Leucostaurite, Pb₂[B₅O₉]Cl·0.5H₂O, from the Atacama Desert: The first Pb-dominant member of the hilgardite group, and micro-determination of boron in minerals by PIGE

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ABSTRACT

Leucostaurite is a new nanoporous lead borate discovered in samples from the Mina Asunción, Sierra Gorda, Atacama Desert, Chile, preserved since 1912 in the collections of the Natural History Museum of Bern, Switzerland. Leucostaurite formed via the oxidation of base-metal ores in the presence of B-rich brines. The mineral name is derived from the Greek "leukos" (white) and "stauros" (cross), and alludes to the white or transparent, colorless cruciform twinned crystals. Leucostaurite forms thin-tabular {010}, striated //[100], interpenetrated twinned crystals, and sheaf-like aggregates up to 0.8 mm on a paralaurionite and boleite matrix. The streak is white and the luster adamantine. Leucostaurite shows a weak, light-yellow fluorescence under short-wavelength UV but no fluorescence under long-wavelength UV light. The mineral is brittle, Mohs hardness ~ 4 , with perfect cleavage parallel to $\{010\}$ and good cleavage parallel to $\{100\}$; calculated density is 5.071 g/cm³. Leucostaurite is biaxial, 2V(meas) ~30°, dispersion: r > v, strong. Optic sign and refractive indices could not be measured, but the average index calculated from the Gladstone-Dale relationship is 1.849. The empirical formula based on Pb + Sr + Ca = 2 atoms per formula unit (apfu), 1 H apfu and B + Si = 5 apfu, is (Pb_{1.967}Sr_{0.026}Ca_{0.007})_{52.000} $(B_{4,983}Si_{0.017})_{\Sigma5.000}(Cl_{1.073}I_{0.004})_{\Sigma1.077}O_{8.971} \cdot 0.5H_2O$, which simplifies to $Pb_2[B_5O_3]Cl \cdot 0.5H_2O$. The boron content was measured on two crystal fragments using proton-induced γ -ray emission spectroscopy; the analytical value $[26.7(3) \text{ wt}\% \text{ B}_2\text{O}_3]$ is within error of the stoichiometric value of 26.5 wt% B_2O_3 . Leucostaurite is orthorhombic, space group Pnn2, a = 11.376(2), b = 11.505(2), c = 6.5558(7) Å, V =858.1(2) Å³, Z = 4. The seven strongest lines measured in the X-ray powder diffraction pattern are [d in Å/ I_{rel} in %]: 4.04/100; 2.84/100; 5.71/80; 2.019/70; 3.29/40; 2.55/40; 1.877/40. The crystal structure of leucostaurite ($R_1 = 6.2\%$) contains a hilgardite-type three-dimensional $[B_5O_9]^{3-}$ framework. Leucostaurite is the first mineral of the hilgardite group with orthorhombic (*Pnn2*) symmetry. However, several borates synthesized for their non-linear optical properties are structurally and chemically closely related to leucostaurite. For example in Na05Pb2(B5O9)Cl(OH)05, one type of channels contains Cl⁻ ions, the other contains OH⁻, Cl⁻, and Na⁺ ions; in leucostaurite these channels are occupied by Cl⁻ ions, and Cl⁻ ions + H₂O groups, respectively.

Keywords: Leucostaurite, new mineral, crystal structure, Mina Asunción, Sierra Gorda, Atacama Desert, Chile

INTRODUCTION: DISCOVERY AND OCCURRENCE OF LEUCOSTAURITE

The new mineral leucostaurite was discovered during the systematic investigation of a historical collection of ore specimens from Mina Asunción, Sierra Gorda, Caracoles District, Antofagasta Province, Chile. These samples were collected by the consul of Switzerland in Chile, Julius Friedrich Häfliger (1834–1911), and donated by his widow in 1912 to the Natural History Museum of Bern (Anonymous 1911). The name leucostaurite is derived from the Greek "*leukos*" (white) and "*stauros*" (cross), and alludes to the white, cruciform twinned crystals. Almost all leucostaurite specimens displayed this habit. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (proposal number IMA 2007-047). The holotype material is deposited in the Musée géologique cantonal, Lausanne, Switzerland, under

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1207

catalog number MGL 90000. A second sample was found by Mike Rumsey in the collections of the British Museum of Natural History, London, where it is preserved under the catalog number BM 1916.446. Purchased in 1879 by F.-W. Crick to J.-R. Gregory, this specimen is from San Rafael Mine, Sierra Gorda, as indicated on the label.

