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Crystal structure of larsenite $PbZnSiO_4$

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Auszug

Larsenit, ein seltenes Mineral aus Franklin, New Jersey, ist orthorhombisch mit $a = 8{,}244$ Å, $b = 18{,}963$ Å, $c = 5{,}06$ Å, $Z = 8$, mit der Raumgruppe $Pna2_1$ und piezoelektrisch. Die Struktur wurde mittels dreidimensionaler Diffraktometerdaten bestimmt und mit Hilfe der Restquadratmethode auf $R = 0{,}055$ für alle Reflexe verfeinert. Sie stellt einen neuen Strukturtyp dar, welcher aus einem Netzwerk von eckenverbundenen Zink- und Siliziumtetraedern und dreiseitigen, beziehungsweise verzerrten vierseitigen Bleipyramiden aufgebaut ist. Die mittleren Kation-Sauerstoff-Abstände sind: Si—O 1,63 Å, Zn—O 1,95 Å, Pb(1)—O 2,33 Å und Pb(2)—O 2,47 Å.

Abstract

Larsenite is a rare mineral reported from Franklin, New Jersey. It is orthorhombic with $a = 8.244$ Å, $b = 18.963$ Å, $c = 5.06$ Å, $Z = 8$, space group $Pna2_1$, and is piezoelectric. The structure was determined using three-dimensional diffractometer data and was refined by least squares to an R of 0.055 for all reflections. It is a new type of structure composed of a network of corner-linked zinc and silicon tetrahedra and three-sided and distorted four-sided lead pyramids, respectively. The mean values of the cation-oxygen distances are Si—O, 1.63 Å; Zn—O, 1.95 Å; Pb(1)—O, 2.33 Å; and Pb(2)—O, 2.47 Å.

Introduction

Larsenite was discovered by Palache, Bauer and Berman (1928) in material from Franklin, New Jersey, U.S.A. As it is orthorhombic and chemically similar to olivine, larsenite was originally thought to

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belong to the olivine group. Layman (1957), however, noted that there were differences in the larsenite and olivine powder patterns and that when the cell axes were oriented with the ~ 5 Å *c* axes parallel, the space group orientations were different. The present structure study was therefore undertaken in order to resolve the problem.

Cell and space group

A slender needle of larsenite (approximately 0.03 mm in diameter) from Franklin material supplied by Professor Clifford Frondel of Harvard University was chosen for x-ray analysis. Precession, Weissenberg, and precision-Weissenberg photographs showed the crystal to be orthorhombic with the cell parameters*

$$\begin{aligned} a &= 8.2441 \pm 0.0001\ \text{Å} \\ b &= 18.9626 \pm 0.0002 \\ c &= 5.06 \pm 0.01 \\ Z &= 8 \end{aligned}$$

We confirmed Layman's (1957) finding that the space group should be either *Pnam* or $Pna2_1$. Later, after an attempt was made to solve the structure assuming *Pnam*, we found that the crystals are piezoelectric, thus establishing that $Pna2_1$ is the correct space group.

At the time the data were collected, the electron microprobe was not in general use and not enough type material was available for the usual quantitative analysis. Palache, Bauer and Berman (1928) had reported an admixture of clinohedrite with larsenite and attributed the 2.42 weight per cent Ca in the larsenite analysis to clinohedrite. We find, however, that their measured specific gravity of 5.90 is low compared to the calculated density (6.12) using the above cell and the formula $PbZnSiO_4$. The refinement results, discussed below, confirmed that Pb in the x-rayed crystal is diminished by about 3 atomic per cent. This would lower the calculated density to 6.04. It is probable, however, that the original specific-gravity measurements are in error because of impurities and extremely small amounts of available sample. Crystals of larsenite from a product of slag from the foundry

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* To obtain the values and errors given above for *a* and *b*, measurements from Straumanis-mounted, precision-Weissenberg type films were refined by least-squares using the Burnham (1962) computer program LCLSQ III. Since the calculated errors seem to be unusually small, it should be emphasized that this is an indication of the statistical precision of the measurements and not necessarily of the accuracy of *a* and *b*.

Kaltwasser, Raibl, Yugoslavia, were supplied by Professor F. Machatschki. The density of these crystals, determined by pycnometry, is 6.15.

Data collection

Three-dimensional diffraction intensities were collected on a Weissenberg diffractometer using a Geiger-tube detector and filtered Cu$K\alpha$ radiation. Although the linear absorption coefficient for larsenite and Cu$K\alpha$ radiation is large (911 cm^{-1}), the small crystal radius resulted in a cylindrical μR of 1.37, a reasonable value. This cylindrical absorption correction was applied to 839 non-equivalent reflections available to the diffractometer. No extinction correction was made.

Structure solution

As was mentioned above, structure solution was attempted at first assuming space group *Pnam*. Under this assumption, examination of the Patterson maps revealed strong peaks on levels $z = 0$ and $z = \frac{1}{2}$, indicating that there were two different lead atoms on the mirror planes at $z = \frac{1}{4}$, $z = \frac{3}{4}$. Then, using the Pb(1)—Pb(1) and Pb(2)—Pb(2) inversion peaks and the two glide planes in the space group, ${}^{\mathrm{Pb(1)}\,+\,\mathrm{Pb(2)}}M_{16}$ minimum-function maps for the mirror planes were formed. Figure 1 shows the map for the mirror plane at $z = \frac{1}{4}$. These maps contained peaks which could be assigned to Pb(1), Pb(2), Zn(1), Zn(2), and, possibly, Si(1) and Si(2). Coordinates corresponding to these peaks were selected for input to a least-squares refinement. Various least-squares trials were then made including some models with possible

