The crystal structure of bartelkeite, with a revised chemical formula, PbFeGe$^{IV}$Ge$_2^{IV}$O$_7$(OH)$_2$, isotypic with high-pressure $P_2_1/m$ lawsonite

MARCUS J. ORIGLIERI, HEXIONG YANG, ROBERT T. DOWNS, ESTHER S. POSNER, KENNETH J. DOMANIK, AND WILLIAM W. PINCH

1Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077 U.S.A.
2Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721-0092 U.S.A.
319 Stonebridge Lane, Pittsford, New York 14534, U.S.A.

ABSTRACT

Bartelkeite from Tsumeb, Namibia, was originally described by Keller et al. (1981) with the chemical formula PbFeGe$_3$O$_7$. By means of electron microprobe analysis, single-crystal X-ray diffraction, and Raman spectroscopy, we examined this mineral from the type locality. Our results show that bartelkeite is monoclinic with space group $P2_1/m$, unit-cell parameters $a = 5.827(2)$, $b = 13.6150(4)$, $c = 6.3097(2)$ Å, $\beta = 127.314(2)^\circ$, and a revised ideal chemical formula PbFeGe$^{IV}$Ge$_2^{IV}$O$_7$(OH)$_2$·H$_2$O (Z = 2). Most remarkably, bartelkeite is isostructural with the high-pressure $P2_1/m$ phase of lawsonite, CaAl$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O, which is only stable above 8.6 GPa and a potential host for H$_2$O in subducting slabs. Its structure consists of single chains of edge-sharing FeO$_6$ and GeO$_6$ octahedra parallel to the c-axis, cross-linked by Ge$_2$O$_7$ tetrahedral dimers. The average $<$Ge-O$>$ bond lengths for the GeO$_6$ and GeO$_2$ polyhedra are 1.889 and 1.744 Å, respectively. The Pb atoms and H$_2$O groups occupy large cavities within the framework. The hydrogen bonding scheme in bartelkeite is similar to that in lawsonite. Bartelkeite represents the first known mineral containing both 4- and 6-coordinated Ge atoms and may serve as an excellent analog for further exploration of the temperature-pressure-composition space of lawsonite.

Keywords: Bartelkeite, germanate, hydrous mineral, crystal structure, X-ray diffraction, Raman spectra

INTRODUCTION

Germanate materials are used as analogues of silicate phases because they can be studied at attainable experimental conditions and provide an understanding of the physical and chemical properties of minerals and melts in the Earth’s interior (e.g., Ringwood and Seabrook 1963; Ross et al. 1986; Hazen et al. 1996; Henderson and Wang 2002; Iezzi et al. 2005; Nestola et al. 2008). Yet, little attention has been devoted to the Ge-analogues of hydrous silicates thus far (Thomas et al. 2008), despite their presumed role in the hydrogen budget of the earth (e.g., Ringwood and Major 1967; Thompson 1992; Frost 2006). Only a few high-pressure hydrous germanates in the Al$_2$O$_3$-GeO$_2$-H$_2$O system have been examined as analogs for phases in the Al$_2$O$_3$-SiO$_2$-H$_2$O system in deeply subducted rocks, where lawsonite and related phases undergo phase transformations (e.g., Schmidt 1995; Wunder and Marler 1997).

While it appears that the number of synthetic germanates has been increasing continuously, there are only 3 anhydrous and 10 hydrous natural germanates in the current list of IMA approved minerals. Unfortunately, until now, seven of these germanate minerals have not been structurally characterized, making it difficult to take full advantage of natural germanates as models of silicates at mantle conditions.

The germanate, bartelkeite, was originally described by Keller et al. (1981) as a new mineral from Tsumeb, Namibia, with chemical formula PbFeGe$_3$O$_7$. And monoclinic symmetry with space group $P2_1$, or $P2_1/m$, unit-cell parameters $a = 5.431(3)$, $b = 13.689(7)$, $c = 5.892(3)$ Å, $\beta = 111.79(4)^\circ$, Z = 2. Since then, no further study has been reported for this mineral. Here, we present the first structure solution of bartelkeite from single-crystal X-ray-diffraction data, demonstrating that its ideal chemical formula is PbFeGe$_3$O$_7$(OH)$_2$·H$_2$O, rather than PbFeGe$_3$O$_7$. Furthermore, we reveal that bartelkeite is isostructural with the high-pressure $P2_1/m$ phase of rock-forming lawsonite, CaAl$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O, which is only stable above 8.6 GPa, opening a new channel for investigating the complex phase transitions in lawsonite.

