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# $LiFe(MoO_4)_2$, $LiGa(MoO_4)_2$ and $Li_3Ga(MoO_4)_3$

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The structures of lithium iron dimolybdate, $LiFe(MoO_4)_2$, and lithium gallium dimolybdate, $LiGa(MoO_4)_2$, are shown to be isomorphous with each other. Their structures consist of segregated layers of $LiO_6$ bicapped trigonal bipyramids and $Fe(Ga)O_6$ octahedra separated and linked by layers of isolated $MoO_4$ tetrahedra. The redetermined structure of trilithium gallium trimolybdate, $Li_3Ga(MoO_4)_3$, shows substitional disorder on the Li/Ga site and consists of perpendicular chains of $LiO_6$ trigonal prisms and two types of differently linked $Li/GaO_6$ octahedra.

## Comment

$LiFe(MoO_4)_2$, (I), is the fourth known compound in the quaternary Li/Fe/Mo/O system, besides two known variants of $Li_2Fe_2(MoO_4)_3$ (Klevtsova & Magarill, 1970; Torardi & Prince, 1986) and $Li_3Fe(MoO_4)_3$ (Klevtsova & Magarill, 1970), whereas its isomorphous variant $LiGa(MoO_4)_2$, (II), is the first compound in the quaternary Li/Ga/Mo/O system. The structures of (I) and (II) appear to be isomorphous with $LiAl(MoO_4)_2$ (Solov'eva & Borisov, 1970). The structure of $Li_3Ga(MoO_4)_3$, (III), the second member in the Li/Ga/Mo/O system, is isomorphous with $Li_3Fe(MoO_4)_3$ (Klevtsova & Magarill, 1970) and $Li_3Sc(MoO_4)_3$ (Kolitsch & Tillmanns, 2003). It is noted that the existence of $Li_3Ga(MoO_4)_3$ was previously reported by Klevtsov (1970) and Trunov & Efremov (1971), and its structure determined by Efremov & Trunov (1975), but the substitutional disorder present in the structure was poorly described. The isomorphous compound $Li_3Cr(MoO_4)_3$ was also reported in the latter study, but with the same poor description of the disorder. For a further determination of this phase, see entry 1200897 in Pearson's Crystal Data (Villars & Cenzual, 2007). These phases are of interest because of their relatively high Li ionic conductivity (Sebastian *et al.*, 2003).

Fig. 1 shows the constituent polyhedra for the structure of (II). The two Mo atoms (oxidation state VI) are in a close to tetrahedral coordination by oxygen, whereas Ga (oxidation state III) is in a close to octahedral coordination. Atom Li4 is surrounded by six O atoms, of which five are within 2.20 Å, and the sixth is at 2.743 (4) and 2.683 (13) Å from the central atom for $LiFe(MoO_4)_2$ and $LiGa(MoO_4)_2$, respectively. The bond-valence contribution (Wills & Brown, 1999) of this atom (O9) is 0.032 and 0.037, respectively, to a total bond-valence sum (BVS) of 0.872 and 0.901, respectively, thus amounting to 3.7 and 4.1% of the total BVS for $LiFe(MoO_4)_2$ and $LiGa(MoO_4)_2$, respectively. According to the Brown criterion that a ligand should contribute at least 4% to the total sum in order to be considered being bonded (Brown, 2002), this O atom is thus on the borderline of being weakly bonded. The five short-bonded O atoms form a trigonal bipyramid, which is capped by the sixth Li atom at a longer distance. This environment is not uncommon in Li-containing oxides; see, for example, Johnston & Harrison (2007) for $Li(VO_2)_3(TeO_3)_2$.