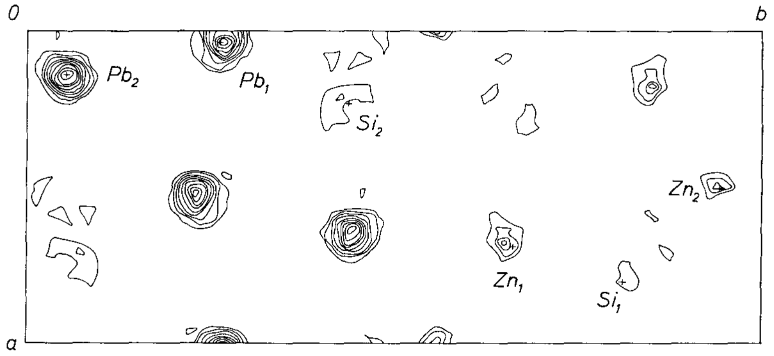


Fig. 1. Minimum function ${}^{\mathrm{Pb(1)}\,+\,\mathrm{Pb(2)}}M_{16}$ for $z = {}^{1}/_{4}$

oxygen positions included, but in no case could R be refined below 19%. At this point we checked the crystals for a piezoelectric effect and found a rather strong response using the Blume (1961)-type apparatus. Since our space group was proven incorrect, we kept only the Pb positions and calculated difference syntheses, using as input coefficients $[F_o(hk0)-F_c(hk0)_{\mathrm{Pb}}]$ and $[F_o(0kl)-F_c(0kl)_{\mathrm{Pb}}]$ for which the phases were determined by Pb. From these syntheses, the Zn(1), Zn(2), Si(1), and Si(2) positions were definitely located and then the same projections were again calculated using signs determined by Pb + Zn + Si. This revealed the eight oxygen positions. Preliminary refinement by difference synthesis resulted in an R of 0.14.

It is interesting to compare the final structure with the minimum-function map in Fig. 1. The crosses and labels show the positions of the cations in the actual structure and confirm that the minimum-function map was giving the correct information. This is because the z coordinates of the cations are close to $\frac{1}{4}$. Another point which should be mentioned is that if the space group really had been *Pnam*, satellite peaks should have occurred along $00z$ for all atoms not on the mirror planes. Since these atoms were thought to be only oxygen, this apparent contradiction was discounted.

Least-squares refinement

The parameters, as obtained in the last section, were used as input to a full-matrix least-squares program (Prewitt, 1964) and refined to a final R of 0.055 ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). Sources of form factors, anomalous dispersion coefficients, and other pertinent data are given in the Appendix. During the last stages of refinement, a form factor corresponding to three atomic per cent calcium substituted for lead in the Pb(1) position was introduced to account for a deficiency in scattering power seen in the difference Fourier syntheses.

Isotropic temperature factors were refined during the first cycles of refinement, and seemed to behave normally except for a rather large variation in oxygen B's. When anisotropic refinement was attempted, several of the oxygen β_{ij}'s became non-positive-definite, probably because the small scattering power of oxygen, with respect to lead, causes oxygen temperature effects to be poorly determined. In further cycles, the cation temperature factors were varied anisotropically, and those of oxygen, isotropically. This resulted in the atom coordinates, isotropic temperature factors, and standard errors given in Table 2.

Table 1. *Observed and calculated structure factors*
The phases may be obtained by using information given in the Appendix

