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**Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>: LEAD ALUMINOSILICATE  
WITH THE NARSARSUKITE-RELATED STRUCTURE**

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Received October 2, 2020; Revised October 5, 2020; Accepted October 7, 2020

The crystal structure of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> (orthorhombic, *Fddd*, *a* = 16.2940(17), *b* = 21.666(2), *c* = 22.655(2) Å, *V* = 7997.8(13) Å<sup>3</sup>, *Z* = 8) had been solved by direct methods and refined to *R*<sub>1</sub> = 0.042 on the basis of 1393 unique observed reflections. The crystal structure of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> contains three symmetrically independent Pb atoms, each having distorted coordination environment due to the stereoactivity of the 6s<sup>2</sup> lone electron pair. There are four tetrahedrally coordinated sites in the structure, *T*<sub>1</sub>–*T*<sub>4</sub>, with the average ⟨*T*–O⟩ bond lengths varying from 1.66 to 1.69 Å. The site occupancies for these sites were assigned to Si<sub>0.5</sub>Al<sub>0.5</sub>. There is one additional Al site that has the fivefold trigonal bipyramidal (TBP) coordination with the O9 site half-occupied. The crystal structure is based upon tubular tetrahedral chains, [*T*<sub>4</sub>O<sub>10</sub>], parallel to the *a* axis and linked into a three-dimensional framework via Pb atoms and dimers of corner-sharing AlO<sub>5</sub> trigonal bipyramids located in between the chains. The comparison between the experimental X-ray powder diffraction pattern for Pb<sub>4</sub>Al<sub>4</sub>Si<sub>3</sub>O<sub>16</sub> (ICDD PDF #32-0505) and theoretical one calculated on the basis of the crystal-structure data shows remarkable similarities, which provides strong evidence in favor of the identity of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> with the “Pb<sub>4</sub>Al<sub>4</sub>Si<sub>3</sub>O<sub>16</sub>” compound reported previously. The crystal-chemical formula of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> can be written as Pb<sub>10</sub>Al<sub>2</sub>O[(Si<sub>2</sub>Al<sub>2</sub>)O<sub>10</sub>]<sub>4</sub> that emphasizes the composition of the tetrahedral chains with disordered distribution of Si and Al over tetrahedral sites. The structure type of the title compound is new for inorganic compounds and may be viewed as a hybrid of the structure types of Pb<sub>6</sub>O[(Si<sub>6</sub>Al<sub>2</sub>)O<sub>20</sub>] and narsarsukite. The unit cell of the title compound corresponds to the 2 × 2 × 2 (eightfold) supercell relative to both narsarsukite and Pb<sub>6</sub>O[(Si<sub>6</sub>Al<sub>2</sub>)O<sub>20</sub>]. The information-based structural complexity parameters are higher than those of the parent structure types with the total structural information per cell (590.100 bits) about 6.2–6.5 times larger.

*Keywords:* aluminosilicate, lead, crystal structure, narsarsukite, superstructure, structural complexity

**DOI:** 10.31857/S0869605520060052

## 1. INTRODUCTION

Lead aluminosilicates represent technologically and mineralogically important group of mineral phases that occur in complex sinters and slugs produced during lead and zinc smelting and are considered as possible matrices for immobilization of Pb (Lu, Shih, 2011, 2012, 2015; Lu et al., 2013; Yang et al., 2020). The “Pb<sub>4</sub>Al<sub>4</sub>Si<sub>3</sub>O<sub>16</sub>” phase was found on Roman coins of the III–IVth centuries, where it most probably formed as a constituent of the patinas the patinas (Mata et al., 2010). Only one Pb aluminosilicate mineral without additional cations (except for H) or anions is known to date, rongibbsite, Pb<sub>2</sub>(Si<sub>4</sub>Al)O<sub>11</sub>(OH), that is based upon a zeolite-like microporous interrupted tetrahedral framework (Yang et al., 2013).

The PbO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system was first investigated by Geller and Bunting (1943), who reported formation in this system of three ternary compounds: Pb<sub>8</sub>Al<sub>2</sub>Si<sub>4</sub>O<sub>19</sub>, Pb<sub>4</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>11</sub>, and Pb<sub>6</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>21</sub>. The existence of these compounds was confirmed by Mylynych et al. (1999) during their studies of crystallization of Pb-containing aluminosilicate glasses. Haensel et al. (1976) described another ternary compound, Pb<sub>4</sub>Al<sub>4</sub>Si<sub>3</sub>O<sub>16</sub>, and reported its X-ray diffraction pattern (ICDD PDF #32-0505). In the detailed study of phase equilibria in the PbO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system, Chen et al. (2001) found eleven different ternary crystalline phases: Pb<sub>8</sub>Al<sub>2</sub>Si<sub>4</sub>O<sub>19</sub>, Pb<sub>4</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>11</sub>, Pb<sub>6</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>21</sub>, Pb<sub>4</sub>Al<sub>4</sub>Si<sub>3</sub>O<sub>16</sub>, PbAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, Pb<sub>3</sub>Al<sub>10</sub>SiO<sub>20</sub>, Pb<sub>4</sub>Al<sub>4</sub>SiO<sub>12</sub>, Pb<sub>4</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>20</sub>, Pb<sub>5</sub>Al<sub>2</sub>Si<sub>10</sub>O<sub>28</sub>, Pb<sub>12</sub>Al<sub>2</sub>Si<sub>17</sub>O<sub>49</sub>, and Pb<sub>12</sub>Al<sub>2</sub>Si<sub>20</sub>O<sub>55</sub>. Dörsam et al. (2008) reported the high-pressure and high-temperature (2 GPa, 650 °C) hydrothermal synthesis of Pb<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>9</sub> that was described as an Al analogue of kentrolite, Pb<sub>2</sub>Mn<sub>2</sub>Si<sub>2</sub>O<sub>9</sub>, and melanotekite, Pb<sub>2</sub>Fe<sub>2</sub>Si<sub>2</sub>O<sub>9</sub>. The high-pressure phase Pb<sub>0.8</sub>Al<sub>1.6</sub>Si<sub>2.4</sub>O<sub>8</sub> with a hollandite-type structure was studied by Downs et al. (1995).

