The crystal structure of Ga-rich plumbogummite from Tsumeb, Namibia

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ABSTRACT

Ga-rich plumbogummite, $(Pb_{0.87},Ca_{0.13})_{\Sigma1.00}H(Al_{1.95},Ga_{1.05})_{\Sigma3.00}(PO_4)_2(OH)_6$, from Tsumeb, Namibia, has rhombohedral symmetry, space group $R\bar{3}m$, with the cell parameters $a = 7.0752(19)$ Å, $c = 16.818(4)$ Å and $V = 729.1(3)$ Å^3. The crystal structure has been refined to $R_1 = 2.05\%$. Ga-rich plumbogummite has an alunite-type structure comprised of a rhombohedral stacking of (001) composite layers of corner-shared $(Al,Ga)O_6$ octahedra and PO_4 tetrahedra, with Pb atoms occupying icosahedrally coordinated sites between the layers. The Pb and H positions are discussed. Ga-rich plumbogummite is nonpleochroic, uniaxial (+), with indices of refraction, $\varepsilon = 1.742(3)$ and $\omega = 1.722(3)$, determined in white light. The five strongest powder-diffraction lines [d in Å, (I/I_o), (hkl)] are: 2.995, (100), (113); 5.766, (95), (101); 2.236, (43), (107, 122); 3.539, (38), (110); 1.919 (32), (303, 033).

Keywords: plumbogummite, Tsumeb, Namibia, gallium, crystal structure, kintoreite, bond valence.

Introduction

Members of the alunite supergroup have the general formula $AB_3(TO_4)_2(OH,H_2O)_6$, where A is a large cation site containing cations such as Na^+, K^+, H_3O^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Pb^{2+} and REE^{3+}. The B site is octahedrally coordinated, containing typically Al^{3+} or Fe^{3+}, but it can also include V^{3+}, Ga^{3+}, Zn^{2+} and Cu^{2+}. The T site is tetrahedrally coordinated and is occupied by S, P or As (Scott, 1987; Jambor, 1999). Most alunite-related minerals have rhombohedral symmetry, $R\bar{3}m$, with hexagonal cell parameters $a_h \approx 7$ Å, $c_h \approx 17$ Å (e.g. crandallite, $(CaAl_3(PO_3[O_{0.5}OH_{0.5}])_2(OH)_6$ – Blount, 1974). The composition often varies due

to solid-solution series encompassing all cation sites. Such modifications include OH substitution for oxygen in the TO_4 tetrahedra, substitution of H_2O or oxygen for OH, and partial occupancy of the A and/or B sites (Jambor, 1999).

At the Tsumeb mine, in the Otjikoto region of Namibia (19°15′S , 17°42′E), Ga is known as an essential constituent in several Pb-bearing members of the alunite supergroup. These minerals include: gallobeudantite, $PbGa_3[(AsO_4),(SO_4)]_2(OH)_6$ (Jambor et al., 1996) and several unnamed Ga analogues of Pb-bearing species of the supergroup. The Tsumeb mine is the type locality for approximately 58 other minerals. An overview of the mineralogy of the Tsumeb deposit can be found in Gebhard (1999). Here, we report the results of two crystal-structure refinements of Ga-rich plumbogummite from Tsumeb, Namibia. This is also the first report of plumbogummite from Tsumeb.

Experimental

Sample

Ga-rich plumbogummite occurs with the unnamed Ga analogue of arsenocrandallite and an unnamed Zn-Fe-Ga oxide (under investigation) in a 20 mm × 10 mm × 10 mm piece of gallite-renierite-germanite ore. A similar assemblage (and host rock) was described by Jambor *et al.* (1996), which included the Ga analogues of several Pb-bearing species of the alunite super-group (gallobeudantite and the unnamed Ga analogues of kintoreite, arsenocrandallite, segnitite and corkite) as zoned crystals. The paragenesis of the Ga-rich plumbogummite specimen differs from that of type gallobeudantite, with only the unnamed Ga analogue of arsenocrandallite (IMA Code: UM1996-04-AsO:CaGaGeH; Smith and Nickel, 2007) being observed. The sample has been deposited in the collections of Mineral Sciences Department, Natural History Museum of Los Angeles County, catalogue number 62425.