EXPERIMENTAL PROCEDURES

The bartelkeite specimen used for the study is from the type locality, Tsumeb, Namibia, and in the collection of the RRUFF Project (http://rruff.info/R070114). Its chemical composition was determined using a Cameca SX-100 electron microprobe at 25 kV and 40 nA with a beam size of 10 μm. The average of 18 analysis points gives (wt%) PbO = 34.1(2), FeO = 10.6(1), GeO$_2$ = 46.2(2), As$_2$O$_5$ = 2.8(3), SiO$_2$ = 10.1(1), ZnO = 0.08(2), P$_2$O$_5$ = 0.04(1), CI = 0.20(6), SO$_3$ = 0.14(4), and total = 94.4(2). The chemical formula was calculated on the basis of 10 (O + Cl) atoms per formula unit, as determined from the structure refinement (see below), by adding 5.64 wt% H$_2$O to achieve charge balance, yielding Pb$_{0.97}$(Fe$^{2+}_{0.94}$Zn$_{0.01}$)O$_{1.99}$Ge$^{IV}_{0.95}$Ge$^{IV}_{1.00}$O$_{7.01}$H$_{2.94}$O$_{1.02}$H$_2$O, which can be simplified as PbFeGe$^{IV}$Ge$^{IV}$O$_7$(OH)$_2$·H$_2$O.

Single-crystal X-ray diffraction data of bartelkeite were collected from a nearly equi-dimensional crystal (~0.09 × 0.09 × 0.08 mm) on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized MoKα radiation.
Reflections with \( l > 2{\AA}l \) were indexed based on a monoclinic unit cell (Table 1). To facilitate a direct comparison with the high-pressure \( P_2/m \) structure of lawsonite (Pawley and Allan 2001), we adopted in this study a unit-cell setting (setting II in Table 1) differing from the one (setting I in Table 1) given by Keller et al. (1981). The matrix for the transformation from setting I to II is \((0 0 1 1 0 1 0 0)\). No satellite or super-lattice reflections were observed. The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The systematic absences of reflections suggest possible space group \( P2_1/m \) or \( P2_1/m \). The crystal structure was solved and refined using SHELX97 (Sheldrick 2008) based on the space group \( P2_1/m \), because it yielded a better refinement in terms of bond lengths and angles, atomic displacement parameters, and \( R \) factors. The positions of all atoms were refined with anisotropic displacement parameters, except for H atoms, which were refined with a fixed isotropic displacement parameter (\( U_{eq} = 0.03 \)). During the structure refinements, ideal chemistry was assumed, as the overall effects of the trace amounts of other elements (Zn, As, Si, S, and Cl) on the final refined structure are negligible. Final refined atomic coordinates and displacement parameters are listed in Table 2 and selected bond lengths and angles in Table 3.

### Results and Discussion

#### Crystal Structure

Most strikingly, bartelkeite is isomorphous with the high-pressure \( P_2/m \) phase of lawsonite (Pawley and Allan 2001). Its structure consists of single chains of edge-sharing FeO_6 and GeO_6 octahedra parallel to the \( c \)-axis, cross-linked by Ge_{2}O_{7} tetrahedral dimers. The Pb atoms and H_{2}O groups occupy large cavities within the framework (Fig. 1). In fact, bartelkeite is the first known mineral containing both 4- and 6-coordinated Ge atoms. Compared to the GeO_{6} octahedron, the FeO_{6} octahedron is markedly distorted, as measured by the octahedral angle variance (OAV) and quadratic elongation (OQE) (Robinson et al. 1971). The OAV and OQE indexes are 136.4 and 1.042, respectively, for the FeO_{6} octahedron, but only 11.4 and 1.004 for the GeO_{6} octahedron. The pronounced distortion of the FeO_{6} octahedron stems primarily from its edge-sharing with the smaller, more strongly bonded GeO_{6} octahedron. To maintain such a linkage, the shared edges of the comparatively large and soft FeO_{6} octahedron have to be shortened substantially to match those of the rigid GeO_{6} octahedron, making the O-Fe-O angle subtending the shared edge \((70.96^\circ)\) deviate considerably from the ideal value of \(90^\circ\). This is similar to the high-pressure \( P2/n \) Na(Mg_{0.5}Si_{0.5})SiO_{3} clinopyroxene, where MgO_{6} and SiO_{6} octahedra also share