However, despite such a rich and outstanding chemical diversity of Pb aluminosilicates, the crystal-structures are known for four of them only: PbAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> (the Pb analogue of feldspar; Benna et al., 1996, 1999; Tribaudino et al., 1998; Curetti et al., 2015), Pb<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>9</sub> (Dörsam et al., 2008), Pb<sub>6</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>21</sub> (Siidra et al., 2009), and Pb<sub>0.8</sub>Al<sub>1.6</sub>Si<sub>2.4</sub>O<sub>8</sub> (Downs et al., 1995).

Herein we report on the crystal structure of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>, a lead aluminosilicate, which is most probably identical to the phase previously reported as Pb<sub>4</sub>Al<sub>4</sub>Si<sub>3</sub>O<sub>16</sub>.

## 2. EXPERIMENTAL

Several tiny colorless transparent crystals of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> were obtained as a by-product during our experiments in the PbO–SiO<sub>2</sub> system (Siidra et al., 2009). The mixture of PbO and SiO<sub>2</sub> in the 1 : 1 ratio was ground, mixed in an agate mortar and placed into an alumina crucible that was heated to 800 °C and kept at that temperature for 1 hour. The crucible was then cooled to room temperature at the rate of 2.5 °C/min. The main product was a vitreous matrix with few tiny crystals of the title compound grown on the border between the matrix and the crucible walls.

One of the crystals was placed onto a Bruker SMART three-circle diffractometer equipped with an APEX CCD area detector. More than a hemisphere of the diffraction data was collected by using the exposure time of 45 s per frame. The absorption correction was done using the SADABS program. The crystal structure was solved and refined by means of the SHELX program package (Sheldrick et al., 2015). The crystal data and experimental parameters of the X-ray diffraction experiment are given in Table 1, atom coordinates, site-occupancies and displacement parameters are provided in Table 2. Table 3 contains selected interatomic distances for the crystal structure.

## 3. RESULTS

The crystal structure of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> contains three symmetrically independent Pb atoms, each having distorted coordination environment due to the stereoactivity of the 6s<sup>2</sup> lone electron pair. The Pb1 and Pb2 atoms form four Pb–O bonds shorter than 2.5 Å, arranged at the corners of the base of PbO<sub>4</sub> square pyramid with Pb atom at the apical corner (Fig. 1). The similar coordination is observed in the crystal structure of litharge, PbO. However, in the title compound the PbO<sub>4</sub> square pyramid is complemented by four and six long Pb–O bonds (Pb–O > 3.0 Å) for the Pb1 and Pb2 atoms, respectively. The Pb3 atoms is coordinated by three O atoms with the Pb–O bonds shorter than 2.6 Å and seven Pb–O bonds with the bond lengths in the range 2.8–3.2 Å.

There are four tetrahedrally coordinated sites in the structure, T1–T4, with the average ⟨T–O⟩ bond lengths varying from 1.66 to 1.69 Å. These bonds are longer than the ideal Si–O bonds

**Table 1.** Crystal parameters, data collection and structure refinement parameters for  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$   
**Таблица 1.** Кристаллографические данные и экспериментальные параметры для  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$

<b>Crystal Data</b>	
Formula	$\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$
Crystal size, mm	$0.12 \times 0.05 \times 0.02$
Crystal system	Orthorhombic
Space group	<i>Fddd</i>
<i>a</i> , Å	16.2940(17)
<i>b</i> , Å	21.666(2)
<i>c</i> , Å	22.655(2)
<i>V</i> , Å <sup>3</sup>	7997.8(13)
<i>Z</i>	8
<i>D<sub>x</sub></i> , g/cm <sup>3</sup>	5.738
<b>Data Collection</b>	
Instrument	Bruker Smart CCD
Radiation	MoK $\alpha$
2 $\Theta$ range (degrees)	3.6–56.60
Total collected reflections	11933
Unique reflections	2459
Unique observed $ F_o  \geq 4\sigma_F$	1393
<i>R</i> <sub>int</sub>	0.108
<i>hkl</i> range	–17→21; –26→28; –25→30
<b>Refinement</b>	
<i>R</i> <sub>1</sub> ( $ F_o  \geq 4\sigma_F$ )	0.042
<i>wR</i> <sub>2</sub>	0.092
<i>S</i>	0.849

and shorter than the ideal Al–O bonds for Si and Al in tetrahedral coordinations, which points out that the *T1–T4* sites are statistically occupied by Si and Al. In order to fulfill the stoichiometry requirements, the site occupancies for these sites were fixed at  $\text{Si}_{0.5}\text{Al}_{0.5}$ . There is one additional Al site that has a fivefold trigonal bipyramidal (TBP) coordination with the O9 site half-occupied and split over two symmetrically equivalent positions located at 1.56 Å from one another (see below). The TBP coordination is typical for Al (Gorelova et al., 2019).

