THE AMERICAN MINERALOGIST, VOL. 52, JULY-AUGUST, 1967

SYNTHESES OF LEAD SILICATES: LARSENITE, BARYSILITE AND RELATED PHASES*

JUN ITO AND CLIFFORD FRONDEL, *Department of Geological Sciences, Harvard University, Cambridge, Massachusetts.*

ABSTRACT

Larsenite, $PbZnSiO_4$, has been synthesized both by heating a precipitated gel of the same composition in air at 1 atm. to temperatures from 500° to 950°C, and by hydrothermal crystallization of the gel at temperatures from 300° to 550°C and a pressure of 2000 bars. Larsenite melts incongruently at 1000°C and 1 atm. to willemite and liquid lead silicate; under hydrothermal conditions larsenite becomes unstable between 550° and 650°C. Efforts failed to synthesize compounds isostructural with larsenite in which Zn is replaced by Mn, Fe, Co, Ni, Mg, Cd or Be. Indexed X-ray powder data are given for synthetic $PbZnSiO_4$.

Barysilite, $MnPb_5(Si_2O_7)_2$, and analogues of this compound in which Mn is wholly replaced by Fe, Co, Ni, Zn, Cd, Mg or Ca have been synthesized either hydrothermally by crystallization of precipitated gels at temperatures from 200° to 550°C and pressures of 1500 to 3000 bars, or by heating gels in air at 1 atm. and temperatures of 600° to 800°C. The idealized formula $Pb_3Si_2O_7$ has been generally attributed to barysilite, but efforts to synthesize this compound failed. The presence of Mn or of another ion in substitution for it, in addition to Pb, appears to be requisite for the formation of the barysilite structure type. X-ray powder spacing data are given for synthetic barysilite and its seven analogues.

SYNTHESIS OF LARSENITE

Larsenite, related to the olivine group, is known as a mineral only from Franklin, New Jersey (Palache, Bauer and Berman, 1928a, b). It has been synthesized by heating a gel with the composition $PbO \cdot ZnO \cdot SiO_2 \cdot nH_2O$ in air at temperatures from 500° to 900°C. The gel was precipitated from a water solution containing 0.4 mM each of lead nitrate, zinc acetate and sodium silicate by the addition of 4 molar NaOH solution to a final pH of 10. The precipitate was stirred magnetically for 5 minutes, centrifuged and washed repeatedly with distilled water. The air dried product contained about 40 percent H_2O. On heating in air, larsenite began to crystallize at an appreciable rate at about 500° and remained stable up to 950°C. At 1000°, larsenite melted incongruently to willemite and liquid lead silicate. The optimum production of larsenite, judging from the X-ray powder pattern, was obtained by a heating period of 20 hours at 800°C. Larsenite also has been synthesized hydrothermally from the same starting materials used for the dry syntheses. The samples were heated in a silver liner in a steel cold-seal rod bomb at temperatures from 300° to 550°C and a water pressure of 2000 bars. The results of this work are given in Table 1. No reduction of Pb^{2+} to Pb metal occurred under the conditions of these experiments. The crystallization of larsenite at an appreciable rate and the point of its thermal breakdown are about 200°C lower under hydrothermal conditions than when heated in air.

The hydrothermally synthesized larsenite crystals are prismatic along [001] and appear to be very similar in habit, as observed under the microscope (Figure 1), to natural crystals figured by Palache (1937). They ranged up to about 0.2 mm in length. The crystals are colorless to white at room temperature but become reddish brown when heated in air to

* Mineralogical Contribution No. 438.