### Table 1. Summary of crystal data and refinement results for bartelkeite

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bartelkeite (this study)</th>
<th>Bartelkeite (Keller et al. 1981)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>( P2_1/m )</td>
<td>( P2_1/m )</td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.4332(2)</td>
<td>5.4331(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.6150(4)</td>
<td>13.6897(7)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.8279(2)</td>
<td>5.892(3)</td>
</tr>
<tr>
<td>( \beta ) (°)</td>
<td>111.760(2)</td>
<td>111.794(4)</td>
</tr>
<tr>
<td>( V (Å^3) )</td>
<td>398.193(9)</td>
<td>406.7</td>
</tr>
<tr>
<td>( Z )</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>( \rho_{o} ) (g/cm(^3))</td>
<td>5.36</td>
<td>4.97</td>
</tr>
<tr>
<td>( \lambda ) (Å)</td>
<td>0.71073</td>
<td></td>
</tr>
<tr>
<td>( \mu ) (mm(^{-1}))</td>
<td>34.08</td>
<td></td>
</tr>
<tr>
<td>29 range for data collection</td>
<td>&lt;70.11</td>
<td></td>
</tr>
<tr>
<td>No. of reflections collected</td>
<td>8266</td>
<td></td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>1798</td>
<td></td>
</tr>
<tr>
<td>No. of reflections with ( l &gt; 2{\AA}l )</td>
<td>1594</td>
<td></td>
</tr>
<tr>
<td>No. of parameters refined</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>( R_{r} )</td>
<td>0.029</td>
<td></td>
</tr>
<tr>
<td>Final R1, r2 factors ( l &gt; 2{\AA}l )</td>
<td>0.023, 0.045</td>
<td></td>
</tr>
<tr>
<td>Final R1, r2 factors (all data)</td>
<td>0.028, 0.045</td>
<td></td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>1.024</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Coordinates and displacement parameters of atoms in bartelkeite

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{eq} )</th>
<th>( U_{11} )</th>
<th>( U_{22} )</th>
<th>( U_{33} )</th>
<th>( U_{12} )</th>
<th>( U_{13} )</th>
<th>( U_{23} )</th>
<th>( U_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.32486(4)</td>
<td>0.75</td>
<td>0.6767(3)</td>
<td>0.0149(1)</td>
<td>0.0142(1)</td>
<td>0.0155(1)</td>
<td>0.0161(8)</td>
<td>0</td>
<td>0.00984(7)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
<td>0.0077(1)</td>
<td>0.0082(3)</td>
<td>0.0087(3)</td>
<td>0.0066(2)</td>
<td>-0.0011(2)</td>
<td>0.0047(2)</td>
<td>-0.0016(2)</td>
<td></td>
</tr>
<tr>
<td>Ge1</td>
<td>0.9013(7)</td>
<td>0.12998(3)</td>
<td>0.9969(4)</td>
<td>0.0069(1)</td>
<td>0.0058(1)</td>
<td>0.0100(3)</td>
<td>0.0055(2)</td>
<td>0.0018(1)</td>
<td>0.0040(2)</td>
<td>0.0028(1)</td>
<td></td>
</tr>
<tr>
<td>Ge2</td>
<td>0.7512(5)</td>
<td>0.1115(2)</td>
<td>0.9530(7)</td>
<td>0.0157(7)</td>
<td>0.0111(7)</td>
<td>0.0062(2)</td>
<td>0.0027(2)</td>
<td>0</td>
<td>0.009(1)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>0.7820(5)</td>
<td>0.3853(2)</td>
<td>0.1337(4)</td>
<td>0.0114(4)</td>
<td>0.013(1)</td>
<td>0.012(1)</td>
<td>0.0084(9)</td>
<td>-0.0008(1)</td>
<td>0.0044(8)</td>
<td>-0.0031(8)</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>0.2383(4)</td>
<td>0.0625(2)</td>
<td>0.1610(4)</td>
<td>0.0088(4)</td>
<td>0.0031(2)</td>
<td>0.0012(1)</td>
<td>0.0012(1)</td>
<td>0.0012(1)</td>
<td>0.0012(1)</td>
<td>0.0040(8)</td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>0.2893(5)</td>
<td>0.0525(2)</td>
<td>0.6036(4)</td>
<td>0.0116(5)</td>
<td>0.0087(9)</td>
<td>0.018(1)</td>
<td>0.0074(8)</td>
<td>0.0017(8)</td>
<td>0.0046(7)</td>
<td>0.0037(8)</td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>0.7617(9)</td>
<td>0.75</td>
<td>0.3216(8)</td>
<td>0.0240(8)</td>
<td>0.028(2)</td>
<td>0.012(2)</td>
<td>0.033(2)</td>
<td>0</td>
<td>0.019(2)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H1</td>
<td>0.143(6)</td>
<td>0.078(4)</td>
<td>0.495(7)</td>
<td>0.03*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>0.713(8)</td>
<td>0.798(2)</td>
<td>0.355(9)</td>
<td>0.03*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* \( U_{eq} \) fixed during refinement.
edges to form single chains (Angel et al. 1988; Yang et al. 2009) and the O-Mg-O angle subtending the shared edge is 69.5°.