The crystal structure is based upon tubular tetrahedral chains, [*T*<sub>4</sub>O<sub>10</sub>], running parallel to the *a* axis and formed by *T1–T4* atoms coordinated by O (Fig. 2*a*). The chains have a square section and belong to the family of tubular silicate anions reviewed by Rozhdestvesnkaya and Krivovichev (2011). The chains are linked into framework *via* Pb atoms and dimers of corner-sharing AlO<sub>5</sub> trigonal bipyramids located in between the chains.

**Table 2.** Fractional atomic coordinates, site occupancies ( $Q$ ), and displacement parameters ( $\text{\AA}^2$ ) for Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>  
**Таблица 2.** Координаты атомов, заселенности позиций ( $Q$ ) и параметры смещения атомов ( $\text{\AA}^2$ ) для кристаллической структуры Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>

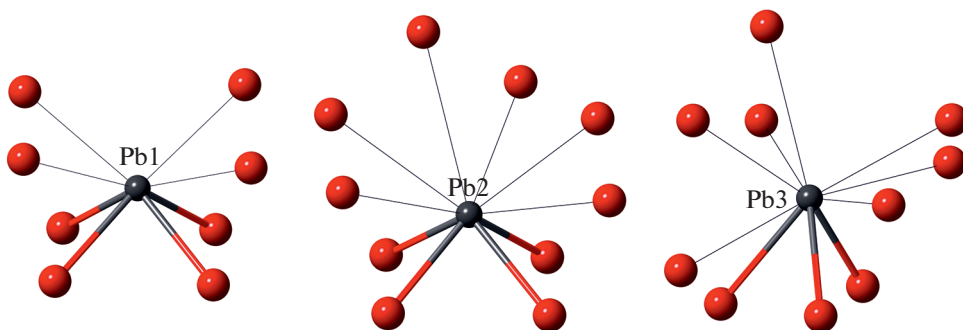
Atom	$Q$	$x$	$y$	$z$	$U_{eq}$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Pb1	Pb	0.12939(4)	0.21467(2)	0.03831(2)	0.01455(17)	0.0171(3)	0.0128(3)	0.0137(3)	0.0025(2)	-0.0009(2)	-0.0003(3)
Pb2	Pb	0.29758(5)	1/8	1/8	0.0161(2)	0.0151(4)	0.0157(4)	0.0176(4)	0.0009(4)	0	0
Pb3	Pb	0.36696(6)	0.28634(4)	0.27293(4)	0.0438(3)	0.0514(6)	0.0372(5)	0.0428(5)	0.0056(3)	-0.0016(4)	-0.0126(5)
T1	Si <sub>0.5</sub> Al <sub>0.5</sub>	0.2661(3)	0.28505(19)	0.1270(2)	0.0176(9)	0.020(2)	0.021(2)	0.012(2)	0.001(3)	-0.0005(19)	-0.0098(17)
T2	Si <sub>0.5</sub> Al <sub>0.5</sub>	0.2709(3)	0.1162(2)	-0.0265(2)	0.0115(11)	0.013(2)	0.011(3)	0.011(2)	0.0010(19)	0.0020(16)	-0.0028(18)
T3	Si <sub>0.5</sub> Al <sub>0.5</sub>	0.0339(3)	0.3879(2)	0.0273(2)	0.0182(13)	0.020(2)	0.015(4)	0.019(2)	0.005(2)	0.0065(19)	0.0023(19)
T4	Si <sub>0.5</sub> Al <sub>0.5</sub>	0.4633(3)	0.26643(19)	0.1258(3)	0.0159(9)	0.024(2)	0.0126(19)	0.011(2)	0.000(2)	0.001(2)	-0.0005(18)
Al	Al	0.4738(5)	3/8	3/8	0.051(3)	0.020(4)	0.034(5)	0.101(8)	0.018(6)	0	0
O1	O	0.2134(6)	0.1226(7)	0.0360(4)	0.018(2)	0.020(5)	0.015(5)	0.021(5)	-0.001(6)	0.006(4)	-0.005(6)
O2	O	0.2137(6)	0.2184(4)	0.1259(5)	0.021(2)	0.021(6)	0.024(6)	0.018(5)	-0.001(6)	0.006(5)	0.000(4)
O3	O	0.2491(8)	0.3197(6)	0.0637(6)	0.032(3)	0.048(9)	0.028(8)	0.019(7)	-0.004(6)	-0.007(6)	-0.002(6)
O4	O	0.4679(8)	0.3649(6)	0.2803(6)	0.042(4)	0.028(7)	0.019(9)	0.079(11)	0.011(7)	0.011(6)	-0.003(6)
O5	O	0.2422(8)	0.1970(6)	0.3125(6)	0.029(3)	0.046(8)	0.019(7)	0.020(7)	-0.007(6)	0.002(6)	0.015(6)
O6	O	0.3679(7)	0.1088(5)	-0.0053(6)	0.030(3)	0.017(6)	0.038(7)	0.036(7)	-0.017(6)	0.007(5)	0.003(5)
O7	O	0.4881(8)	0.2049(7)	0.3142(6)	0.037(4)	0.043(9)	0.030(8)	0.039(9)	0.009(7)	-0.015(6)	0.001(7)
O8	O	0.0206(11)	0.3244(7)	0.0669(7)	0.058(5)	0.098(14)	0.030(9)	0.046(11)	0.027(8)	0.038(9)	0.015(9)
O9	O	3/8	0.3390(14)	3/8	0.022(7)	0.009(14)	0.041(18)	0.016(15)	0	-0.002(14)	0
O10	O	0.4852(18)	0.1913(8)	0.1149(7)	0.126(11)	0.33(3)	0.040(10)	0.008(9)	0.002(7)	0.000(13)	0.065(15)
O11	O	0.3654(9)	0.2714(10)	0.1393(8)	0.092(7)	0.028(9)	0.162(19)	0.084(13)	0.064(13)	-0.004(8)	0.006(10)

