 103.8 (7) |
| O1vii—Zr1—O1iv | 93.45 (7) | Li2viii—Li1—Li2xxv | 135.9 (7) |
| O1v—Zr1—O1iv | 86.55 (7) | Li2viii—Li1—Li2xxv | 7.0 (9) |
| O1viii—Zr1—O1iv | 93.45 (7) | Li2viii—Li1—Li2xxv | 135.9 (7) |
| O1vii—Zr1—O1iv | 93.45 (7) | O1viii—Li1—Li2xxv | 79.0 (4) |
| O1v—Zr1—O1iv | 93.45 (7) | O1viii—Li1—Li2xxv | 96.8 (2) |
| O1viii—Zr1—O1iv | 93.45 (7) | O1viii—Li1—Li2xxv | 92.1 (7) |
| O1v—Zr1—O1iv | 93.45 (7) | O1i—Li1—Li2xxv | 160.7 (4) |
| O1viii—Zr1—O1iv | 93.45 (7) | O1i—Li1—Li2xxv | 79.0 (4) |
| O1v—Zr1—O1iv | 86.55 (7) | Li2viii—Li1—Li2xxvi | 103.8 (7) |
| O1viii—Zr1—O1iv | 180.00 (9) | Li2viii—Li1—Li2xxvi | 135.9 (7) |
| O1vii—Zr1—Li2x | 93.0 (3) | Li2viii—Li1—Li2xxvi | 7.0 (9) |
| O1v—Zr1—Li2x | 87.0 (3) | O1viii—Li1—Li2xxvi | 79.0 (4) |
| O1vii—Zr1—Li2x | 87.0 (3) | O1v—Li1—Li2xxvi | 59.6 (4) |
| O1v—Zr1—Li2x | 134.2 (3) | O1vii—Li1—Li2xxvi | 75.7 (3) |
| O1vii—Zr1—Li2x | 45.8 (3) | O1i—Li1—Li2xxvi | 160.7 (4) |
| O1v—Zr1—Li2x | 47.8 (3) | Li2viii—Li1—Li2xxvi | 96.8 (2) |
| O1vii—Zr1—Li2x | 132.2 (3) | Li2viii—Li1—Li2xxvi | 96.8 (2) |
| O1v—Zr1—Li2x | 87.0 (3) | Li2xxiv—Li1—Li2xxvi | 139.6 (7) |
| O1vii—Zr1—Li2x | 87.0 (3) | Li2xxiv—Li1—Li2xxvi | 79.0 (4) |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|
| O1 — Zr1 — Li2      | 93.0 (3)     | Li2 — Li2 — Al1      | 158 (3)      |
| O1 — Zr1 — Li2     | 45.8 (3)     | Li2 — Li2 — Li1      | 158 (3)      |
| O1 — Zr1 — Li2     | 134.2 (3)    | Al1 — Li2 — Li1      | 0            |
| O1 — Zr1 — Li2     | 132.2 (3)    | Li2 — Li2 — O1       | 101.9 (17)   |
| O1 — Zr1 — Li2    | 47.8 (3)     | Al1 — Li2 — O1       | 66.2 (5)     |
| O1 — Zr1 — Li2    | 180.0 (7)    | Li1 — Li2 — Al1      | 66.2 (5)     |
| O1 — Zr1 — Li2   | 134.2 (3)    | Li2 — Li2 — O1xx     | 141 (3)      |
| O1 — Zr1 — Li2  | 45.8 (3)     | Al1 — Li2 — O1xx     | 60.4 (4)     |
| O1 — Zr1 — Li2  | 47.8 (3)     | Li1xx — Li2 — O1xxii | 60.4 (4)     |
| O1 — Zr1 — Li2 | 132.2 (3)    | O1 — Li2 — O1xxii   | 108.0 (7)    |
| O1 — Zr1 — Li2 | 93.0 (3)     | Li2 — Li2 — O1v     | 57.2 (15)    |
| O1 — Zr1 — Li2 | 87.0 (3)     | Al1 — Li2 — O1v     | 140.1 (8)    |
| Li2 — Li2 — Li2  | 119.82 (4)   | Li1 — Li2 — O1v     | 140.1 (8)    |
| Li2 — Li2 — Li2  | 60.18 (4)    | O1 — Li2 — O1v      | 99.9 (6)     |
| Li2 — Li2 — Li2  | 45.8 (3)     | O1xxii — Li2 — O1v   | 92.6 (6)     |
| Li2 — Li2 — Li2 | 134.2 (3)    | Li2 — Li2 — O1xxi   | 112.5 (10)   |
| Li2 — Li2 — Li2 | 132.2 (3)    | Al1 — Li2 — O1xxi   | 56.4 (4)     |
| Li2 — Li2 — Li2 | 47.8 (3)     | Li1xx — Li2 — O1xxi | 56.4 (4)     |
| Li2 — Li2 — Li2 | 87.0 (3)     | O1 — Li2 — O1xxi    | 101.8 (7)    |
| Li2 — Li2 — Li2 | 93.0 (3)     | O1xxii — Li2 — O1xxi| 85.7 (5)     |
| Li2 — Li2 — Li2 | 60.18 (4)    | O1 — Li2 — O1xxi    | 157.6 (7)    |
| Li2 — Li2 — Li2 | 119.82 (4)   | Li2 — Li2 — Al1xxvii| 14.6 (19)    |
| Li2 — Li2 — Li2 | 180.0 (6)    | Al1 — Li2 — Al1xxvii| 170.3 (9)    |
| Li2 — Li2 — Li2 | 47.8 (3)     | Li1xx — Li2 — Al1xxvii| 170.3 (9)    |
| Li2 — Li2 — Li2 | 132.2 (3)    | O1 — Li2 — Al1xxvii | 114.1 (6)    |
| Li2 — Li2 — Li2 | 93.0 (3)     | O1xxii — Li2 — Al1xxvii| 126.4 (7)    |
| Li2 — Li2 — Li2 | 87.0 (3)     | O1 — Li2 — Al1xxvii | 49.5 (3)     |
| Li2 — Li2 — Li2 | 134.2 (3)    | O1xxii — Li2 — Al1xxvii| 115.1 (6)    |
| Li2 — Li2 — Li2 | 45.8 (3)     | Li2 — Li2 — Li1xxviii| 14.6 (19)    |
| Li2 — Li2 — Li2 | 119.82 (4)   | Al1 — Li2 — Li1xxviii| 170.3        |
| Li2 — Li2 — Li2 | 60.18 (4)    | Li1xx — Li2 — Li1xxviii| 170.3 (9)    |
| Li2 — Li2 — Li2 | 119.82 (4)   | O1 — Li2 — Li1xxviii| 114.1 (6)    |
| Li2 — Li2 — Li2 | 60.18 (4)    | O1xxii — Li2 — Li1xxviii| 126.4 (7)    |
| Li2 — Li2 — Li2 | 132.2 (3)    | O1 — Li2 — Li1xxviii| 49.5 (3)     |
| Li2 — Li2 — Li2 | 47.8 (3)     | O1xxi — Li2 — Li1xxviii| 115.1 (6)    |
| Li2 — Li2 — Li2 | 87.0 (3)     | Al1 — Li2 — Li1xxviii| 0            |
| Li2 — Li2 — Li2 | 93.0 (3)     | Li2 — Li2 — Li2xxii | 150.2 (6)    |
| Li2 — Li2 — Li2 | 45.8 (3)     | Al1 — Li2 — Li2xxii | 40.45 (19)   |
| Li2 — Li2 — Li2 | 134.2 (3)    | Li1xx — Li2 — Li2xxii| 40.45 (19)   |
| Li2 — Li2 — Li2 | 60.18 (4)    | O1 — Li2 — Li2xxii  | 60.7 (7)     |
| Li2 — Li2 — Li2 | 119.82 (4)   | O1xxii — Li2 — Li2xxii| 47.3 (4)     |
| Li2 — Li2 — Li2 | 60.18 (4)    | O1 — Li2 — Li2xxii  | 99.7 (8)     |
| Li2 — Li2 — Li2 | 119.82 (4)   | O1xxi — Li2 — Li2xxii| 95.5 (4)     |
| Li2 — Li2 — Li2 | 180.0 (8)    | Al1 — Li2 — Li2xxii | 148.9 (8)    |
| Li2 — Li2 — Li2 | 50.9 (4)     | Li1xxvii — Li2 — Li2xxii| 148.9 (8)    |
| Li2 — Li2 — Li2 | 50.9 (4)     | Li2 — Li2 — Li2xxii | 118 (3)      |
| Al1 — Li2 — Li1xxvii| 0           | Al1 — Li2 — Li2xxii | 40.45 (19)   |
| Li2 — Li2 — Li2xxiv| 77.1 (6)     | Li1xx — Li2 — Li2xxiv| 40.45 (19)   |
### Crystal data

$\text{Al}_{1.15}\text{H}_{5.52}\text{La}_{2.88}\text{Li}_{1.64}\text{O}_{12}\text{Zr}_{1.95}$

$M_r = 790.95$

Cubic, $\overline{I}43d$

Hall symbol: $I-4bd$

$a = 13.0738 (2)$ Å

$V = 2234.63 (10)$ Å³

$Z = 8$

$F(000) = 2804.4$

### Data collection

Bruker SMART APEX
diffractometer

Graphite monochromator
rotation, $\omega$–scans at 4 different $\phi$ positions

Absorption correction: multi-scan
(APEX2; Bruker, 2012)

$\theta_{\text{min}} = 0.21$, $\theta_{\text{max}} = 0.36$

34201 measured reflections

Refinement

Refinement on $F^2$

$S = 1.27$

Least-squares matrix: full

$R(F^2 > 2\sigma(F^2)) = 0.013$

$wR(F^2) = 0.029$

819 independent reflections

819 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 34.9^\circ$, $\theta_{\text{min}} = 3.8^\circ$

$h = -21 \rightarrow 21$

$k = -21 \rightarrow 21$

$l = -21 \rightarrow 21$

Cell parameters from 34201 reflections

$D_c = 4.707$ Mg m$^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

$T = 298$ K

Cuboid, colorless

0.13 × 0.12 × 0.08 mm

### Supporting information

Symmetry codes: (i) $x, y, z$; (ii) $-z+1/4, -y+1/4, -x+1/4$; (iii) $z, -x, -y+1/2$; (iv) $-z+1/4, -y+1/4, x+1/4$; (v) $-x+1/4, z-1/4, y+1/4$; (vi) $x, -y, -z+1/2$; (vii) $-x+1/4, -z+1/4, y+1/4$; (viii) $-z+3/4, -y+1/4, x+1/4$; (ix) $x+1/2, -x, y$; (x) $z+1/2, x, -y+1/2$; (xi) $-z+3/4, -y+1/4, -x+1/4$; (xii) $x+1/2, 0, -z+1/2$; (xiii) $-x+1/2, -y+1/2, -z+1/2$; (xiv) $-x+1/2, -z+1/2, -y+1/2$; (xv) $-z+1/2, y+1/4, -x+1/4$; (xvi) $-z+1/2, y+1/4, x+1/4$; (xvii) $x, -z+1/2, y+1/4$; (xviii) $-y+1/4, -z+3/4, -x+1/4$; (xix) $-y+1/4, -z+3/4, x+1/4$; (xx) $-y+1/4, z-1/4, x+1/4$; (xxi) $-y+1/4, z-1/4, -x+1/4$; (xxii) $-y+1/4, -z+3/4, x+1/4$; (xxiii) $-y+1/4, -z+3/4, x+1/4$; (xxiv) $-y+1/4, -z+3/4, -x+1/4$; (xxv) $-y+1/4, -z+3/4, -x+1/4$; (xxvi) $-y+1/4, -z+3/4, -x+1/4$; (xxvii) $-y+1/4, x-1/4, -z+1/4$; (xxviii) $y, z+1/2, x+1/2$.
Hydrogen site location: difference Fourier map