Gallium-rich plumbogummite occurs as white, transparent, rhombohedral single crystals up to 300 μm across, which sit perched on the gallite-renierite-germanite ore. Ga-rich plumbogummite rarely forms as intergrown crystals, which may be up to 0.5 mm across. Its streak is white, it has a vitreous lustre; forms are dominated by the rhombohedron {112} and it is visually indistinguishable from the unnamed Ga analogue of arsenocrandallite.

Structure refinement

The single-crystal study was done using a Bruker X8 ApexII single-crystal diffractometer at the Department of Chemistry, University of British Columbia. A rhombohedral crystal with the dimensions 0.3 mm × 0.2 mm × 0.1 mm was used for collection of intensity data at 293 K (Table 1). A second crystal structure refinement was completed on another crystal. A summary of these results are listed in an Appendix.

The intensity data were processed with the Bruker Apex program suite, with data reduction using *the SAINT* program (Bruker, 2005) and absorption correction by the multi-scan method

TABLE 1. Summary of data collection conditions and refinement parameters for Ga-rich plumbogummite.

Crystal data	
Cell parameters	$a = 7.0752(19)$ Å
	$c = 16.818(4)$ Å
	$V = 729.1(3)$ Å^3
	$Z = 3$
Space group	$R\bar{3}m$
Data collection	
Temperature (K)	293(2)
λ (Mo-$K\alpha$) Å	0.71073
Crystal shape, size (mm)	rhombohedron, $0.03 \times 0.03 \times 0.02$
2θ max (°)	59.99
Reflection range	$-6 \leqslant h \leqslant 9$; $-9 \leqslant k \leqslant 9$; $-22 \leqslant l \leqslant 21$
Total no. reflections	1846
No. unique reflections	271
No. reflections, $F_o > 4\sigma(F)$	267
Absorption correction	$\mu = 26.04$ mm^{-1}
R_{merg} on F^2	0.0287
Refinement	
No. parameters refined	39
R_1, $F_o > 4\sigma(F)$	0.0205
R_1, all data	0.021
wR_2 (F^2)*, all data	0.0437
Goodness of Fit	1.339
$\Delta\sigma_{\mathrm{min}}$, $\Delta\sigma_{\mathrm{max}}$ (e/Å^3)	-0.48, 0.43

* $w = 1/[\sigma^2(F_o^2) + (0.0075\mathrm{P}^2 + 5.64\mathrm{P})]$, P $= [2F_c^2 + \mathrm{Max}(F_o^2, 0)]/3$.

using *SADABS* (Bruker, 2005). Minor splitting of the spots was observed, indicating the presence of two twin individuals. However, the spots could be integrated with a single spot size and preceded normally to convergence. Twinning is a common phenomenon in alunite supergroup minerals (e.g. kintoreite − Kharisun *et al*., 1997*a*; segnitite − Birch *et al*., 1992), whereas twin sector zoning is less common (e.g. alunite − Bajnóczi *et al*., 2004).

The crystal structure of Ga-rich plumbogummite was refined in space group $R\bar{3}m$ (No. 166), using *SHELXL−97* (Sheldrick, 2008) with the starting coordinates of Kolitsch *et al*. (1999*a*). In the Kolitsch *et al*. model, the Pb atom is at the 18*f* site [*x*, *x*, *z*], whereas in kintoreite, the Fe^{3+} analogue of plumbogummite, the Pb atom has been reported at the 36*i* general position (Kharisun *et al*., 1997*a*) and the 18*f* position [*x*, 0, 0] by Grey *et al*. (2009). As reported for kintoreite (Grey *et al*., 2009), there is little difference in the *R* factor of Ga-rich plumbogummite when Pb is assigned to any of the sites [*x*, *x*, *z*], [*x*,; 0, 0] and the 18*h* site [*x*, −*x*, *z*] (where *z* ∼ 0), as all three sites describe adequately the statistical distribution of Pb about the (001) plane. We note that in the structure of Ga-rich plumbogummite, refinement of Pb at the origin (0, 0, 0) dramatically increased the *R* factor, indicating that the Pb atom is displaced off the origin. Giuseppetti and Tadini (1980, 1987) reported the Pb atom on the origin in the structures of osarizawaite and corkite; however, the Pb atom had large thermal ellipsoids, which indicate stereochemical activity of the $6s^2$ lone pair. Here, we report off-centring to the [*x*, 0, 0] position for the Pb, consistent with other refinements.