Leucostaurite most probably formed by the interaction of evaporitic brines within the oxidation zone of a base-metal deposit. In the Atacama Desert, evaporites are the product of volcanism, either directly from sulfurous fumaroles (solfataras), or indirectly from thermal springs, where leaching of large volumes of rock is caused by high-temperature water-rock interactions. In this way, large amounts of sulfur, boron, and chlorine, as well as locally high concentrations of iodine and nitrate, are transported from volcanoes to endorheic basins within or near the volcanic complexes (Pueyo et al. 2001). The oxidation of base-metal deposits in the presence of these dispersed salts and/or brines leads to complex and unusual mineral associations. The exotic geochemical signature of these evaporite deposits is reflected in some typical minerals from Atacama deposits, such as bandylite Cu₂[B(OH)₄]₂Cl₂ (Li and Burns 2000; Palache and Foshag 1938), santarosaite (Cu,Pb) B_2O_4 (Schlueter et al. 2008), bellingerite $Cu_3^{2+}(IO_3)_6 \cdot 2H_2O_4$ (Berman and Wolfe 1940; Ghose and Wan 1974), salesite Cu²⁺(IO₃)(OH) (Ghose and Wan 1978; Palache and Jarrell 1939), schwartzembergite H₂Pb₅²⁺I³⁺O₆Cl₃ (Domeyko, 1864; Welch et al. 2001), and seeligerite Pb₃O(IO₃)Cl₃ (Bindi et al. 2008; Mücke 1971).

APPEARANCE, PHYSICAL AND OPTICAL PROPERTIES

Leucostaurite forms thin colorless to white crystals tabular on {010} and striated //[100], sometimes grouped into sheaflike aggregates up to 0.8 mm in length on a paralaurionite and boleite matrix. Apart from {010}, the {100}, {201}, and {001} forms were observed. Many crystals show interpenetrated twinning [most probably either on (101) or (011)], forming a cruciform assemblage (Fig. 1).

The following minerals were found on the specimens containing leucostaurite: boleite, paralaurionite, caracolite, bindheimite, gypsum, penfieldite, challacolloite, schwartzembergite, cesanite, and seeligerite. Leucostaurite has a white streak and adamantine luster. It displays a weak, light-yellow fluorescence under short-wavelength UV light and no fluorescence under long-wavelength UV light. The mineral is brittle, with a Mohs hardness ~4. Leucostaurite displays a perfect cleavage parallel to $\{010\}$, and a good cleavage parallel to {100}. The mineral sinks in a Clerici solution (mixture of water and thallium malonate/formate) with a density of 4.32 g/cm³, and not enough material was available for density measurement via a pycnometer. The density calculated on the basis of the empirical formula and unit-cell dimensions from the crystalstructure refinement is 5.071 g/cm3. Leucostaurite releases HCl and H₂O on heating at about 1000 °C in air.

Optically, leucostaurite is biaxial (sign undetermined), with n > 1.790 (589 nm wavelength). Accurate determination of the refractive index was not possible by the immersion method, because the mineral is immediately destroyed (whitening) by liquid AsBr₃-As₂S₃-S mixtures with $n \ge 1.800$. The average



FIGURE 1. Morphology of leucostaurite. (**a**) Scanning electron microscope image (backscattered electron mode, 20 keV) of cruciform leucostaurite twin. (**b**) Reflected light microscope image of a polished twinned crystal under crossed polars.

refractive index calculated using the Gladstone-Dale relationship, with the constants listed in Mandarino (1976), for the empirical formula is 1.849. Dispersion was strong, r > v, with 2V (meas): ~30°. The mineral did not display pleochroism under polarized light.

CHEMICAL COMPOSITION

Chemical analyses were carried out with a Cameca SX51 electron microprobe operated at 20 kV with a 20 nA beam current. Counting times were 10 s on the peaks and 5 s on each side of the peak for background. The beam was slightly defocused to \sim 5 µm in diameter to limit beam damage. Characteristic X-ray lines were measured in wavelength-dispersive spectroscopic (WDS) mode; the X-ray lines, Bragg crystals, and external quantification standards used are listed in Table 1.