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Revised as a 2-component inversion twin.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|       | x       | y       | z       | Uiso*/Ueq | Occ. (<1) |
|-------|---------|---------|---------|-----------|-----------|
| La1   | 0.11936 (3) | 0.25   | 0.01005 (9) | 0.961 (10) |
| Zr1A  | -0.01161 (12) | 0.006 (3) | 0.024 (5)* | 0.061 (6) |
| Zr1B  | -0.0073 (15) | 0.1429 (2) | 0.00149 (7) |
| O1    | 0.0970 (2) | 0.1899 (2) | 0.0132 (6) |
| O2    | 0.0335 (3) | 0.4452 (3) | 0.00149 (7) |
| Li1   | 0.375   | 0.25   | 0.016*   | 0.62 (6)  |
| Al1   | 0.375   | 0.25   | 0.016*   | 0.1      |
| Li2   | 0.875   | 0.25   | 0.017 (9) | 0.47 (9)  |
| H1    | 0.098 (6) | 0.180 (6) | 0.025*   | 0.92 (17) |

### Atomic displacement parameters (Å²)

|       | U¹¹   | U²²   | U³³   | U¹²   | U¹³   | U²³   |
|-------|-------|-------|-------|-------|-------|-------|
| La1   | 0.00938 (13) | 0.00852 (14) | 0.01224 (15) | 0.0000 (2) | 0.0000 (2) | 0.00403 (8) |
| Zr1A  | 0.0069 (4) | 0.0069 (4) | 0.0069 (4) | 0.0000 (2) | 0.0000 (2) | 0.0000 (2) |
| O1    | 0.0112 (12) | 0.0115 (13) | 0.0169 (15) | 0.0014 (9) | -0.0002 (10) | 0.0028 (10) |
| O2    | 0.0193 (15) | 0.0142 (13) | 0.0110 (14) | 0.0028 (10) | 0.0005 (10) | 0.0038 (10) |
| Li2   | 0.012 (14) | 0.020 (12) | 0.020 (12) | 0.0000 (2) | 0.0000 (2) | 0.0000 (2) |

### Geometric parameters (Å, °)

|       | O1—Li¹     | Li1—La¹     | O1—Zr1A     | Zr1A—Li¹     |
|-------|------------|-------------|-------------|-------------|
| La1—O1i | 2.506 (3) | 1.998 (3) | 2.007 (4) | 2.14 (3) |
| La1—O1ii| 2.506 (3) | 2.19 (3)  | 2.19 (3)  | 2.36 (3) |
| La1—O1  | 2.518 (3) | 2.14 (3)  | 2.14 (3)  | 2.14 (3) |
| La1—O1ii| 2.518 (3) | 2.36 (3)  | 2.36 (3)  | 2.36 (3) |
| La1—O2v | 2.544 (3) | 2.506 (3) | 2.506 (3) | 2.14 (3) |
| La1—O2i | 2.506 (3) | 2.007 (4) | 2.007 (4) | 2.14 (3) |
| La1—O2v | 2.544 (3) | 2.19 (3)  | 2.19 (3)  | 2.19 (3) |
| La1—O2i | 2.506 (3) | 2.36 (3)  | 2.36 (3)  | 2.36 (3) |
| La1—O2vi| 3.1947 (4) | 1.85 (3)  | 1.85 (3)  | 1.85 (3) |
| La1—Li² | 3.3422 (4) | 1.976 (3) | 1.976 (3) | 1.976 (3) |

Acta Cryst. (2022). C78, 1-6
| Bond                  | Distance (Å) |
|-----------------------|--------------|
| La1—Zr1Aⅱ            | 3.487 (2)    |
| La1—H1                | 2.55 (8)     |
| Zr1A—Zr1Bⅲ           | 0.39 (3)     |
| Zr1A—Zr1Bⅲ           | 0.39 (3)     |
| Zr1A—O1ⅰ             | 2.007 (4)    |
| Zr1A—O1ⅰ             | 2.007 (4)    |
| Zr1A—O2ⅱ             | 2.217 (4)    |
| Zr1A—O2ⅲ             | 2.217 (4)    |
| Zr1A—O2ⅳ             | 2.217 (4)    |
| Zr1A—O2ⅷ             | 2.217 (4)    |
| Zr1A—La1xi            | 3.487 (2)    |
| Zr1A—La1ⅸ            | 3.487 (2)    |
| Zr1A—Li1ⅹ             | 3.487 (2)    |
| Zr1B—Zr1Bⅲ           | 0.32 (5)     |
| Zr1B—Zr1Bⅲ           | 0.32 (5)     |
| Zr1B—O2ⅳ             | 1.85 (3)     |
| Zr1B—O2ⅷ             | 2.06 (3)     |
| Zr1B—O2ⅸ             | 2.10 (3)     |
| Zr1B—O1ⅰ             | 2.14 (3)     |
| Zr1B—O1ⅱ             | 2.19 (3)     |
| Zr1B—O1ⅲ             | 2.36 (3)     |
| Zr1B—Li2ⅱ            | 3.47 (3)     |
| Zr1B—La1ⅸ             | 3.49 (4)     |
| Zr1B—Li1ⅹ             | 3.54 (3)     |
| O1—Al1ⅸ              | 1.998 (3)    |
| O1ⅰ—La1—O1ⅱ          | 73.10 (16)   |
| O1ⅱ—La1—O1            | 68.42 (15)   |
| O1ⅱ—La1—O1            | 123.66 (7)   |
| O1ⅱ—La1—O1ⅳ          | 123.66 (7)   |
| O1ⅲ—La1—O1ⅲ          | 68.42 (15)   |
| O1ⅲ—La1—O1ⅳ          | 166.67 (15)  |
| O1ⅲ—La1—O1ⅸ          | 108.41 (9)   |
| O1ⅳ—La1—O2ⅴ          | 161.19 (8)   |
| O1ⅴ—La1—O2ⅴ          | 72.41 (10)   |
| O1ⅵ—La1—O2ⅵ          | 96.88 (11)   |
| O1ⅵ—La1—O2ⅶ          | 161.19 (8)   |
| O1ⅶ—La1—O2ⅶ          | 108.41 (9)   |
| O1ⅶ—La1—O2ⅷ          | 96.88 (11)   |
| O1ⅷ—La1—O2ⅷ          | 161.19 (8)   |
| O1ⅷ—La1—O2ⅸ          | 108.41 (9)   |
| O1ⅸ—La1—O2ⅸ          | 97.31 (11)   |
| O1ⅸ—La1—O2ⅹ          | 71.54 (10)   |
| O1ⅹ—La1—O2ⅹ          | 74.30 (10)   |
| O1ⅹ—La1—O2ⅹ          | 107.34 (10)  |
| O2ⅰ—La1—O2ⅰ          | 76.42 (15)   |
| O2ⅰ—La1—O2ⅰ          | 97.31 (11)   |
| O2ⅱ—La1—O2ⅱ          | 71.54 (10)   |
| O2ⅰ—La1—O2ⅰ          | 74.30 (10)   |
| O2ⅱ—La1—O2ⅰ          | 107.34 (10)  |
| O2ⅱ—La1—O2ⅱ          | 125.74 (7)   |
| O2ⅱ—La1—O2ⅱ          | 66.49 (14)   |
O1—La1—O2ii 71.54 (10)  
O1i—La1—O2ii 97.31 (11)  
O1—La1—O2ii 107.34 (10)  
O1—La1—O2ii 74.30 (10)  
O2—La1—O2ii 66.49 (14)  
O2—La1—O2ii 125.74 (7)  
O2—La1—O2ii 166.47 (14)  
O1i—La1—Li2vi 143.45 (8)  
O1i—La1—Li2vi 143.45 (8)  
O1—La1—Li2vi 83.33 (7)  
O1i—La1—Li2vi 83.33 (7)  
O2—La1—Li2vi 38.21 (8)  
O2—La1—Li2vi 38.21 (8)  
O2—La1—Li2vi 96.77 (7)  
O2—La1—Li2vi 96.77 (7)  
O1—La1—Li1 36.55 (8)  
O1—La1—Li1 36.55 (8)  
O1—La1—Li1 96.67 (7)  
O1—La1—Li1 96.67 (7)  
O2—La1—Li1 141.79 (8)  
O2—La1—Li1 141.79 (8)  
O2—La1—Li1 83.23 (7)  
O2—La1—Li1 83.23 (7)  
Li2vi—La1—Li1 180  
O1—La1—Zr1Avii 34.45 (8)  
O1—La1—Zr1Avii 96.17 (8)  
O1—La1—Zr1Avii 34.50 (7)  
O1—La1—Zr1Avii 158.08 (7)  
O2—La1—Zr1Avii 94.29 (8)  
O2—La1—Zr1Avii 128.79 (7)  
O2—La1—Zr1Avii 80.78 (8)  
O2—La1—Zr1Avii 93.16 (8)  
Li2vi—La1—Zr1Avii 116.505 (14)  
Li1—La1—Zr1Avii 63.495 (14)  
O1—La1—H1 74.9 (17)  
O1—La1—H1 116 (2)  
O1—La1—H1 15 (2)  
O1—La1—H1 160.1 (18)  
O2—La1—H1 82 (2)  
O2—La1—H1 88.1 (17)  
O2—La1—H1 60 (2)  
O2—La1—H1 122 (2)  
Li2vi—La1—H1 83.6 (18)  
Li1—La1—H1 96.4 (18)  
Zr1A—La1—H1 40.8 (17)  
Zr1B—Zr1A—Zr1Biv 49 (4)  
Zr1B—Zr1A—O1ix 105 (4)  
Zr1B—Zr1A—O1viii 113 (5)  