The Pb2+ cation in bartelkeite, due probably to its lone-pair electron activities, displays a (6+3) coordination, with six Pb-O bond lengths shorter than 2.70 Å and three longer than 3.15 Å (Table 3). By comparison, Sr2+ in the isostructural P

contrary to the work by Keller et al. (1981), our structure analysis clearly indicates the presence of both OH and H2O in bartelkeite, as shown by our bond-valence calculations using the parameters given by Brese and O’Keeffe (1991) (Table 4), as well as by our Raman spectroscopic measurements (see below). The hydrogen bonding scheme in bartelkeite (Table 3) is similar to that in lawsonite. However, OH in bartelkeite appears to be engaged in only one hydrogen bond, but two in lawsonite (Fig. 1).

Raman spectra

The Raman spectrum of bartelkeite is plotted in Figure 2. Based on previous Raman spectroscopic studies on various germanate materials (e.g., Ross et al. 1986; Baran et al. 2004; Takahashi et al. 2008), we made the following tentative assignments for the major bands. The two broad bands at 3293 and 3490 cm⁻¹ are due to O-H stretching vibrations. According to Libowitzky (1999), these two bands correspond to estimated O···O distances of ~2.75 and 2.95 Å, respectively, which are compared to the O5H···O3 (2.76 Å) and O6w···O5H (2.78 Å) distances from the structure refinement (Table 3). The very weak and broad band at 1558 cm⁻¹ is characteristic of the H-O-H bending vibration. The two bands at 758 (the strongest) and 812 cm⁻¹ are attributed to the symmetric and antisymmetric stretching vibrations of Ge-O bonds within the GeO4 tetrahedron, respectively, whereas the band at 492 cm⁻¹ is assigned to the Ge-O stretching vibrations within the GeO6 octahedron. The two bands at 549 (the second strongest) and 393 cm⁻¹ are ascribed to the Ge IV-O-GeIV and GeVI-O-GeIV bending vibrations, respectively. The bands below 320 cm⁻¹ are of complex nature and mostly associated with the rotational and translational modes of GeO4 and GeO6 polyhedra, Fe-O interactions, and the lattice vibrational modes.

Implications for lawsonite

Lawsonite is an index mineral for high-pressure low-temperature metamorphism (such as blueschist facies). Its high H2O content (11.5 wt%) and high-pressure stability, up to ~12 GPa at 1240 K, make it a potential host for water in subducting slabs down to as much as 250 km (Pawley 1994; Schmidt 1995). Recent experimental studies have uncovered the intricate behavior of this mineral as a function of temperature, pressure, and composition. On the one hand, lawsonite undergoes two reversible phase transitions attributed to the order-disorder of hydrogen bonding at low temperatures, one from Cmcm to Pmcn at 273 K and the other from Pmcn to P2₁cn at 155 K (Libowitzky and Armbruster 1995). The FeO₆ octahedra in bartelkeite are beneath the Ge₁O₆ octahedra. The large, medium, and small spheres represent Pb, O6w, and H atoms, respectively, in bartelkeite, and Ca, O5w, and H atoms in lawsonite.

![Figure 1.](image1.png) **Figure 1.** Comparison of crystal structures of (a) bartelkeite and (b) lawsonite at 295 K (Libowitzky and Armbruster 1995). The FeO₆ octahedra in bartelkeite are beneath the Ge₁O₆ octahedra. The large, medium, and small spheres represent Pb, O6w, and H atoms, respectively, in bartelkeite, and Ca, O5w, and H atoms in lawsonite.

