The Canadian Mineralogist
Vol. 47, pp. 153-158 (2009)
DOI: 10.3749/canmin.47.1.153

THE CRYSTAL STRUCTURE OF KRIVOVICHEVITE, $Pb_3[Al(OH)_6](SO_4)(OH)$

Sergey V. KRIVOVICHEV[§]

Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia

Thomas ARMBRUSTER

Mineralogical Crystallography, Institute of Geological Sciences, Universität Bern,
Freiestrasse 3, CH–3012 Bern, Switzerland

Victor N. YAKOVENCHUK

Geological Institute, Kola Science Center, Russian Academy of Sciences, 14 Fersman Str.,
Apatity 184200, Murmansk Region, Russia

Abstract

The crystal structure of krivovichevite, $Pb_3[Al(OH)_6](SO_4)(OH)$, a new mineral species from hydrothermal deposits of the Mt. Lepkhe–Nelm, Lovozero alkaline massif, Kola Peninsula, in Russia, has been solved from single-crystal X-ray-diffraction data by direct methods and refined to $R_1 = 0.034$ for 681 unique reflections with $|F_o| \geq 4\sigma_F$. The mineral is acentric trigonal, space group $R3c$, a 7.742(2), c 32.082(9) Å, V 1665.2(7) Å^3, $Z = 6$. The structure of krivovichevite contains one symmetrically unique Pb position coordinated by four OH groups and three O atoms. The coordination of the Pb^{2+} cation is highly asymmetrical owing to the localized $6s^2$ lone pairs of electrons. On one side, the Pb^{2+} cation is coordinated by three OH groups that form rather short Pb^{2+}–OH bonds (2.28–2.50 Å). The resulting $Pb(OH)_3$ configuration is complemented by one intermediate Pb^{2+}–O4 bond (2.76 Å) and three longer Pb^{2+}–φ bonds (φ: O, OH; 2.81–3.03 Å). There is one Al^{3+} cation in the structure, coordinated by six OH groups to form isolated $Al(OH)_6^{3-}$ octahedra. One symmetrically independent S^{6+} cation is coordinated by four O^{2-} anions to form SO_4^{2-} sulfate tetrahedra. The structure of krivovichevite is based upon layers of Pb^{2+} cations and OH^- groups (**A**) separated by layers of $Al(OH)_6^{3-}$ octahedra and SO_4^{2-} tetrahedra (**B**). The **A** layer is a hexagonal array of Pb consisting of Pb_3 triangles, with every sixth triangle centered by the OH^- group. The sheets are stacked in the sequence ...**ABAB**... The stacking sequence of the Pb sheets corresponds to a hexagonal close-packing sequence …*ababab*..., whereas the stacking sequence of the Al sulfate sheets is that of a cubic close-packing sequence ...*abcabc*... Combination of these two stacking sequence leads to the 12-layer sequence ...$\mathbf{A}^a\mathbf{B}^a\mathbf{A}^b\mathbf{B}^b\mathbf{A}^a\mathbf{B}^c\mathbf{A}^b\mathbf{B}^a\mathbf{A}^a\mathbf{B}^b\mathbf{A}^b\mathbf{B}^c$..., where $\mathbf{M}^n$ ($\mathbf{M} = \mathbf{A}, \mathbf{B}$; $n = a, b, c$) corresponds to the **M** sheet in the *n* position. It seems likely that krivovichevite represents a metastable ephemeral phase that forms in the early stages of oxidation of galena prior to a transformation to stable plumbojarosite–hinsdalite-like phases.

Keywords: krivovichevite, Kola Peninsula, crystal structure, lead, sulfate, galena oxidation.