Aliv—O1—Zr1Bvii 121.3 (8)  
Liiv—O1—Zr1Bvii 121.3 (8)  
Zr1Avii—O1—Zr1Bvii 9.5 (8)  
Zr1Bv—O1—Zr1Bvii 8.5 (11)  
Aliv—O1—Zr1Bvix 123.4 (5)  
Liiv—O1—Zr1Bvix 123.4 (5)  
Zr1Aviii—O1—Zr1Bviii 4.3 (4)  
Zr1Bv—O1—Zr1Bviii 6.0 (8)  
Zr1Bv—O1—Zr1Bviii 6.9 (12)  
Aliv—O1—La1viii 95.15 (12)  
Liiv—O1—La1viii 95.15 (12)  
Zr1Aviii—O1—La1viii 100.61 (15)  
Zr1Bv—O1—La1viii 103.0 (8)  
Zr1Bv—O1—La1viii 109.2 (13)  
Zr1Bv—O1—La1viii 102.3 (8)  
Aliv—O1—La1 122.82 (15)  
Liiv—O1—La1 122.82 (15)  
Zr1Aviii—O1—La1 100.20 (13)  
Zr1Bv—O1—La1 108.8 (8)  
Zr1Bv—O1—La1 101.1 (7)  
Zr1Bv—O1—La1 103.4 (8)  
La1viii—O1—La1 105.71 (13)  
Aliv—O1—H1 56 (7)  
Liiv—O1—H1 56 (7)  
Zr1Aviii—O1—H1 106 (7)  
Zr1Bv—O1—H1 101 (7)  
Zr1Bv—O1—H1 97 (7)  
Zr1Bv—O1—H1 103 (7)  
La1viii—O1—H1 149 (7)  
La1—O1—H1 85 (7)  
Zr1Bv—O2—Li2vii 129.6 (7)  
Zr1Bv—O2—Li2vii 7.3 (16)  
Li2vi—O2—Zr1Bviii 130.6 (8)  
Zr1Bv—O2—Zr1Bviii 5.9 (9)  
Li2vi—O2—Zr1Bviii 135.6 (10)  
Zr1Bv—O2—Zr1Bviii 8.8 (12)  
Zr1Bv—O2—Zr1Bviii 4.1 (5)  
Li2vi—O2—Zr1Bviii 125.57 (17)  
Zr1Bv—O2—Zr1Bviii 9.7 (9)  
Zr1Bv—O2—Zr1Bviii 10.0 (9)  
Zr1Bv—O2—La1iv 105.3 (10)  
Li2vi—O2—La1iv 89.03 (12)  
Zr1Bv—O2—La1iv 97.9 (10)  
Zr1Bv—O2—La1iv 104.4 (9)  
Zr1Bv—O2—La1iv 106.84 (13)  
Zr1Bv—O2—La1iv 101.5 (11)  
Li2vi—O2—La1viii 122.70 (14)  
Zr1Bv—O2—La1viii 103.6 (8)
| Bond                  | Length (Å) | Error (Å) |
|----------------------|------------|-----------|
| Zr1B—Zr1A—O1x        | 113 (5)    |           |
| Zr1B—Zr1A—O1x        | 153 (3)    |           |
| O1x—Zr1A—O1x         | 89.46 (17) |           |
| Zr1B—Zr1A—O1xi       | 153 (3)    |           |
| Zr1B—Zr1A—O1vi       | 105 (4)    |           |
| O1vi—Zr1A—O1vi       | 89.46 (17) |           |
| O1—Zr1A—O1vi         | 89.46 (17) |           |
| Zr1B—Zr1A—O2xii      | 20 (3)     |           |
| Zr1B—Zr1A—O2xii      | 68 (4)     |           |
| O1—Zr1A—O2xii        | 94.57 (13) |           |
| O1—Zr1A—O2xii        | 96.47 (13) |           |
| O1—Zr1A—O2xii        | 172.9 (2)  |           |
| Zr1B—Zr1A—O2iv       | 68 (4)     |           |
| Zr1B—Zr1A—O2iv       | 62 (4)     |           |
| Zr1B—Zr1A—O2iv       | 172.9 (2)  |           |
| Zr1B—Zr1A—O2iv       | 94.57 (13) |           |
| Zr1B—Zr1A—O2iv       | 96.47 (13) |           |
| Zr1B—Zr1A—O2iv       | 79.14 (16) |           |
| Zr1B—Zr1A—O2iv       | 79.14 (16) |           |
| Zr1B—Zr1A—La1xi      | 150 (6)    |           |
| Zr1B—Zr1A—La1xi      | 139 (6)    |           |
| O1—Zr1A—La1x         | 95.88 (14) |           |
| O1—Zr1A—La1x         | 44.94 (11) |           |
| O1—Zr1A—La1x         | 45.30 (10) |           |
| O2—Zr1A—La1x         | 139.67 (9) |           |
| O2—Zr1A—La1x         | 91.13 (9)  |           |
| O2—Zr1A—La1x         | 137.69 (9) |           |
| Zr1B—Zr1A—La1x       | 139 (6)    |           |
| Zr1B—Zr1A—La1x       | 110 (2)    |           |
| O1—Zr1A—La1x         | 45.30 (10) |           |
| O1—Zr1A—La1x         | 95.88 (14) |           |
| O1—Zr1A—La1x         | 44.94 (11) |           |
| O2—Zr1A—La1x         | 137.69 (9) |           |
| O2—Zr1A—La1x         | 137.69 (9) |           |
| Zr1B—Zr1A—La1x       | 91.13 (9)  |           |
| Zr1B—Zr1A—La1x       | 70.09 (5)  |           |
| Zr1B—Zr1A—La1x       | 110 (2)    |           |
| Zr1B—Zr1A—La1x       | 150 (6)    |           |
| O1—Zr1A—La1x         | 44.94 (11) |           |
| O1—Zr1A—La1x         | 45.30 (10) |           |
| O1—Zr1A—La1x         | 95.88 (14) |           |
| O2—Zr1A—La1x         | 91.13 (9)  |           |

**Bond Angles (°) and Errors:**

| Bond                  | Angle (°)  | Error (°) |
|----------------------|------------|-----------|
| Zr1B—Zr1A—O1x        | 113 (5)    |           |
| Zr1B—Zr1A—O1x        | 153 (3)    |           |
| O1x—Zr1A—O1x         | 89.46 (17) |           |
| Zr1B—Zr1A—O1xi       | 153 (3)    |           |
| Zr1B—Zr1A—O1vi       | 105 (4)    |           |
| O1vi—Zr1A—O1vi       | 89.46 (17) |           |
| O1—Zr1A—O1vi         | 89.46 (17) |           |
| Zr1B—Zr1A—O2xii      | 20 (3)     |           |
| Zr1B—Zr1A—O2xii      | 68 (4)     |           |
| O1—Zr1A—O2xii        | 94.57 (13) |           |
| O1—Zr1A—O2xii        | 96.47 (13) |           |
| O1—Zr1A—O2xii        | 172.9 (2)  |           |
| Zr1B—Zr1A—O2iv       | 68 (4)     |           |
| Zr1B—Zr1A—O2iv       | 62 (4)     |           |
| Zr1B—Zr1A—O2iv       | 172.9 (2)  |           |
| Zr1B—Zr1A—O2iv       | 94.57 (13) |           |
| Zr1B—Zr1A—O2iv       | 96.47 (13) |           |
| Zr1B—Zr1A—O2iv       | 79.14 (16) |           |
| Zr1B—Zr1A—O2iv       | 79.14 (16) |           |
| Zr1B—Zr1A—La1xi      | 150 (6)    |           |
| Zr1B—Zr1A—La1xi      | 139 (6)    |           |
| O1—Zr1A—La1x         | 95.88 (14) |           |
| O1—Zr1A—La1x         | 44.94 (11) |           |
| O1—Zr1A—La1x         | 45.30 (10) |           |
| O2—Zr1A—La1x         | 139.67 (9) |           |
| O2—Zr1A—La1x         | 91.13 (9)  |           |
| O2—Zr1A—La1x         | 137.69 (9) |           |
| Zr1B—Zr1A—La1x       | 139 (6)    |           |
| Zr1B—Zr1A—La1x       | 110 (2)    |           |
| O1—Zr1A—La1x         | 45.30 (10) |           |
| O1—Zr1A—La1x         | 95.88 (14) |           |
| O1—Zr1A—La1x         | 44.94 (11) |           |
| O2—Zr1A—La1x         | 137.69 (9) |           |
| O2—Zr1A—La1x         | 137.69 (9) |           |
| Zr1B—Zr1A—La1x       | 91.13 (9)  |           |
| Zr1B—Zr1A—La1x       | 70.09 (5)  |           |
| Zr1B—Zr1A—La1x       | 110 (2)    |           |
| Zr1B—Zr1A—La1x       | 150 (6)    |           |
| O1—Zr1A—La1x         | 44.94 (11) |           |
| O1—Zr1A—La1x         | 45.30 (10) |           |
| O1—Zr1A—La1x         | 95.88 (14) |           |
| Zr1B—Zr1A—La1x       | 70.09 (5)  |           |
| Bond                        | Bond Angle (°) ± Standard Deviation       |
|-----------------------------|------------------------------------------|
| O2iv—Zr1A—La1x              | 137.69 (9)                               |
| O2ii—Zr1A—La1x              | 139.67 (9)                               |
| La1x—Zr1A—La1x              | 70.09 (5)                                |
| La1x—Zr1A—La1x              | 70.09 (5)                                |
| Zr1Bvi—Zr1A—Li1xii          | 127 (3)                                  |
| Zr1Bv—Zr1A—Li1xii           | 79 (4)                                   |
| O1x—Zr1A—Li1xii             | 100.02 (10)                              |
| O1x—Zr1A—Li1xii             | 113.16 (12)                              |
| O1x—Zr1A—Li1xii             | 26.09 (10)                               |
| O2xiii—Zr1A—Li1xii          | 146.86 (13)                              |
| O2v—Zr1A—Li1xii             | 83.83 (9)                                |
| O2v—Zr1A—Li1xii             | 69.81 (9)                                |
| La1x—Zr1A—Li1xii            | 68.24 (3)                                |
| La1x—Zr1A—Li1xii            | 56.29 (2)                                |
| Zr1Bviii—Zr1B—Zr1Bi         | 60.00 (6)                                |
| Zr1Bviii—Zr1B—Zr1Bi         | 138 (5)                                  |
| Zr1B—Zr1B—O2iv              | 126 (9)                                  |
| Zr1Bviii—Zr1B—O2xvii        | 47 (7)                                   |
| Zr1B—Zr1B—O2xv               | 93 (9)                                   |
| O2iv—Zr1B—O2xv               | 92.3 (15)                                |
| Zr1Bviii—Zr1B—O1x            | 78 (9)                                   |
| Zr1B—Zr1B—O1x               | 36 (5)                                   |
| O2iv—Zr1B—O2xv               | 90.9 (12)                                |
| O2v—Zr1B—O2v                | 85.5 (5)                                 |
| Zr1Bviii—Zr1B—O1x            | 95 (9)                                   |
| Zr1B—Zr1B—O1x               | 130 (4)                                  |
| O2iv—Zr1B—O1x               | 101.9 (13)                               |
| O2v—Zr1B—O1x                | 97.3 (16)                                |
| O2v—Zr1B—O1x                | 166.7 (19)                               |
| Zr1Bviii—Zr1B—O1x            | 119 (7)                                  |
| Zr1B—Zr1B—O1x               | 77 (9)                                   |
| O2iv—Zr1B—O1x               | 102.2 (13)                               |
| O2v—Zr1B—O1x                | 165.4 (18)                               |
| O2v—Zr1B—O1x                | 92.7 (16)                                |
| O1x—Zr1B—O1x                | 81.4 (6)                                 |
| Zr1Bviii—Zr1B—O1x           | 44 (4)                                   |
| Zr1B—Zr1B—O1x               | 54 (7)                                   |
| O2v—Zr1B—O1x                | 178.7 (12)                               |
| O2v—Zr1B—O1x                | 89.0 (11)                                |
| O2v—Zr1B—O1x                | 89.6 (12)                                |
| O1x—Zr1B—O1x                | 77.5 (10)                                |
| O1x—Zr1B—O1x                | 76.6 (11)                                |
| Zr1Bviii—Zr1B—Li2x           | 164 (6)                                  |
| Zr1B—Zr1B—Li2x              | 126 (10)                                 |
| O2iv—Zr1B—Li2x              | 26.1 (4)                                 |
| O2v—Zr1B—Li2x               | 117.1 (14)                               |
| O2v—Zr1B—Li2x               | 100.0 (11)                               |
| O1x—Li1—Zr1Axxv             | 26.21 (10)                               |
| O1ii—Li1—Zr1Axxv             | 90.93 (10)                               |
| O1i—Li1—Zr1Axxv              | 130.14 (9)                               |
| O1xii—Li1—Zr1Axxv            | 103.67 (10)                              |
| La1—Li1—Zr1Axxv              | 119.79 (3)                               |
| La1x—Li1—Zr1Axxv             | 60.21 (3)                                |
| Zr1Bviii—Li1—Zr1Axxv         | 107.3 (5)                                |
| Zr1Bxiv—Li1—Zr1Axxv          | 6.2 (5)                                  |
| Zr1Biii—Li1—Zr1Axxv          | 98.1 (5)                                 |
| Zr1B—Li1—Zr1Axxv             | 123.8 (5)                                |
| O1x—Li1—Zr1Axxv              | 130.14 (9)                               |
| O1ii—Li1—Zr1Axxv             | 26.21 (10)                               |
| O1i—Li1—Zr1Axxv              | 103.67 (10)                              |
| O1xi—Li1—Zr1Axxv             | 90.93 (10)                               |
| La1—Li1—Zr1Axxv              | 60.21 (3)                                |
| La1x—Li1—Zr1Axxv             | 119.79 (3)                               |
| Zr1Bviii—Li1—Zr1Axxv         | 6.2 (5)                                  |
| Zr1B—Li1—Zr1Axxv             | 98.1 (5)                                 |
| Zr1B—Li1—Zr1Axxv             | 123.8 (5)                                |
| Zr1B—Li1—Zr1Axxv             | 104.29 (3)                               |
| Zr1Bviii—Li1—Zr1Axxv         | 123.8 (5)                                |
| Zr1B—Li1—Zr1Axxv             | 107.3 (5)                                |
| Zr1B—Li1—Zr1Axxv             | 111.48 (10)                              |
| Zr1B—Li1—Zr1Axxv             | 111.48 (10)                              |
| O2xvii—Li1—Zr1Axxv           | 105.53 (19)                              |
| O2xv—Li1—Zr1Axxv             | 105.53 (19)                              |
| O2xvi—Li1—Zr1Axxv            | 111.48 (10)                              |
| O2xv—Li1—Zr1Axxv             | 111.48 (10)                              |
| O2xvi—Li1—Zr1Axxv            | 127.23 (9)                               |
| O2xv—Li1—Zr1Axxv             | 52.77 (9)                                |
| O2xv—Li1—Zr1Axxv             | 52.77 (9)                                |
| O2xvi—Li1—Zr1Axxv            | 52.77 (9)                                |
| O2xvi—Li1—Zr1Axxv            | 52.77 (9)                                |
| O2xvi—Li1—Zr1Axxv            | 52.77 (9)                                |
| O2xvi—Li1—Zr1Axxv            | 52.77 (9)                                |
| O2xv—Li1—Zr1Axxv             | 125.3 (7)                                |
| O2xv—Li1—Zr1Axxv             | 24.3 (5)                                 |
| O2xvi—Li1—Zr1Axxv            | 112.0 (5)                                |
| O2xvi—Li1—Zr1Axxv            | 87.6 (4)                                 |
| O2xvi—Li1—Zr1Axxv            | 63.6 (4)                                 |
| O2xvi—Li1—Zr1Axxv            | 116.4 (4)                                |
| O2xvi—Li1—Zr1Axxv            | 24.3 (5)                                 |
| O2xvi—Li1—Zr1Axxv            | 87.6 (4)                                 |
| O2xvi—Li1—Zr1Axxv            | 125.3 (7)                                |
| O2xvi—Li1—Zr1Axxv            | 112.0 (5)                                |
| O2xvi—Li1—Zr1Axxv            | 116.4 (4)                                |
| O2xvi—Li1—Zr1Axxv            | 63.6 (4)                                 |
**Crystal data**