**Table 3.** Selected interatomic distances (Å) for  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$   
**Таблица 3.** Избранные межатомные расстояния (Å) для  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$

Pb1–O2	2.416(12)	T1–O3	1.642(14)
Pb1–O1	2.420(14)	T1–O8	1.643(14)
Pb1–O1	2.422(13)	T1–O11	1.668(15)
Pb1–O2	2.467(11)	T1–O2	1.677(10)
Pb1–O8	3.035(15)	⟨T1–O⟩	1.66
Pb1–O5	3.047(13)		
Pb1–O3	3.052(13)	T2–O3	1.658(14)
Pb1–O3	3.133(14)	T2–O6	1.659(12)
⟨Pb1–O⟩	2.75	T2–O5	1.662(13)
		T2–O1	1.702(10)
Pb2–O2	2.442(10) 2x	⟨T2–O⟩	1.67
Pb2–O1	2.439(10) 2x		
Pb2–O6	3.185(12) 2x	T3–O8	1.656(14)
Pb2–O11	3.37(2) 2x	T3–O6	1.678(12)
Pb2–O10	3.38(3) 2x	T3–O4	1.693(14)
⟨Pb2–O⟩	2.96	T3–O7	1.713(15)
		⟨T3–O⟩	1.69
Pb3–O4	2.374(13)		
Pb3–O4	2.553(14)	T4–O11	1.628(16)
Pb3–O9	2.582(13)	T4–O10	1.685(16)
Pb3–O7	2.808(13)	T4–O7	1.693(15)
Pb3–O5	2.947(14)	T4–O5	1.703(13)
Pb3–O10	3.03(2)	⟨T4–O⟩	1.68
Pb3–O11	3.045(19)		
Pb3–O7	3.084(15)	Al–O10	1.600(16) 2x
Pb3–O8	3.14(2)	Al–O9	1.789(15) 2x
Pb3–O6	3.169(11)	Al–O9	2.158(15)
⟨Pb3–O⟩	2.87	⟨Al–O⟩	1.79

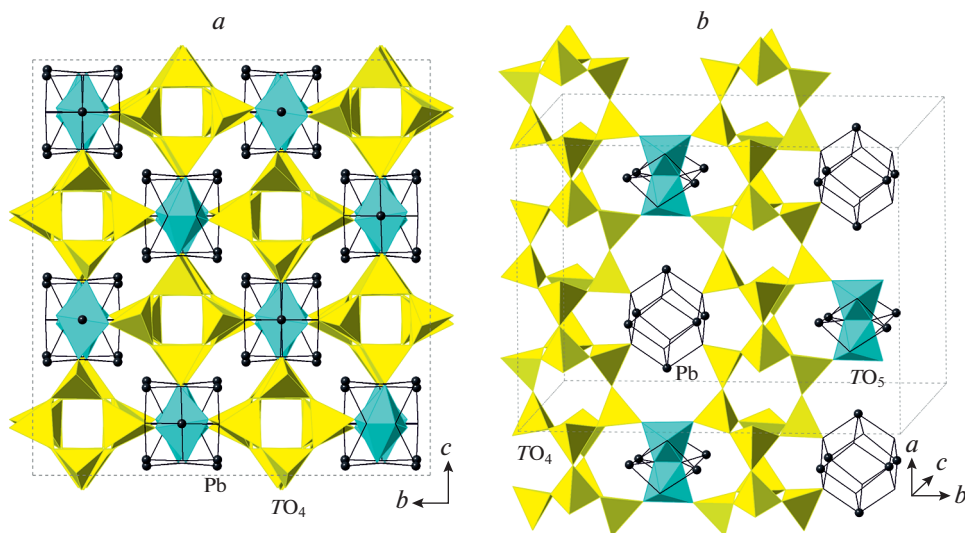
#### 4. DISCUSSION

The  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$  stoichiometry has not been observed previously for the  $\text{PbO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system (see Introduction), but possesses some similarity to the  $\text{Pb}_4\text{Al}_4\text{Si}_3\text{O}_{16}$  stoichiometry first reported by Haensel et al. (1976). The Pb : Al : Si ratios for the  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$  and  $\text{Pb}_4\text{Al}_4\text{Si}_3\text{O}_{16}$  compositions are equal to 5 : 5 : 4 and 4 : 4 : 3, or 1 : 1 : 0.80 and 1 : 1 : 0.75, respectively, which are rather close to each other and can potentially be mixed up in the chemical analyses. The comparison between the experimental X-ray powder diffraction pattern for  $\text{Pb}_4\text{Al}_4\text{Si}_3\text{O}_{16}$  (ICDD PDF #32-0505; Haensel et al., 1976) and theoretical one calculated on



**Fig. 1.** Coordination of Pb<sup>2+</sup> cations in the crystal structure of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>. Pb and O atoms are shown as black and red, respectively. The Pb–O bonds longer than 2.6 Å are shown as black lines.