Sommaire

Nous avons résolu la structure cristalline de la krivovichevite, $Pb_3[Al(OH)_6](SO_4)(OH)$, nouvelle espèce minérale provenant des zones hydrothermalement altérées au mont Lepkhe–Nelm, complexe alcalin de Lovozero, péninsule de Kola, en Russie, à partir de données prélevées sur monocristal par méthodes directes, et nous l'avons affinée jusqu'à un résidu R_1 de 0.034 en utilisant 681 réflexions uniques ayant $|F_o| \geq 4\sigma_F$. Le minéral est acentrique trigonal, groupe spatial $R3c$, a 7.742(2), c 32.082(9) Å, V 1665.2(7) Å^3, $Z = 6$. La structure de la krivovichevite contient une position de Pb symétriquement unique, coordonnée par quatre groupes OH et trois atomes d'oxygène. La coordinence du cation Pb^{2+} est fortement assymétrique à cause de l'emplacement des paires d'électrons $6s^2$ isolés. D'un côté, le cation Pb^{2+} est coordonné par trois groupes OH qui forment des liaisons Pb^{2+}–OH plutôt courtes (2.28–2.50 Å). A la configuration $Pb(OH)_3$ qui en résulte s'ajoutent une liaison Pb^{2+}–O4 de longueur intermédiaire (2.76 Å) et trois liaisons Pb^{2+}–φ plus longues (φ: O, OH; 2.81–3.03 Å). Il y a un cation Al^{3+} dans la structure, en coordinence avec six groupes OH pour former des octaèdres $Al(OH)_6^{3-}$ isolés. Un cation S^{6+} symétriquement indépendant est coordonné par quatre anions O^{2-} pour donner des tétraèdres SO_4^{2-}. La structure de la krivovichevite est fondée sur des couches de cations Pb^{2+} et de groupes OH^- (**A**) intercalées avec des couches d'octaèdres $Al(OH)_6^{3-}$ et de tétraèdres SO_4^{2-} (**B**). La couche

---

[§] *E-mail address*: skrivovi@mail.ru

A définit un agencement hexagonal d'atomes Pb en triangles Pb_3, chaque sixième triangle ayant au centre un groupe OH^-. Les feuillets sont empilés dans une séquence ...**ABAB**... La séquence d'empilement des feuillets Pb correspond à une séquence à serrage compact hexagonal ...*ababab*..., tandis que la séquence d'empilement les feuillets à sulfate de Al est celle d'un serrage compact cubique ...*abcabc*... La combinaison de ces deux séquences d'empilement mène à une séquence de douze couches ...$\mathbf{A}^a\mathbf{B}^a\mathbf{A}^b\mathbf{B}^b\mathbf{A}^a\mathbf{B}^c\mathbf{A}^b\mathbf{B}^a\mathbf{A}^a\mathbf{B}^b\mathbf{A}^b\mathbf{B}^c$..., dans laquelle $\mathbf{M}^n$ (**M** = **A**, **B**; *n* = *a*, *b*, *c*) correspond à un feuillet **M** dans la position *n*. La krivovichevite représenterait une phase éphémère métastable typique des stades précoces de l'oxydation de la galène et de sa transformation à un assemblage stable de phases de type plumbojarosite–hinsdalite.

(Traduit par la Rédaction)

Mots-clés: krivovichevite, péninsule de Kola, structure cristalline, plomb, sulfate, oxydation de la galène.

INTRODUCTION

Krivovichevite, $Pb_3[Al(OH)_6](SO_4)(OH)$ (IMA 2004–053), is a new mineral species recently described by Yakovenchuk *et al.* (2007) from hydrothermal deposits of the Mt. Lepkhe – Nelm, Lovozero alkaline massif, Kola Peninsula, Russia. Krivovichevite was found in close association with anglesite, cerussite, hydrocerussite and lanarkite, and, along with these minerals, is a result of the secondary alteration of galena. Its chemical composition was determined with an electron microprobe as: PbO 76.49, CaO 0.02, Al_2O_3 5.38, SO_3 9.27 wt.%. The H_2O content, 7.20 wt.%, was obtained using the Penfield method, for a total of 98.36 wt.%. The empirical formula, calculated on the basis of Pb + Ca + Al + S = 5 *apfu*, is $Pb_{3.04}Al_{0.94}(S_{1.03}O_{3.98})(OH)_{7.08}$. The aim of this paper is to report the crystal structure of krivovichevite and to comment on the possible role of this phase in the process of alteration of galena.

EXPERIMENTAL

The crystal of krivovichevite from the holotype specimen described by Yakovenchuk *et al.* (2007) was mounted on a Bruker three-circle X-ray diffractometer operating at 50 kV and 40 mA and equipped with an SMART 1K CCD area detector. More than one hemisphere of data was collected using monochromatic Mo$K\alpha$ radiation, with frame widths of 0.3° in ω, and with a 60 s count for each frame. The unit-cell parameters (Table 1) were refined using least-squares techniques. The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. The absorption correction was done by a semi-empirical pseudo-y-scan method by modeling the crystal as an ellipsoid.

