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One-dimensional lone electron pair micelles in the crystal structure of $Pb_5(SiO_4)(VO_4)_2$

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Abstract

The structure of $Pb_5(SiO_4)(VO_4)_2$ (hexagonal, $P6_3/m$, $a = 9.9865(11)$, $c = 7.3599(12)$ Å, $V = 635.67(14)$ Å^3, $Z = 2$) has been solved by direct methods and refined to $R_1 = 0.051$ on the basis of 440 unique observed reflections with $|F_o| \geq 4\sigma_F$. The compound belongs to the apatite structure type. The Pb coordination polyhedra are distorted due to the presence of stereoactive lone electron pairs Ψ. The structure contains channels running along the c axis and centered at $(00z)$. The channels are most probably occupied by the lone electron pairs of the Pb^{2+} cations and thus represent lone electron pair micelles. The existence of such micelles in the structure may well be the reason for the electrogyratory effect and protonic conductivity observed in crystals of the title compound.
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1. Introduction

The apatite-related compounds $Pb_5(GeO_4)(VO_4)_2$ and $Pb_5(SiO_4)(VO_4)_2$ have received considerable attention due to their interesting physical properties such as electrogyratory effect (crystals of these compounds become optically active when the applied electric field and the light beam are along the optical axis) [1–5] and protonic conductivity [6]. The former effect was suggested to be used in electrogyratory communication devices where information is transmitted by a modulated laser beam [7]. Both compounds were first reported in 1957 by Merker and Wondratschek [8] and were

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subsequently studied by other authors using different techniques [9–11]. The structure of $Pb_5(GeO_4)(VO_4)_2$ was studied by Ivanov and Zavodnik [12] and Ivanov [13] using X-ray single-crystal and powder diffraction methods, respectively, whereas the structure of $Pb_5(SiO_4)(VO_4)_2$ has never been reported.

The aim of this work is to describe results of a single-crystal X-ray diffraction study of $Pb_5(SiO_4)(VO_4)_2$ and to discuss some interesting aspects of its crystal structure.

2. Experimental

2.1. Synthesis

The crystals of $Pb_5(SiO_4)(VO_4)_2$ were synthesized from a stoichiometric mixture of PbO, SiO_2 and V_2O_5. The mixture was placed into *a* platinum crucible and heated to 940 °C. After 14 h of heating at this temperature, the oven was turned off and was allowed to cool overnight. As a product of the synthesis, transparent elongated yellow crystals of $Pb_5(SiO_4)(VO_4)_2$ were recovered.

2.2. Single-crystal X-ray diffraction study

A crystal selected for data collection was mounted on a Bruker PLATFORM goniometer equipped with an 1 K SMART CCD detector with a crystal-to-detector distance of 5.4 cm. The data were collected using Mo Kα X-radiation and frame widths of 0.3° in ω, with 30 s used to acquire each frame. More than a hemisphere of three-dimensional data was collected. The unit-cell dimensions were

Table 1
Crystallographic data and refinement parameters for $Pb_5(SiO_4)(VO_4)_2$

a (Å)	9.9865(11)
c (Å)	7.3599(12)
V (Å^3)	635.67(14)
Space group	$P6_3/m$
$F_{0\,0\,0}$	1132
Z	2
μ (cm^{-1})	675.20
D_{calc} (g/cm^3)	7.095
Crystal size (mm)	$0.24 \times 0.12 \times 0.12$
Radiation	Mo Kα
Total ref.	3654
$2\theta_{max}$	56.02
Unique ref.	534
Unique $|F_o| \geq 4\sigma_F$	440
R_1	0.051
wR_2	0.144

Note: $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\sum[w(F_o^2 - F_c^2)/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

Table 2
Atomic coordinates and displacement parameters ($\mathring{A}^2$) for $Pb_5(SiO_4)(VO_4)_2$