Na₂O, K₂O, Al₂O₃, and SO₃ were sought, and found to be below the detection limit (~0.05 wt%). The following components were also included in the analysis routine, but found to be present only in minor amounts: MgO ≤ 0.14 wt%; ZnO ≤ 0.11 wt%; BaO ≤ 0.11 wt%; Br ≤ 0.08 wt%; MnO ≤ 0.08 wt%; FeO ≤ 0.07 wt%; CuO ≤ 0.07 wt%; SiO₂ ≤ 0.07 wt%; P₂O₅ ≤ 0.07 wt%. H₂O was calculated by stoichiometry from the results of

 TABLE 1. Electron microprobe micro-chemical analysis of leucostaurite (average of 23 analyses)

Constituent	wt%	Range	St.dev.	X-ray line/analyzer crystal/ probe standard
CI	5.68	5.38-5.91	0.12	CIKa/PET/tugtupite
1	0.07	<0.05-0.25	0.25	IKa/LIF/Pbl ₂
PbO	65.54	63.54-68.38	1.46	PbMa/PET/crocoite
CaO	0.06	<0.05-0.44	0.09	CaKa/PET/wollastonite
SrO	0.40	0.25-0.69	0.12	SrLa/TAP/strontianite†
SiO ₂	0.15	0.02-0.40	0.07	SiKα/PET/wollastonite
$B_2O_3^*$	26.73	-	0.26	PIGE: hilgardite-1 <i>Tc</i>
H_2O (calc)	1.34			-
-O=(Cl,l)	-1.29	1.22-1.34	0.03	
Total‡	98.68			

* PIGE analyses on two different crystal fragments (see text). The amount of boron required to obtain 5 (B+Si) in the empirical formula is 25.90 wt% B_2O_3 .

 \dagger The background was measured only on one side of the SrLa peak, because of an interference with PbLB_3/PbLB_4.

 \pm Similarly low average totals for electron-microprobe analyses were found for hilgardite-1*Tc*, Ca₂B₅O₈Cl(OH)₂, from the Boulby mine, U.K.

the crystal-structure refinement, as there was insufficient material for carbon-hydrogen-nitrogen (CHN) analysis.

We used particle-induced γ -ray emission (PIGE) spectroscopy to obtain quantitative analyses of B in leucostaurite. In this method, the sample is exposed to a beam of protons (3.0 MeV). At this energy, the protons can penetrate the Coulomb barrier on light elements and induce various nuclear reactions (Tesmer and Nastasi 1995; Ryan 1995); many of these reactions involve the emission of y-rays. PIGE provides quantitative analysis based on y-ray spectroscopy, suitable standards, and knowledge of the individual reaction cross sections. The lower Coulomb barrier of light elements makes PIGE particularly suitable for the analysis of light elements such as Li, Be, B, F, Na, and Al. With detection limits as low as 10 ppm for some elements, and the ability to work in situ with horizontal beam sizes in the order of $1 \,\mu\text{m}^2$, PIGE has found many applications in Earth Sciences, ranging from the analysis of trace light elements in fluid inclusions, fossils, pigments, atmospheric aerosols, minerals, and glasses (e.g., d'Errico et al. 2010; Lucarelli et al. 2011; Quattropani et al. 1999; Rio et al. 1995; Robertson and Dyar 1996; Ryan 1995; Volfinger 2002). However, this appears to be the first application of the method for B-analysis to a new mineral description.

We used the CSIRO-GEMOC nuclear microprobe (Ryan et al. 2001) in Melbourne, Australia, to monitor the proton-induced nuclear reaction $[^{10}B(p,\alpha\gamma)^7Be]$ by γ -ray spectroscopy (Courel et al. 1991; Tesmer and Nastasi 1995). Detection of the 429.2 keV γ-rays used a 30% intrinsic germanium solid-state detector in close geometry (20 mm from sample) at 0° to the beam. Proton-induced X-ray emission (PIXE) spectra were collected concurrently, and were quantified using the GeoPIXE software (Ryan et al. 1996, 2002). Boron concentrations were estimated using the assumption that the sample was thick enough (>20 mg/ cm²) so that the proton beam stops within the sample. The depth sampled by the beam was corrected by taking into account the matrix effects on stopping powers (dE/dx). The concentration C of an element in an unknown can be related to the concentration of this element C_s in a standard using the relation (Tesmer and Nastasi 1995):

$$C = C_s \cdot \left(\frac{Y}{Y_s}\right) \cdot \left(\frac{\left[\frac{\mathrm{d}E}{\mathrm{d}x}\right]}{\left[\frac{\mathrm{d}E}{\mathrm{d}x}\right]_s}\right)$$
(1)