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR KRIVOVICHEVITE

a (Å)	7.742(2)	D_{calc} (g/cm³)	5.17
c (Å)	32.082(9)	Crystal size (mm)	0.22 × 0.04 × 0.01
V (Å³)	1665.2(7)		
Space group	*R*3*c*	F_{000}	2220
μ (cm⁻¹)	456.97	Z	6
		Radiation	Mo*K*α
Total Reflections	2855	Unique Reflections	740
Unique $\lvert F_o\rvert > 4\sigma_F$	681	*p*	53
Flack parameter *x*	-0.023(31)	R_1	0.034
wR_2	0.083	S	0.472

Note: $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2) / 3$; $S = \{\Sigma[w(F_o^2 - F_c^2)] / (n - p)\}^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

The Bruker SHELXTL Version 5 system of programs was used for determination and refinement of the crystal structure. The structure was solved by direct methods and refined to an R_1 value of 0.034, calculated for the 681 unique observed ($|F_o| \geq 4\sigma_F$) reflections. No indications of racemic twinning were observed. Final coordinates and anisotropic displacement parameters of the atoms are given in Table 2, and selected interatomic distances are listed in Table 3. Table 4 provides a bond-valence analysis calculated using bond-valence parameters of Krivovichev & Brown (2001) for the Pb^{2+}–O bonds and of Brese & O'Keeffe (1991) for other bonds. Calculated and observed structure-factors are available from the Depository of Unpublished Data on the MAC website [document Krivovichevite CM47_153].

RESULTS

Cation coordination

The structure of krivovichevite contains one symmetrically unique Pb position. It is coordinated by four OH groups and three O atoms (Fig. 1a). The coordination of the Pb^{2+} cation is highly asymmetrical owing to the localized $6s^2$ lone-pair electrons. On one side, Pb^{2+} is coordinated by three OH groups that form rather short Pb^{2+}–OH bonds (2.28–2.50 Å). The resulting $Pb(OH)_3$ configuration is complemented by one intermediate Pb^{2+}–O4 bond (2.76 Å) and three longer Pb^{2+}–φ bonds (φ = O, OH; 2.81–3.03 Å). The coordination of Pb may be considered as strongly distorted and in an octahedral configuration. Its core consists of four Pb^{2+}–φ bonds with four φ–Pb^{2+}–φ angles between adjacent bonds in the range of 74–97° (Fig. 1b). This core can be considered as being derived from an ideal octahedral coordination by removing two vertices and bending the φ–Pb^{2+}–φ angle between diametrally opposite Pb^{2+}–φ bonds. The resulting configuration is complemented by three additional longer Pb^{2+}–φ bonds (Fig. 1c). The character of the Pb^{2+} coordination (short Pb^{2+}–φ bonds in one half of the coordination sphere and longer Pb^{2+}–φ bonds in the other) is typical for Pb oxysalts with "additional" O^{2-} and OH^- anions that behave as strong Lewis bases (Li *et al.* 2000, 2001, Krivovichev *et al.* 2001, 2002a, b).

There is one Al^{3+} in the structure, coordinated by six OH groups to form isolated $Al(OH)_6^{3-}$ octahedra. One symmetrically independent S^{6+} is coordinated by four O^{2-} ions to form SO_4^{2-} sulfate tetrahedra with a configuration typical of that observed in other sulfate minerals (Hawthorne *et al.* 2000).

TABLE 2. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN KRIVOVICHEVITE

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	0.31619(9)	0.27974(8)	0.85506(8)	0.0154(3)	0.0168(4)	0.0141(3)	0.0161(4)	0.0012(2)	0.0018(3)	0.0083(3)
Al	0	0	0.9403(3)	0.012(1)	0.012(2)	0.012(2)	0.012(3)	0	0	0.0060(10)
S	⅔	⅓	0.9359(2)	0.014(1)	0.014(2)	0.014(2)	0.015(3)	0	0	0.0071(9)
O1	-0.0221(19)	0.1852(18)	0.9033(4)	0.017(3)	0.024(7)	0.013(6)	0.024(9)	0.005(5)	0.003(6)	0.017(5)
O2	0.0356(18)	-0.1776(18)	0.9761(4)	0.017(3)	0.017(6)	0.017(6)	0.014(8)	0.001(5)	0.000(5)	0.006(5)
O3	0	0	0.8259(7)	0.019(4)	0.017(6)	0.017(6)	0.022(12)	0	0	0.008(3)
O4	⅔	⅓	0.8894(8)	0.021(5)	0.020(6)	0.020(6)	0.024(13)	0	0	0.010(3)
O5	0.5547(18)	0.1231(18)	0.9506(4)	0.017(3)	0.009(5)	0.012(5)	0.026(8)	0.006(5)	-0.002(5)	0.001(4)