Ga$_{0.28}$La$_{2.94}$Li$_{6.44}$O$_{12.00}$Zr$_{2.00}$

D$_c$ = 5.165 Mg m$^{-3}$

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 35033 reflections

θ = 3.9 – 38.9°

μ = 13.88 mm$^{-1}$

T = 298 K

Cuboid, colorless

0.13 × 0.13 × 0.10 mm

**Data collection**

Bruker SMART APEX

X-ray diffractometer

Graphite monochromator

ω-scan for CrysAlis PRO

23040 measured reflections

48 independent reflections

1045 reflections with I > 2σ(I)

R$_{int}$ = 0.038

θ$_{max}$ = 38.9°, θ$_{min}$ = 3.9°

h = -22 to 22

k = -22 to 22

l = -22 to 22

35033 measured reflections

**Refinement**

Refinement on F$^2$

Least-squares matrix: full

R(F$^2$ > 2σ(F$^2$)) = 0.013

wR(F$^2$) = 0.026

S = 1.29

1054 reflections

(R) = 0.001

where P = (F$^2$ + 2F$^2$) / 3
\( \Delta \rho_{\text{max}} = 0.53 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.65 \text{ e Å}^{-3} \)

Extinction correction: SHELXL2014 (Sheldrick, 2015),
\( F_c^* = k F_c [1 + 0.001 x F_c^2 / \sin (2 \theta)]^{1/4} \)

Extinction coefficient: 0.00103 (4)

Absolute structure: Refined as an inversion twin.

Absolute structure parameter: 0.50 (4)

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refined as a 2-component inversion twin.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|       | x       | y       | z       | \( U_{\text{iso}}^* / U_{eq} \) | Occ. (<1) |
|-------|---------|---------|---------|-------------------------------|-----------|
| La1   | 0.11966 (2) | 0 | 0.25 | 0.00584 (5) | 0.9814 (19) |
| Zr1   | 0.00014 (2) | 0 | 0.00014 (2) | 0.00502 (8) |
| O1    | 0.09727 (14) | 0.19681 (14) | 0.27989 (14) | 0.0087 (3) |
| O2    | 0.03322 (15) | 0.44478 (16) | 0.14725 (13) | 0.0105 (3) |
| Li1   | 0.375 | 0 | 0.25 | 0.0038 (5) | 0.818 (3) |
| Ga1   | 0.375 | 0 | 0.25 | 0.0038 (5) | 0.182 (3) |
| Li2   | 0.875 | 0 | 0.25 | 0.021 (3) | 0.995 (3) |
| Ga2   | 0.875 | 0 | 0.25 | 0.021 (3) | 0.005 (3) |
| Li3   | 0.0971 (7) | 0.1868 (6) | 0.4268 (6) | 0.014 (2) | 0.62 (3) |

### Atomic displacement parameters (Å²)

|       | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{12} \) | \( U_{13} \) | \( U_{23} \) |
|-------|---------------|---------------|---------------|---------------|---------------|---------------|
| La1   | 0.00591 (7) | 0.00574 (8) | 0.00587 (8) | 0 | 0 | 0.00065 (5) |
| Zr1   | 0.00502 (8) | 0.00502 (8) | 0.00502 (8) | 0.00015 (6) | 0.00015 (6) | 0.00015 (6) |
| O1    | 0.0079 (7) | 0.0087 (7) | 0.0095 (7) | -0.0008 (6) | 0.0013 (5) | -0.0002 (6) |
| O2    | 0.0134 (8) | 0.0122 (8) | 0.0059 (7) | 0.0021 (6) | -0.0003 (5) | 0.0009 (6) |
| Li1   | 0.0043 (8) | 0.0035 (6) | 0.0035 (6) | 0 | 0 | 0 |
| Ga1   | 0.0043 (8) | 0.0035 (6) | 0.0035 (6) | 0 | 0 | 0 |
| Li2   | 0.013 (4) | 0.025 (4) | 0.025 (4) | 0 | 0 | 0 |
| Ga2   | 0.013 (4) | 0.025 (4) | 0.025 (4) | 0 | 0 | 0 |
| Li3   | 0.022 (4) | 0.014 (4) | 0.007 (3) | -0.005 (3) | 0.004 (3) | 0.001 (2) |