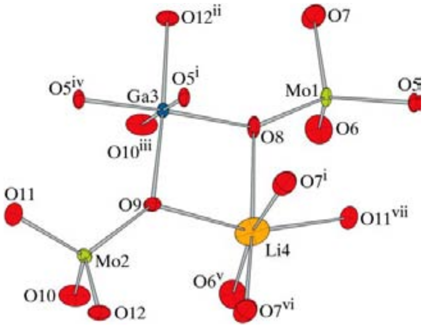

**Figure 1**
The full coordination environment around each unique metal centre in the asymmetric unit of (II). Symmetry codes are as given in Table 1. Displacement ellipsoids are drawn at the 75% probability level. It is noted that the structure of (I) is isomorphous with that of (II).

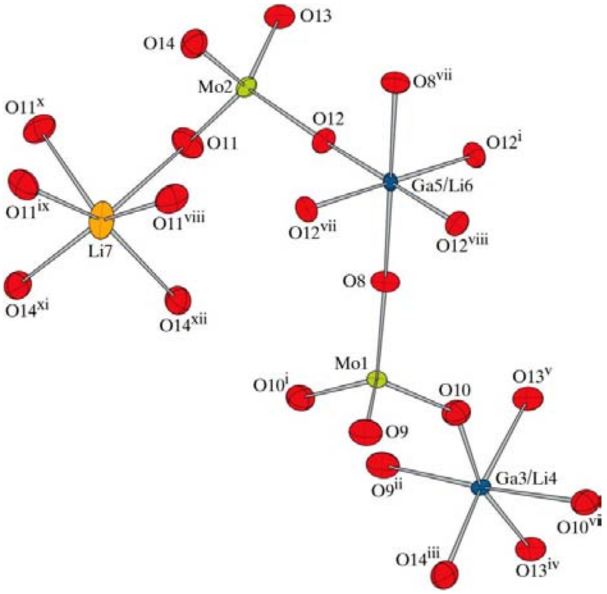

**Figure 2**
The full coordination environment around each unique metal centre in the asymmetric unit of (III). Symmetry codes are as given in Table 1. Displacement ellipsoids are drawn at the 75% probability level.

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The constituent polyhedra in the structure of (III) are shown in Fig. 2. The tetrahedral coordination of Mo is very similar to that in the structures of (I) and (II). The fully occupied Li7 site has sixfold O coordination, with distances ranging between 2.088 (9) and 2.252 (11) Å in a close to trigonal-prismatic environment. The two remaining metal sites are found to be substitutionally occupied by both Ga and Li, with occupation probabilities of 0.2909 (17)/0.7191 (17) and 0.421 (3)/0.579 (3) for the Ga5/Li6 and the Ga3/Li4 sites, respectively. The mixed Ga/Li sites have a close to octahedral coordination, with Ga/Li—O distances between 2.029 (3) and 2.155 (3) Å for the Ga3/Li4—O polyhedron, and between 2.000 (3) and 2.078 (3) Å for the Ga5/Li6—O polyhedron, somewhat larger than the Ga—O distances found in (I) and (II). This is expected because of the mixed occupancy of the sites, which also gives rise to too small artificial bond-valence sums for Ga3 and Ga5 (2.395 and 2.710, respectively) and too high sums for Li4 and Li6 (1.173 and 1.328, respectively). The higher average Li/Ga—O distance for the Ga3/Li4 polyhedron is in line with the lower proportion of Ga on that site compared with the Ga5/Li6 polyhedron.

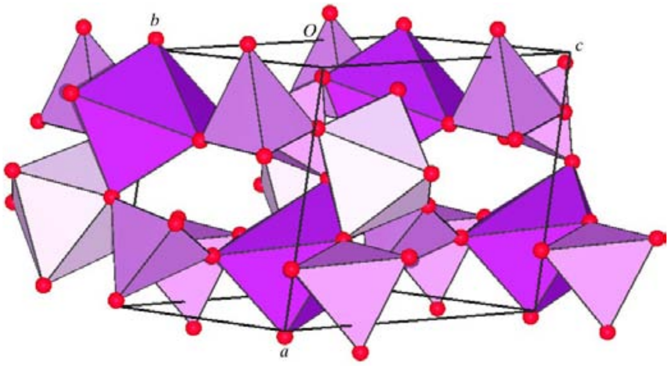

**Figure 3**
The polyhedral connectivity of the structures of (I) and (II). Ga(Fe) octahedra are depicted with light shading, Mo tetrahedra with medium shading and Li-bicapped trigonal bipyramids with dark shading.