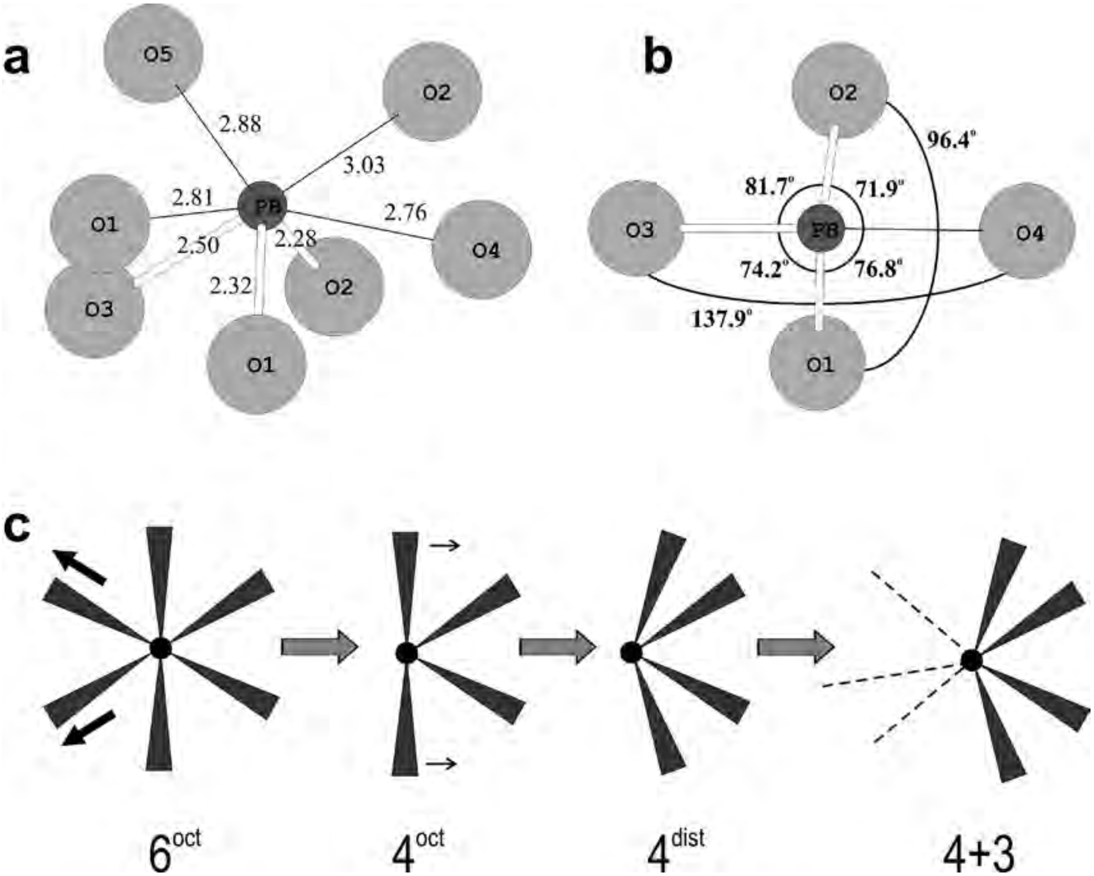

FIG. 1. Coordination of Pb^{2+} cation in the structure of krivovichevite (a), its core consisting of four Pb^{2+}–O bonds (b), and transformation pathway from regular octahedral coordination to irregular (4 + 3) coordination (c).

Bond-valence analysis

Bond-valence sums (Table 4) for most of the atoms are consistent with their expected values. The relatively low bond-valence sum incident upon the O5 site (1.60 valence units, *vu*) can be explained by its participation in hydrogen bonding. We were unable to locate the positions of H atoms in the presence of such a heavy absorber as Pb. However, some details of the hydrogen bonding system can be inferred by inspection of the OH...O distances. Thus, the O5 site has two neighboring OH sites, OH2 and OH1, located at 2.76 and 2.84 Å, respectively. The value of 1.60 *vu* for the O5 bond-valence sum may be explained by acceptance of two relatively strong hydrogen bonds (~0.2 *vu* each).