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	0.00092(11)	0.74940(12)	1/4	0.0302(5)	0.0253(7)	0.0185(7)	0.0526(9)	0	0	0.0153(5)
Pb(2)	1/3	2/3	−0.00731(12)	0.0227(5)	0.0266(6)	0.0266(6)	0.0151(7)	0	0	0.0133(3)
T^*	0.3797(5)	0.9840(5)	1/4	0.013(1)	0.015(2)	0.008(2)	0.013(2)	0	0	0.004(2)
O(1)	0.5005(18)	0.9072(21)	1/4	0.029(4)	0.016(9)	0.028(10)	0.042(11)	0	0	0.012(8)
O(2)	0.2655(14)	0.9166(13)	0.0697(15)	0.026(3)	0.028(7)	0.011(6)	0.022(5)	0.006(5)	−0.005(5)	−0.003(5)
O(3)	0.4862(20)	0.1810(18)	1/4	0.021(4)	0.031(10)	0.007(7)	0.019(7)	0	0	0.006(7)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
  * Occupancy of the T site: $V_{0.67}Si_{0.33}$.

refined on the basis of 564 reflections. The data were reduced using the Bruker program SAINT. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied, and the data were corrected for Lorentz, polarization, and background effects. A total of 3654 intensities was measured; there were 534 unique reflections with 440 classified as observed ($F_o \geq 4\sigma F_o$). Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from [14]. The Bruker SHELXTL Version 5.1 system of programs was used for the structure solution and refinement. The structure was solved by direct methods in the space group $P6_3/m$ and refined to an agreement index (R_1) of 0.051, calculated for the unique observed reflections, and a goodness-of-fit (S) of 1.133. The maximal electron density residuals (2.10–3.92 e/$\mathring{A}^3$) were close to Pb sites (~1 Å). The occupancy of the V/Si site was found close to the V:Si = 2:1 ratio and in the final refinement was fixed at this ratio. Further details pertinent to data collection and structure refinement are given in Table 1. The final atomic parameters are listed in Table 2, selected interatomic distances are in Table 3. Table of observed and calculated structure factors may be obtained from the authors upon request.

Table 3
Selected bond lengths (Å) in the structure of $PB_5(SiO_4)(VO_4)_2$

Pb(1)– O(1)	2.17(2)
Pb(1)– O(2)	2.53(1) 2×
Pb(1)– O(2)	2.67(1) 2×
Pb(1)– O(3)	2.77(2)
<Pb(1)–O>	2.56
Pb(2)–O(3)	2.45(1) 3×
Pb(2)–O(1)	2.85(1) 3×
Pb(2)–O(2)	2.95(1) 3×
<Pb(2)–O>	2.75
T–O(2)	1.66(1) 2×
T–O(3)	1.71(2)
T–O(1)	1.72(2)
<T–O>	1.69

3. Results

3.1. Cation coordination

There are two symmetrically non-equivalent Pb sites in the structure of $Pb_5(SiO_4)(VO_4)_2$. The Pb(1) site is coordinated by six O atoms arranged at the vertices of a pentagonal pyramid (Fig. 1a). The apical Pb(1)–O(1) bond is very short (2.17 Å), whereas five equatorial bonds are longer (2.53–2.77 Å). The coordination is very distorted which is undoubtedly a consequence of the stereoactivity of a $6s^2$ lone electron pair (Ψ) on the Pb^{2+} cation. The lone electron pair Ψ is located on the opposite side of the short Pb(1)–O(1) bond. The Pb(2) site is more symmetric but still possesses a distorted coordination. Three relatively short Pb(2)–O(3) bonds (2.45 Å) are arranged in such a way that a $Pb(2)O_3$ trigonal pyramid is formed with three equal O(3)–Pb(2)–O(3) valence angles of 72.8°. The Pb(2)O3 configuration is complemented by six long Pb(2)–O bonds (2.85–2.95 Å). In contrast to the Pb(1) site, the Pb(2) site does not have an obvious gap in its coordination sphere.