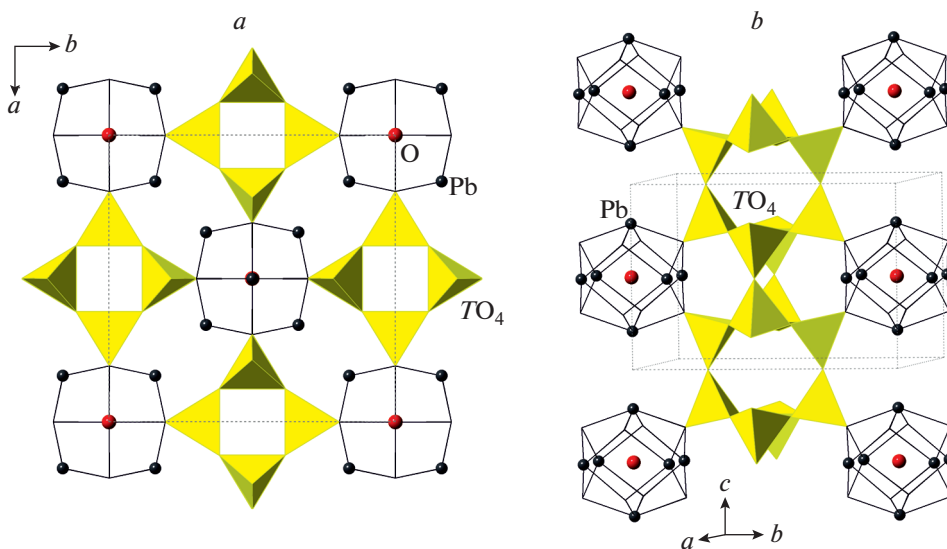
**Рис. 1.** Координация катионов Pb<sup>2+</sup> в кристаллической структуре Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>. Атомы Pb и O изображены черным и красным, соответственно. Связи Pb–O с длиной выше 2.6 Å показаны черными линиями.



**Fig. 2.** The crystal structure of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> projected along [100] (*a*) and its slice along the (001) plane showing linkage of aluminosilicate tetrahedral chains via Pb<sup>2+</sup> cations and dimers of (AlO<sub>5</sub>) trigonal bipyramids (*b*).

**Рис. 2.** Кристаллическая структура Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> в проекции вдоль [100] (*a*) и ее срез по плоскости (001), показывающий связь алюмосиликатных тетраэдрических цепочек через катионы Pb<sup>2+</sup> и димеры тригональных бипирамид (AlO<sub>5</sub>) (*b*).

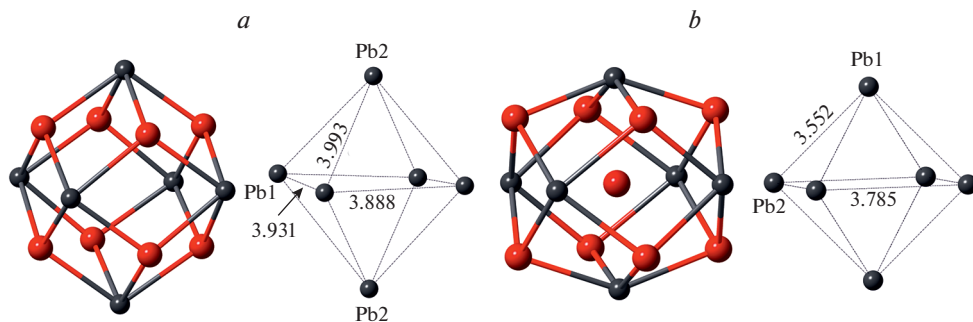
the basis of crystal-structure data reported herein show remarkable similarities, except for the reflection with  $d = 4.36$  Å versus the calculated value of 4.27 Å (in our opinion, a misprint cannot be excluded). The closeness of the two diffraction patterns provides strong evidence in favor of the identity of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> studied by us with the Pb<sub>4</sub>Al<sub>4</sub>Si<sub>3</sub>O<sub>16</sub> compound reported previously.



**Fig. 3.** The crystal structure of  $\text{Pb}_6\text{O}[(\text{Si}_6\text{Al}_2)\text{O}_{20}]$  projected along [001] (a) and the linkage of aluminosilicate tetrahedral chains to the  $(\text{OPb}_6)$  units (b).

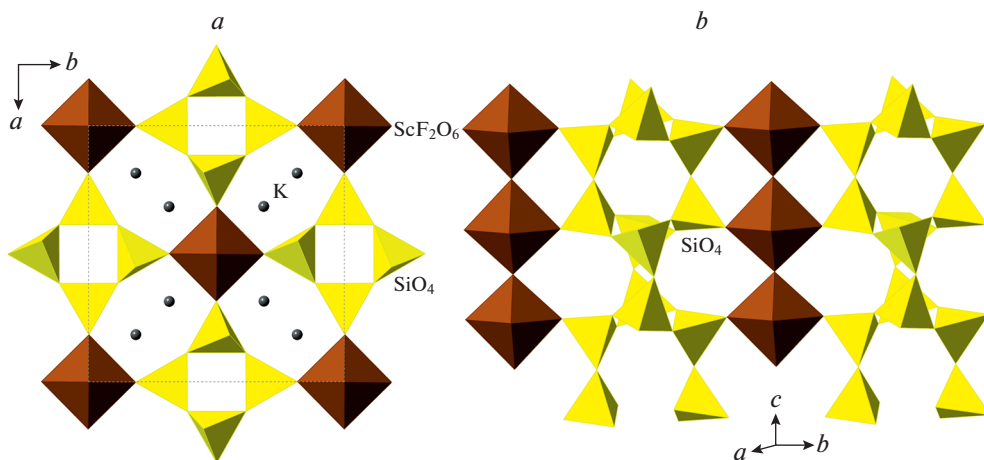
**Рис. 3.** Кристаллическая структура  $\text{Pb}_6\text{O}[(\text{Si}_6\text{Al}_2)\text{O}_{20}]$  в проекции вдоль [001] (a) и объединение алюмосиликатных тетраэдрических цепочек с группами  $(\text{OPb}_6)$  (b).