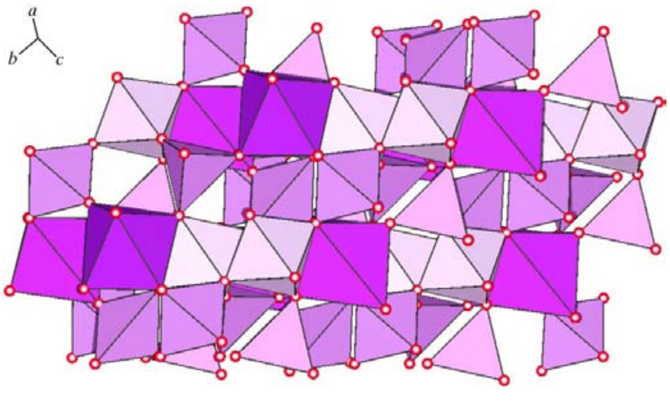

**Figure 4**
The layer-type structures of (I) and (II), in which the Mo tetrahedra are segregated from the other polyhedra. The shading is as in Fig. 2

Fig. 3 shows the resulting polyhedral connectivity of (I) and (II). All Mo tetrahedra are isolated from each other, and they are linked to adjacent polyhedra only by corner-sharing. Three corners are shared with Li-monocapped trigonal bipyramids, whereas two corners are shared with two Ga octahedra, thus giving one corner that is shared simultaneously with a Ga octahedron and a Li-monocapped trigonal bipyramid. The Li and Ga polyhedra appear solely as dimers, sharing one edge. The resulting layer structure is given in Fig. 4: the Li and Fe(Ga) polyhedra line up in layers and are clearly separated and linked by $MoO_4$ tetrahedra.

Fig. 5 shows the resulting polyhedral connectivity of (III). Mo tetrahedra are again isolated from each other and corner-linked to Ga/Li octahedra and Li trigonal prisms. The latter form infinite chains in the *a* direction, where the individual

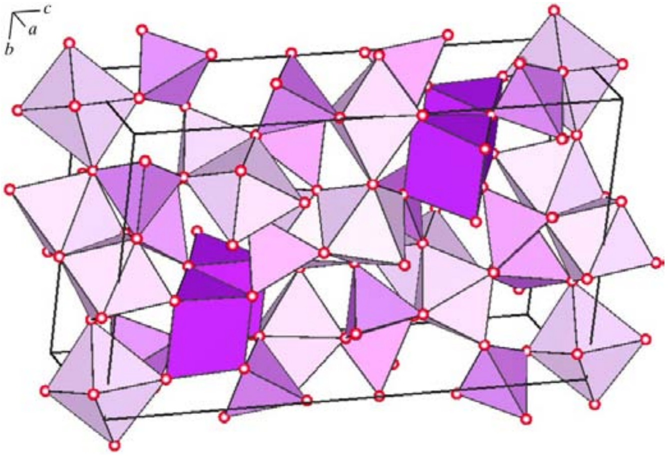

**Figure 5**
The polyhedral connectivity of the structure of (III). Ga/Li octahedra are depicted with light shading, Mo tetrahedra with medium shading and Li trigonal prisms with dark shading.