The only tetrahedral T position in the structure is occupied by V and Si with the V:Si ratio of 2:1. As a consequence, the average <T–O> bond length (1.69 Å) is longer than the typical Si^{4+}–O bond (1.624 Å [15]) but shorter than the typical V^{5+}–O bond (1.718 Å [15]).

3.2. Bond-valence analysis

The bond-valence analysis was calculated using the equation

$$v_{ij} = \exp\left(\frac{R_{ij} - d_{ij}}{b}\right),$$

where d_{ij} and v_{ij} are a bond length and a bond valence, respectively. R_{ij} and b are empirical parameters taken for Pb^{2+}–O bonds from [16], and for V^{5+}–O, Si^{4+}–O bonds from [17]. Since the T site is simultaneously occupied by V and Si, we have used for this site an R_{ij} value of 1.743 Å which was calculated as $(2 \times 1.803 + 1.624)/3$ where 1.803 and 1.624 are R_{ij} values for V^{5+}–O and Si^{4+}–O bonds, respectively.
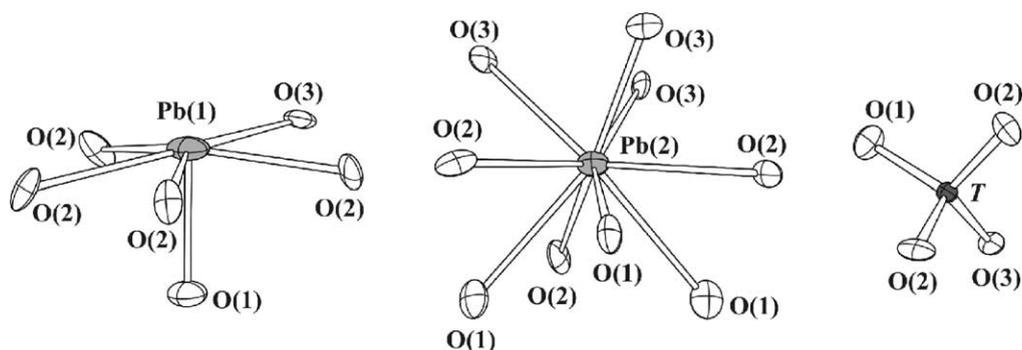

Fig. 1. Coordination of cations in the structure of $Pb_5(SiO_4)(VO_4)_2$.
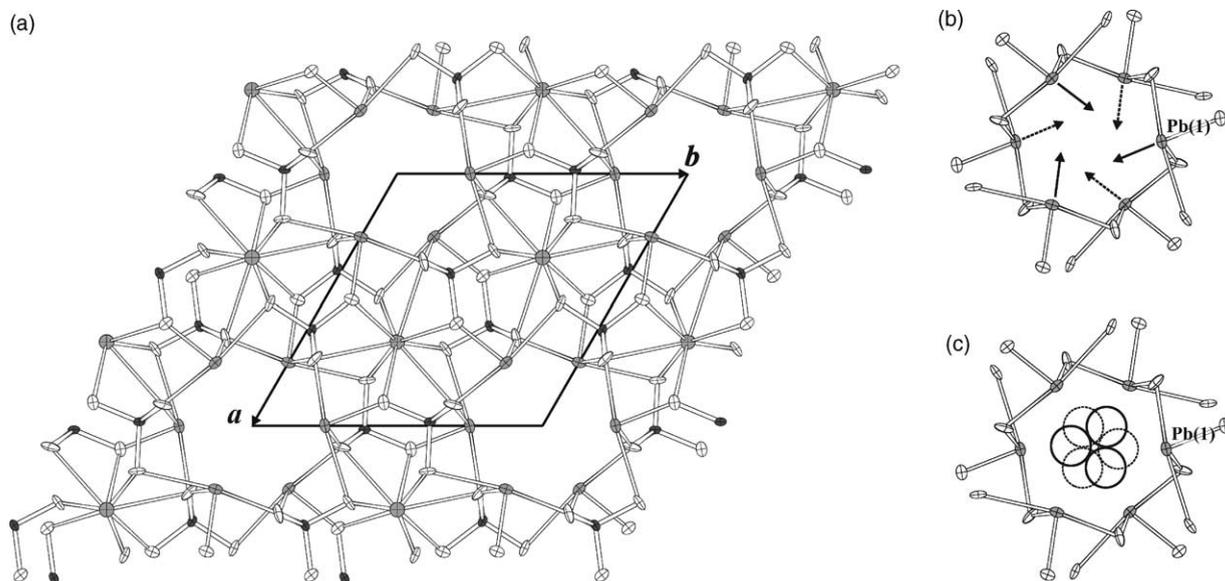
Fig. 2. The structure of $Pb_5(SiO_4)(VO_4)_2$ projected along the c axis (a), the arrangement of Pb(1) cations around the channel with the arrows showing approximate directions of the Pb-Ψ vectors (b), and imaginary packing of lone electron pairs represented as spheres in the channel (c). Dashed arrows and circles are at $z = 0.25$, single arrows and circles are at $z = 0.75$.