![Figure 2.](image2.png) **Figure 2.** Raman spectrum of bartelkeite.

<table>
<thead>
<tr>
<th>Table 4. Bond-valence sums for bartelkeite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>O₁</td>
</tr>
<tr>
<td>O₂</td>
</tr>
<tr>
<td>O₃</td>
</tr>
<tr>
<td>O₄</td>
</tr>
<tr>
<td>O₅H</td>
</tr>
<tr>
<td>O₆W</td>
</tr>
<tr>
<td>∑M</td>
</tr>
</tbody>
</table>
The stability field of this high-pressure $P_2_1/m$ phase is still undefined. In addition, Liesbercher et al. (2010) noticed a $Cmcm$-to-$P_2_1/m$ symmetry change as the substitution of Sr for Ca increases in lawsonite, whereas Dörsam et al. (2011) synthesized $Pbnm$ Pb-lawsonite, $PbAlSi_3O_5(OH)\cdot H_2O$ at 2 GPa and 600 °C. The determination of the bartelkeite-type structure implies that the lawsonite-or bartelkeite-type structure or topologically similar structures can be rather compliant and complex, and a variety of such compounds with different cation sizes and valences may be synthesized or found in nature, such as CaMgSiVI(Si2O7)(OH)2·H2O, NaAlSiVI(SiO7)(OH)2·H2O, and BaFeTi(SiO7)(OH)2·H2O. Furthermore, it suggests that bartelkeite-type compounds can serve as good models for further exploration of the temperature-pressure-composition space of lawsonite and the discovery of more exotic phases at various temperatures and pressures.

**ACKNOWLEDGMENTS**

This study was funded by the Science Foundation Arizona.

**REFERENCES CITED**


Yang, H., Konzett, J., Frost, D.J., and Downs, R.T. (2009) X-ray diffraction and Raman spectroscopic studies of clinopyroxenes with six-coordinated Si in the Na(Mg$_{0.5}$Si$_{0.5}$)Si$_2$O$_6$–NaAlSi$_2$O$_5$ system. American Mineralogist, 94, 942–949.
data_bart2

_audit_creation_method  SHELXL-97
_chemical_name_systematic
;
;
_chemical_name_common
;
_chemical_melting_point
;
_chemical_formula_moiety
;
_chemical_formula_sum
'H2 Fe Ge3 O10 Pb'
_chemical_formula_weight 642.83

loop_
_atom_type_symbol
_atom_type_description
_atom_type_scat_dispersion_real
_atom_type_scat_dispersion_imag
_atom_type_scat_source
'O'  'O'   0.0106   0.0060
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'H'  'H'   0.0000   0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Fe'  'Fe'   0.3463   0.8444
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Ge'  'Ge'   0.1547   1.8001
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Pb'  'Pb'  -3.3944  10.1111
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting

_symmetry_space_group_name_H-M

loop_
_symmetry_equiv_pos_as_xyz
'x, y, z'
'-x, y+1/2, -z'
'-x, -y, -z'
'x, -y-1/2, z'

_cell_length_a  5.8279(2)
_cell_length_b  13.6150(4)
_cell_length_c  6.3097(2)
_cell_angle_alpha  90.00
_cell_angle_beta  127.314(2)
_cell_angle_gamma  90.00
_cell_volume  398.18(2)
_cell_formula_units_Z  2
_cell_measurement_temperature  293(2)
_cell_measurement_reflns_used
_cell_measurement_theta_min
_cell_measurement_theta_max