where Y is the measured yield (peak area divided by the integrated proton charge) and (dE/dx) is the stopping power given in units of MeV/mg/cm². Two standards were used, hilgardite-1Tc $[Ca_2B_5O_9Cl (H_2O)]$ from the Boulby mine, U.K. (MGL 90384), and danburite $[CaB_2(SiO_4)_2]$ from Oman (MGL 58602). The nature of the standards was confirmed by powder XRD. Three fragments of leucostaurite (labeled A, B, and C) were embedded with the standards in an epoxy resin block and polished. The beam was scanned over each fragment, and counts were integrated for each fragment. When hilgardite-1Tc was used as a standard, the larger fragments B and C both gave 26.7(3) wt% B_2O_3 consistent with the stoichiometric value expected for leucostaurite, which is 26.5 wt% B₂O₃. Fragment A gave a lower value of 22.2 wt% B₂O₃, suggesting insufficient thickness to include the strong resonance at 1.5 MeV. The danburite sample was fine grained ($\sim 20 \times 60 \,\mu m^2$ typical grain size) with interstitial filling making it unsuitable as an effective standard. It gave B₂O₃ values biased toward higher values (23.8 wt%) for fragment A and 29.0 wt% for fragments B and C). These difficulties highlight the need for standards and samples with grain sizes and sample thickness that exceed the range of the protons penetration depths.

The empirical formula, based on Pb + Sr + Ca = 2 atoms per formula unit (apfu), 1 H apfu from the structure refinement and B + Si = 5 apfu from the structure refinement, is $(Pb_{1.967}Sr_{0.026}Ca_{0.007})_{\Sigma 2.000}(B_{4.983}Si_{0.017})_{\Sigma 5.000}(Cl_{1.073}I_{0.004})_{\Sigma 1.077}O_{8.971}O.SH_2O$. The end-member formula is $Pb_2[B_5O_9]Cl\cdot0.5H_2O$, which requires: PbO 67.95, B_2O_3 26.50, Cl 5.40, H_2O 1.37, -O = Cl 1.22; total 100.00 wt%. The B_2O_3 concentration measured by PIGE is within error of the stoichimetric value.

POWDER X-RAY DIFFRACTION STUDY

The X-ray powder diffraction pattern of leucostaurite was collected using a 114.6 mm diameter Gandolfi camera and CuK α_1 /Ni-filtered X-ray radiation ($\lambda = 1.5418$ Å). The powder pattern is in good agreement with the results of the crystal-structure analysis in terms of the comparison between calculated and observed *d*-spacings and intensities (Table 2). Because most lines have multiple indexes, it was not attempted to refine the unit cell from the powder data.

CRYSTAL STRUCTURE AND RELATION WITH OTHER MINERALS

Single-crystal X-ray diffraction intensity data were collected on a $0.12 \times 0.10 \times 0.03$ mm³ large crystal using a Stoe IPDS II image plate 2-circle diffractometer and MoK α X-ray radiation. Details of the data collection are reported in Table 3. The data were processed using the CrysAlisPro program (Oxford Diffraction 2009) and corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm, as implemented in CrysAlisPro. The unit-cell dimensions are a = 11.376(2), b =11.505(2), c = 6.5568(7) Å; V = 858.1(2) Å³, and the *a:b:c* ratio calculated from these unit-cell parameters is 0.9888:1:0.5699. The crystal structure was solved in space group *Pnn*2 by direct methods using SHELXS-97 and refined by full-matrix leastsquares on F^2 , using SHELXL-97 (Sheldrick 2008). The final R_1 index with anisotropic displacement parameters for the Pb