The final model for the refinement converged to R_1 = 2.05% for 267 reflections [$F_o > 4\sigma(F_o)$], and 2.10 for all 271 reflections. The refined atom coordinates, site occupancies and displacement parameters are given in Table 2; bond distances in Table 3, and a bond-valence analysis in Table 4.

X-ray powder diffraction

Powder data were obtained using a Rigaku R-AXIS SPIDER large-area curved-imaging-plate microdiffractometer with monochromatized Mo-*K*α (λ = 0.71075 Å) radiation on the same crystal used for single-crystal structure refinement. Unit-cell data (parameters refined from the powder data using *Chekcell* − Laugier and Bochu, 2004) are given in Table 5.

TABLE 2. Atomic coordinates and displacement parameters ($\mathring{A}^2$) for Ga-rich plumbogummite.

Atom	*x*	*y*	*z*	Occupancy	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb/Ca	0.033(4)	0.0	0.0	0.88/0.12*	0.022(4)	0.025(4)	0.024(11)	0.0164(3)	−0.0018(11)	−0.0009(6)	0.012(6)
Al/Ga	0.5	0.0	0.5	0.65/0.35	0.0088(3)	0.0063(4)	0.0060(5)	0.0139(5)	0.0014(3)	0.00070(17)	0.0030(3)
P	0.0	0.0	0.30898(10)		0.0099(5)	0.0088(6)	0.0088(6)	0.0121(8)	0	0	0.0044(3)
O(1)	0.0	0.0	0.6014(3)		0.0171(11)	0.0190(16)	0.0190(16)	0.013(2)	0	0	0.0095(8)
O(2)	0.2155(2)	−0.2155(2)	−0.05658(16)		0.0146(6)	0.0142(10)	0.0142(10)	0.0162(13)	0.0000(5)	0.0000(5)	0.0078(11)
O(3)	0.1255(2)	−0.1255(2)	0.13598(16)		0.0117(6)	0.0096(9)	0.0096(9)	0.0169(13)	−0.0007(5)	0.0007(5)	0.0055(10)
H(1)	0.192(6)	−0.192(6)	0.114(4)		0.05(2)						

* The occupancy is integrated over the six 18*f* sites.

TABLE 3. Polyhedral bond distances (Å) in Ga-rich plumbogummite.

(Al/Ga)−O(2)	1.947(1)	×2
(Al/Ga)−O(3)	1.914(1)	×4
<(Al/Ga)−O>	1.925	
P−O(1)	1.507(5)	
P−O(2)	1.542(3)	×3
<P−O>	1.533	
(Pb/Ca)−O(2)	2.614	×2
(Pb/Ca)−O(2)	2.817	×2
(Pb/Ca)−O(2)	3.007	×2
(Pb/Ca)−O(3)	2.647	×2
(Pb/Ca)−O(3)	2.766	×2
(Pb/Ca)−O(3)	2.880	×2
<Pb/Ca>−O(3)	2.789	

Optical characterization

The crystal used for the structure determination was also used for optical characterization. The crystal showed some layering and possible sector zoning or twinning in parts, confirming the twinning observations noted above; however the majority of the crystal was homogeneous. The crystal was split up into fragments, where the individuals showed the following characteristics: nonpleochroic, uniaxial (+), with indices of refraction, ε = 1.742(3) and ω = 1.722(3) determined in white light. The crystal showed some bluish colours prior to splitting; this seems to be an interference effect related to the growth layers as opposed to actual bluish interference colours observed for some alunite-supergroup members (e.g. dussertite − Kolitsch *et al.*, 1999*b*).