### Geometric parameters (Å, °)

|       | \( \text{La1—O2}^i \) | \( \text{O2—Li3}^v \) | \( \text{O2—La1}^iv \) | \( \text{La1—O1}^v \) | \( \text{La1—Li3}^v \) |
|-------|-------------------|------------------|-------------------|-------------------|-------------------|
| La1   | 2.4935 (19) | 2.108 (9) | 2.4936 (19) | 2.587 (2) | 2.639 (8) |
| La1   | 2.4935 (19) | 2.108 (9) | 2.4936 (19) | 2.587 (2) | 2.639 (8) |
| La1   | 2.5264 (19) | 2.587 (2) | 1.645 (8) | 1.645 (8) | 1.645 (8) |
| La1   | 2.5264 (19) | 2.587 (2) | 1.645 (8) | 1.645 (8) | 1.645 (8) |
| La1   | 2.5975 (19) | 1.645 (8) | 1.645 (8) | 1.645 (8) | 1.645 (8) |
| La1   | 2.5976 (19) | 1.645 (8) | 1.645 (8) | 1.645 (8) | 1.645 (8) |
La₁—Li₃vi 3.037 (8) Li₁—O₁vi 1.8941 (18)
La₁—Li₃vii 3.037 (8) Li₁—O₁v 1.8941 (18)
La₁—Ga₂viii 3.1725 (2) Li₁—O₁iv 1.8941 (18)
La₁—Li₂viii 3.1725 (2) Li₁—O₁vii 1.8941 (18)
Zr₁—O₂ix 2.0823 (18) Li₁—La₁xx 3.3109 (2)
Zr₁—O₂iv 2.0823 (18) Li₂—O₂xxi 1.9246 (9)
Zr₁—O₂i 2.0823 (18) Li₂—O₂xxii 1.9246 (9)
Zr₁—O₁x 2.1346 (18) Li₂—O₂xxiii 1.9246 (9)
Zr₁—O₁xi 2.1346 (18) Li₂—O₂xxiv 1.9246 (9)
Zr₁—La₁ 3.1726 (2) Li₂—Li₃xxv 2.340 (9)
Zr₁—Li₃xiii 2.890 (8) Li₂—Li₃xxvi 2.340 (9)
Zr₁—Li₃v 2.890 (8) Li₂—Li₃xxvii 2.340 (9)
Zr₁—Li₃xiv 2.890 (8) Li₂—Li₃xxviii 2.340 (9)
Zr₁—Li₃x 3.140 (7) Li₂—Li₃xxix 2.340 (9)
Zr₁—Li₃xi 3.140 (7) Li₂—Li₃xxx 2.340 (9)
O₁—Ga₁xv 1.8941 (18) Li₃—Ga₂xxix 2.340 (9)
O₁—Li₁xv 1.8941 (18) Li₃—Ga₂xxx 2.340 (9)
O₁—Li₃ 1.909 (8) Li₃—Ga₂xxxi 2.340 (9)
O₁—Li₃i 2.075 (8) Li₃—Li₂xxx 2.340 (9)
O₁—Zr₁xiv 2.1346 (18) Li₃—Li₂xxxi 2.340 (9)
O₁—Li₃viii 2.229 (8) Li₃—Li₂xxii 2.340 (9)
O₁—La₁xv 2.5264 (19) Li₃—Li₂xxiii 2.340 (9)
O₂—Ga₂xxix 1.9247 (19) Li₃—Li₂xxiv 2.340 (9)
O₂—Li₂xxix 1.9247 (19) Li₃—Li₂xxv 2.340 (9)
O₂—Zr₁i 2.0823 (18) Li₃—Zr₁v 2.890 (8)
O₂—La₁—O₂ii 74.68 (9) Li₃v—O₂—La₁i 161.4 (2)
O₂—La₁—O₁iii 111.38 (5) Ga₂xxix—O₂—La₁iv 124.19 (9)
O₂—La₁—O₁iv 160.56 (5) Li₂xxix—O₂—La₁iv 124.19 (9)
O₂—La₁—O₁iv 160.56 (5) Zr₁v—O₂—La₁iv 100.00 (7)
O₂—La₁—O₁iv 111.38 (5) Li₃v—O₂—La₁iv 90.4 (2)
O₁iii—La₁—O₁iv 69.36 (8) La₁—O₂—La₁iv 102.82 (7)
O₂—La₁—O₁iv 125.72 (4) Ga₂xxix—O₂—Li₃xvi 59.26 (19)
O₂—La₁—O₂ii 68.66 (8) Li₂xxix—O₂—Li₃xvi 59.26 (19)
O₁iii—La₁—O₂ii 94.00 (6) Zr₁v—O₂—Li₃xvi 170.9 (2)
O₁iv—La₁—O₂iii 72.71 (6) Li₃v—O₂—Li₃xvi 94.3 (2)
O₂—La₁—O₂iv 68.66 (8) La₁—O₂—Li₃xvi 78.05 (18)
O₂—La₁—O₂iv 125.72 (4) La₁v—O₂—Li₃xvi 71.06 (19)
O₁iii—La₁—O₂iv 72.71 (6) Li₃v—Li₁—Li₃vi 131.8 (5)
O₁iv—La₁—O₂iv 94.00 (6) Li₃v—Li₁—Li₃vi 99.6 (2)
O₂—La₁—O₂iv 164.10 (8) Li₃v—Li₁—Li₃vi 99.6 (2)
O₂—La₁—O₁v 96.52 (6) Li₃v—Li₁—Li₃iv 99.6 (2)
O₂—La₁—O₁v 73.06 (6) Li₃v—Li₁—Li₃iv 99.6 (2)
O₁iii—La₁—O₁iv 122.80 (4) Li₃v—Li₁—Li₃iv 131.8 (5)
O₁iv—La₁—O₁v 69.03 (8) Li₃v—Li₁—Li₃iv 163.0 (3)
O₂—La₁—O₁v 108.95 (5) Li₃v—Li₁—O₁vi 64.8 (3)
O₂—La₁—O₁v 72.92 (5) Li₃v—Li₁—O₁vi 77.7 (3)
| Bond                  | Angle (°)     | Bond                  | Angle (°)     |
|-----------------------|---------------|-----------------------|---------------|
| O2—La1—O1            | 73.06 (6)     | Li3vi—Li1—O1iv       | 71.4 (3)      |
| O2—La1—O1            | 96.52 (6)     | Li3v—Li1—O1iv        | 71.4 (3)      |
| O1iii—La1—O1         | 69.03 (8)     | Li3v—Li1—O1iv        | 77.7 (3)      |
| O1iv—La1—O1          | 122.80 (4)    | Li3v—Li1—O1iv        | 163.0 (3)     |
| O2iv—La1—O1          | 72.92 (5)     | Li3v—Li1—O1iv        | 64.8 (3)      |
| O2v—La1—O1           | 108.95 (5)    | Li3v—Li1—O1iv        | 115.09 (6)    |
| O1v—La1—O1           | 167.16 (8)    | Li3v—Li1—O1iv        | 77.7 (3)      |
| O2i—La1—Li3vi        | 146.61 (16)   | Li3v—Li1—O1iv        | 71.4 (3)      |
| O2i—La1—Li3vi        | 123.17 (17)   | Li3v—Li1—O1iv        | 64.8 (3)      |
| O1iii—La1—Li3vi      | 42.58 (16)    | Li3v—Li1—O1iv        | 163.0 (3)     |
| O1iv—La1—Li3vi       | 46.12 (15)    | Li3v—Li1—O1iv        | 98.74 (12)    |
| O2iii—La1—Li3vi      | 55.27 (17)    | Li3v—Li1—O1iv        | 64.8 (3)      |
| O2ii—La1—Li3vi       | 109.23 (16)   | Li3v—Li1—O1iv        | 163.0 (3)     |
| O1v—La1—Li3vi        | 115.09 (16)   | Li3v—Li1—O1iv        | 71.4 (3)      |
| O1—La1—Li3vi         | 76.72 (16)    | Li3v—Li1—O1iv        | 77.7 (3)      |
| O2v—La1—Li3vi        | 123.17 (17)   | Li3v—Li1—O1iv        | 98.74 (12)    |
| O2—it—Li3vi          | 146.61 (16)   | Li3v—Li1—O1iv        | 115.09 (6)    |
| O1iv—La1—Li3vi       | 46.12 (15)    | Li3v—Li1—O1iv        | 115.09 (6)    |
| O1—La1—Li3vi         | 109.23 (16)   | Li3v—Li1—O1iv        | 164.1 (3)     |
| Li3v—La1—Li3vii      | 59.3 (3)      | Li3v—Li1—O1iv        | 65.9 (3)      |
| O2—La1—Ga2viii       | 37.34 (4)     | O1vi—Li1—La1xx       | 49.37 (6)     |
| O2—La1—Ga2viii       | 37.34 (4)     | O1iv—Li1—La1xx       | 130.63 (6)    |
| O1v—La1—Ga2viii      | 145.32 (4)    | O1iv—Li1—La1xx       | 130.63 (6)    |
| O1—La1—Ga2viii       | 145.32 (4)    | O1iv—Li1—La1xx       | 49.37 (6)     |
| O2—La1—Ga2viii       | 97.95 (4)     | Li3v—Li1—La1xx       | 65.9 (3)      |
| O2—La1—Ga2viii       | 97.95 (4)     | Li3v—Li1—La1xx       | 65.9 (3)      |
| O1—La1—Ga2viii       | 83.58 (4)     | Li3v—Li1—La1xx       | 114.1 (3)     |
| O1—La1—Ga2viii       | 83.58 (4)     | O1iv—Li1—La1xx       | 114.1 (3)     |
| Li3v—La1—Ga2viii     | 150.36 (16)   | Li3v—Li1—La1xx       | 130.63 (6)    |
| Li3v—La1—Ga2viii     | 150.36 (16)   | Li3v—Li1—La1xx       | 49.37 (6)     |
| O2—La1—La2viii       | 37.34 (4)     | O1iv—Li1—La1xx       | 49.37 (6)     |
| O2—La1—La2viii       | 37.34 (4)     | O1iv—Li1—La1xx       | 130.63 (6)    |
| O1—La1—La2viii       | 145.32 (4)    | La1xxvii—Li1—La1xx   | 180           |
| O1iv—La1—La2viii     | 145.32 (4)    | O2xxi—Li2—O2xxii     | 112.48 (6)    |
| O2—La1—La2viii       | 97.95 (4)     | O2xxi—Li2—O2xxii     | 103.61 (12)   |
| O2—La1—La2viii       | 97.95 (4)     | O2xxi—Li2—O2xxii     | 112.48 (6)    |
| O1v—La1—La2viii      | 83.58 (4)     | O2xxi—Li2—O2xxii     | 103.60 (12)   |
| O1—La1—La2viii       | 83.58 (4)     | O2xxi—Li2—O2xxii     | 112.48 (6)    |
| Li3—La1—Li2viii      | 150.36 (16)   | O2xxi—Li2—Li3xxiv    | 161.7 (2)     |
| Li3—La1—Li2viii      | 150.36 (16)   | O2xxi—Li2—Li3xxiv    | 79.8 (2)      |
| Ga2viii—La1—La2viii  | 0             | O2xxi—Li2—Li3xxiv    | 58.3 (2)      |
| O2—Zr1—O2v           | 86.98 (8)     | O2xxi—Li2—Li3xxiv    | 75.8 (2)      |
| O2—Zr1—O2v           | 86.98 (8)     | O2xxi—Li2—Li3xxiv    | 58.3 (2)      |
| O2—Zr1—O2v           | 86.98 (8)     | O2xxi—Li2—Li3xxiv    | 75.8 (2)      |
| Atom 1—Atom 2—Atom 3 | O1x—Zr1—O1x | 94.92 (8) | O2xiii—Li2—Li3xv | 161.7 (2) |
|---------------------|---------------|-----------|-------------------|-----------|
|                     | O2x—Zr1—O1x  | 177.97 (8)| O2xxx—Li2—Li3xxv | 79.8 (2)  |
|                     | O2—Zr1—O1x   | 92.40 (7) | Li3xiv—Li2—Li3xxv| 140.0 (4) |
|                     | O2—Zr1—O1xi  | 92.40 (7) | O2xxi—Li2—Li3xxvi| 75.8 (2)  |
|                     | O2—Zr1—O1xi  | 94.92 (8) | O2xxii—Li2—Li3xxvi| 161.7 (2) |
|                     | O2—Zr1—O1xii | 177.97 (8)| O2xxiii—Li2—Li3xxvi| 79.8 (2)  |
|                     | O1—Zr1—O1xi  | 85.72 (7) | O2xxiv—Li2—Li3xxvi| 58.3 (2)  |
|                     | O2—Zr1—O1xii | 177.97 (8)| Li3xxiv—Li2—Li3xxvi| 96.73 (13)|
|                     | O2—Zr1—O1xii | 92.40 (7) | Li3xxv—Li2—Li3xxvi| 79.8 (2)  |
|                     | O1—Zr1—O1xii | 85.72 (7) | O2xxv—Li2—Li3xxvi | 75.8 (2)  |
|                     | O1—Zr1—O1xii | 85.72 (7) | O2xxvi—Li2—Li3xxvi| 161.7 (2) |
|                     | O2—Zr1—Li3xiii | 46.76 (18)| O2xxvii—Li2—Li3xxvi| 96.73 (13)|
|                     | O2—Zr1—Li3xiii | 94.45 (17)| Li3xxviii—Li2—Li3xxvi| 79.8 (2)  |
|                     | O1—Zr1—Li3xiii | 131.42 (18)| Li3xxix—Li2—Li3xxvi| 140.0 (4) |
|                     | O1—Zr1—Li3xiii | 133.42 (18)| O2xxi—Li2—La1xx | 51.80 (6) |
|                     | O1—Zr1—Li3xiii | 46.76 (18) | O2xxii—Li2—La1xx | 128.20 (6) |
|                     | O1—Zr1—Li3xiii | 94.45 (17) | O2xxiii—Li2—La1xx | 128.20 (6) |
|                     | O1—Zr1—Li3xiii | 131.42 (18) | Li3xxx—Li2—La1xx | 110.0 (2) |
|                     | O1—Zr1—Li3xiii | 87.38 (16) | Li3xxx—Li2—La1xx | 110.0 (2) |
|                     | O1—Zr1—Li3xiii | 45.80 (18) | Li3xxxii—Li2—La1xx | 70.0 (2)  |
|                     | O1—Zr1—Li3xiii | 131.42 (18) | Li3xxxii—Li2—La1xx | 70.0 (2)  |
|                     | O1—Zr1—Li3xiii | 87.38 (16) | Li3xxxii—Li2—La1xx | 128.20 (6) |
|                     | O1—Zr1—Li3xiii | 45.80 (18) | Li3xxxiii—Li2—La1xx | 128.20 (6) |
|                     | O1—Zr1—Li3xiii | 131.42 (18) | Li3xxxiii—Li2—La1xx | 51.80 (6) |
|                     | O1—Zr1—Li3xiii | 87.38 (16) | Li3xxxiii—Li2—La1xx | 128.20 (6) |
|                     | O1—Zr1—Li3xiii | 45.80 (18) | Li3xxxiii—Li2—La1xx | 70.0 (2)  |
|                     | O1—Zr1—Li3xiii | 131.42 (18) | Li3xxxiii—Li2—La1xx | 128.20 (6) |
|                     | O1—Zr1—Li3xiii | 87.38 (16) | Li3xxxiii—Li2—La1xx | 110.0 (2) |
|                     | O1—Zr1—Li3xiii | 45.80 (18) | Li3xxxiii—Li2—La1xx | 110.0 (2) |
|                     | O1—Zr1—Li3xiii | 131.42 (18) | O1—Li3—Li3xviii | 0 |
|                     | O1—Zr1—Li3xiii | 87.38 (16) | O1—Li3—Li3xviii | 63.9 (3)  |
|                     | O1—Zr1—Li3xiii | 45.80 (18) | O1—Li3—Li3xviii | 63.9 (3)  |
|                     | O1—Zr1—Li3xiii | 131.42 (18) | O1—Li3—Li3xviii | 59.9 (3)  |
|                     | O1—Zr1—Li3xiii | 87.38 (16) | O1—Li3—Li3xviii | 59.9 (3)  |
|                     | O1—Zr1—Li3xiii | 45.80 (18) | O1—Li3—Li3xviii | 106.6 (4) |
|                     | O1—Zr1—Li3xiii | 131.42 (18) | O1—Li3—Li3xviii | 138.8 (5) |
|                     | O1—Zr1—Li3xiii | 87.38 (16) | O1—Li3—Li3xviii | 138.8 (5) |
|                     | O1—Zr1—Li3xiii | 45.80 (18) | O1—Li3—Li3xviii | 100.0 (4) |
|                     | O1—Zr1—Li3xiii | 131.42 (18) | O1—Li3—Li3xviii | 93.4 (3)  |
|                     | O1—Zr1—Li3xiii | 87.38 (16) | O1—Li3—Li3xviii | 56.1 (3)  |
|                     | O1—Zr1—Li3xiii | 45.80 (18) | O1—Li3—Li3xviii | 56.1 (3)  |
|                     | O1—Zr1—Li3xiii | 131.42 (18) | O1—Li3—Li3xviii | 100.9 (4) |
|                     | O1—Zr1—Li3xiii | 87.38 (16) | O1—Li3—Li3xviii | 83.7 (3)  |
|                     | O1—Zr1—Li3xiii | 45.80 (18) | O1—Li3—Li3xviii | 158.8 (4) |
| Bond                  | Angle (°) | Standard Error |
|----------------------|-----------|----------------|
| Li³⁻·Zr¹·Li³⁺         | 49.0 (3)  |                |
| Li³⁻·Zr¹·Li³⁺         | 70.8 (3)  |                |
| Li³⁻·Zr¹·Li³⁺         | 166.5 (3) |                |
| Li³⁻·Zr¹·Li³⁺         | 119.11 (5)|                |
| O²⁻·Zr¹·Li³⁺         | 145.12 (16)|              |
| O²⁻·Zr¹·Li³⁺         | 81.85 (16)|                |
| O²⁻·Zr¹·Li³⁺         | 59.62 (16)|                |
| O¹⁻·Zr¹·Li³⁺         | 96.18 (16)|                |
| O¹⁻·Zr¹·Li³⁺         | 121.32 (16)|              |
| O¹⁻·Zr¹·Li³⁺         | 36.53 (16)|                |
| O¹⁻·Zr¹·Li³⁺         | 166.5 (3) |                |
| O¹⁻·Zr¹·Li³⁺         | 49.0 (3)  |                |
| O¹⁻·Zr¹·Li³⁺         | 70.8 (3)  |                |
| Li³⁻·Zr¹·Li³⁺         | 119.11 (5)|                |
| Ga¹⁺·O¹·Li¹⁺          | 51.3 (3)  |                |
| Ga¹⁺·O¹·Li¹⁺          | 51.3 (3)  |                |
| Li¹⁺·O¹·Li¹⁺          | 48.7 (2)  |                |
| Li¹⁺·O¹·Li¹⁺          | 48.7 (2)  |                |
| Li¹⁺·O¹·Li¹⁺          | 78.1 (3)  |                |
| Ga¹⁺·O¹·Zr¹⁺          | 128.17 (10)|              |
| Li¹⁺·O¹·Zr¹⁺          | 128.17 (10)|              |
| Li¹⁺·O¹·Zr¹⁺          | 101.7 (3) |                |
| Li¹⁺·O¹·Zr¹⁺          | 86.7 (2)  |                |
| Ga¹⁺·O¹·Li¹⁺          | 46.1 (2)  |                |
| Ga¹⁺·O¹·Li¹⁺          | 46.1 (2)  |                |
| Li³⁺·O¹·Li³⁺          | 74.3 (3)  |                |
| Li³⁻·O¹·Li³⁺          | 88.4 (4)  |                |
| Zr¹⁺·O¹·Li³⁺          | 174.3 (2) |                |
| Ga¹⁺·O¹·La¹⁺          | 95.95 (7) |                |
| Li¹⁺·O¹·La¹⁺          | 95.95 (7) |                |
| Li³⁺·O¹·La¹⁺          | 147.0 (3) |                |
| Li³⁻·O¹·La¹⁺          | 82.0 (2)  |                |
| Zr¹⁺·O¹·La¹⁺          | 103.10 (7)|                |
| Li³⁺·O¹·La¹⁺          | 79.11 (19)|                |
| Ga¹⁺·O¹·La¹⁺          | 121.96 (8)|                |
| Li¹⁺·O¹·La¹⁺          | 121.96 (8)|                |
| Li³⁺·O¹·La¹⁺          | 94.7 (3)  |                |
| Li³⁻·O¹·La¹⁺          | 176.0 (2) |                |
| Zr¹⁺·O¹·La¹⁺          | 100.81 (7)|                |
| Li³⁺·O¹·La¹⁺          | 83.8 (2)  |                |
| La¹⁺·O¹·La¹⁺          | 101.62 (6)|                |
| Ga²⁺·O²·La²⁺          | 0        |                |
| Ga²⁺·O²·Zr¹⁺          | 129.42 (11)|              |
| La²⁺·O²·Zr¹⁺          | 129.42 (11)|              |
| Ga²⁺·O²·Li³⁺          | 70.8 (2)  |                |
| Li²⁺·O²·Li³⁺          | 70.8 (2)  |                |