h	k	l	F_o	F_c
2	0	0	77	71
4			45	48
6			241	265
8			20	22
10			150	143
1	1	0	60	61
2			208	213
3			308	363
4			151	153
5			66	75
6			159	178
7			115	125
8			139	139
9			111	111
10			99	119
0	2	0	32	22
1			46	39
2			148	152
3			88	85
4			213	230
5			181	194
6			68	70
7			13	14
8			142	150
9			41	59
10			37	12
1	3	0	48	49
2			104	103
3			15	13
4			230	250
5			105	114
6			223	241
7			74	75
8			12	26
9			37	35
10			30	36
0	4	0	185	167
1			182	180
2			245	272
3			158	165
4			94	91
5			159	161
6			26	15
7			125	126
8			0	6
9			150	158
10			62	60
1	5	0	139	126
2			352	405
3			122	118
4			63	58
5			42	36
6			59	53
7			45	40
8			221	228
9			73	76
0	6	0	294	274
1			139	129
2			178	179
3			100	93
4			73	73
5			285	302
6			67	62
7			53	51
8			86	86
9			0	4
1	7	0	198	187
2			61	60
3			291	308
4			142	141
5			180	185
6			151	146
7			131	124
8			20	12
9			30	32
0	8	0	261	234
1			38	35
2			151	146
3			107	103
4			142	132
5			140	142
6			155	156
7			100	105
8			101	95
9			115	115
1	9	0	288	297
2			81	76
3			207	205
4			181	181
5			51	47
6			69	64
7			89	85
8			43	38
9			165	169
0	10	0	415	432
1			128	117
2			29	27
3			193	195
4	10	0	47	39
5			52	49
6			174	174
7			142	140
8			48	51
9			112	114
1	11	0	177	170
2			149	152
3			251	255
4			41	32
5			108	106
6			54	47
7			73	69
8			76	74
9			0	4
0	12	0	30	29
1			42	19
2			95	93
3			36	32
4			69	71
5			267	276
6			28	23
7			115	122
8			50	45
1	13	0	134	134
2			163	164
3			155	147
4			50	40
5			58	59
6			94	94
7			51	42
8			114	115
0	14	0	160	149
1			245	254
2			23	15
3			131	127
4			0	6
5			46	36
6			64	59
7			152	147
8			27	37
1	15	0	166	163
2			132	132
3			22	22
4			154	143
5			37	26
6			83	83
7			46	57
0	16	0	105	95
1			74	68
2			64	61
3			100	98
4			84	85
5			142	143
6			92	99
7			95	92
1	17	0	79	76
2			18	11
3			241	259
4			118	111
5			80	75
6			23	21
7			42	55
0	18	0	222	228
1			67	66
2			71	76
3			49	47
4			30	28
5			157	150
6			127	135
1	19	0	116	122
2			132	128
3			78	85
4			0	10
5			25	20
6			36	31
0	20	0	44	38
1			76	71
2			61	58
3			86	85
4			88	77
5			35	29
1	21	0	50	42
2			36	30
3			51	49
4			80	80
1	22	0	67	70
2			97	96
3			28	24
1	23	0	25	19
2			122	131
2	0	1	377	430
4			12	9
8			260	275
10			75	75
0	1	1	260	239
1			163	170
2	1	1	224	230
3			87	84
4			55	52
5			236	251
6			49	45
7			57	60
8			15	16
9			86	83
10			144	140
1	2	1	65	63
2			78	75
3			68	65
4			247	263
5			65	67
6			218	229
7			168	177
8			66	67
9			26	22
10			47	45
0	3	1	91	78
1			89	85
2			331	390
3			88	88
4			280	310
5			54	54
6			67	70
7			54	51
8			73	69
9			93	99
10			58	56
1	4	1	352	408
2			61	61
3			131	131
4			202	204
5			134	134
6			130	130
7			192	194
8			111	112
9			85	80
0	5	1	481	530
1			86	79
2			63	54
3			133	127
4			154	155
5			48	51
6			142	139
7			104	100
8			67	68
9			73	72
1	6	1	41	33
2			190	191
3			227	230
4			103	101
5			37	33
6			63	62
7			176	177
8			122	123
9			24	24
0	7	1	132	111
1			64	55
2			158	157
3			13	6
4			208	212
5			270	273
6			43	41
7			100	104
8			65	64
9			31	28
1	8	1	194	194
2			152	146
3			178	171
4			166	165
5			41	29
6			188	186
7			40	32
8			49	45
9			30	25
0	9	1	12	13
1			242	232
2			134	136
3			214	208
4			77	71
5			80	73
6			37	30
7			185	184
8			20	15
9			173	175
1	10	1	257	256
2			235	242
3			142	145
4			101	101
5			42	28
6			42	32
7			106	103
8			141	136
9			81	78
0	11	1	137	126
1			104	100
2	11	1	51	53
3			116	110
4			105	104
5			228	228
6			46	43
7			94	92
8			52	51
1	12	1	17	38
2			33	31
3			218	214
4			12	13
5			48	35
6			52	44
7			157	157
8			19	22
0	13	1	176	174
1			16	18
2			136	136
3			86	88
4			157	154
5			186	189
6			76	73
7			64	71
8			29	24
1	14	1	292	318
2			124	126
3			34	34
4			66	66
5			117	116
6			29	21
7			128	127
8			49	47
0	15	1	38	33
1			106	99
2			96	91
3			153	145
4			161	160
5			30	27
6			60	69
7			112	108
1	16	1	83	76
2			76	77
3			117	114
4			75	75
5			38	33
6			142	144
7			55	54
0	17	1	15	32
1			62	59
2			93	90
3			0	7
4			41	26
5			198	189
6			13	11
1	18	1	46	44
2			162	162
3			124	115
4			0	6
5			36	33
6			24	20
0	19	1	150	158
1			153	158
2			37	29
3			63	61
4			38	36
5			34	31
1	20	1	145	148
2			36	33
3			43	43
4			122	121
5			34	30
0	21	1	50	46
1			0	16
2			131	138
3			36	30
4			150	155
1	22	1	52	55
3			93	94
0	23	1	155	135
1			47	69
2	0	2	153	149
4			92	98
6			213	234
8			34	34
1	1	2	88	89
2			135	133
3			300	318
4			155	161
5			57	56
6			120	126
7			106	104
8			142	140
9			92	91
0	2	2	57	53
1			107	112
2			192	206
3			24	19
4	2	2	174	178
5			140	144
6			82	82
7			51	47
8			138	139
9			42	38
1	3	2	123	124
2			115	116
3			42	46
4			231	241
5			90	92
6			238	245
7			63	55
8			50	49
9			59	57
0	4	2	211	187
1			236	236
2			220	221
3			175	180
4			103	104
5			150	146
6			50	46
7			134	139
8			0	6
9			139	133
1	5	2	152	142
2			303	321
3			68	64
4			24	14
5			34	28
6			72	67
7			48	44
8			230	234
9			67	68
0	6	2	313	291
1			144	136
2			191	192
3			74	65
4			78	83
5			252	253
6			84	75
7			54	51
8			79	76
9			43	38
1	7	2	162	157
2			56	48
3			269	266
4			154	144
5			140	138
6			140	132
7			105	101
8			47	38
9			23	18
0	8	2	211	196
1			58	58
2			132	124
3			117	110
4			155	147
5			148	142
6			125	116
7			72	66
8			103	100
1	9	2	261	254
2			46	46
3			150	146
4			109	106
5			38	30
6			50	44
7			102	96
8			38	38
0	10	2	310	300
1			110	106
2			33	31
3			146	141
4			96	98
5			59	60
6			174	171
7			143	140
8			42	38
1	11	2	152	152
2			124	123
3			249	252
4			43	36
5			108	103
6			68	59
7			78	75
8			91	85
0	12	2	45	45
1			102	96
2			68	65
3			54	45
4			37	29
5			261	263
6			28	24
7			119	117
8			45	37
1	13	2	140	141
2			166	171