TABLE 2. X-ray powder diffraction data for leucostaurite

hkl	d_{calc}	I/I _{max}	d_{meas}	I_{meas}	hkl	d_{calc}	I/I _{max}	d_{meas}	I_{meas}
011	5.70	68.3			342	1.878	5.8		
200	5.69	4.9	5.71(2)	80	531	1.875	14.1	1.877(2)	40
101	5.68	53.3			432	1.874	7.6		
120	5.13	3.1			260	1.817	6.6 j	1 0 2 1 (2)	10
210	5.10	8.9	5.11(2)	20	161	1.817	5.1	1.021(2)	10
111	5.09	5.4			233	1.801	3		
220	4.04	100			620	1.801	1.3	1 001(2)	20
121	4.04	44.6	4.04(1)	100	611	1,799	1.7	1.801(2)	20
211	4.03	33.1			323	1.799	11.9		
031	3.31	23.1			442	1.721	3.3 \		
301	3.28	31.2	3.29(1)	40	143	1.720	8	/	
002	3.28	12.1			413	1.714	6.2	1.720(1)	10
131	3.18	11.6			360	1.711	3.2		
320	3.17	1.5	3.16(1)	30	171	1.579	361		
311	3.16	21.7	5	50	622	1.578	2.2		
040	2.88	46.3	0.00(4)		701	1.577	2.3		
231	2.86	23.9	2.88(1)	30	024	1 576	85	1.580(1)	30
321	2.851	12.2			503	1.576	2.1		
022	2.031	43.8			204	1.575	531		
400	2.010	33.0	2.844(4)	100	731	1 4 5 9	41)		
202	2.044	48.8			533	1.458	16	1.460(1)	10
122	2.040	47			180	1 4 2 7	24		
410	2.761	72	2 759(4)	30	642	1.127	2.1		
212	2.701	0.1	2.759(4)	50	042	1 4 2 4	2.0	1 /25(1)	10
141	2.756	18.2			470	1 4 2 3	28	1.423(1)	10
420	2.500	2.8			272	1 4 2 3	14		
220	2.547	16.4	2.553(4)	40	741	1 3 8 3	17		
411	2.517	15.2			543	1 382	2.6		
331	2 4 9 4	81	2 501(3)	20	244	1 382	6.2		
430	2.121	881	2.301(3)	20	820	1 380	2.1	1.379(1)	15
232	2.201	5 1	2.284(3)	20	811	1 380	0.7		
051	2 1 7 1	82	_		4 2 4	1 379	62		
341	2.163	13.3			571	1.306	5.4		
042	2.162	83	2,156(2)	30	472	1.305	1.4		
431	2157	8.9	21130(2)	50	173	1 305	16		
013	2.137	83	_		802	1 305	0.6		
103	2.146	9.4			703	1.304	2	1.304(1)	10
511	2 1 1 3	15.2			015	1 303	15		
412	2112	11 5	2.113(2)	30	105	1 303	0.8		
440	2.022	12			751	1.301	4.9		
242	2.022	34			553	1 300	63		
521	2.021	114	2 010(2)	70	373	1 2 4 1	5.9		
422	2.013	19.2	2.019(2)	70	901	1 2 4 1	29		
122	2.013	117			035	1 2 4 1	1.5		
213	2.011	12.8			604	1 240	0.8		
160	1 891	27			760	1 240	1.2	1.238(1)	² 0
351	1 884	11 5	1.892(2)	10	3 0 5	1 2 3 9	19		-
551	1.004	,,			164	1 2 3 9	1.9		
					837	1.235	23		
					732	1 235	4		
					, , , ,	1.235	- -		

and Cl atoms was 6.2% for 2034 unique observed reflections with $F_o > 4\sigma(F_o)$. The H atoms could not be located from the inspection of electron-density difference Fourier maps, most probably due to the presence of Pb²⁺ cations with heavy and diffuse electron shells. Refinement of the extinction coefficient did not result in any physically realistic value and in any improvement of the refinement. The atomic coordinates, isotropic displacement parameters and bond-valence sums for leucostaurite are reported in Table 4, anisotropic displacement parameters in Table 5, and selected bond distances in Table 6.

The structure is based upon the three-dimensional framework $[B_5O_9]^{3-}$, consisting of edge-sharing BO₃ triangles and BO₄ tetrahedra (Fig. 2). Pb1²⁺ is coordinated by eight O²⁻ and two Cl⁻ anions, whereas the Pb2²⁺ site is coordinated by seven O²⁻ anions, two Cl⁻ anions and one H₂O molecule. The Pb²⁺ cations, Cl⁻ anions and H₂O groups are located in the cavities of the borate framework (Fig. 2): channels parallel to [001] contain either Cl⁻ or H₂O + Cl⁻; channels parallel to [010] contain Pb1²⁺