_exptl_crystal_description
Refinement of $F^2$ against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on $F^2$, conventional R-factors R are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>_refine_ls_structure_factor_coef</td>
<td>Fsqd</td>
</tr>
<tr>
<td>_refine_ls_matrix_type</td>
<td>full</td>
</tr>
<tr>
<td>_refine_ls_weighting_scheme</td>
<td>calc</td>
</tr>
<tr>
<td>_refine_ls_weighting_details</td>
<td></td>
</tr>
<tr>
<td>_atom_sites_solution_primary</td>
<td>direct</td>
</tr>
<tr>
<td>_atom_sites_solution_secondary</td>
<td>difmap</td>
</tr>
<tr>
<td>_atom_sites_solution_hydrogens</td>
<td>geom</td>
</tr>
<tr>
<td>_refine_ls_hydrogen_treatment</td>
<td>mixed</td>
</tr>
<tr>
<td>_refine_ls_extinction_method</td>
<td>SHELXL</td>
</tr>
<tr>
<td>_refine_ls_extinction_coef</td>
<td>0.0024(2)</td>
</tr>
<tr>
<td>_refine_ls_extinction_expression</td>
<td></td>
</tr>
<tr>
<td>_refine_ls_number_reflns</td>
<td>1797</td>
</tr>
<tr>
<td>_refine_ls_number_parameters</td>
<td>83</td>
</tr>
<tr>
<td>_refine_ls_number_restraints</td>
<td>2</td>
</tr>
<tr>
<td>_refine_ls_R_factor_all</td>
<td>0.0283</td>
</tr>
<tr>
<td>_refine_ls_R_factor_gt</td>
<td>0.0230</td>
</tr>
<tr>
<td>_refine_ls_wR_factor_ref</td>
<td>0.0441</td>
</tr>
<tr>
<td>_refine_ls_wR_factor_gt</td>
<td>0.0430</td>
</tr>
<tr>
<td>_refine_ls_goodness_of_fit_ref</td>
<td>1.029</td>
</tr>
<tr>
<td>_refine_ls_restrained_S_all</td>
<td>1.031</td>
</tr>
<tr>
<td>_refine_ls_shift/su_max</td>
<td>0.004</td>
</tr>
<tr>
<td>_refine_ls_shift/su_mean</td>
<td>0.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Loop</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>_atom_site_label</td>
<td>Pb 0.32487(4) 0.7500 0.67674(3) 0.01488(6) Uani 1 2 d S ..</td>
</tr>
<tr>
<td>_atom_site_type_symbol</td>
<td>Fe 0.5000 0.0000 0.0000 0.00769(12) Uani 1 2 d S ..</td>
</tr>
<tr>
<td>_atom_site_frc_x</td>
<td>Ge1 Ge 0.5000 0.0000 0.5000 0.00773(9) Uani 1 2 d S ..</td>
</tr>
<tr>
<td>_atom_site_frc_y</td>
<td>Ge2 Ge 0.96137(6) 0.12998(3) 0.99604(6) 0.00688(7) Uani 1 1 d ..</td>
</tr>
<tr>
<td>_atom_site_frc_z</td>
<td>O1 O 0.9013(7) 0.7500 0.9350(7) 0.0157(7) Uani 1 2 d S ..</td>
</tr>
<tr>
<td>_atom_site_U_iso_or_equiv</td>
<td>O2 O 0.7512(5) 0.11151(19) 0.6545(4) 0.0128(5) Uani 1 1 d ..</td>
</tr>
<tr>
<td>_atom_site_adp_type</td>
<td>O3 O 0.7821(5) 0.38529(19) 0.1337(4) 0.0114(4) Uani 1 1 d ..</td>
</tr>
<tr>
<td>_atom_site_occupancy</td>
<td>O4 O 0.2837(4) 0.38529(19) 0.0114(4) Uani 1 1 d ..</td>
</tr>
<tr>
<td>_atom_site_symmetry_multiplicity</td>
<td>O5H O 0.2837(4) 0.0524(2) 0.6036(4) 0.0116(5) Uani 1 1 d D ..</td>
</tr>
<tr>
<td>_atom_site_disorder_assembly</td>
<td>O6W O 0.7617(9) 0.7500 0.3216(8) 0.0239(8) Uani 1 2 d SD ..</td>
</tr>
</tbody>
</table>

http://www.minsocam.org/MSA/AmMin/TOC/2012/Oct12_Data/Origlieri_p1812_12.cif
H1  H  0.144(8)  0.077(4)  0.497(8)  0.030  Uiso 1 1 d D . .
H2  H  0.712(9)  0.799(3)  0.356(9)  0.030  Uiso 1 1 d D . .

loop_
_atom_site_aniso_label
_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_12
_atom_site_aniso_U_13

Pb  0.01415(8)  0.01555(11)  0.01618(8)  0.000  0.00984(7)  0.000
Fe  0.0082(3)  0.0087(4)  0.0066(2)  -0.00110(19)  0.0047(2)  -0.0016(2)
Ge1  0.00759(18)  0.0100(3)  0.00554(16)  0.00176(14)  0.00397(15)  0.00282(14)
Ge2  0.00581(13)  0.00720(18)  0.00654(12)  0.00011(10)  0.00318(10)  0.00054(10)
O1  0.0105(14)  0.0064(19)  0.0266(17)  0.000  0.0093(13)  0.000
O2  0.0120(10)  0.0146(14)  0.0084(8)  -0.0001(8)  0.0044(8)  -0.0031(8)
O3  0.0129(10)  0.0117(13)  0.0132(9)  0.0042(8)  0.0097(8)  0.0040(8)
O4  0.0083(9)  0.0119(12)  0.0063(8)  0.0032(8)  0.0044(7)  0.0053(7)
O5H  0.0087(9)  0.0179(15)  0.0074(8)  0.0017(8)  0.0046(8)  0.0037(8)
O6W  0.028(2)  0.012(2)  0.033(2)  0.000  0.0190(17)  0.000