Table 1. *(Continued)*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
3	13	2	175	171	4	2	3	201	218	0	11	3	161	155	7	2	4	51	50	4	13	4	60	59
4			83	78	5			56	57	1			83	86	1	3	4	76	75	5			48	51
5			37	33	6			205	216	2			21	18	2			129	127	0	14	4	88	88
6			85	78	7			113	118	3			83	86	3			86	90	1			114	115
7			36	37	8			72	75	4			96	96	4			185	185	2			0	19
0	14	2	127	132	0	3	3	137	128	5			193	191	5			63	69	3			95	96
1			166	168	1			73	83	6			88	85	6			179	186	4			44	34
2			17	16	2			257	273	7			81	78	7			47	52	1	15	4	141	149
3			138	133	3			93	90	1	12	3	45	38	0	4	4	158	139	2			64	65
4			47	45	4			239	251	2			48	40	1			147	142	3			52	51
5			39	35	5			50	52	3			204	208	2			161	158	0	16	4	70	77
6			54	46	6			93	94	4			31	31	3			134	127	1			38	28
7			149	141	7			49	43	5			50	46	4			79	76	2			63	63
1	15	2	148	152	8			67	60	6			44	37	5			93	92	3			72	73
2			104	105	1	4	3	276	282	7			129	128	6			30	39	1	17	4	81	86
3			50	46	2			85	91	0	13	3	168	178	7			81	81					
4			117	113	3			120	122	1			0	19	1	5	4	118	112	2	0	5	194	186
5			32	30	4			123	125	2			81	77	2			213	207	4			55	72
6			65	64	5			101	99	3			88	90	3			67	57	0	1	5	227	185
7			82	79	6			99	98	4			143	142	4			40	36	1			105	109
0	16	2	99	106	7			143	144	5			153	148	5			28	29	2			119	121
1			41	36	8			94	94	6			87	87	6			79	83	3			32	31
2			50	47	0	5	3	399	360	1	14	3	228	244	7			43	36	4			38	45
3			78	77	1			76	68	2			102	102	0	6	4	232	214	5			125	136
4			90	95	2			111	98	3			55	52	1			110	104	1	2	5	36	37
5			119	123	3			88	84	4			39	32	2			134	140	2			88	98
6			68	64	4			71	65	5			97	93	3			40	35	3			143	158
1	17	2	83	88	5			36	38	6			47	48	4			96	88	4			129	136
2			25	17	6			119	116	0	15	3	83	93	5			198	202	5			16	19
3			203	215	7			94	98	1			96	106	6			85	83	0	3	5	187	155
4			78	83	8			73	78	2			93	89	7			53	55	1			82	82
5			76	70	1	6	3	31	14	3			107	106	1	7	4	141	136	2			173	170
6			44	46	2			160	160	4			114	118	2			79	79	3			49	45
0	18	2	221	259	3			215	209	5			48	46	3			201	198	4			163	169
1			41	41	4			59	49	1	16	3	73	76	4			113	108	5			64	70
2			92	69	5			48	35	2			87	92	5			103	103	1	4	5	159	155
3			43	41	6			76	80	3			107	112	6			109	110	2			79	78
4			49	52	7			132	132	4			83	85	0	8	4	141	133	3			108	105
5			138	127	8			122	120	5			50	47	1			69	62	4			102	101
1	19	2	106	109	0	7	3	212	198	0	17	3	40	40	2			117	114	5			81	80
2			129	132	1			136	123	1			74	79	3			97	85	0	5	5	251	221
3			63	65	2			108	108	2			81	87	4			189	175	1			56	52
4			0	10	3			21	16	3			18	21	5			120	115	2			93	86
5			14	11	4			164	151	4			32	22	6			95	96	3			64	58
0	20	2	40	41	5			233	235	1	18	3	60	60	1	9	4	207	203	4			68	63
1			68	79	6			62	60	2			131	133	2			22	25	5			46	50
2			58	64	7			91	94	3			96	90	3			77	67	1	6	5	35	37
3			77	77	8			60	50	4			42	35	4			97	86	2			111	117
4			97	100	1	8	3	183	172	0	19	3	138	133	5			40	31	3			159	160
1	21	2	57	50	2			145	138	1			116	118	6			46	45	4			72	70
2			59	64	3			159	156	2			35	32	0	10	4	184	182	0	7	5	152	151
3			46	48	4			147	143	3			48	46	1			94	95	1			127	133
0	22	2	38	41	5			44	39	1	20	3	117	117	2			45	46	2			96	95
1			71	67	6			175	169						3			109	106	3			44	42
					7			18	23	2	0	4	106	104	4			83	77	4			93	92
2	0	3	295	299	8			74	72	4			107	119	5			59	61	1	8	5	91	102
4			34	30	0	9	3	41	29	6			151	155	6			96	99	2			117	122
6			93	105	1			190	181	1	1	4	90	95	1	11	4	122	129	3			111	115
8			218	224	2			104	101	2			145	146	2			108	117	4			105	107
0	1	3	262	239	3			161	156	3			186	185	3			168	178	0	9	5	34	34
1			175	183	4			76	72	4			105	107	4			66	65	1			102	113
2			180	186	5			58	58	5			33	36	5			73	73	2			52	54
3			86	84	6			21	13	6			101	109	0	12	4	54	54	3			107	108
4			65	61	7			143	144	7			122	126	1			98	109	1	10	5	147	167
5			169	180	1	10	3	211	208	0	2	4	101	89	2			53	46	2			101	104
6			77	85	2			177	177	1			101	103	3			47	51	3			92	94
7			36	24	3			138	139	2			149	158	4			46	35	0	11	5	113	131
8			0	0	4			76	62	3			30	27	5			193	196	1			22	31
1	2	3	54	53	5			47	32	4			159	166	1	13	4	105	118	2			11	14
2			92	95	6			52	49	5			120	125	2			116	125	1	12	5	53	60
3			139	151	7			86	89	6			60	55	3			108	115					

The expressions used for obtaining these values are given in the Appendix. Table 3*a* is a compilation of the cation anisotropic temperature factors and Table 3*b* gives the corresponding root mean square vibration amplitudes.

Explanation of the magnitudes of the individual temperature factors is rather difficult because of the dominance of lead. However, the average isotropic *B*'s for each atom type, Pb (.9), Zn (.7), Si (.7), and O (1.0), are all reasonable except that B_{Si} is probably larger than it should be. The "abnormal" oxygen, O(4), has the next-to-largest *B*, but O(1), which has the largest *B*, has a similar environment to O(2),

Table 2. *Final larsenite atom coordinates, equivalent isotropic temperature factors (cations), isotropic temperature factors (oxygen), and standard errors*