Ga-rich plumbogummite shows higher refractive indices than the typical range for plumbogummite: ω = 1.653−1.688 and ε = 1.675−1.704 (Anthony *et al.*, 2000) in accord with the high Ga content. Plumbogummite has also been noted as being biaxial (+) with a small 2V value (e.g. Hintze, 1933; Slansky, 1977); however, this was not observed in the Ga-rich plumbogummite crystals. Recently, however, several biaxial species − pattersonite, a dimorph of kintoreite, $PbFe_3(PO_4)_2(OH)_4[(H_2O)_{0.5}(OH)_{0.5}]_2$ (Kolitsch *et al.*, 2008) and kolitschite, $PbZn_{0.5}Fe_3(AsO_4)_2(OH)_6$, related to segnitite (Grey *et al.*, 2008; Mills *et al.*, 2008) − have been shown to be new minerals related to the alunite supergroup members. These new discoveries shed light on the complex crystal chemistry of the alunite supergroup. A re-examination of some of these previously described plumbogummites, such as those described by Hintze (1933) and Slansky (1977), seems highly desirable.

Discussion

Crystal structure

The crystal structure of plumbogummite (Kolitsch *et al.*, 1999*a*), is a typical rhombohedral alunite-type structure (e.g. Blount, 1974) made up of (001) sheets of corner-shared Al octahedra and P tetrahedra that stack along *c* (Fig. 1). The Pb atoms occupy icosahedrally coordinated sites between the layers. The stacking of two composite octahedral/tetrahedral layers, with interlayer Pb atoms, is shown in Fig. 2. The octahedra share corners *via* hydroxyl anions, O(3), to form a planar network of triangular clusters encompassing hexagonal voids. Such networks are often described as hexagonal tungsten bronze (HTB) layers (e.g. Grey *et al.*, 2006). The apical oxygen

TABLE 4. Bond-valence analysis for Ga-rich plumbogummite.

	Pb/Ca[KB]	Pb/Ca[BO]		Al/Ga		P		H(1)	Total[KB]	Total[BO]
O(1)						1.34		0.27	1.61	1.61
O(2)	0.18	0.16	↓×6	0.47	↓×2	1.22	↓×3		2.26	2.20
O(3)	0.19	0.17	↓×6	0.50	↓×4			0.73	1.92	1.86
	2.19	1.97		2.94		5.00		1.00		

[KB] = Using the Pb−O parameters of Krivovichev and Brown (2001).
[BO] = Using the Pb−O parameters of Breese and O'Keeffe (1991).

TABLE 5. X-ray powder diffraction data for Ga-rich plumbogummite.

$I_{obs.}$	$d_{obs.}$	$d_{calc.}$	$I_{calc.}$*	h	k	l
95	**5.766**	**5.76**	**100**	**1**	**0**	**1**
7	4.96	4.955	6	0	1	2
38	**3.539**	**3.539**	**36**	**1**	**1**	**0**
11	3.46	3.47	11	1	0	4
100	**2.995**	**2.994**	**97**	**1**	**1**	**3**
17	2.886	2.88	28	2	0	2
11	2.807	2.806	15	0	0	6
19	2.479	2.478	19	0	2	4
13	2.296	2.295	13	2	1	1
43	2.236	2.239	31	1	0	7
		2.235	16	1	2	2
9	2.199	2.199	9	1	1	6
6	2.029	2.03	7	2	1	4
32	**1.919**	**1.92**	**5**	**3**	**0**	**3**
		1.92	**23**	**0**	**3**	**3**
23	1.769	1.77	20	2	2	0
5	1.737	1.735	6	2	0	8
8	1.665	1.667	<1	3	1	2
		1.667	6	2	1	7
10	1.654	1.654	8	1	1	9
8	1.518	1.518	6	3	1	5
		1.517	5	0	4	2
16	1.498	1.497	12	2	2	6
12	1.474	1.476	14	0	2	10
5	1.442	1.44	4	4	0	4
4	1.4	1.402	3	3	2	1
6	1.388	1.388	5	1	3	7
5	1.381	1.38	1	3	0	9
		1.38	4	0	3	9
11	1.301	1.301	5	4	1	3
		1.301	3	1	4	3

* Using the crystal structure data with a =7.0752 Å, c = 16.8183 Å.