*Acta Cryst. (2022). C78, 1-6*
Zr1—O2—Li3
87.2 (2)
Li3—Li3—Zr1
142.5 (4)
Ga2—O2—La1
90.85 (7)
Li3—Li3—Zr1
70.7 (3)
Li2—O2—La1
90.85 (7)
O2—Li3—Zr1
92.8 (2)
Zr1—O2—La1
103.05 (8)

Symmetry codes: (i) −x, −y+1/2, −z; (ii) −x, y−1/2, −z+1/2; (iii) z, x, y; (iv) z, −x, −y+1/2; (v) x, −y, −z+1/2; (vi) −z+3/4, −y+1/4, x+1/4; (vii) −z+3/4, −y−1/4, −x+1/4; (viii) x, y, z; (ix) −y+1/2, z, −x; (x) x−1/4, z−1/4, y−1/4; (xi) z+1/4, y−1/4, x−1/4; (xii) x+1/4, x−1/4, y−1/4, z−1/4; (xiii) −z+1/2, x, −y, −z+1/2; (xiv) −y, −z+1/2, x; (xv) y, z, −x; (xvi) y−1/4, x+1/4, −z+3/4; (xvii) y+1/4, x+1/4, z+1/4; (xviii) y−1/4, −x+1/4, −z+3/4; (xix) −x+1, −y+1/2, z; (xx) −x−3/4, z−1/4, y−1/4, x−1/4; (xxi) −y+1, x−1/2, −z+1/2; (xxii) x+1/2, y−1/4, −z+3/4; (xxiii) y+1/4, −x+1/4, −z+3/4; (xxiv) y+1/4, −x+1/4, −z+3/4; (xxv) y+1/4, x−1/4, z−1/4; (xxvi) −y+1, −z+1/2, x; (xxvii) −y−1, z−1/2, −x+1/2; (xxviii) x+1, y, z; (xxix) −y−1/4, −x+1/4, z−3/4, −z+3/4.

(LLOZ-Ga40-hydro-150C)

Crystal data

Ga$_{0.26}$H$_{3.30}$La$_{2.96}$Li$_{1.99}$O$_{11.72}$Zr$_2$

$M_r$ = 821.46

Cubic, $I43d$

Hall symbol: $I$-4bd 2c 3

$a$ = 13.06720 (12) Å

$V$ = 2231.25 (6) Å$^3$

$Z$ = 8

$F(000) = 2901.2$

Data collection

Bruker SMART APEX diffractometer

Graphite monochromator

rotation, $ω$-scans at 4 different $φ$ positions

Absorption correction: multi-scan

(APEX2; Bruker, 2012)

$T_{\text{min}} = 0.21$, $T_{\text{max}} = 0.36$

35657 measured reflections

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.037$

$S = 1.12$

918 reflections

43 parameters

3 restraints

0 constraints

Hydrogen site location: difference Fourier map

Only H-atom coordinates refined

$w = 1/[σ^2(F^2) + (0.0072P)^2 + 28.9201P]$

where $P = (F^2 + 2F_c^2)/3$

$\Delta F_{\text{max}} = 0.54$ e Å$^{-3}$

$\Delta F_{\text{min}} = -0.52$ e Å$^{-3}$

Extinction correction: SHELXL2014

$E$-factor: 0.00055 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x       | y       | z       | Uiso*/Ueq | Occ. (<1) |
|----|---------|---------|---------|-----------|-----------|
| La1| 0.11790 (3) | 0       | 0.25    | 0.00993 (9) | 0.986 (4) |
| Zr1| −0.01020 (3) | −0.01020 (3) | −0.01020 (3) | 0.01011 (17) |          |
| O1 | 0.0963 (3) | 0.1906 (3) | 0.2735 (3) | 0.0106 (6)  |          |
| O2 | 0.0339 (3) | 0.4448 (3) | 0.1420 (3) | 0.0138 (6)  |          |
| Li1| 0.375    | 0       | 0.25    | 0.0068 (7)  | 0.824 (3) |
| Ga1| 0.375    | 0       | 0.25    | 0.0068 (7)  | 0.176 (3) |
| Li2| 0.875    | 0       | 0.25    | 0.007*     | 0.34 (5)  |
| Li3| 0.070 (16) | 0.283 (15) | 0.457 (16) | 0.01*      | 0.04 (3)  |
| H1 | 0.104 (11) | 0.183 (10) | 0.321 (8)  | 0.025*     | 0.65 (19) |