_geom_special_details
;
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.
;
loop_
_geom_bond_atom_site_label_1
_geom_bond_atom_site_label_2
_geom_bond_distance
_geom_bond_site_symmetry_2
_geom_bond_publ_flag

Pb  O3  2.473(2)  2_656  ?
Pb  O3  2.473(2)  3_666  ?
Pb  O6W  2.623(4)  1_455  ?
Pb  O2  2.645(2)  2_656  ?
Pb  O2  2.645(2)  3_666  ?
Pb  O1  2.703(3)  .  ?
Fe  O3  2.042(2)  4_565  ?
Fe  O3  2.042(2)  2_645  ?
Fe  O5H  2.133(2)  1_554  ?
Fe  O5H  2.133(2)  3_656  ?
Fe  O4  2.213(2)  3_655  ?
Fe  O4  2.213(2)  .  ?
Ge1  O5H  1.849(2)  3_656  ?
Ge1  O5H  1.849(2)  .  ?
Ge1  O4  1.902(2)  3_656  ?
Ge1  O4  1.902(2)  .  ?
Ge1  O2  1.915(2)  .  ?
Ge1  O2  1.915(2)  3_656  ?
Ge2  O3  1.729(2)  4_566  ?
<table>
<thead>
<tr>
<th>Atom</th>
<th>Atomic Position</th>
<th>Symmetry Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge2</td>
<td>O2 1.734(2)</td>
<td></td>
</tr>
<tr>
<td>Ge2</td>
<td>O1 1.7544(12)</td>
<td>3.767</td>
</tr>
<tr>
<td>Ge2</td>
<td>O4 1.757(2)</td>
<td>1.656</td>
</tr>
<tr>
<td>O1</td>
<td>Ge2 1.7544(12)</td>
<td>3.767</td>
</tr>
<tr>
<td>O1</td>
<td>Ge2 1.7544(12)</td>
<td>2.757</td>
</tr>
<tr>
<td>O2</td>
<td>Pb 2.645(2)</td>
<td>3.666</td>
</tr>
<tr>
<td>O3</td>
<td>Ge2 1.729(2)</td>
<td>4.564</td>
</tr>
<tr>
<td>O3</td>
<td>Fe 2.042(2)</td>
<td>2.655</td>
</tr>
<tr>
<td>O3</td>
<td>Pb 2.473(2)</td>
<td>3.666</td>
</tr>
<tr>
<td>O4</td>
<td>Ge2 1.757(2)</td>
<td>1.454</td>
</tr>
<tr>
<td>O5H</td>
<td>Fe 2.133(2)</td>
<td>1.556</td>
</tr>
<tr>
<td>O5H</td>
<td>H1 0.77(4)</td>
<td></td>
</tr>
<tr>
<td>O6W</td>
<td>Pb 2.623(4)</td>
<td>1.655</td>
</tr>
<tr>
<td>O6W</td>
<td>H2 0.81(4)</td>
<td></td>
</tr>
</tbody>
</table>

```plaintext
loop_
  _geom_angle_atom_site_label_1
  _geom_angle_atom_site_label_2
  _geom_angle_atom_site_label_3
  _geom_angle
  _geom_angle_site_symmetry_1
  _geom_angle_site_symmetry_3
  _geom_angle_publ_flag
  O3 Pb O3 96.29(11) 2.656 3.666
  O3 Pb O6W 82.03(8) 2.656 1.455
  O3 Pb O6W 82.03(8) 3.666 1.455
  O3 Pb O2 160.47(7) 2.656 2.656
  O3 Pb O2 83.14(8) 3.666 2.656
  O6W Pb O2 78.55(8) 1.455 2.656
  O3 Pb O2 83.14(8) 2.656 3.666
  O3 Pb O2 160.47(7) 3.666 3.666
  O6W Pb O2 78.55(8) 1.455 3.666
  O2 Pb O2 90.93(11) 2.656 3.666
  O3 Pb O1 107.09(7) 2.656