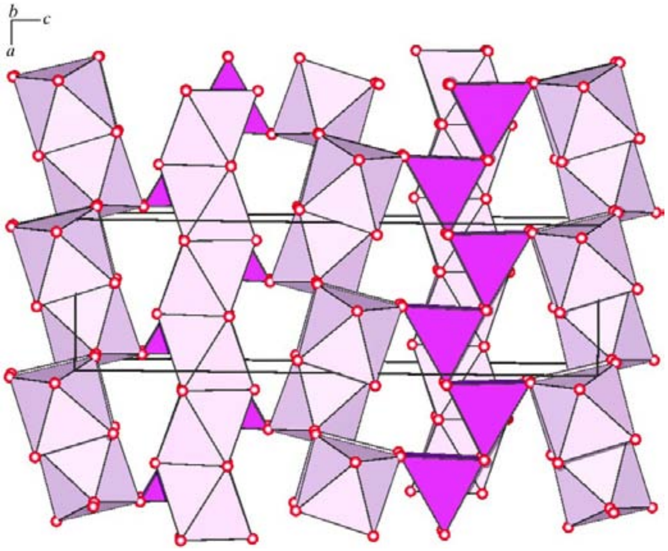

**Figure 6**
The chain network in the structure of (III). The shading is as in Fig. 5. The Mo tetrahedra have been omitted for clarity.

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trigonal prisms are joined by edge-sharing. The Ga/Li octahedra form two types of mutually perpendicular chains. The first type consists of face-shared octahedra travelling along the *a* axis, whereas the other type of Ga/Li octahedra form infinite parallel chains along the *b* axis, each chain being composed of edge-sharing octahedron dimers, which are themselves linked by corner-sharing (Fig. 6). The chains are linked into parallel chains by corner-sharing. Sebastian *et al.* (2003) reported that the Li ionic mobility in the isotypic phases $Li_3Fe(MoO_4)_3$ and $Li_3Cr(MoO_4)_3$ takes place in the one-dimensional trigonal-prismatic chains.

## Experimental

The lithium trimolybdate starting material, $Li_3Mo_3O_{10}$, was synthesized following the solid-state reaction described previously by Beaurain *et al.* (2006). The $GaPO_4$ powder compound with the $\alpha$-quartz structure was obtained by dissolving 4 *N* Ga metal in nitric acid followed by precipitation with phosphoric acid. $FePO_4{\cdot}nH_2O$ used as starting material was a commercial product (LABOSI). The crystal-growth experiments were carried out in air in a single temperature zone in an SiC resistance heater furnace with a Eurotherm temperature controller. Different amounts [70 and 85 wt% for (III) and (II), respectively] of $Li_2Mo_3O_{10}$ were mixed with $\alpha$-$GaPO_4$ and homogenized in an agate mortar. The mixtures were placed in Pt crucibles covered with a lid, heated from room temperature to 1223 K at a ramp rate of 100 K h$^{-1}$ and held at this temperature for 5 h for homogenization. The melted charges were then cooled slowly at a rate of 1 K h$^{-1}$ to 873 K. After 5 h at 873 K, the charges were cooled to room temperature at a rate of 200 K h$^{-1}$. In order to obtain crystals of (I), 15 wt% of $FePO_4{\cdot}nH_2O$ was thoroughly mixed with 85 wt% of $Li_2Mo_3O_{10}$ and charged in a Pt crucible. In order to release the water molecules, the mixture was heated at 623 K for 3 h. The temperature of the furnace was then increased at a rate of 100 K h$^{-1}$ to 973 K and kept at this temperature for 5 h for homogenization. Slow cooling (2 K h$^{-1}$) to 723 K was programmed before switching off the furnace.

### Compound (I)

*Crystal data*

$LiFe(MoO_4)_2$
$M_r = 382.66$
Triclinic, $P\overline{1}$
$a = 6.7592$ (2) Å
$b = 7.1773$ (2) Å
$c = 7.2398$ (2) Å
$\alpha = 90.806$ (3)°
$\beta = 110.315$ (3)°
$\gamma = 105.3850$ (15)°
$V = 315.38$ (2) Å$^3$
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 6.19$ mm$^{-1}$
$T = 173$ K
0.49 × 0.28 × 0.16 mm