FIG. 1. Crystal structure of Ga-rich plumbogummite projected onto (100). Lead atoms are indicated as spheres.

The BO_6 octahedron in the alunite structure-type has two long $B-O(2)$ distances and four short $B-O(3)$ distances. In Ga-rich plumbogummite, these distances are 1.947 and 1.914 Å respectively, giving an $<Al/Ga-O>$ of 1.925 Å, and a refined site occupancy of $Al_{0.66}Ga_{0.34}$.

The large A cation site in the alunite-type structure is in 12-coordination. In the ideal case, the cation is located at the origin and has symmetrical coordination with bonds of equal length to six O(2) and to six O(3) atoms. However, as described above, in the majority of Pb members of the alunite supergroup, the Pb coordination environment is displaced and distorted, and the Pb atom exhibits stereochemical activity of the $6s^2$ lone-pair electrons (Mills, 2007). The stereochemical activity of the Pb $6s^2$ lone-pair electrons has been described in a number of minerals and compounds (e.g. joesmithite – Moore, 1988; wherryite – Cooper and Hawthorne, 1994; mawbyite – Kharisun et al., 1997b; synthetic $Pb_4BiO_4PO_4$ – Giraud et al.

anions, O(2), of the triangular groupings of octahedra are shared with the PO₄ tetrahedra.

The TO_4 tetrahedron in the alunite structure-type has one short apical $T-O(1)$ distance and three longer $T-O(2)$ distances. In Ga-rich plumbogummite, these distances are 1.507 and 1.541 Å respectively, giving a $<P-O>$ of 1.533 Å. The average bond length matches well with the value of 1.537 Å reported by Huminicki and Hawthorne (2002) for phosphate minerals and 1.56 Å reported by Kolitsch et al. (1999a) for plumbogummite with 5% As. Approximately 2−3% S might be substituting at the site; however, refinements were unable to determine this unambiguously.
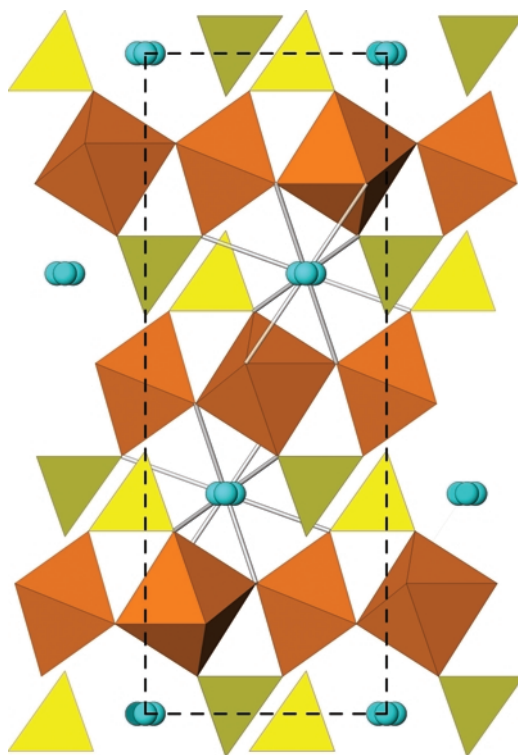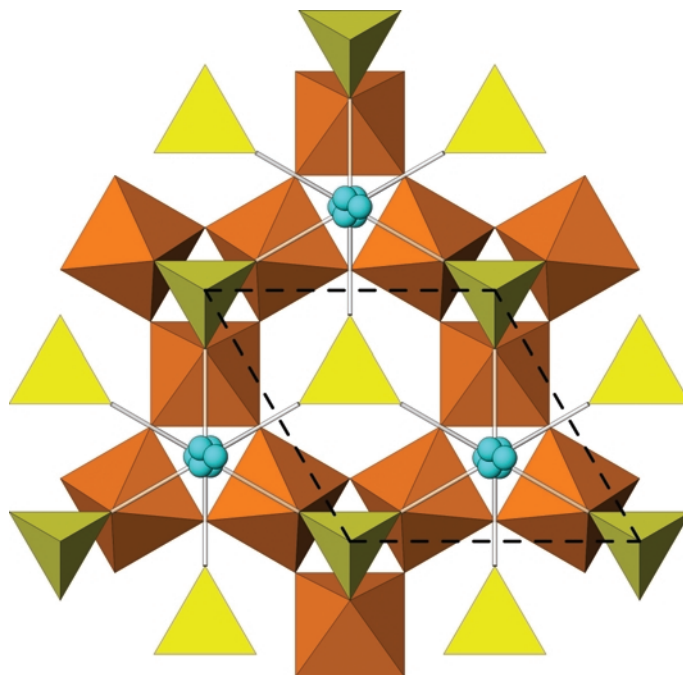
FIG. 2. Crystal structure of Ga-rich plumbogummite projected onto (001). Lead atoms are indicated as spheres.