Description of the structure

The structure of krivovichevite is shown in Figure 2a. Owing to the highly irregular coordination of the Pb^{2+}, a description in terms of Pb-centered coordination polyhedra does not provide a clear interpretation. Thus, we adopt another approach that is based upon subdivision of the structure into layers **A** of heavy Pb^{2+} cations (Fig. 2b) separated by layers **B** of $Al(OH)_6^{3-}$ octahedra and SO_4^{2-} tetrahedra (Fig. 2c). This approach has been employed by Steele *et al.* (1998, 1999) for the description of structures of the $Pb_4(SO_4)(CO_3)_2(OH)_2$ polymorphs susannite, macphersonite, and leadhillite, and by Krivovichev & Burns (2000) for the description of the structures of ”plumbonacrite” and $NaPb_2(OH)(CO_3)_2$.

The **A** layer (Fig. 2b) is a hexagonal array of Pb atoms consisting of Pb_3 triangles with every sixth triangle centered by the OH^- group. Layers of this type have been observed in a number of Pb oxysalt minerals reviewed by Krivovichev & Burns (2000). In most of the structures, the Pb sheets stack along the axis perpendicular to the plane of the sheet to form ordered pseudo-close-packed arrangements. However, in synthetic hydrocerussite (Martinetto *et al.* 2002), the stacking is disordered, as is manifested in local disorder of Pb sites. The typical Pb...Pb interatomic distance in hexagonal Pb sheets is ~5.2 Å. Owing to the presence of tricoordinated OH^- groups in krivovichevite, the sheets are considerably compressed, with an average Pb...Pb distance of 4.49 Å.

In the **B** layer (Fig. 2c) of $Al(OH)_6^{3-}$ octahedra and SO_4^{2-} tetrahedra, both polyhedra have their triangular faces oriented parallel to (001), *i.e.*, to the plane of the sheets. Position of the sulfate tetrahedra is especially noteworthy, as their apical corners are invariably oriented along the same direction of the *c* axis. This uniform orientation accounts clearly for the non-centrosymmetrical character of the structure.

The sheets are stacked in the sequence ...**ABAB**... It is of interest, however, that, if one looks at the stacking sequence of the Pb sheets only, it corresponds to a hexagonal close-packing sequence ...*ababab*..., whereas the stacking sequence of the Al sulfate sheets is that of a cubic close-packing sequence ...*abcabc*... Combination of these two stacking sequence leads to the observed 12-layer sequence ...$\mathbf{A}^a\mathbf{B}^a\mathbf{A}^b\mathbf{B}^b\mathbf{A}^a\mathbf{B}^c\mathbf{A}^b\mathbf{B}^a\mathbf{A}^a\mathbf{B}^b\mathbf{A}^b\mathbf{B}^c$..., where $\mathbf{M}^n$ (**M** = **A**, **B**; *n* = *a*, *b*, *c*) corresponds to the **M** sheet in the *n* position.

DISCUSSION

As krivovichevite is soluble in water (Yakovenchuk *et al.* 2007) and occurs in the rim developed around altered crystals of galena, it can be considered as an intermediate phase that forms during the oxidation of galena. It is well known that galena is unstable under oxidizing conditions and reacts with atmospheric oxygen to form a rind of anglesite around a galena core: $PbS + 2O_2 \rightarrow PbSO_4$. Davies *et al.* (1993) investigated paragenetic sequences that occur upon alteration of galena in soils. The presence of Fe^{3+} in mineral-forming solutions (*e.g.*, due to microbe-mediated dissolution of pyrite) leads to the formation of plumbojarosite, $PbFe_6(SO_4)_4(OH)_{12}$, which is usually not rimmed by the late Pb-bearing phases and is thus considered as a final product of the reaction. Similarly, the presence of Al^{3+} in hydrothermal solutions reacting with galena (*e.g.*, as a result of nepheline or feldspar dissolution) may lead to the formation of a hypothetical phase $PbAl_6(SO_4)_4(OH)_{12}$, which is chemically closely related to krivovichevite, $Pb_3[Al(OH)_6](SO_4)(OH)$. Since krivovichevite contains more Pb than $PbAl_6(SO_4)_4(OH)_{12}$, we suggest that it represents a metastable ephemeral phase that forms at the early stages of galena oxidation before transformation into stable plumbojarosite or hinsdalite-like phases. The **B**

