inorganic papers

The layered monodiphosphate Li$_9$Ga$_3$(P$_2$O$_7$)$_3$(PO$_4$)$_2$ refined from X-ray powder data

Xiao-Xuan Liu,[a] **Cheng-Xin Wang,**[a] **Shu-Ming Luo**[a] **and Jin-Xiao Mi**[a,b]*

[a]Xiamen University, Department of Materials Science and Engineering, Xiamen 361005, Fujian Province, People's Republic of China, and [b]Key Laboratory of Nonferrous Materials and Processing Technology, (Guilin University of Technology), Ministry of Education, People's Republic of China

Correspondence e-mail: jxmi@xmu.edu.cn

Nonalithium trigallium(III) tris[pyrophosphate(V)] diphosphate(V), Li$_9$Ga$_3$(P$_2$O$_7$)$_3$(PO$_4$)$_2$, has been synthesized by a hydrothermal method and its crystal structure solved from X-ray powder diffraction data using Rietveld analysis. The structure is based on separate layers parallel to (001), consisting of GaO$_6$ octahedra that share corners with PO$_4$ tetrahedra and P$_2$O$_7$ groups. The lithium ions are located in the interstitial space.

Comment

The title compound, together with the three analogues Li$_9$Fe$_3$(P$_2$O$_7$)$_3$(PO$_4$)$_2$, Li$_9$Cr$_3$(P$_2$O$_7$)$_3$(PO$_4$)$_2$ and Li$_9$Al$_3$-(P$_2$O$_7$)$_3$(PO$_4$)$_2$, was first synthesized by Poisson *et al.* (1998). Its crystal structure has not yet been reported, although the structures of the iron and aluminium analogues are available. The structure has now been refined by the Rietveld method from powder diffraction data.

Li$_9$Ga$_3$(P$_2$O$_7$)$_3$(PO$_4$)$_2$ has a two-dimensional layered structure. The layers, which are parallel to (001) and are separated by lithium ions, consist of GaO$_6$ octahedra that share corners with PO$_4$ tetrahedra and P$_2$O$_7$ groups. The GaO$_6$ octahedron shares two contiguous O4 with a diphosphate group P2$_2$O$_7$. It is also connected to two other P2$_2$O$_7$ groups by sharing a single O5. Each of the two spare O atoms of the GaO$_6$ octahedron is shared with a P1O$_4$ tetrahedron. The GaO$_6$ octahedra, together with PO$_4$ tetrahedra and P$_2$O$_7$ groups, form an infinite layered structure which is parallel to the *ab* plane. Channels,
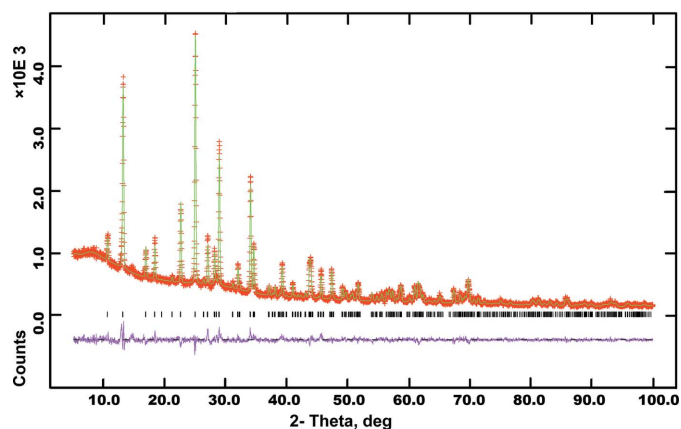

Figure 1
A comparison of observed (top crosses) and calculated (top solid line) intensity profiles for Li$_9$Ga$_3$(P$_2$O$_7$)$_3$(PO$_4$)$_2$; intensity differences (bottom solid line) and allowed Bragg reflections (tick marks) are also shown.

Figure 2
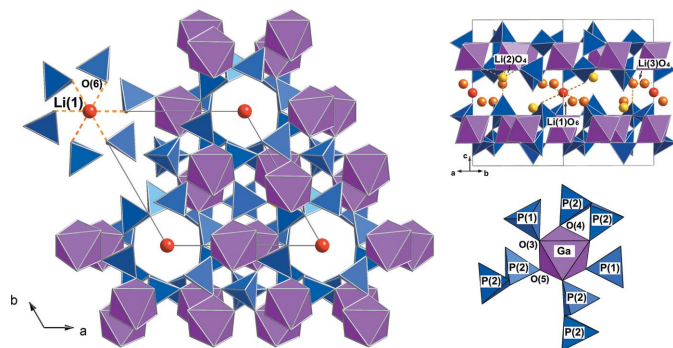Three views of the crystal structure of $Li_9Ga_3(P_2O_7)_3(PO_4)_2$.

which result from the way the layers stack along the *c* axis, contain the Li1 sites. Other lithium ions are located between two layers.