Atomic displacement parameters (Å²)

|    | U11  | U22  | U33  | U12  | U13  | U23  |
|----|------|------|------|------|------|------|
| La1| 0.00856 (14) | 0.00800 (14) | 0.01322 (16) | 0      | 0      | 0.00411 (10) |
| Zr1| 0.01011 (17) | 0.01011 (17) | 0.01011 (17) | −0.00033 (13) | −0.00033 (13) | −0.00033 (13) |
| O1 | 0.0076 (11) | 0.0106 (13) | 0.0135 (14) | −0.0005 (10) | −0.0005 (10) | 0.0019 (10) |
| O2 | 0.0191 (15) | 0.0128 (14) | 0.0095 (13) | 0.0025 (11) | 0.0030 (10) | 0.0032 (11) |
| Li1| 0.0055 (13) | 0.0075 (10) | 0.0075 (10) | 0      | 0      | 0      |
| Ga1| 0.0055 (13) | 0.0075 (10) | 0.0075 (10) | 0      | 0      | 0      |

Geometric parameters (Å, º)

|    | x       | y       | z       | Uiso*/Ueq | Occ. (<1) |
|----|---------|---------|---------|-----------|-----------|
| La1—Li3ix | 2.5 (2) | 0       | 0.25    | 0.00993 (9) | 0.986 (4) |
| La1—Li3ix | 2.5 (2) | 0       | 0.25    | 0.00993 (9) | 0.986 (4) |
| La1—O1xi  | 2.514 (3) | 0.1906 (3) | 0.2735 (3) | 0.0106 (6)  |          |
| La1—O1xi  | 2.514 (3) | 0.1906 (3) | 0.2735 (3) | 0.0106 (6)  |          |
| La1—O1vii | 2.525 (3) | 0.1906 (3) | 0.2735 (3) | 0.0106 (6)  |          |
| La1—O1vii | 2.525 (3) | 0.1906 (3) | 0.2735 (3) | 0.0106 (6)  |          |
| O2—La1viii | 2.603 (4) | 0.1906 (3) | 0.2735 (3) | 0.0106 (6)  |          |
| O2—La1viii | 2.603 (4) | 0.1906 (3) | 0.2735 (3) | 0.0106 (6)  |          |