 TABLE 3.
 Crystallographic data and refinement parameters for leucostaurite, Pb₂[B₅O₉]Cl·0.5H₂O

a (Å)	11.376(2)
b (Å)	11.505(2)
c (Å)	6.5568(7)
V (Å3)	858.1(2)
Space group	Pnn2
μ (mm ⁻¹)	39.536
Z	4
D _{calc} (g/cm ³)	5.077
Crystal size (mm ³)	$0.12 \times 0.10 \times 0.03$
Diffractometer	Stoe IPDS II
Radiation	ΜοΚα
Reflections (total)	7924
Reflections (unique)	2193
2θ range, °	5.04-59.38
$h_{\min} \rightarrow h_{\max}, k_{\min} \rightarrow k_{\max}, l_{\min} \rightarrow l_{\max}$	$-15 \rightarrow 15, -9 \rightarrow 7, -15 \rightarrow 15$
Unique $ F_o \ge 4\sigma_F$	2034
Flack parameter	0.06(3)
R _{int}	0.083
R_{σ}	0.053
<i>R</i> ₁	0.062
wR ₂	0.176
GoF	1.379
Note: $\mathbf{D} = \nabla [\mathbf{\Gamma}] = \mathbf{\Gamma} / \nabla \mathbf{\Gamma} $ with $\mathbf{D} = (\nabla [w/\mathbf{\Gamma}])$	$\Gamma^{2}(2)/\Sigma[m(\Gamma^{2}(2))]/2, m = 1/[\sigma^{2}(\Gamma^{2}) + (\sigma \Gamma)]$

Note: $R_1 = \Sigma ||F_0| - |F_c||/\Sigma|F_0|$; $wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2]/\Sigma [w(F_0^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, where $P = (F_0^2 + 2F_c^2)/3$; $GoF = \{\Sigma [w(F_0^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

 TABLE 4.
 Atomic coordinates, displacement parameters (Å²), and bond-valence sums* (BVS; valence units) for leucostaurite, Pb₂[B₂O₂]Cl-0.5H₂O

	1 02[0509]	CI 0.51120			
Atom	X	У	Ζ	U_{eq}	BVS
Pb1	0.0379(1)	0.76058(6)	0.3457(2)	0.0189(2)	1.70
Pb2	0.7276(1)	0.97810(8)	0.5167(2)	0.0257(2)	1.77
Cl1	0.5	0	0.780(2)	0.036(2)	0.26
Cl2	0	0	0.474(2)	0.032(2)	0.32
B1	0.820(2)	0.735(2)	0.641(4)	0.013(4)	3.19
B2	0.741(2)	0.531(2)	0.517(6)	0.010+	3.16
B3	0.988(2)	0.753(2)	0.869(4)	0.010†	3.17
B4	0.712(2)	0.321(2)	0.503(4)	0.012(3)	2.98
B5	0.710(2)	0.713(2)	0.315(4)	0.015(4)	2.99
01	0.944(2)	0.728(2)	0.691(3)	0.022(3)	2.33
02	0.761(2)	0.625(2)	0.690(3)	0.022(3)	1.63
03	0.811(2)	0.766(2)	0.432(2)	0.010(2)	2.05
04	0.714(2)	0.583(2)	0.343(3)	0.023(3)	2.15
05	0.919(2)	0.793(2)	0.019(3)	0.020(3)	2.06
06	0.764(2)	0.822(2)	0.777(2)	0.014(3)	1.95
07	0.776(2)	0.229(2)	0.597(3)	0.015(3)	2.04
08	0.608(2)	0.760(2)	0.419(3)	0.017(3)	1.97
09	0.740(2)	0.434(2)	0.597(3)	0.022(3)	2.37
O _w 10	0.0	0.5	0.818(9)	0.07(2)	0.28
* C . I I.	and the state of the second			12.2	10

* Calculated using bond-valence parameters taken from Krivovichev and Brown (2001) for the Pb²⁺-O²⁻ bonds and from Brese and O'Keefe (1991) for all other bonds.

+ Fixed during refinement.

TABLE 5. Anisotropic displacement parameters (in Å ²)								
Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂		
Pb1	0.0206(4)	0.0240(4)	0.0121(4)	0.0002(5)	-0.0003(3)	0.0004(3)		
Pb2	0.0334(5)	0.0262(4)	0.0174(4)	0.0029(3)	0.0014(4)	0.0034(3)		
Cl1	0.023(4)	0.035(4)	0.050(6)	0	0	0.004(4)		
Cl2	0.030(4)	0.021(3)	0.045(7)	0	0	-0.006(3)		

and Cl⁻; and channels parallel to [100] contain Pb2²⁺, H₂O, and Cl⁻ (Fig. 2). The bond-valence sum incident upon the O_w10 site is 0.28 valence units (v.u.), in agreement with its assignment to an oxygen atom of an H₂O molecule. The bond-valence sums for the Cl sites are very low (0.26–0.32 v.u.), which is typical for the Cl⁻ anions located within cavities of three-dimensional framework structures.