*Data collection*

Oxford Diffraction Xcalibur-I diffractometer
Absorption correction: multi-scan [*CrysAlis RED* (Oxford Diffraction, 2007); empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
$T_{min} = 0.420$, $T_{max} = 1.000$ (expected range = 0.156–0.372)
5166 measured reflections
1977 independent reflections
1966 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.014$
$wR(F^2) = 0.035$
$S = 1.20$
2007 reflections
109 parameters
$\Delta\rho_{max} = 0.46$ e Å$^{-3}$
$\Delta\rho_{min} = -0.66$ e Å$^{-3}$

**Table 1**
Selected bond lengths (Å) for (I).

| | | | |
|---|---|---|---|
| Mo1—O5 | 1.8736 (13) | Fe3—O5$^{iii}$ | 1.9537 (13) |
| Mo1—O6 | 1.7074 (15) | Fe3—O10$^{iv}$ | 1.9514 (15) |
| Mo1—O7 | 1.7148 (15) | Fe3—O8 | 1.9543 (14) |
| Mo1—O8 | 1.8792 (13) | Fe3—O9 | 2.0397 (14) |
| Mo2—O9 | 1.7851 (14) | Li4—O6$^{v}$ | 2.112 (4) |
| Mo2—O10 | 1.7608 (15) | Li4—O7$^{vi}$ | 2.001 (4) |
| Mo2—O11 | 1.7417 (14) | Li4—O7$^{i}$ | 2.743 (4) |
| Mo2—O12 | 1.7835 (14) | Li4—O8 | 2.217 (4) |
| Fe3—O5$^{i}$ | 2.0444 (14) | Li4—O9 | 2.202 (4) |
| Fe3—O12$^{ii}$ | 1.9977 (14) | Li4—O11$^{vii}$ | 2.139 (4) |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $x, y-1, z$; (iv) $-x+1, -y, -z$; (v) $-x+1, -y+1, -z$; (vi) $x+1, y, z$; (vii) $x, y+1, z$.

### Compound (II)

*Crystal data*

$LiGa(MoO_4)_2$
$M_r = 396.54$
Triclinic, $P\overline{1}$
$a = 6.7232$ (3) Å
$b = 7.0982$ (3) Å
$c = 7.2580$ (4) Å
$\alpha = 90.915$ (4)°
$\beta = 110.648$ (4)°
$\gamma = 105.253$ (4)°
$V = 310.43$ (3) Å$^3$
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 8.29$ mm$^{-1}$
$T = 293$ K
0.43 × 0.32 × 0.11 mm

*Data collection*

Oxford Diffraction Xcalibur diffractometer
Absorption correction: multi-scan [*CrysAlis RED* (Oxford Diffraction, 2007); empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
$T_{min} = 0.173$, $T_{max} = 1.000$ (expected range = 0.069–0.402)
5166 measured reflections
1977 independent reflections
1880 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.116$
$S = 0.82$
1977 reflections
109 parameters
$\Delta\rho_{max} = 1.34$ e Å$^{-3}$
$\Delta\rho_{min} = -3.97$ e Å$^{-3}$

**Table 2**
Selected bond lengths (Å) for (II).

| | | | |
|---|---|---|---|
| Mo1—O5 | 1.870 (4) | Ga3—O10$^{iii}$ | 1.919 (4) |
| Mo1—O6 | 1.709 (4) | Ga3—O5$^{iv}$ | 1.916 (4) |
| Mo1—O7 | 1.709 (4) | Ga3—O8 | 1.921 (4) |
| Mo1—O8 | 1.874 (4) | Ga3—O9 | 2.014 (4) |
| Mo2—O9 | 1.786 (4) | Li4—O6$^{v}$ | 2.188 (13) |
| Mo2—O10 | 1.763 (4) | Li4—O7$^{vi}$ | 1.985 (13) |
| Mo2—O11 | 1.739 (4) | Li4—O7$^{i}$ | 2.679 (13) |
| Mo2—O12 | 1.775 (4) | Li4—O8 | 2.183 (13) |
| Ga3—O5$^{i}$ | 2.014 (4) | Li4—O9 | 2.167 (14) |
| Ga3—O12$^{ii}$ | 1.972 (4) | Li4—O11$^{vii}$ | 2.099 (14) |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, -y, -z$; (iv) $x, y-1, z$; (v) $-x+1, -y+1, -z$; (vi) $x+1, y, z$; (vii) $x, y+1, z$.