According to the crystal-structure study, the crystal-chemical formula of  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$  can be written as  $\text{Pb}_{10}\text{Al}_2\text{O}[(\text{Si}_2\text{Al}_2)\text{O}_{10}]_4$  that emphasizes the composition of tetrahedral chains with disordered distribution of Si and Al over tetrahedral sites. The crystal structure of the title compound is related to that of  $\text{Pb}_6\text{O}[(\text{Si}_6\text{Al}_2)\text{O}_{20}]$  (Siidra et al., 2009), which is based upon the tubular  $[(\text{Si}_6\text{Al}_2)\text{O}_{20}]^{10-}$  chains with the same topology as observed in  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$  (Fig. 3a). However, the linkage of the chains is different and is provided by the oxocentered  $(\text{Pb}_6\text{O})^{10+}$  units located in between the chains (Fig. 3b). In fact, each of these units forms a core of the larger  $\{(\text{Pb}_6\text{O}_8^T)\text{O}_a\}$  units, where  $\text{O}^T$  and  $\text{O}_a$  notations correspond to the O atoms bonded to T atoms and additional O atoms, respectively. The  $(\text{Pb}_6\text{O}_8^{\text{Si}})$  configuration has the shape of a rhombododecahedron with Pb atoms at the tetravalent corners and O atoms at the trivalent corners. The similar units are present in the title compound as well. Figure 4 compares geometries of the  $(\text{Pb}_6\text{O}_8^{\text{Si}})$  units in  $\text{Pb}_{10}\text{Al}_2\text{O}[(\text{Si}_2\text{Al}_2)\text{O}_{10}]_4$  and  $\text{Pb}_6\text{O}[(\text{Si}_6\text{Al}_2)\text{O}_{20}]$  (Figs. 4a and b, respectively). It can be seen that the units in the latter compound are more compressed, most likely due to the presence of the additional  $\text{O}_a$  atom at the center of the  $(\text{Pb}_6)$  octahedron. The  $\text{Pb}\cdots\text{Pb}$  distances in the octahedron are in the range 3.89–3.99 Å in the title compound (with “empty”  $(\text{Pb}_6)$  octahedron) and 3.55–3.79 Å in  $\text{Pb}_6\text{O}[(\text{Si}_6\text{Al}_2)\text{O}_{20}]$  (with the  $(\text{Pb}_6)$  octahedron centered by the  $\text{O}_a$  atom). The occurrence of the same structural units in similar structure types with occupied and non-occupied polyhedral cavities has been observed previously in inorganic structures with lone-electron-pair cations [e.g., the “empty”  $(\text{Pb}_6)$  octahedron in  $\text{Pb}_{21}[\text{Si}_7\text{O}_{22}]_2[\text{Si}_4\text{O}_{13}]$  (Siidra et al., 2014) versus  $(\text{ClPb}_6)$  octahedron in



**Fig. 4.** Rhombododecahedral Pb–O units in the crystal structures of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> (a) and the geometrical parameters of Pb<sub>6</sub> octahedral motifs. See text for details.

**Рис. 4.** Ромбододекаэдрические Pb–O единицы в кристаллических структурах Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> (a) и Pb<sub>6</sub>O[(Si<sub>6</sub>Al<sub>2</sub>)O<sub>20</sub>] (b) и геометрические параметры октаэдров Pb<sub>6</sub>. См. пояснения в тексте.



**Fig. 5.** The crystal structure of K<sub>2</sub>ScF[Si<sub>4</sub>O<sub>10</sub>] projected along [001] (a) and the linkage of octahedral and tetrahedral chains through sharing common corners (b).

**Рис. 5.** Кристаллическая структура K<sub>2</sub>ScF[Si<sub>4</sub>O<sub>10</sub>] в проекции вдоль [001] (a) и объединение тетраэдрических и октаэдрических цепочек через общие вершины (b).

hyttsjöite, Pb<sub>18</sub>Ba<sub>2</sub>Ca<sub>5</sub>Mn<sub>2</sub><sup>2+</sup>Fe<sub>2</sub><sup>3+</sup>Si<sub>30</sub>O<sub>90</sub>Cl · 6H<sub>2</sub>O (Grew et al., 1996)]. It should be noted that, in the title compound, only Pb1 and Pb2 atoms participate in the formation of (Pb<sub>6</sub>) octahedra, whereas the Pb3 atom is associated with the dimers of (AlO<sub>5</sub>) trigonal bipyramids.

The crystal structure of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> is also similar to that of narsarsukite, Na<sub>2</sub>TiO[Si<sub>4</sub>O<sub>10</sub>] (Pyatenko, Pudovkina, 1960; Peacor, Buerger, 1962), and isotypic compound K<sub>2</sub>ScF[Si<sub>4</sub>O<sub>10</sub>] (Kolitsch, Tillmanns, 2004). Both structures are based upon tubular chains of four-membered rings, which are interlinked by the chains of octahedra running parallel to the silicate chains. Figure 5 shows general features of the crystal structure of K<sub>2</sub>ScF[Si<sub>4</sub>O<sub>10</sub>].