TABLE 3. SELECTED BOND-LENGTHS (Å) IN THE STRUCTURE OF KRIVOVICHEVITE

Pb-OH2	2.28(1)	Al-OH2	1.91(1) 3×
Pb-OH1	2.32(1)	Al-OH1	1.94(1) 3×
Pb-OH3	2.501(9)	<Al-OH>	1.93
Pb-O4	2.76(1)		
Pb-OH1	2.81(1)	S-O5	1.49(1) 3×
Pb-O5	2.89(1)	S-O4	1.49(3)
Pb-OH2	3.03(1)	<S-O>	1.49
<Pb-O>	2.66		

TABLE 4. BOND-VALENCE ANALYSIS FOR KRIVOVICHEVITE

Atom	OH1	OH2	OH3	O4	O5	Σ
Pb	0.48, 0.18	0.52, 0.11	0.33 3×↓	0.20 3×↓	0.15	1.97
Al	0.46 3×→	0.49 3×→				2.87
S				1.45	1.45 3×→	5.80
Σ	1.12	1.12	0.99	2.04	1.60	

Bond-valence sums are expressed in valence units (*vu*).

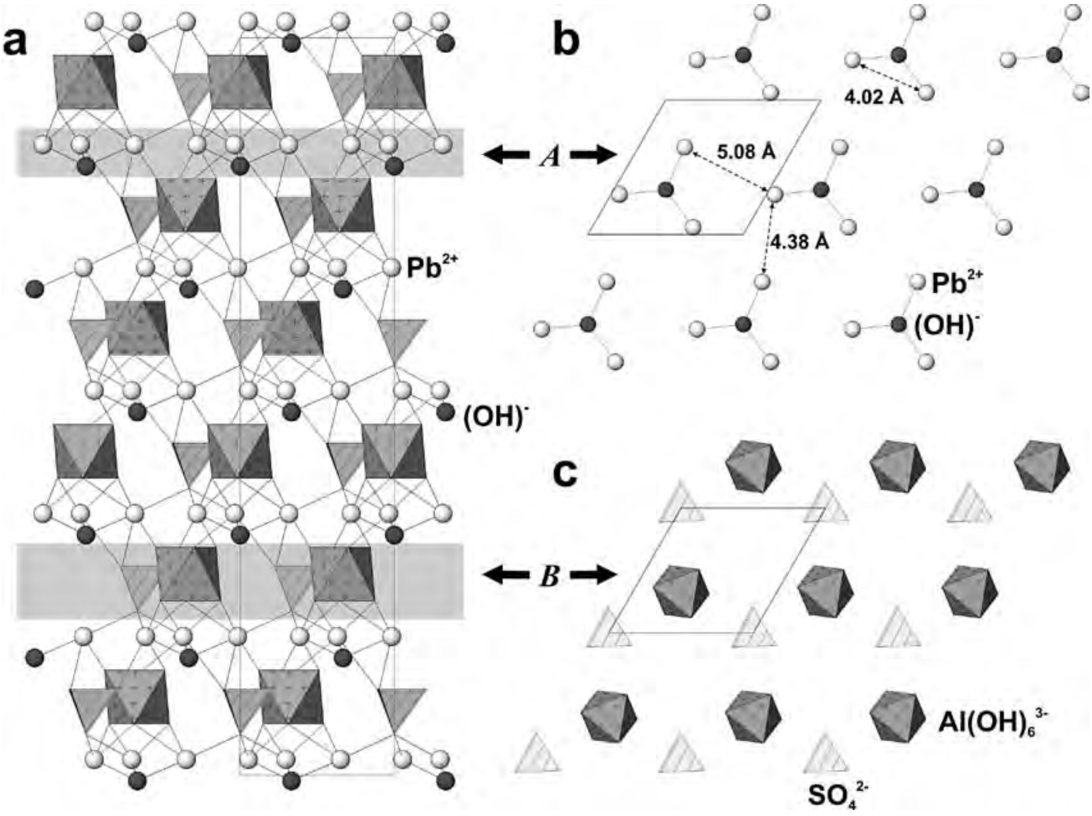

FIG. 2. The crystal structure of krivovichevite projected along the *a* axis (a), consisting of layers **A** of Pb^{2+} cations and (OH)$^-$ groups (b), and layers **B** of Al(OH)$_6^{3-}$ octahedra and SO$_4^{2-}$ tetrahedra (c).

layers in the structure, consisting of the Al(OH)$_6^{3-}$ octahedra and SO$_4^{2-}$ tetrahedra, provide necessary structural elements for condensation of hexagonal sheets of octahedra and tetrahedra typical of jarosite- and alunite-type minerals (Hawthorne *et al.* 2000).