### Compound (III)

*Crystal data*

$Li_3Ga(MoO_4)_3$
$M_r = 570.51$
Orthorhombic, *Pnma*
$a = 5.04022$ (13) Å
$b = 10.4054$ (3) Å
$c = 17.4541$ (5) Å
$V = 915.39$ (4) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 7.00$ mm$^{-1}$
$T = 293$ K
0.35 × 0.30 × 0.25 mm

*Data collection*

Oxford Diffraction Xcalibur diffractometer
Absorption correction: multi-scan [*CrysAlis RED* (Oxford Diffraction, 2007); empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
$T_{\min} = 0.768$, $T_{\max} = 1.000$ (expected range = 0.134–0.174)
17688 measured reflections
1610 independent reflections
1353 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.085$
$S = 1.14$
1610 reflections
96 parameters
2 restraints
$\Delta\rho_{\max} = 1.35$ e Å$^{-3}$
$\Delta\rho_{\min} = -3.02$ e Å$^{-3}$

**Table 3**
Selected bond lengths (Å) for (III).

| | | | |
|---|---|---|---|
| Mo1—O8 | 1.766 (3) | Ga3—O10 | 2.076 (2) |
| Mo1—O9 | 1.795 (2) | Ga5—O8$^{\rm vii}$ | 2.078 (3) |
| Mo1—O10 | 1.7621 (17) | Ga5—O12$^{\rm i}$ | 2.0025 (18) |
| Mo1—O10$^{\rm i}$ | 1.7621 (17) | Ga5—O12$^{\rm viii}$ | 2.0004 (19) |
| Mo2—O11 | 1.734 (2) | Ga5—O12$^{\rm vii}$ | 2.0004 (19) |
| Mo2—O12 | 1.785 (2) | Ga5—O8 | 2.071 (3) |
| Mo2—O13 | 1.788 (2) | Ga5—O12 | 2.0025 (18) |
| Mo2—O14 | 1.7656 (15) | Li7—O11 | 2.252 (3) |
| Ga3—O9$^{\rm ii}$ | 2.1003 (13) | Li7—O11$^{\rm ix}$ | 2.1808 (16) |
| Ga3—O14$^{\rm iii}$ | 2.044 (3) | Li7—O11$^{\rm x}$ | 2.252 (3) |
| Ga3—O13$^{\rm iv}$ | 2.0314 (18) | Li7—O11$^{\rm viii}$ | 2.1808 (16) |
| Ga3—O13$^{\rm v}$ | 2.029 (3) | Li7—O14$^{\rm xi}$ | 2.088 (3) |
| Ga3—O10$^{\rm vi}$ | 2.155 (2) | Li7—O14$^{\rm xii}$ | 2.088 (3) |

Symmetry codes: (i) $x, -y+\frac{3}{2}, z$; (ii) $x-1, -y+\frac{3}{2}, z$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$; (v) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{3}{2}$; (vi) $-x+1, -y+2, -z+1$; (vii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{3}{2}$; (viii) $x+\frac{1}{2}, y, -z+\frac{3}{2}$; (ix) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{3}{2}$; (x) $x, -y+\frac{1}{2}, z$; (xi) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{3}{2}$; (xii) $x-\frac{1}{2}, y, -z+\frac{3}{2}$.