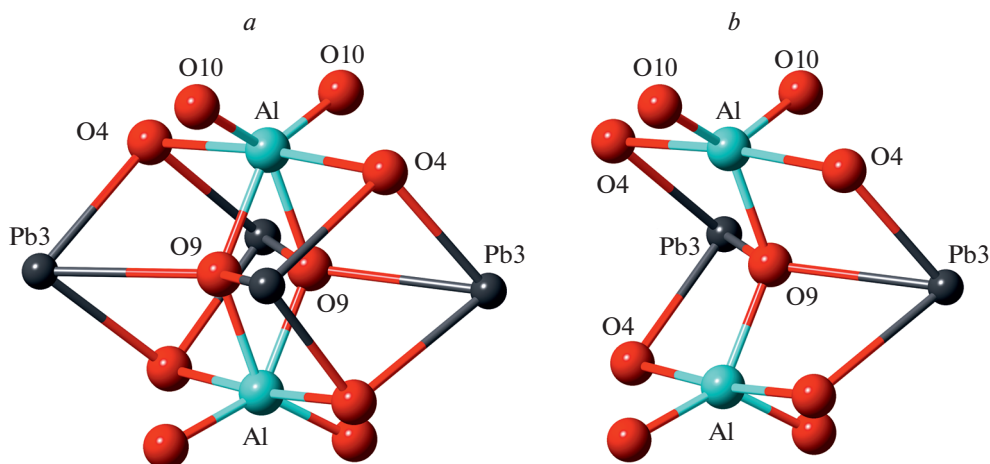


**Table 4.** Comparison of experimental X-ray powder diffraction pattern for  $\text{Pb}_4\text{Al}_4\text{Si}_3\text{O}_{16}$  (ICDD PDF #32-0505) and theoretical\* X-ray powder pattern for  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$ **Таблица 4.** Сравнение экспериментальных порошковых данных для  $\text{Pb}_4\text{Al}_4\text{Si}_3\text{O}_{16}$  (ICDD PDF #32-0505) и теоретической\* рентгенограммы для  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$ 

ICDD PDF #32-0505		Calculated for $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$		
$d, \text{Å}$	$I/I_0$	$d, \text{Å}$	$I/I_0$	$hkl$
7.78	30	7.83	60	022
6.57	16	6.61	17	202
		6.53	12	113
6.48	18	6.51	26	220
5.63	16	5.66	14	004
5.41	7	5.42	7	211
5.13	6	5.13	8	311
4.36	20	4.27 (?)	15	115
4.18	11	4.19	16	242
4.06	7	4.07	10	400
3.90	11	3.91	11	044
3.75	9	3.76	13	333
3.41	70	3.43	100	206
3.29	100	3.31	50	404
		3.30	99	260
3.25	40	3.26	39	440
3.08	10	3.09	8	353
2.883	13	2.90	14	137
2.843	25	2.85	25	264
2.816	25	2.823	19	444
2.748	13	2.758	6	317
2.671	20	2.683	26	426
2.623	40	2.628	23	462
2.601	60	2.610	49	066
2.318	45	2.313	2	375
2.258	6	2.258	1	555
		2.255	2	480
2.207	20	2.205	3	606
2.192	25	2.197	22	466
2.171	20	2.170	8	660
2.143	7	2.149	2	268
2.122	8	2.128	2	0.10.2
2.089	11	2.094	9	2.10.0
2.031	45	2.042	24	646
		2.027	27	664

\* Calculated using VESTA (Momma, Izumi, 2011).

The structure type of the title compound is new for inorganic compounds and may be viewed as a hybrid of the structure types of  $\text{Pb}_6\text{O}[(\text{Si}_6\text{Al}_2)\text{O}_{20}]$  and narsarsukite. On one hand, it can be obtained from narsarsukite by replacing each second pair of corner-sharing ( $\text{TiO}_6$ ) octahedra by ( $\text{Pb}_6$ ) octahedron (as a consequence, the sixfold coordination of Ti transforms into fivefold coordination of Al). On the other hand, the crystal structure of  $\text{Pb}_{10}\text{Al}_{10}\text{Si}_8\text{O}_{41}$  can be obtained from that of  $\text{Pb}_6\text{O}[(\text{Si}_6\text{Al}_2)\text{O}_{20}]$  by the replacement of each second ( $\text{Pb}_6\text{O}$ ) octahedron by the TBP dimer surrounded by four  $\text{Pb}_3$  atoms. The disordered and ordered configurations of the dimer are shown in Fig. 6. The O9 site that is shared between two adjacent ( $\text{AlO}_3$ ) units is half-occupied so that the averaged configuration (Fig. 6a) is the overlap of two ordered configurations (Fig. 6b). As a result, the atoms involved in the disordered moiety (es-



**Fig. 6.** The disordered (*a*) and ordered (*b*) configurations of trigonal bipyramidal dimers in the crystal structure of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>.

**Рис. 6.** Разупорядоченная (*a*) и упорядоченная (*b*) конфигурации тригонально-бипирамидальных димеров в кристаллической структуре Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>.

pecially Al, O9 and O10) possess strongly elongated displacement parameters, indicating that the observed Al–O bond lengths are strongly distorted due to the libration effects.