ACKNOWLEDGEMENTS

We are grateful to P.A. Williams and Stuart Mills for their comments on the manuscript, and Robert F. Martin for language corrections. This work was supported by the Russian Federation Ministry of Science and Education through the grant RNP 2.1.1.3077.

REFERENCES

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.

DAVIES, A., DREXLER, J.W., RUBY, M.V. & NICHOLSON, A. (1993): Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. *Environ. Sci. Technol.* **27**, 1415-1425.

HAWTHORNE, F.C., KRIVOVICHEV, S.V. & BURNS, P.C. (2000): The crystal chemistry of sulfate minerals. *In* Sulfate Minerals – Crystallography, Geochemistry, and Environmental Significance (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 1-112.

KRIVOVICHEV, S.V. & BROWN, I.D. (2001): Are the compressive effects of encapsulation an artifact of the bond valence parameters? *Z. Kristallogr.* **216**, 245-247.

KRIVOVICHEV, S.V. & BURNS, P.C. (2000): Crystal chemistry of basic lead carbonates. III. Crystal structures of $Pb_3O_2(CO_3)$ and $NaPb_2(OH)(CO_3)_2$. *Mineral. Mag.* **64**, 1077-1087.

KRIVOVICHEV, S.V. & BURNS, P.C. (2001): Crystal chemistry of lead oxide chlorides. I. Crystal structures of synthetic mendipite, $Pb_3O_2Cl_2$, and synthetic damaraite, $Pb_3O_2(OH)Cl$. *Eur. J. Mineral.* **13**, 801-809.

KRIVOVICHEV, S.V. & BURNS, P.C. (2002a): Crystal chemistry of lead oxide chlorides. II. Crystal structure of $Pb_7O_4(OH)_4Cl_2$. *Eur. J. Mineral.* **14**, 135-139.

KRIVOVICHEV, S.V. & BURNS, P.C. (2002b): Crystal structure of $Pb_{10}O_7(OH)_2F_2(SO_4)$ and crystal chemistry of lead oxysulfate minerals and inorganic compounds. *Z. Kristallogr.* **217**, 451-459.

LI, YAPING, KRIVOVICHEV, S.V. & BURNS, P.C. (2000): Crystal chemistry of lead oxide hydroxide nitrates. I. The crystal structure of $[Pb_6O_4](OH)(NO_3)(CO_3)$. *J. Solid State Chem.* **153**, 365-370.

LI, YAPING, KRIVOVICHEV, S.V. & BURNS, P.C. (2001): Crystal chemistry of lead oxide hydroxide nitrates. II. The crystal structure of $[Pb_{13}O_8](OH)_6(NO_3)_4$. *J. Solid State Chem.* **158**, 74-77.

MARTINETTO, P., ANNE, M., DOORYHÉE, E., WALTER, P. & TSOUCARIS, G. (2002): Synthetic hydrocerussite, $2(PbCO_3)•(Pb(OH)_2)$, by X-ray powder diffraction. *Acta Crystallogr.* **C58**, i82-i84.

STEELE, I.M., PLUTH, J.J. & LIVINGSTONE, A. (1998): Crystal structure of macphersonite ($Pb_4SO_4(CO_3)_2(OH)_2$): comparison with leadhillite. *Mineral. Mag.* **62**, 451-459.

STEELE, I.M., PLUTH, J.J. & LIVINGSTONE, A. (1999): Crystal structure of susannite, $Pb_4SO_4(CO_3)_2(OH)_2$: a trimorph with macphersonite and leadhillite. *Eur. J. Mineral.* **11**, 493-499.

YAKOVENCHUK, V.N., PAKHOMOVSKY, YA.A., MEN'SHIKOV, YU.P., MIKHAILOVA, J.A., IVANYUK, G.YU. & ZALKIND, O.A. (2007): Krivovichevite, $Pb_3[Al(OH)_6](SO_4)(OH)$, a new mineral species from the Lovozero alkaline massif, Kola Peninsula, Russia. *Can. Mineral.* **45**, 451-456.

Received August 20, 2008, revised manuscript accepted January 26, 2009.