The obtained bond-valence sums are 1.95, 2.00, 4.66, 2.04, 2.03 and 2.02 valence units (v.u.) for the Pb(1), Pb(2), T, O(1), O(2) and O(3) sites, respectively. These values are in good agreement with the expected valences of these sites.

3.3. Structure description and discussion

The structure of $Pb_5(SiO_4)(VO_4)_2$ (Fig. 2) is isostructural with $Pb_5(GeO_4)(VO_4)_2$. It belongs to the apatite structure type, but differs from the classic apatite (e.g., $Ca_5(PO_4)_3OH$) in two aspects: (1) The Pb coordination polyhedra are distorted due to the presence of stereoactive lone electron pairs Ψ. (2) The structure channels which are occupied in apatites by halogen ions (and sometimes OH^- or O^{2-} anions [18]) are empty. These channels run parallel to the c axis and are centered at $00z$. The walls of these channels are "decorated" by the Pb(1) atoms (Fig. 2) located at $z = 1/4$ or $3/4$. If one chooses the Pb-Ψ direction as opposite to the short Pb(1) bond, the Pb(1)-Ψ vectors are oriented as shown in Fig. 2b. It is noteworthy that the Pb(1)-Ψ vectors do not intersect in one point. This is in agreement with the suggestion that the stereoactive lone electron pairs Ψ occupy a space region approximately equal to the volume of a O^{2-} ion (i.e. 15–20 Å^3) [19]. In order to pack as densely as possible, they would form triangular arrangements as shown in Fig. 2c. Indeed, with this arrangement, the Pb(1)-Ψ vectors do not intersect at the center of the channel. In normal apatite structures, the channels are usually occupied by anions. However, in $Pb_5(SiO_4)(VO_4)_2$, these channels are empty and thus provide space for the lone electron pairs of the Pb^{2+} cations. Such arrangements are typical for the structures of compounds with stereoactive lone electron pair cations and the corresponding spaces have been called lone pair micelles [20]. Such micelles may have different size and dimensionality and their major role is the accommodation of lone electron pairs in certain regions of the structure.

It is tempting to relate the existence of one-dimensional lone electron pair micelles in the structure of $Pb_5(SiO_4)(VO_4)_2$ with its interesting physical properties. The micelle has the shape of a channel running along the c axis. This direction coincides with the optical axis of the compound. Application of an external electric field and guiding light along this direction is imposed to cause a certain, yet unknown, effect on the electrons within the channels which then results in an electrogyratory effect actually observed in crystals of $Pb_5(SiO_4)(VO_4)_2$. The existence of channels and lone pair micelles may also favor migration of protons along the c axis thus proposing a possible explanation for the protonic conductivity of this compound [6].

Acknowledgements

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