  O3 Pb O1 107.09(7) 3.666
  O6W Pb O1 165.86(12) 1.455
  O2 Pb O1 91.61(7) 2.656
  O2 Pb O1 91.61(7) 3.666
  O3 Fe O3 180.00(9) 4.565 2.645
  O3 Fe O5H 88.59(9) 4.565 1.554
  O3 Fe O5H 91.41(9) 2.645 1.554
  O3 Fe O5H 91.41(9) 4.565 3.656
  O3 Fe O5H 88.59(9) 2.645 3.656
  O5H Fe O5H 180.00(14) 1.554 3.656
  O3 Fe O4 86.79(9) 4.565 3.655
  O3 Fe O4 93.21(9) 2.645 3.655
  O5H Fe O4 70.95(8) 1.554 3.655
  O5H Fe O4 109.05(8) 3.656 3.655
  O3 Fe O4 93.21(9) 4.565
  O3 Fe O4 86.79(9) 2.645
  O5H Fe O4 109.05(8) 1.554
  O5H Fe O4 70.95(8) 3.656
  O4 Fe O4 180.00(13) 3.655
  O5H Ge1 O5H 180.0 3.656
  O5H Ge1 O4 95.48(9) 3.656 3.656
  O5H Ge1 O4 84.52(9) 3.656
```
O5H Ge1 O4 95.48(9) . . ?
O4 Ge1 O4 180.00(10) 3_656 . ?
O5H Ge1 O2 91.13(11) 3_656 . ?
O5H Ge1 O2 88.87(11) . . ?
O4 Ge1 O2 90.07(10) 3_656 . ?
O4 Ge1 O2 89.93(10) . . ?
O5H Ge1 O2 88.87(11) 3_656 3_656 ?
O5H Ge1 O2 91.13(11) . 3_656 ?
O4 Ge1 O2 89.93(10) 3_656 3_656 ?
O4 Ge1 O2 90.07(10) . 3_656 ?
O2 Ge1 O2 180.00(10) . 3_656 ?
O3 Ge2 O2 114.84(11) 4_566 . ?
O3 Ge2 O1 108.13(14) 4_566 3_767 ?
O2 Ge2 O1 108.40(14) . 3_767 ?
O3 Ge2 O4 113.22(10) 4_566 1_656 ?
O2 Ge2 O4 110.89(11) . 1_656 ?
O1 Ge2 O4 100.19(13) 3_767 1_656 ?
Ge2 O1 Ge2 137.32(19) 3_767 2_757 ?
Ge2 O1 Pb 111.28(10) 3_767 . ?
Ge2 O1 Pb 111.28(10) 2_757 . ?
Ge2 O2 Ge1 119.58(13) . . ?
Ge2 O2 Pb 122.17(12) . 3_666 ?
Ge1 O2 Pb 116.90(9) . 3_666 ?
Ge2 O3 Fe 117.68(12) 4_564 2_655 ?
Ge2 O3 Pb 124.03(13) 4_564 3_666 ?
Fe O3 Pb 113.18(9) 2_655 3_666 ?
Ge2 O4 Ge1 129.93(11) 1_454 . ?
Ge2 O4 Fe 129.13(10) 1_454 . ?
Ge1 O4 Fe 99.83(9) . . ?
Ge1 O5H Fe 104.58(10) 1_556 ?
Ge1 O5H H1 118(4) . . ?
Fe O5H H1 136(4) 1_556 . ?
Pb O6W H2 104(3) 1_655 . ?

loop_
__geom_hbond_atom_site_label_D
__geom_hbond_atom_site_label_H
__geom_hbond_atom_site_label_A
__geom_hbond_distance_DH
__geom_hbond_distance_HA
__geom_hbond_distance_DA
__geom_hbond_angle_DHA
__geom_hbond_site_symmetry_A
O5H H1 O3 0.77(4) 2.02(4) 2.761(3) 160(5) 4_465
O6W H2 O5H 0.81(4) 2.03(4) 2.777(3) 152(5) 3_666

__differn_measured_fraction_theta_max 0.986
__differn_reflns_theta_full 35.05
__differn_measured_fraction_theta_full 0.986
__refine_diff_density_max 1.953
__refine_diff_density_min -1.194
__refine_diff_density_rms 0.256