1999). In Ga-rich plumbogummite, the *A* cation is located at a $(x, 0, 0)$ site and is displaced from the origin by 0.242 Å. The *A* cation has two short (2.614 Å), two medium (2.817 Å) and two long bonds (3.007 Å) to O(2), whereas to O(3), the two short bonds are 2.647 Å, and there are two pairs of medium length bonds of 2.766 and 2.880 Å. During refinement, the *R*-factor is substantially reduced by refining the occupancy, as Ca or Ba commonly occupies this site in Pb-bearing members (Mills, 2007). In Ga-rich plumbogummite, the site refined to $Pb_{0.88}Ca_{0.12}$, indicating partial solid solution toward crandallite. The <Pb/Ca−O> distance of 2.789 Å is in accord with literature values for alunite supergroup minerals. It is interesting to note that the Pb atom in the plumbogummite structure of Kolitsch *et al.* (1999*a*) refined to full occupancy, and it seems that the Pb in the gallobeudantite structure also has full occupancy (Jambor *et al.*, 1996).

Two published sets of parameters can be used for the determination of the bond valence for the *A* site. Recently, Krivovchev and Brown (2001) re-determined the bond valence parameters for Pb for structures where Pb is encapsulated by O^{2-} as OPb_4. The result was a change in the parameters

from $r_0 = 2.112$ Å and $b = 0.37$ Å (Brese and O'Keeffe, 1991) to $r_0 = 1.963$ Å and $b = 0.49$ Å for Pb−O bonds. For Ga-rich plumbogummite, a bond valence sum (BVS) of 2.19 v.u. for the *A* site is obtained using the parameters of Krivovichev and Brown (2001). In contrast, if the parameters of Brese and O'Keeffe (1991) are used, the valence sum is 1.97 v.u. Thus, the parameters of Krivovichev and Brown (2001) tend to over-estimate the bonding to Pb in the *A* site. Although OM_4 bonds fit the general $r_0−b$ trend for MO_n (in this case M = Pb), they appear to, on average, overestimate the valence of the ion, which may reflect *M*...*M* repulsion in the M_4 tetrahedron. Recalculation of the BVS for the plumbogummite of Kolitsch *et al.* (1999*a*) shows the same overbonding features. Using the parameters of Brese and O'Keeffe, the fully occupied Pb site has a BVS of 2.11 v.u., whereas Krivovchev and Brown's parameters give a significantly larger sum of 2.35 v.u. In contrast, the O(2) oxygen bonded to Pb has a valence sum of 2.26 v.u. using the Krivovichev and Brown parameters or 2.20 using those of Brese and O'Keeffe (1991), so this atom is overbonded to a similar degree for either choice of parameters, implying that the para-

meterization for the Pb−O bonds is not the cause, but rather geometrical constraints on the maximum possible lengthening of the other cation−O(2) bonds.