The data for the structure of (I) were collected at 173 K by placing the crystal in a stream of nitrogen (Cryojet, Oxford Instruments). The structures of (I) and (II) were solved using default charge-flipping parameters as determined by *JANA2000* (Petrícek *et al.*, 2000). The Li atoms were found in difference Fourier maps. The refinement of these two structures proceeded without problems. The presence of the inversion centre in the structure was established using an analysis of the electron-density map before attribution of the atom types (Palatinus & Chapuis, 2007).

The structure of (III) was also solved using default parameters, and the proper space-group symmetry *Pnma* was established on the basis of an analysis of the electron-density map before attribution of the atom types; the agreement factors for the three generators $n_x$, $m_y$ and $a_z$ are 0.23, 1.89, and 0.64%, respectively, proving that the inversion centre is indeed present. It is noted that the same space group was proposed for the previously determined structure (Efremov & Trunov, 1975), and also for the isomorphous compounds $Li_3Fe(MoO_4)_3$ (Klevtsova & Magarill, 1970) and $Li_3Sc(MoO_4)_3$ (Kolitsch & Tillmanns, 2003). The occupancy of the presumed Ga site needed to be set at 0.50 in order to have acceptable displacement parameters. Only one Li atom could be located in the difference map, which is not sufficient for charge balance, but no accessible voids could be located in the resulting structure. Therefore, a substitutional disorder of Ga/Li was proposed, approximately in line with what was found in the structure of $Li_3Fe(MoO_4)_3$ for the Fe/Li sites (Klevtsova & Magarill, 1970). There, the occupancies of the two sites were fixed at 0.3333/0.66667 for Fe and Li, respectively. In the present case, the occupancies of the Ga3/Li4 and Ga5/Li6 sites in the structure of (III) were constrained to a value of 1.00, whereas restraints with an s.u. value of 0.001 were used for keeping the total number of Li atoms in the structural formula at 3.0 and the total number of Ga atoms at 1.0, *i.e.* 0.5 × occupancy(Ga3) + occupancy(Ga5) = 0.5, and 0.5 × occupancy(Li4) + occupancy(Li6) = 1.0. There is no indication that the third trigonal prismatic site contains a small amount of Ga.

For all compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996) and *DRAWxtl* (Finger *et al.*, 2007); software used to prepare material for publication: *CRYSTALS*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3035). Services for accessing these data are described at the back of the journal.

## References

Beaurain, M., Armand, P. & Papet, P. (2006). *J. Cryst. Growth*, **294**, 396–400.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model.* Oxford University Press.
Efremov, V. A. & Trunov, V. K. (1975). *Inorg. Mater.* **11**, 229–232.
Finger, L. W., Kroeker, M. & Toby, B. H. (2007). *J. Appl. Cryst.* **40**, 188–192.
Johnston, M. G. & Harrison, W. T. A. (2007). *Acta Cryst.* C**63**, i57–i59.
Klevtsov, P. V. (1970). *Kristallografiya*, **15**, 797–802.
Klevtsova, R. F. & Magarill, S. A. (1970). *Kristallografiya*, **15**, 710–715.
Kolitsch, U. & Tillmanns, E. (2003). *Acta Cryst.* E**59**, i55–i58.
Oxford Diffraction (2007). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.32.5. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.
Petrícek, V., Dusek, M. & Palatinus, L. (2000). *JANA2000*. Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic.
Sebastian, L., Piffard, Y., Shukla, A. K., Taulellec, F. & Gopalakrishnan, J. (2003). *J. Mater. Chem.* **13**, 1797–1802.
Solov'eva, L. P. & Borisov, S. V. (1970). *Kristallografiya*, **15**, 577–581.
Torardi, C. C. & Prince, E. (1986). *Mater. Res. Bull.* **21**, 719–726.
Trunov, V. K. & Efremov, V. A. (1971). *Zh. Neorg. Khim.* **16**, 2026–2027.
Villars, P. & Cenzual, K. (2007). Pearson's Crystal Data. Release 2007/8. ASM International, Materials Park, Ohio, USA.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.
Wills, A. S. & Brown, I. D. (1999). *VaList*. CEA, France.