The gallium ion, which occupies the 6*f* position, together with six O atoms, forms a GaO_6 octahedron. P1 and P2 are on the 4*d* special positions and 12*g* general positions, respectively. Two P_2O_4 tetrahedra form a P_2O_7 pyrophosphate ion by sharing an O2 atom. The lithium ions are located on three sites; Li1 and Li2 are on the 2*b* and 4*d* special positions, and Li3 is on a 12*g* general position. In the $Li1O_6$ trigonal antiprism, Li1 is coordinated by six O6 atoms; Li2 is coordinated by one O1 and three O4, and the $Li2O_4$ tetrahedron exhibits a threefold internal symmetry; Li3 is coordinated by a tetrahedron which is distorted.

Experimental

$Li_9Ga_3(P_2O_7)_3(PO_4)_2$ was synthesized under hydrothermal conditions. The reaction was carried out with mixtures of Li_2HPO_4 and $GaCl_3$ (0.23 g gallium metal dissolved in 2.5 ml 37% HCl) in a Li:Ga:P molar ratio of 1:20:10. The container was about 50% full of solution. The autoclave was placed in an oven with subsequent heating at 493 K for 7 d. All starting materials were of analytical grade and used without further purification.

Crystal data

$Li_9Ga_3(P_2O_7)_3(PO_4)_2$	$D_x = 2.933$ Mg m^{-3}
$M_r = 983.39$	Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation
Trigonal, $P\bar{3}c1$	$T = 295$ (2) K
$a = 9.72879$ (13) Å	Specimen shape: flat sheet
$c = 13.5827$ (3) Å	$10 \times 10 \times 0.1$ mm
$V = 1113.36$ (3) Å^3	Particle morphology: laminar, white
$Z = 2$	

Data collection

PANalytical X'pert PRO diffractometer	Scan method: continuous
Specimen mounting: packed powder	$2\theta_{min} = 5.0$, $2\theta_{max} = 100.0°$
Specimen mounted in reflection mode	Increment in $2\theta = 0.008°$

Table 1
Selected bond lengths (Å).

P1—O1	1.535 (17)	Ga1—O5[ii]	2.016 (8)
P1—O3	1.535 (7)	Li1—O6[iii]	2.492 (6)
P2—O2	1.565 (5)	Li2—O1[iv]	1.97 (6)
P2—O4	1.500 (8)	Li2—O4	2.076 (15)
P2—O5	1.492 (9)	Li3—O3[v]	2.106 (27)
P2—O6[i]	1.509 (9)	Li3—O5	2.051 (28)
Ga1—O3	1.990 (8)	Li3—O6[iii]	1.974 (24)
Ga1—O4	2.001 (7)	Li3—O6	1.857 (26)

Symmetry codes: (i) $x, y - 1, z$; (ii) $-y + 1, x - y, z$; (iii) $x, y - 1, z - 1$; (iv) $y - x + 1, y, z + \frac{1}{2}$; (v) $y - x + 1, y, z - \frac{1}{2}$.

Data collection: *X'pert Data collector* (PANalytical, 2003); cell refinement: *GSAS* (Larson & Von Dreele, 2000) and *EXPGUI* (Toby, 2001); data reduction: *GSAS*; method used to solve structure: atomic coordinates of the isotypic iron compound $Li_9Fe_3(P_2O_7)_3(PO_4)_2$ (Poisson *et al.*, 1998) used as starting parameters; program(s) used to refine structure: *GSAS* and *EXPGUI*; molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
Brandenburg, K. (2004). *DIAMOND*. Version 3.0. Crystal Impact GbR, Bonn, Germany.
Dollase, W. A. (1986). *J. Appl. Cryst.* **19**, 267–272.
Finger, L. W., Cox, D. E. & Jephcoat, A. P. (1994). *J. Appl. Cryst.* **27**, 892–900.
Larson, A. C. & Von Dreele, R. B. (2000). *GSAS*. Los Alamos National Laboratory, New Mexico, USA.
March, A. (1932). *Z. Kristallogr.* **81**, 285–297.
PANalytical, B. V. (2003). *X'pert Data collector*. Version 1.0. PANalytical BV, Almelo, The Netherlands.
Poisson, S., d'Yvoire, F., Bretey, E. & Berthet, P. (1998). *J. Solid State Chem.* **138**, 32–40.
Thompson, P., Cox, D. E. & Hastings, J. B. (1987). *J. Appl. Cryst.* **20**, 79–83.
Toby, B. H. (2001). *J. Appl. Cryst.* **34**, 210–213.