The three-dimensional framework of leucostaurite is similar to that of hilgardite, a family of framework borates

PD ₂			
Pb1-01	2.53(2)	B2-O9	1.23(3)
Pb1-05	2.56(2)	B2-O4	1.32(4)
Pb1-O3	2.64(2)	B2-O2	1.59(4)
Pb1-07	2.69(2)	<b2-o></b2-o>	1.38
Pb1-06	2.78(2)		
Pb1-Cl2	2.912(3)	B3-O1	1.30(3)
Pb1-08	2.92(2)	B3-O5	1.34(3)
Pb1-O2	3.03(2)	B3-O8	1.42(3)
Pb1-Cl1	3.059(2)	<b3-o></b3-o>	1.35
Pb2-06	2.51(2)	B4-07	1.42(3)
Pb2-04	2.54(2)	B4-O9	1.48(3)
Pb2-O3	2.68(1)	B4-O6	1.51(3)
Pb2-O2	2.74(2)	B4-O5	1.52(2)
Pb2-09	2.82(2)	<b4-o></b4-o>	1.48
Pb2-O _w 10	2.91(3)		
Pb2-08	2.92(2)	B5-O7	1.45(3)
Pb2-07	2.99(2)	B5-O8	1.45(3)
Pb2-Cl2	3.122(1)	B5-O4	1.51(3)
Pb2-Cl1	3.123(7)	B5-O3	1.51(3)
		<b5-o></b5-o>	1.48
B1-O3	1.42(3)		
B1-O1	1.45(3)		
B1-O2	1.47(3)		
B1-O6	1.48(3)		
<b1-o></b1-o>	1.46		

 TABLE 6.
 Selected distances (Å) in the structure of leucostaurite, Ph_IB_O_ICL0.5H_O

(Ghose 1982, 1985; Ghose and Wan 1979; Grice et al. 1999; Hawthorne et al. 1996). Hence, leucostaurite is a member of the hilgardite group, and belongs to class 6.ED.05 according to the classification of Strunz and Nickel (2001). The members of the hilgardite group are listed together with related synthetic compounds in Table 7. Leucostaurite is the first mineral of the hilgardite group in which the dominant cation is Pb instead of Ca or (Ca+Sr). Leucostaurite has a composition very close to that of the end-member, containing only minor amounts of Ca (≤ 0.44 wt% CaO) and Sr (≤ 0.69 wt% SrO; Table 1). Leucostaurite is also the first mineral of the hilgardite group to display an orthorhombic symmetry.

Hilgardite was described from the insoluble residue from a brine well in the Choctaw Salt Dome, Louisiana (Hurlbut and Taylor 1937). Ghose and Wan (1977, 1979) recognized hilgardite as a potential precursor of a new family of borate zeolites, and described its mild piezoelectric properties. The building block of all these structures, the pentaborate polyanion $[B_5O_{12}]^{9-}$, can exist in two stereoisomeric configurations, left- or right-handed (Ghose 1982, 1985). The arrangement of these isomeric blocks gives rise to a series of polytypes; trigonal and monoclinic polytypes are known (1*Tc*, 3*Tc*, 4*M*; Ghose 1982). Kurgantaite and tiretskite (Kondrat'eva 1964; Pekov et al. 2001) are isostructural with hilgardite-1*Tc*, differing by having (OH)⁻ instead of Cl⁻, and one of the two Ca positions occupied by Sr in kurgantaite.

The first orthorhombic derivative of the hilgardite-type structure, $Ba_2[B_5O_9]Br$, was synthesized by Lloyd et al. (1973). In the past 12 years, several structurally closely related compounds were synthesized, because of their potential as nonlinear-optical materials (e.g., Belokoneva et al. 2000; Plachinda et al. 2005; Table 7). Lead-containing borates in particular can display very high optical nonlinearity (Belokoneva et al. 2007), and $Pb_2B_5O_9I$ has the largest second-harmonic generation response of all borates (Huang et al. 2010).

Leucostaurite is the first natural occurrence of a hilgardite-



FIGURE 2. Crystal structure of leucostaurite. Pb^{2+} cations as large light-colored spheres, Cl^- anions as medium gray spheres, and H_2O groups as black spheres.