Standard errors are in parentheses

Atom	x	y	z	B
Pb(1)	0.0373(1)	0.2702(1)	$\frac{1}{4}$*	1.0
Pb(2)	.1476(1)	.0588(1)	.2780(4)	.9
Zn(1)	.8220(4)	.1560(2)	.7170(9)	.8
Zn(2)	.5017(4)	.0579(2)	.7220(9)	.6
Si(1)	.2008(8)	.1781(4)	.726(2)	.6
Si(2)	.7312(8)	.0739(4)	.215(2)	.8
O(1)	.220(3)	.257(1)	.593(6)	1.4(4)
O(2)	.351(2)	.130(1)	.646(5)	.7(3)
O(3)	.037(2)	.147(1)	.584(5)	.8(4)
O(4)	.173(3)	.183(1)	.042(5)	1.3(4)
O(5)	.748(3)	.152(1)	.081(5)	.9(4)
O(6)	.572(2)	.034(1)	.081(5)	.7(4)
O(7)	.886(3)	.024(1)	.144(5)	.8(4)
O(8)	.703(3)	.079(1)	.532(5)	1.1(4)

* The z parameter of Pb(1) was fixed at $\frac{1}{4}$ during the refinements to establish a reference coordinate in the c direction.

which has one of the smallest B's. Since these variations are nearly all within one σ of the mean, they may not be significant. The possibility does exist that there may be some exchange of atoms between the Zn(2) and Si(2) tetrahedra since the $B_{\mathrm{Zn}(2)}$ is too small and the $B_{\mathrm{Si}(2)}$ is too large.

The Pb and Zn thermal ellipsoids are rather anisotropic, with approximately 2:1 ratios of the major to minor axes. For Si, the thermal vibrations are nearly isotropic. It is interesting that the major axes of the lead and zinc ellipsoids are approximately parallel with b. No explanation for this is immediately apparent except that for lead this direction makes a right angle with the general direction to the

Table 3*a*. *Final cation anisotropic temperature factors for larsenite*

Standard errors are in parentheses (all values $\times 10^{-4}$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb(1)	38 (2)	10 (0)	61 (5)	2 (0)	−20 (3)	−2 (1)
Pb(2)	35 (1)	8 (0)	57 (5)	0 (0)	1 (3)	−4 (1)
Zn(1)	28 (5)	9 (1)	45 (21)	−2 (2)	2 (9)	2 (4)
Zn(2)	18 (5)	7 (1)	39 (19)	−4 (2)	0 (9)	2 (4)
Si(1)	39 (10)	4 (2)	38 (38)	3 (3)	−14 (17)	−12 (7)
Si(2)	20 (9)	7 (2)	95 (47)	0 (4)	2 (18)	−2 (7)

Table 3*b*. *Magnitudes and orientations of the cation thermal ellipsoids in larsenite*

R		rms displacement	+*a*	+*b*	+*c*
Pb(1)	1	.075 (5)	61 (3)	88 (3)	29 (3)
	2	.121 (3)	38 (6)	117 (7)	115 (4)
	3	.136 (2)	67 (6)	27 (7)	104 (4)
Pb(2)	1	.083 (4)	94 (6)	75 (4)	16 (4)
	2	.110 (2)	173 (6)	85 (8)	95 (6)
	3	.123 (2)	84 (8)	16 (4)	105 (7)
Zn(1)	1	.08 (2)	98 (26)	96 (10)	10 (23)
	2	.098 (9)	167 (18)	100 (12)	99 (26)
	3	.131 (7)	101 (11)	12 (10)	85 (9)
Zn(2)	1	.07 (2)	60 (*)	74 (32)	145 (*)
	2	.07 (1)	143 (*)	103 (38)	124 (*)
	3	.122 (7)	110 (8)	21 (8)	84 (10)
Si(1)	1	.0 (1)	86 (16)	53 (17)	37 (16)
	2	.10 (2)	49 (22)	129 (23)	65 (19)
	3	.13 (2)	41 (22)	60 (16)	115 (15)
Si(2)	1	.08 (2)	4 (40)	89 (26)	94 (42)
	2	.11 (2)	93 (42)	121 (98)	148 (97)
	3	.12 (2)	87 (27)	31 (98)	121 (97)

* Sigma larger than 99°.

bonded oxygens. The errors of orientation are fairly large and it is felt that it is not advisable to further interpret these orientations. For Zn(2) the orientations of r_1 and r_2 are nearly indeterminate since the magnitudes of r_1 and r_2 are similar.

Discussion of the structure

Figures 2*a* and 2*b* are different views of polyhedral models of larsenite. The principal features of the models are the corner-sharing zinc and silicon tetrahedra. These tetrahedra are linked at all vertices [except O(4) of the Si(1) tetrahedron and O(7) of the Si(2) tetrahedron which are coordinated to lead] to form a network structure. This network is made up of double chains of five-membered Zn(1)-Si(1)-Zn(1)-Si(1)-Zn(2) rings which lie in the *ab* plane and extend along *a*. These chains are interconnected by three-membered Zn(1)-Zn(2)-Si(2) and Zn(2)-Zn(2)-Si(2) rings. Pb(1) occupies the intersections of three channels in the tetrahedral network, one parallel to *a*, one to *c*, and the other to

[210]. Pb(2) also occupies the [210] channel plus another parallel to *c*. These lead atoms are covalently bonded and form three-sided and distorted four-sided pyramids, respectively.

The five-membered rings mentioned above are similar (although the ring interconnections are different) to those in the melilite structure (Smith, 1953). In particular, they should correspond to the rings in the melilite hardystonite, $Ca_2ZnSi_2O_7$ and a synthetic compound, $Pb_2ZnSi_2O_7$, which has also been reported to have the melilite structure (Brisi, 1964).