The structure type of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>, being the ordered hybrid version of the narsarsukite and Pb<sub>6</sub>O[(Si<sub>6</sub>Al<sub>2</sub>)O<sub>20</sub>] structure types, can be considered as a superstructure of both of them. The analysis of the unit-cell parameters for the three structure types (Table 5) shows that the unit cell of the title compound corresponds to the 2 × 2 × 2 (eightfold) supercell relative to both narsarsukite and Pb<sub>6</sub>O[(Si<sub>6</sub>Al<sub>2</sub>)O<sub>20</sub>]. The information-based structural complexity parameters (Krivovichev, 2013) of Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> (Table 5) are therefore higher than those of the parent structure types with the total structural information per cell (590.100 bits) about 6.2–6.5 times larger. This agrees well to the previous observations on structural complexity for the minerals with the “structure-superstructure” relations (Krivovichev et al., 2019).

The author is grateful to Igor Pekov for the useful remarks on the manuscript. The reported study was funded by the Russian Science Foundation, project number 19-17-00038.

**Table 5.** Crystallographic data and complexity parameters for narsarsukite-related compounds\*

**Таблица 5.** Кристаллографические данные и параметры структурной сложности для нарсарсуки-топодобных соединений\*

Chemical formula	Mineral name	Sp. gr.	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	Reference	<i>I<sub>G</sub></i> , bits/atom	<i>I<sub>G,total</sub></i> , bits/cell
Na <sub>2</sub> TiO[Si <sub>4</sub> O <sub>10</sub> ]	Narsarsukite	<i>I4/m</i>	10.727	= <i>a</i>	<b>7.948</b>	Peacor, Buerger, 1962	2.670	96.117
K <sub>2</sub> ScF[Si <sub>4</sub> O <sub>10</sub> ]	—	<i>I4/m</i>	10.207	= <i>a</i>	<b>8.166</b>	Kolitsch, Tillmanns, 2004	2.670	96.117
Rb <sub>2</sub> ScF[Si <sub>4</sub> O <sub>10</sub> ]	—	<i>I4/m</i>	11.262	= <i>a</i>	<b>8.305</b>	Kahlenberg et al., 2014	2.670	96.117
Pb <sub>6</sub> O[(Si <sub>6</sub> Al <sub>2</sub> )O <sub>20</sub> ]	—	<i>I4/mmm</i>	11.716	= <i>a</i>	<b>8.044</b>	Siidra et al., 2009	2.558	89.525
Pb <sub>10</sub> Al <sub>2</sub> O[(Si <sub>2</sub> Al <sub>2</sub> )O <sub>10</sub> ] <sub>4</sub>	—	<i>Fddd</i>	<b>16.294</b>	21.666	22.655	This work	4.215	590.100

\* The unit-cell parameter that corresponds to the extension of tetrahedral chains is shown in bold.

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**Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>: АЛЮМОСИЛИКАТ СВИНЦА  
С НАРСАРСУКИТОПОДОБНОЙ СТРУКТУРОЙ**© 2020 г. д. чл. С. В. Кривовичев<sup>a, b, \*</sup><sup>a</sup>Центр наноматериаловедения, Кольский научный центр, Российская академия наук,  
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Кристаллическая структура Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> (ромб., *Fddd*,  $a = 16.2940(17)$ ,  $b = 21.666(2)$ ,  $c = 22.655(2)$  Å,  $V = 7997.8(13)$  Å<sup>3</sup>,  $Z = 8$ ) решена прямыми методами и уточнена  $R_1 = 0.042$  на основе 1393 независимых рефлексов. Структура содержит три позиции Pb с координацией, искаженной за счет стереоактивности неподеленной электронной пары 6s<sup>2</sup>. Четыре позиции T1–T4 координированы тетраэдрически со средними длинами связи (T–O) в пределах от 1.66 до 1.69 Å. Заселенности этих позиций определены как Si<sub>0.5</sub>Al<sub>0.5</sub>. Позиция Al имеет тригонально-бипирамидальную координацию с наполовину заселенной позицией O9. Кристаллическая структура состоит из трубчатых тетраэдрических цепочек [T<sub>4</sub>O<sub>10</sub>], вытянутых параллельно оси *a* и связанных в каркас атомами Pb и димерами тригональных бипирамид AlO<sub>5</sub>. Сравнение экспериментальной дифракционной картины для соединения Pb<sub>4</sub>Al<sub>4</sub>Si<sub>3</sub>O<sub>16</sub> (ICDD PDF #32-0505) и теоретической картины для Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub>, вычисленной на основании структурных данных, указывает на возможную идентичность Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> с соединением “Pb<sub>4</sub>Al<sub>4</sub>Si<sub>3</sub>O<sub>16</sub>”, исследованным ранее. Кристаллохимическая формула Pb<sub>10</sub>Al<sub>10</sub>Si<sub>8</sub>O<sub>41</sub> может быть записана как Pb<sub>10</sub>Al<sub>2</sub>O[(Si<sub>2</sub>Al<sub>2</sub>)O<sub>10</sub>]<sub>4</sub>, что подчеркивает присутствие в структуре тетраэдрических цепочек со смешенной заселенностью тетраэдрических позиций. Структурный тип соединения является новым и может быть представлен как гибрид структурных типов Pb<sub>6</sub>O[(Si<sub>6</sub>Al<sub>2</sub>)O<sub>20</sub>] и нарсарсукита. Элементарная ячейка соединения соответствует восьмерной 2 × 2 × 2-сверхструктуре по отношению к нарсарсукиту и Pb<sub>6</sub>O[(Si<sub>6</sub>Al<sub>2</sub>)O<sub>20</sub>]. Информационная сложность нового структурного типа примерно в 6.2–6.5 раз выше таковой для материнских структурных типов с количеством структурной информации на ячейку, равной 590.100 бит.

**Ключевые слова:** алюмосиликат, свинец, кристаллическая структура, нарсарсукист, сверхструктура, структурная сложность

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