In the alunite structure type, it is common to determine the H(1) atom position. It has generally been described on a $[x, -x, z]$ site where it forms as an O(3)−H(1)...O(1) bond. In Ga-rich plumbogummite, it has a distance of 1.008 Å and an O−O distance of 2.81 Å, categorized as a weak hydrogen bond (Libowitzky and Beran, 2004). The contribution to the BVS is 0.73 v.u. to O(3) and 0.27 v.u. to O(1) which leaves both O atoms undersaturated (Table 4). It has often been speculated that a second hydrogen bond exists within the structure (e.g. Blount, 1974 in crandallite); however, this has yet to be confirmed. In Ga-rich plumbogummite, O(1) has a valence of 1.61 indicating that it is at least partially protonated. As O(2) is significantly overbonded, an inter-PO_4 hydrogen bond of the type O(1)−H(2)···O(2), as is proposed for kintoreite by Grey *et al*., (2009), is impossible. One more likely scenario involves an O(1)−H(2)...O(1) hydrogen bond which is formed between the proton, H(2), and the O(1) atoms of opposing tetrahedra on either side of the hexagonal rings. This O(1)−O(1) distance is considerably larger at ~3.4 Å than the distance noted for crandallite (2.99 Å) and kintoreite (3.21 Å). For this to occur, the O(1)−H(2) distance would be expected to be very short (Nakamoto *et al*., 1955) and the P−O(1) distance should be correspondingly elongated (Ferraris and Ivaldi, 1984). However, the P−O(1) distance is much shorter (1.509 Å) than the three P−O(2) distances of 1.544 Å.

Formation conditions

Mills (2007) was able to synthesize Ge- and Ga-rich equivalents of segnitite, the As- and Fe-analogue of plumbogummite. Here, under only a limited pH range (1−1.5), crystals with the alunite structure type were produced. During that study (Mills, 2007), attempts to synthesize the Ga and P equivalent (between pH 1 and 4 in a Ga saturated hydrothermal solution) were unsuccessful. In all cases, the P-analogue of schultenite precipitated and the Ga remained unreacted. In the presence of Fe and Ge, the new compound $Pb_3Fe_2(PO_4)_4(H_2O)$ was synthesized. This phase also has the potential to be discovered as a new mineral.

Considering that Ga-rich plumbogummite occurs on Ga-rich ore, it is somewhat surprising that only about one third of the Al is substituted by Ga considering the octahedral radii of Al is 0.535 Å *vs*. 0.62 Å for Ga. Ideally, it should be possible for a complete solid solution to exist between plumbogummite and the, as yet unidentified, Ga-analogue. It seems that more than abundant Ga is required for the Ga-dominant end-member ($PbGa_3H(AsO_4)_2(OH)_6$) to form − pH and Eh conditions must therefore play a major role. We note that in gallobeudantite, substantial Fe^{3+} and Al substitution occurs for Ga, and that a pure Ga end-member of that mineral is yet to be discovered.

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Appendix

A second crystal structure refinement was completed on another rhombohedral crystal of Ga-rich plumbogummite. The unit-cell parameters are: a = 7.1012(7) Å, c = 16.842(4) Å, V = 735.5(2) Å^3, with an R_1 = 0.0296 for 254 reflections. The refined Pb/Ca and Al/Ga ratios are: $Pb_{0.85}Ca_{0.15}$ and $Al_{0.67}Ga_{0.33}$. The average bond lengths are: <(Al/Ga)−O> 1.929 Å, <P−O> 1.541 Å and <Pb/Ca−O> 2.797 Å, with a O(3)−H(1)...O(1) distance of 1.052 Å. Atomic coordinates can be obtained from the corresponding author.