Name	Chemical formula	Space grou	o Unit cell (Å)	Cell volume (Å ³)	References and comments
Hilgardite-1 <i>Tc</i>	$Ca_2[B_5O_9]Cl·H_2O$	<i>P</i> 1	$a = 6.452(1); \alpha = 61.60(1)^{\circ}$ $b = 6.559(1); \beta = 118.72(1)^{\circ}$ $c = 6.286(1); \gamma = 105.86(1)^{\circ}$	204.90(6)	Polytypes 1 <i>Tc</i> , 3 <i>Tc</i> , and 4 <i>M</i> are known. Original description, Hurlbut and Taylor (1937). Cell parameters shown for the 1 <i>T</i> c polymorph (Burns and Hawthorne 1994).
Kurgantaite	$CaSr[B_5O_9]Cl\cdot H_2O$	Р1	$a = 6.5732(6); a = 60.995(2)^{\circ}$ $b = 6.4445(6); \beta = 61.257(2)^{\circ}$ $c = 6.3693(6); \gamma = 77.191(2)^{\circ}$	206.88(3)	Pekov et al. (2001); Ferro et al. (2000b)
Synthetic	Sr ₂ [B ₅ O ₉]OH·H ₂ O	C2	a = 10.2571(6) $b = 8.048(2); \beta = 127.860(2)^{\circ}$ c = 6.4043(4)	417.43(4)	Barbier and Park (2001)
Tiretskite	$Ca_2[B_5O_9](OH) \cdot H_2O$	<i>P</i> 1	$a = 6.44; \alpha = 61.77^{\circ}$ $b = 6.45; \beta = 61.25^{\circ}$ $c = 6.41; \gamma = 77.50^{\circ}$		Kondrat'eva (1964); Davies and Machin (1968)
Leucostaurite	Pb ₂ [B ₅ O ₉]Cl·0.5H ₂ O	Pnn2	<i>a</i> = 11.376(2); <i>b</i> = 11.505(2) <i>c</i> = 6.5568(7)	858.1(2)	This study
Synthetic	$M_2[B_5O_9]X;$ M = Pb,Ca,Sr,Ba; $X = Cl,Br,l^*$	Pnn2	a = 11.257(8)-11.635(8) b = 11.138(7)-11.581(7) c = 6.12(9)-6.680(3)	767.4–900.1	Belokoneva et al. (2003, 2007); Egorova et al. (2008); Huang et al. (2010); Lloyd et al. (1973); Plachinda et al. (2005)
Synthetic	$Ba_2[B_5O_9]CI \cdot 0.5H_2O$	Pnn2	<i>a</i> = 11.716(2); <i>b</i> = 11.574(2); <i>c</i> = 6.700(1)	908.5(2)	Ferro et al. (2000a)
Synthetic	$Na_{0.5}Pb_2[B_5O_9]Cl \cdot 0.5H_2O$	Pnn2	<i>a</i> = 11.51(1); <i>b</i> = 11.45(4); <i>c</i> = 6.563(4)	865(4)	Belokoneva et al. (2000)
Synthetic N	Na _{0.5} Pb ₂ [B ₅ O ₉](OH) _{1.5} ·0.5H ₂ C) Pnn2	<i>a</i> = 11.426(5); <i>b</i> = 11.328(4); <i>c</i> = 6.5735(8)	850.8(8)	Al-Ama et al. (2006)
Synthetic	$Pb_2[B_5O_9](OH) \cdot 0.5H_2O$	P112 ₁ /n	a = 11.32(1); b = 6.632(1) $c = 11.549(8); \gamma = 91.03(5)^{\circ}$	860(2)	Borisova et al. (2002)
Synthetic	Pb ₂ [B₅O ₉](OH)·H ₂ O	P112 ₁ /n	a = 11.32(1); b = 6.631(2) $c = 11.440(9); \gamma = 91.03(6)^{\circ}$	859(2)	Belokoneva et al. (1998)

TABLE 7. Minerals of the hilgardite group and related synthetic compounds

type compound with the orthorhombic *Pnn*2 space group. Leucostaurite is most closely related to the synthetic compounds $Na_{0.5}Pb_2(B_5O_9)Cl(OH)_{0.5}$ (Belokoneva et al. 2000) and $Pb_2[B_5O_9]$ (OH) $\cdot 0.5H_2O$ (Borisova et al. 2002; Table 7). In $Na_{0.5}Pb_2(B_5O_9)$ Cl(OH)_{0.5}, one type of channel parallel to [001] contains Clions, the other channel is disordered and contains OH⁻, Cl⁻, and Na⁺ ions; in leucostaurite these channels are occupied by Cl⁻ ions and Cl⁻ ions + H₂O groups, respectively. Pb₂[B₅O₉] (OH) $\cdot 0.5H_2O$ and leucostaurite differ only by the replacement of (OH)⁻ for Cl⁻.

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