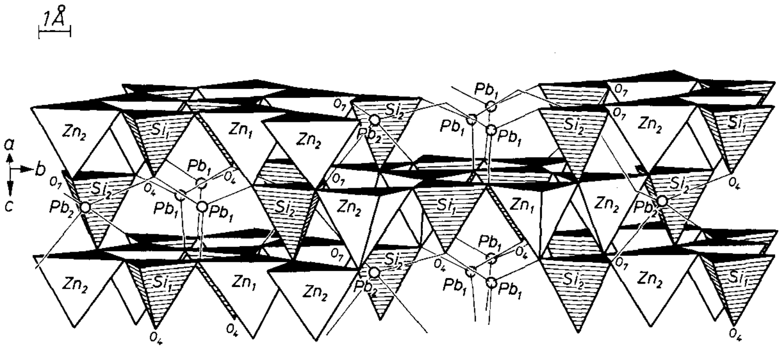


Fig. 2a. Polyhedral model for larsenite viewed approximately along *a*

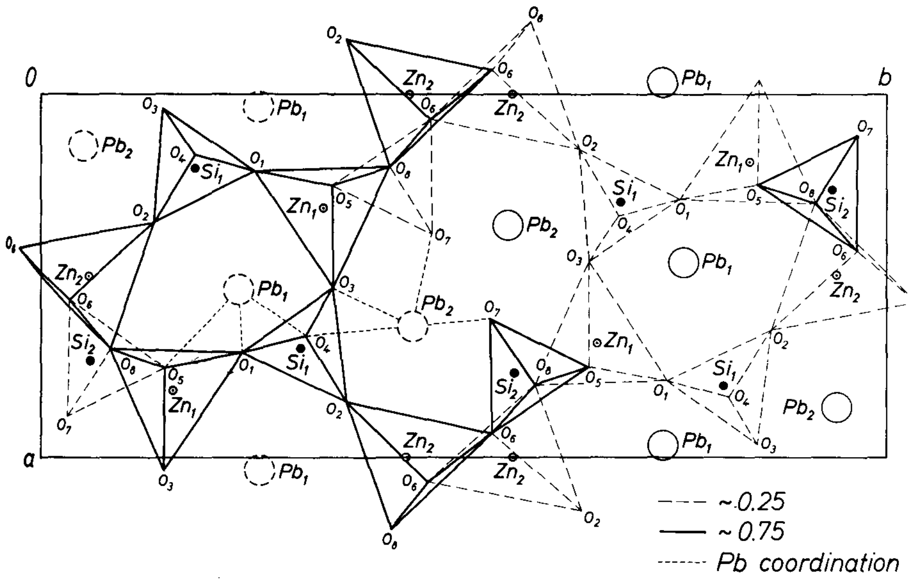


Fig. 2b. Polyhedral model of larsenite viewed along *c*

Figure 3 shows a ball and stick model of larsenite projected along the z axis, in which all short distances of the cation-oxygen bonds are indicated by full lines. It is interesting to note that the atoms occur in fairly distinct layers parallel to the ab plane with the cations being close to $z = 0.25$, $z = 0.75$ and oxygen atoms close to $z = 0.10$, $z = 0.60$. This results in the tetrahedra and pyramids all being aligned in approximately the same way and is also the reason for the polar space group.

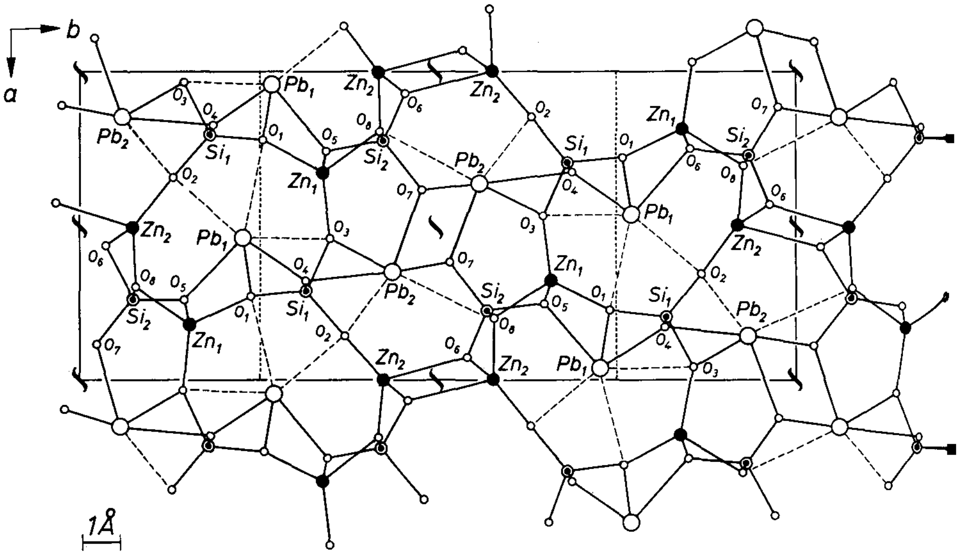


Fig. 3. Structure of larsenite projected along c. Full lines: short cation-oxygen distances

Interatomic distances and interbond angles for larsenite are given in Table 4 and Fig. 4. The most interesting of these are the Pb—O distances and angles. Pb(1) is coordinated by three oxygen atoms at an average distance of 2.33 Å to form a three-sided pyramid, and Pb(2) is coordinated by four oxygen atoms at an average distance of 2.47 Å to form a distorted four-sided pyramid. Other Pb—O distances are larger than 2.85 Å (Fig. 4). The situation is similar to that found for orthorhombic PbO (Leciejewicz, 1961a; Kay, 1961), where the lead-oxygen polyhedra are in the form of distorted PbO(4) pyramids with an average distance of 2.35 Å; for tetragonal PbO (Leciejewicz, 1961b), wherein the distances of the PbO(4) pyramids are 2.37 Å; for linarite, $PbCuSO_4(OH)_2$ (Bachmann and Zemann, 1961; Araki, 1962) with an average distance of 2.42 Å for a three-sided

Table 4. *Interatomic distances in larsenite*
(± 0.01 Å)