Acta Cryst. (2022), C78, 1-6
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| Zr1—La1x             | 3.5178 (5)   | Li3—Ga1xvi           | 1.5 (2)      |
| O1—Li3xvi            | 0.9 (2)      | Li3—Li1xvi           | 1.5 (2)      |
| O1—Ga1xvi            | 1.987 (4)    | Li3—Li3xvi           | 2.0 (4)      |
| O1—Li1xvi            | 1.987 (4)    | Li3—O1xvi            | 2.4 (2)      |
| O1—Zr1xvii           | 2.031 (3)    | Li3—La1xvii          | 2.5 (2)      |
| O1—Li3xviii          | 2.4 (2)      | Li3—Li3x            | 2.6 (4)      |
| O1—La1xvi            | 2.514 (3)    | Li3—La1xviii         | 2.7 (2)      |
| O2—Li2xix            | 1.982 (4)    | Li3—Zr1xviii         | 2.9 (2)      |
| O2—Zr1vi             | 2.187 (4)    | Li3—Zr1xvii          | 3.2 (2)      |
| O2—La1vi             | 2.539 (4)    | Li3—Li2xviii         |             |
| Li3—La1—Li3xii       | 48 (9)       | Li3—Li1—Li3i         | 86 (10)      |
| Li3—La1—O1ii         | 57 (5)       | Li3—Li1—Li3i         | 122 (10)     |
| Li3—La1—O1iv         | 20 (5)       | Li3—Li1—O1i          | 24 (8)       |
| Li3—La1—O1v          | 20 (5)       | Li3—Li1—O1i          | 140 (8)      |
| Li3—La1—O1vii        | 57 (5)       | Li3—Li1—O1i          | 87 (8)       |
| O1—La1—O1xvi         | 72.06 (16)   | Li3—Li1—O1i          | 102 (8)      |
| O1—La—O1x            | 89 (5)       | Li3—Li1—O1iv         | 140 (8)      |
| Li3—La1—O1x          | 103 (5)      | Li3—Li1—O1iv         |             |
| O1—La1—O1v           | 123.13 (7)   | O1—Li1—O1iv          | 87 (8)       |
| O1—La1—O1v           | 68.54 (15)   | O1—Li1—Li1—O1xvi    |             |
| Li3—La1—O1           | 103 (5)      | O1—Li1—Li1—O1xvi    |             |
| Li3—La1—O1           | 89 (5)       | O1—Li1—Li1—O1xvi    |             |
| O1—La1—O1            | 68.54 (15)   | O1—Li1—Li1—O1xvi    |             |
| O1—La1—O1            | 123.13 (7)   | O1—Li1—Li1—O1xvi    |             |
| O1—La1—O1            | 167.17 (15)  | O1—Li1—Li1—O1xvi    |             |
| Li3—La1—O2xiv        | 165 (5)      | O1—Li1—Li1—O1xvii   |             |
| Li3—La1—O2xiv        | 118 (5)      | O1—Li1—Li1—O1xvii   |             |
| O1—La1—O2xiv         | 108.54 (10)  | O1—Li1—Li1—O1xvii   |             |
| O1—La1—O2xiv         | 161.05 (10)  | O1—Li1—Li1—O1xvii   |             |
| O1—La1—O2vi          | 97.21 (12)   | O1—Li1—Li1—O1xvii   |             |
| O1—La1—O2vi          | 72.54 (11)   | O1—Li1—Li1—O1xvii   |             |
| Li3—La1—O2vii        | 118 (5)      | O1—Li1—Li1—O1xvii   |             |
| Li3—La1—O2vii        | 165 (5)      | O1—Li1—Li1—O1xvii   |             |
| O1—La1—O2vii         | 161.05 (10)  | O1—Li1—Li1—O1xvii   |             |
| O1—La1—O2vii         | 108.54 (10)  | O1—Li1—Li1—O1xvii   |             |
| O1—La1—O2vi          | 72.54 (11)   | O1—Li1—Li1—O1xvii   |             |
| O1—La1—O2vi          | 97.21 (12)   | O1—Li1—Li1—O1xvii   |             |
| O2—La1—O2vi          | 77.23 (18)   | O1—Li1—Li1—O1xvii   |             |
| Li3—La1—O2vii        | 64 (5)       | O1—Li1—Li1—La1      | 137 (8)      |
| Li3—La1—O2vii        | 102 (5)      | O1—Li1—Li1—La1      | 43 (8)       |
| O1—La1—O2vii         | 96.82 (12)   | O1—Li1—Li1—La1      | 43 (8)       |
| O1—La1—O2vii         | 71.66 (11)   | O1—Li1—Li1—La1      | 131.89 (10)  |
| O1—La1—O2vii         | 107.49 (10)  | O1—Li1—Li1—La1      | 48.11 (10)   |
| O1—La1—O2vii         | 74.13 (11)   | O1—Li1—Li1—La1      | 48.11 (10)   |
| O2—La1—O2vii         | 126.12 (8)   | O1—Li1—Li1—La1      | 43 (8)       |
| O2—La1—O2vii         | 66.40 (16)   | O1—Li1—Li1—La1      | 137 (8)      |
| Li3—La1—O2vii        | 102 (5)      | O1—Li1—Li1—La1      | 137 (8)      |
| Bond                  | Bond Angle (°) |
|----------------------|----------------|
| Li₃ᵢ—La₁—O₂ᵣ        | 64 (5)         |
| O₁ᵣ—La₁—O₂ᵣ        | 71.66 (11)     |
| O₁ᵣ—La₁—O₂ᵣ        | 96.82 (12)     |
| O₁ᵣ—La₁—O₂ᵣ        | 74.13 (11)     |
| O₁ᵣ—La₁—O₂ᵣ        | 107.49 (10)    |
| O₂ᵢᵣ—La₁—O₂ᵣ       | 66.40 (16)     |
| O₂ᵢᵣ—La₁—O₂ᵣ       | 126.12 (8)     |
| O₂ᵢᵣ—La₁—O₂ᵣ       | 166.09 (15)    |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 108 (9)        |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 117 (2)        |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 136 (5)        |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 88 (4)         |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 19 (4)         |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 148 (4)        |
| O₂ᵢᵣ—La₁—Li₃ᵢᵣ     | 79 (4)         |
| O₂ᵢᵣ—La₁—Li₃ᵢᵣ     | 63 (5)         |
| O₂ᵢᵣ—La₁—Li₃ᵢᵣ     | 114 (4)        |
| O₂ᵢᵣ—La₁—Li₃ᵢᵣ     | 72 (4)         |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 117 (2)        |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 108 (9)        |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 88 (4)         |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 136 (5)        |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 148 (4)        |
| O₂ᵢᵣ—La₁—Li₃ᵢᵣ     | 19 (4)         |
| O₂ᵢᵣ—La₁—Li₃ᵢᵣ     | 63 (5)         |
| O₂ᵢᵣ—La₁—Li₃ᵢᵣ     | 79 (4)         |
| O₂ᵢᵣ—La₁—Li₃ᵢᵣ     | 72 (4)         |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 114 (4)        |
| Li₃ᵢ—La₁—Li₃ᵢᵣ     | 131 (9)        |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 88.64 (15)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 88.64 (15)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 88.64 (15)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 173.91 (17)    |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 96.82 (14)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 94.15 (14)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 94.15 (14)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 173.91 (17)    |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 80.15 (16)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 94.15 (14)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 173.91 (17)    |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 96.82 (14)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 80.15 (16)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 80.15 (16)     |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 89 (4)         |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 3 (4)          |
| O₁ᵢᵢ—Zr₁—O₁ᵢᵢ      | 92 (4)         |
| O₂ᵢᵢ—Zr₁—Li₃ᵢᵣ     | 96 (4)         |
| Bond                            | Distance (Å) | E (kJ/mol) |
|--------------------------------|--------------|------------|
| $O_{2}^{ii} - Zr - Li_{3}^{iii}$ | 91 (4)       | 76 (4)     |
| $O_{2}^{ii} - Zr - Li_{3}^{iii}$ | 171 (4)      | 78 (4)     |
| $O_{1}^{i} - Zr - Li_{3}^{iv}$  | 3 (4)        | 50 (4)     |
| $O_{1}^{i} - Zr - Li_{3}^{iv}$  | 92 (4)       | 130 (4)    |
| $O_{2}^{ii} - Zr - Li_{3}^{iv}$ | 89 (4)       | 115 (4)    |
| $O_{2}^{ii} - Zr - Li_{3}^{iv}$ | 171 (4)      | 76 (4)     |
| $O_{2}^{ii} - Zr - Li_{3}^{iv}$ | 96 (4)       | 78 (4)     |
| $O_{2}^{ii} - Zr - Li_{3}^{iv}$ | 91 (4)       | 58 (4)     |
| $Li_{3}^{iii} - Zr - Li_{3}^{iv}$ | 92 (6)  | 169 (4)    |
| $O_{1}^{i} - Zr - Li_{3}^{iii}$ | 92 (4)       | 50 (4)     |
| $O_{1}^{i} - Zr - Li_{3}^{iii}$ | 89 (4)       | 130 (4)    |
| $O_{1}^{i} - Zr - Li_{3}^{iii}$ | 3 (4)        | 115 (4)    |
| $O_{2}^{ii} - Zr - Li_{3}^{iii}$ | 91 (4)       | 99 (7)     |
| $O_{2}^{ii} - Zr - Li_{3}^{iii}$ | 171 (4)      | 78 (4)     |
| $O_{2}^{ii} - Zr - Li_{3}^{iii}$ | 96 (4)       | 58 (4)     |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 92 (6)       | 169 (4)    |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 92 (6)       | 76 (4)     |
| $Li_{3}^{ii} - Zr - Li_{3}^{iii}$ | 94.85 (10)  | 130 (4)    |
| $Li_{3}^{ii} - Zr - Li_{3}^{iii}$ | 44.88 (10)  | 50 (4)     |
| $Li_{3}^{ii} - Zr - Li_{3}^{iii}$ | 44.58 (10)  | 97 (9)     |
| $Li_{3}^{ii} - Zr - Li_{3}^{iii}$ | 90.93 (10)  | 115 (4)    |
| $Li_{3}^{ii} - Zr - Li_{3}^{iii}$ | 136.97 (10) | 115 (4)    |
| $Li_{3}^{ii} - Zr - Li_{3}^{iii}$ | 139.95 (10) | 113 (10)   |
| $Li_{3}^{ii} - Zr - Li_{3}^{iii}$ | 48 (4)       | 113 (10)   |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 97 (4)       | 0          |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 45 (4)       | 106 (10)   |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 44.58 (10)  | 47 (8)     |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 94.85 (10)  | 47 (8)     |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 44.88 (10)  | 122 (10)   |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 136.97 (10) | 56 (7)     |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 139.95 (10) | 56 (7)     |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 90.93 (10)  | 20 (7)     |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 97 (4)       | 81 (10)    |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 45 (4)       | 113 (10)   |
| $Li_{3}^{ii} - Zr - Li_{3}^{ii}$ | 48 (4)       | 113 (10)   |
| $La_{1}^{i} - Zr - La_{1}^{i}$  | 69.360 (12)  | 66 (5)     |
| $La_{1}^{i} - Zr - La_{1}^{i}$  | 44.88 (10)  | 62 (5)     |
| $La_{1}^{i} - Zr - La_{1}^{i}$  | 44.58 (10)  | 89 (10)    |
| $La_{1}^{i} - Zr - La_{1}^{i}$  | 94.85 (10)  | 89 (10)    |
| $La_{1}^{i} - Zr - La_{1}^{i}$  | 90.93 (10)  | 81 (5)     |
| $La_{1}^{i} - Zr - La_{1}^{i}$  | 136.97 (10) | 81 (5)     |
| $Li_{3}^{ii} - Zr - La_{1}^{i}$ | 45 (4)       | 127 (9)    |
| $Li_{3}^{ii} - Zr - La_{1}^{i}$ | 48 (4)       | 135 (10)   |
| $Li_{3}^{ii} - Zr - La_{1}^{i}$ | 97 (4)       | 29 (5)     |
| $La_{1}^{i} - Zr - La_{1}^{i}$  | 69.360 (12)  | 29 (5)     |
| $La_{1}^{i} - Zr - La_{1}^{i}$  | 69.360 (12)  | 29 (5)     |
| $Li_{3}^{ii} - O_{1} - Ga_{1}^{vi}$ | 43 (10) | 66 (5)     |
| Bond  | Distance (Å) | Symmetry Code |
|-------|--------------|---------------|
| Li₃ₓ—O₁—Li₁ₓvi  | 43 (10) | La₁xxii—Li₃—Li₃ₓ |
| Ga₁ₓvi—O₁—Li₁ₓvi  | 0 | Li₃ₓvi—Li₃—Li₃ₓ |
| Li₃ₓ—O₁—Zr₁xvii  | 170 (10) | O₁xxvi—Li₃—La₁xviii |
| Ga₁ₓvi—O₁—Zr₁xvii  | 127.29 (18) | Ga₁xxvi—Li₃—La₁xviii |
| Li₃ₓ—O₁—Li₃xviii  | 54 (10) | Li₃xxvi—Li₃—La₁xviii |
| Ga₁ₓvi—O₁—Li₃xviii  | 38 (5) | O₁xx—Li₃—La₁xviii |
| Li₁xvi—O₁—Zr₁xvii  | 127.29 (18) | Li₁xxvi—Li₃—La₁xviii |
| Ga₁xvi—O₁—Zr₁xvii  | 0L i 3 xviii—Li3—Li3ix |
| Li₁xvi—O₁—Zr₁xvii  | 127.29 (18) | Ga₁xxvi—Li₃—La₁xviii |
| Li₁xvi—O₁—Zr₁xvii  | 54 (10) | Li₃xxvi—Li₃—La₁xviii |
| Ga₁xvi—O₁—Zr₁xvii  | 38 (5) | O₁xx—Li₃—La₁xviii |
| Li₁xvi—O₁—Zr₁xvii  | 127.29 (18) | Li₁xxvi—Li₃—La₁xviii |
| Ga₁xvi—O₁—Zr₁xvii  | 54 (10) | Li₃xxvi—Li₃—La₁xviii |
| Li₁xvi—O₁—Zr₁xvii  | 38 (5) | O₁xx—Li₃—La₁xviii |
| Zr₁xvii—O₁—Li₃xviii  | 117 (5) | Li₃xviii—Li₃—La₁xviii |
| Li₃xvi—O₁—Li₃xviii  | 79 (10) | Li₃vi—Li₃—La₁xviii |
| Ga₁xvi—O₁—Li₃xviii  | 95.85 (13) | O₁xvi—Li₃—Zr₁xxii |
| Li₁xvi—O₁—Li₃xviii  | 95.85 (13) | Ga₁xxvi—Li₃—Zr₁xxii |
| Zr₁xvii—O₁—Li₃xviii  | 100.89 (14) | Ga₁xxvi—Li₃—Zr₁xxii |
| Li₃xviii—O₁—Li₃xviii  | 61 (5) | Li₃vi—Li₃—Zr₁xxii |
| Li₃xvi—O₁—La₁  | 89 (10) | O₁ix—Li₃—Li₁xxii |
| Ga₁xvi—O₁—La₁  | 122.52 (15) | La₁xxvi—Li₃—Zr₁xxii |
| Li₁xvi—O₁—La₁  | 122.52 (15) | Li₃xxvi—Li₃—Zr₁xxii |
| Zr₁xvii—O₁—La₁  | 100.55 (13) | Li₃xvi—Li₃—Zr₁xxii |
| Li₃xviii—O₁—La₁  | 142 (5) | Li₃vi—Li₃—Zr₁xxii |
| La₁xvi—O₁—La₁  | 105.20 (13) | O₁xvi—Li₃—Li₂xxii |
| Li₂xx—O₂—Zr₁vi  | 126.18 (19) | Ga₁xxvi—Li₃—Li₂xxii |
| Li₂xx—O₂—La₁vi  | 88.28 (13) | Ga₁xxvi—Li₃—Li₂xxii |
| Zr₁xvii—O₂—La₁vi  | 106.46 (15) | Li₃xxvi—Li₃—Li₂xxii |
| Li₂xx—O₂—La₁vi  | 123.00 (16) | Li₃vi—Li₃—Li₂xxii |
| Zr₁xvii—O₂—La₁vi  | 105.20 (13) | Li₃vi—Li₃—Li₂xxii |
| Li₃xvi—O₁—La₁  | 122.52 (15) | O₁ix—Li₃—Li₂xxii |
| Li₃xvi—O₁—La₁  | 105.20 (13) | La₁xxvi—Li₃—Zr₁xxii |
| Li₃xvi—O₁—La₁  | 122.52 (15) | Li₃xxvi—Li₃—Zr₁xxii |
| Zr₁xvii—O₂—La₁vi  | 100.55 (13) | Li₃vi—Li₃—Zr₁xxii |
| Li₃xvi—O₁—La₁  | 122.52 (15) | Li₃vi—Li₃—Zr₁xxii |
| Li₂xx—O₂—La₁vi  | 88.28 (13) | Li₃vi—Li₃—Zr₁xxii |
| Zr₁xvii—O₂—La₁vi  | 106.46 (15) | Li₃vi—Li₃—Zr₁xxii |
| Li₂xx—O₂—La₁vi  | 123.00 (16) | Li₃vi—Li₃—Zr₁xxii |
| Zr₁xvii—O₂—La₁vi  | 105.20 (13) | Li₃vi—Li₃—Zr₁xxii |
| La₁xvi—O₁—La₁  | 102.25 (13) | Li₃vi—Li₃—Zr₁xxii |
| Li₁xvi—O₁—Li₃  | 86 (10) | Li₃vi—Li₃—Zr₁xxii |
| Li₁xvi—O₁—Li₃  | 122 (10) | Li₃vi—Li₃—Zr₁xxii |
| Li₂xx—O₂—La₁vi  | 88.28 (13) | Li₃vi—Li₃—Zr₁xxii |
| Li₂xx—O₂—La₁vi  | 123.00 (16) | Li₃vi—Li₃—Zr₁xxii |
| Li₂xx—O₂—La₁vi  | 106.46 (15) | Li₃vi—Li₃—Zr₁xxii |
| Li₂xx—O₂—La₁vi  | 123.00 (16) | Li₃vi—Li₃—Zr₁xxii |

Symmetry codes: (i) −z+3/4, −y+1/4, x+1/4; (ii) −z+3/4, y−1/4, −x+1/4; (iii) x, y, z; (iv) z, −x, −y+1/2; (v) x, −y, −z+1/2; (vi) −x, −y+1/2, z; (vii) −x, y−1/2, −z+1/2; (viii) y−1/4, −x+1/4, −z−1/4; (ix) y+1/4, −x−1/4, z+3/4; (x) x−1/4, z−1/4, y−1/4, (xi) y−1/4, y−1/4, y−1/4, (xii) −y+1/2, z, −x; (xiii) −z+1/2, −x, −y−1/2; (xiv) −y+1/2, −x+1/2, −z−1/2; (xv) −y−1/4, −x+1/4, −z−1/4; (xvi) y, z, x; (xvii) y+1/4, x+1/4, z+1/4; (xviii) −y+1/4, x+1/4, −z−3/4; (xix) −x−1, −y+1/2, z; (xx) −xx+3/4, z−1/4, −y+1/4; (xxi) −xx+1/2, −y+1/2; (xxii) y+1/4, −x−1/4, −z−1/4; (xxiii) x+3/4, z−1/4, y−1/4, (xxiv) −x−1, y−1/2, −z+1/2; (xxv) y+3/4, −x+1/4, −y+1/4; (xxvi) x+1, y, z; (xxvii) y+3/4, −x+1/4, −z−3/4; (xxviii) y−1/4, −z−1/2, (xxix) −y+1, z−1/2, −x+1/2; (xxx) y+3/4, x−1/4, y−1/4, (xxxi) z−1/4, −y+1/4, −z−1/2; (xxiiii) −x, y+1/2, −z+1/2; (xxiii) −y+1/4, x−3/4, −z−3/4.