Pb(1)—O(1)	2.31 Å	Pb(2)—O(3)	2.45 Å
Pb(1)—O(4)	2.26	Pb(2)—O(4)	2.65
Pb(1)—O(5)	2.43	Pb(2)—O(7)	2.35
Pb(1)—O$_{av}$	2.33	Pb(2)—O(7′)	2.44
Pb(1)—O(3)	2.88	Pb(2)—O$_{av}$	2.47
Pb(1)—O(1′)	3.18	Pb(2)—O(2)	2.85
Pb(1)—O(2)	3.15	Pb(2)—O(8)	3.15
Zn(1)—O(1)	1.96	Zn(2)—O(2)	1.89
Zn(1)—O(3)	1.90	Zn(2)—O(6)	1.96
Zn(1)—O(5)	1.94	Zn(2)—O(6′)	1.98
Zn(1)—O(8)	1.99	Zn(2)—O(8)	1.96
Zn(1)—O$_{av}$	1.95	Zn(2)—O$_{av}$	1.95
Si(1)—O(1)	1.65	Si(2)—O(5)	1.63
Si(1)—O(2)	1.59	Si(2)—O(6)	1.66
Si(1)—O(3)	1.64	Si(2)—O(7)	1.63
Si(1)—O(4)	1.62	Si(2)—O(8)	1.62
Si(1)—O$_{av}$	1.63	Si(2)—O$_{av}$	1.63
About Si(1):	(± 0.03 Å)	About Si(2): (± 0.03 Å)	
O(1)—O(2)	2.65	O(5)—O(6)	2.67
O(1)—O(3)	2.58	O(5)—O(7)	2.70
O(1)—O(4)	2.70	O(5)—O(8)	2.70
O(2)—O(3)	2.63	O(6)—O(7)	2.62
O(2)—O(4)	2.68	O(6)—O(8)	2.67
O(3)—O(4)	2.66	O(7)—O(8)	2.69
(O—O)$_{av}$	2.65	(O—O)$_{av}$	2.67
About Zn(1): (± 0.03 Å)		About Zn(2): (± 0.03 Å)	
O(1)—O(3)	3.19	O(2)—O(6)	3.39
O(1)—O(5)	3.12	O(2)—O(6′)	3.19
O(1)—O(8)	3.13	O(2)—O(8)	3.11
O(3)—O(5)	3.47	O(6)—O(6′)	3.08
O(3)—O(8)	3.05	O(6)—O(8)	3.10
O(5)—O(8)	3.13	O(6)—O(8)	3.13
(O—O)$_{av}$	3.18	(O—O)$_{av}$	3.17

pyramid; for pyrobelonite, PbMnVO$_4$(OH) (Donaldson and Barnes, 1955) with an average distance of 2.47 Å for a distorted four-sided pyramid. For Pb—O, the sum of the ionic radii is about 2.64 Å and of the covalent radii, about 2.40 Å. It seems that the bond of Pb—O in larsenite has a covalent character.

Average Si—O and Zn—O distances are 1.63 Å and 1.95 Å, respectively. The Si—O distances are similar to 1.63 Å found for individual silicate tetrahedra by Smith and Bailey (1963). The Zn—O distances are comparable with that of 1.92 Å in willemite, Zn_2SiO_4 (Bragg and

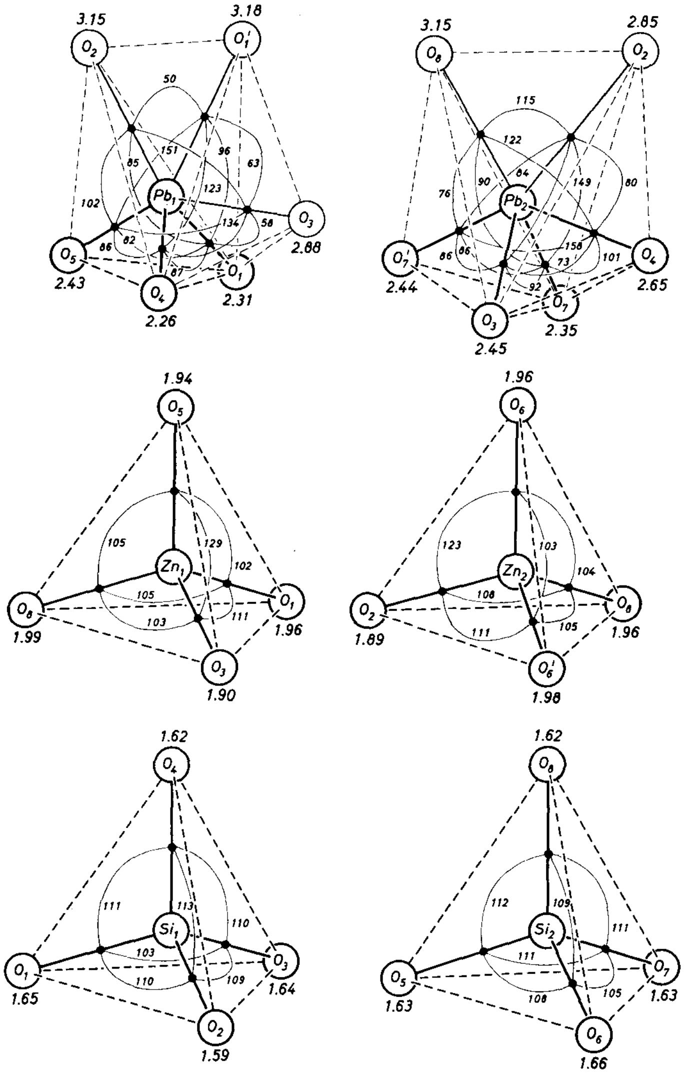
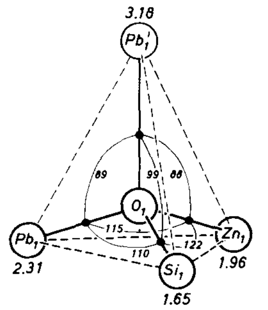
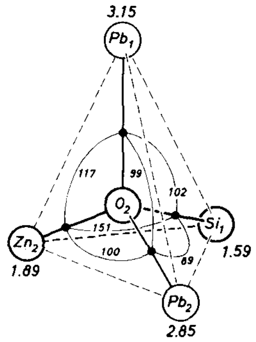
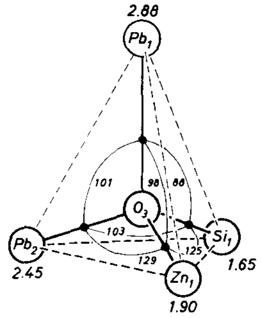
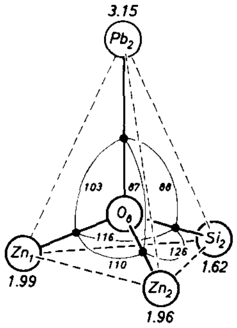


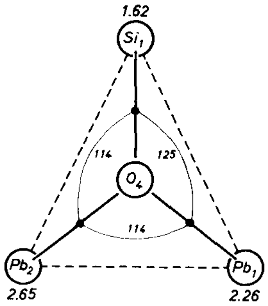
Fig. 4. Interatomic distances in Å and interbond angles in degrees

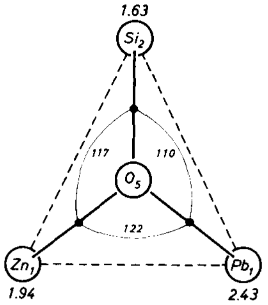

3.18
Pb_1'
89
99
88
O_1
115
122
110
Pb_1
Zn_1
2.31
1.96
Si_1
1.65

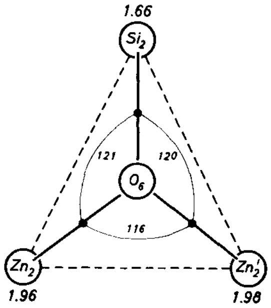

3.15
Pb_1
117
99
102
O_2
151
Si_1
Zn_2
100
89
1.59
1.89
Pb_2
2.85

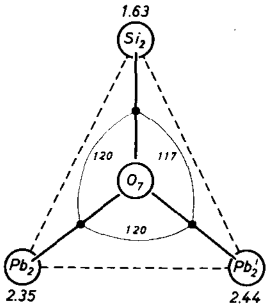

2.88
Pb_1
101
98
88
O_3
103
Si_1
Pb_2
125
129
2.45
1.65
Zn_1
1.90


3.15
Pb_2
103
87
88
O_8
116
126
Si_2
Zn_1
110
1.99
1.62
Zn_2
1.96


1.62
Si_1
114
125
O_4
114
Pb_2
Pb_1
2.65
2.26


1.63
Si_2
117
110
O_5
122
Zn_1
Pb_1
1.94
2.43


1.66
Si_2
121
120
O_6
116
Zn_2
Zn_2'
1.96
1.98


1.63
Si_2
120
117
O_7
120
Pb_2
Pb_2'
2.35
2.44

ZACHARIASEN, 1930) and of 1.97 Å in hodgkinsonite, $Zn_2Mn(OH)_2SiO_4$ (RENTZEPERIS, 1963).

Each oxygen atom, except O(2), is nearly planar-coordinated at short distances by three atoms, Si—Zn—Pb, or Si—Zn—Zn, or Si—Pb—Pb. The O(2) is coordinated only by two atoms, one Si and one Zn. The distances Si—O (1.59 Å) and Zn—O (1.89 Å) are here shorter than the average distances and the angle Zn—O—Si is 151 °.

It is worthwhile to compare the larsenite structure with that of esperite (formerly called calcium larsenite). MOORE and RIBBE (1965) found that esperite, $Ca_3Pb(ZnSiO_4)_4$ is monoclinic and structurally very similar to beryllonite, $NaBePO_4$ (GOLOVASTIKOV, 1962) and trimerite, $CaMn_2[BeSiO_4]_3$. It is apparent that although the larsenite and esperite structures both contain networks of tetrahedra, the actual configurations are different. A detailed comparison, however, will not be possible until results of an esperite refinement are available.

Appendix

Data for reconstructing the refinement and interatomic distances

Refinement

Final refinement was done on an IBM 7044 computer using a full-matrix least-squares program SFLS4 written by PREWITT (1964). The standard errors for the various parameters were calculated from

$$\sigma_{(p)} = b_{ii}^{\frac{1}{2}} \{[\sum_{m}(w\Delta^2) - \sum_{i=1}^{n} \Delta p_i v_i]/[m-n]\}^{\frac{1}{2}} \qquad (A.1)$$

where $b_{ii}^{\frac{1}{2}}$ is a diagonal element of the inverted matrix, w is the observational weight, Δ is $F_o - F_c$, v_i is the vector of the normal equations, m the number of observations, and n the number of parameters. The weights were obtained from

$$w = 1/[10.0 + 0.5\,|F_o| + 0.0026 - |F_o|^2]. \qquad (A.2)$$

After the last cycle of refinement, interatomic distances and angles were computed using the BUSING, MARTIN and LEVY (1964) program ORFFE. Errors were computed using the variance-covariance matrix from the atom parameter refinement, but did not include the errors of the cell-parameter refinement.

Equivalent B's were derived from an expression given by HAMILTON (1959):

$$B_{\mathrm{equiv}} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij}\,(\mathbf{a}_i \cdot \mathbf{a}_j) \qquad (A.3)$$

where the **a** are the cell axes. For anisotropic refinement,

$$T = \exp\{-[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]\}.$$

Form factors and anomalous-dispersion coefficients were taken from International Tables for X-Ray Crystallography, Vol. III (1962). Reference symbols are those given in International Tables.

Atom	Reference	$\Delta f'$	$\Delta f''$
Pb^{+2}	S-66	-4.5	9.5
Zn^{+2}	SX-45	-1.7	.75
Si^{+2}	SX-19, SX-70	.20	.40
O^{-1}	SX-31a	.10	.0
Ca^{+1}	SX-40	.30	1.4

The $|F_c|$'s listed in Table 1 were computed from

$$|F_c| = \{(A_r - B_i)^2 + (B_r + A_i)^2\}^{\frac{1}{2}} \tag{A.4}$$

where $A_r = \Sigma\,(f + \Delta f')\,\zeta\cos\varphi, \quad A_i = \Sigma\Delta f''\,\zeta\cos\varphi$

$B_r = \Sigma\,(f + \Delta f')\,\zeta\sin\varphi, \quad B_i = \Sigma\Delta f''\,\zeta\sin\varphi$

and ζ and φ are scale and temperature factors and trigonometric parts of the structure factors. Reversing the signs of *hkl* at the end of refinement resulted in a slightly larger *R* factor (~ 0.01 larger), so that the signs in (A.4) above probably are correct.

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