TABLE 1. SYNTHESES OF LARSENITE, $PbZnSiO_4$

	Gel composition	Pressure (bars)	Temperature (°C)	Time (hours)	Phases observed
1.	$PbZnSiO_4$	1	500	20	Larsenite
2.	$PbZnSiO_4$	1	600	20	Larsenite
3.	$PbZnSiO_4$	1	800	20	Larsenite
4.	$PbZnSiO_4$	1	900	20	Larsenite
5.	$PbZn_2Si_2O_7$	1	900	20	Larsenite, willemite
6.	$PbZn_2Si_2O_7$	1	800	30	Larsenite, Zn-barysilite
7.	$Pb_4ZnSi_3O_{11}$	1	700	20	Larsenite, Zn-barysilite
8.	$Pb_4ZnSi_3O_{11}$	1	600	30	Zn-barysilite, larsenite
9.	$Pb_3ZnSi_2O_8$	1	700	20	Zn-barysilite, larsenite
10.	$PbZnSi_2O_6$	1	700	20	Larsenite
11.	$Pb_{2.5}Zn_{0.5}Si_2O_7$	1	700	20	Zn-barysilite
12.	$PbZnSiO_4$	1	1050	20	Willemite
13.	$PbZnSiO_4$	2000	500	48	Larsenite
14.	$PbZnSiO_4$	2000	450	96	Larsenite
15.	$PbZnSiO_4$	2000	650	48	Willemite
16.	$PbZnSiO_4$	2000	550	24	Larsenite, willemite
17.	$PbZnSiO_4$	2000	280	72	Larsenite
18.	$PbZnSiO_4$	1500	400	3 weeks	Larsenite

temperatures over about 500°C. Optically, the crystals are biaxial negative with parallel extinction; $Y=c$ with $\alpha\sim1.91$ and $\gamma\sim1.96$. Larsenite synthesized dry or hydrothermally does not fluoresce in either long-wave or short-wave ultraviolet radiation.

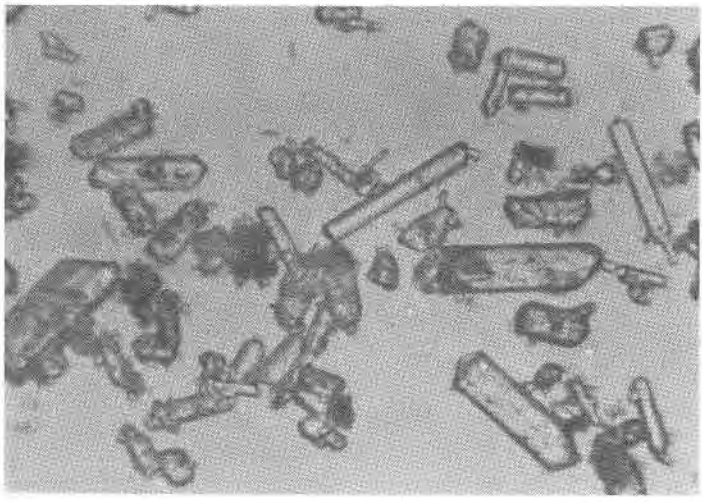

FIG. 1. Crystals of synthetic larsenite (run no. 13, Table 1) ×100.

Synthetic larsenite gave a very sharp X-ray diffractometer pattern. This has been indexed (Table 2) using the orthorhombic cell obtained by Layman (1957) on natural material. The cell dimensions are a 8.24 Å $\pm$.02, b 19.00$\pm$.04, c 5.05$\pm$.01. These values are slightly larger than those of Layman (a 8.23, b 18.94, c 5.06 Å), probably because of the presence of relatively small ions such as Ca, Mn, and Mg in solid solution in small amounts in the natural material. The calculated density is 6.12.

Efforts failed to synthesize compounds isostructural with larsenite that contained other divalent ions in place of Zn, including Mg, Fe, Co, Ni, Mn, Cd and Be.

Syntheses of Barysilite and Analogues

Barysilite, for which the new formula $MnPb_5(Si_2O_7)_2$ is suggested, has been synthesized hydrothermally at temperatures from 380° to 550°C and pressures from 1500 to 2000 bars. Gels of the compositions indicated in Table 3 were employed as starting materials. The gels were precipitated by addition of NaOH solution to a final pH of 10 from appropriate amounts of 0.2 molar solutions of lead nitrate, sodium metasilicate, and manganous carbonate dissolved in dilute HCl containing ascorbic acid as reducing agent. The gels were washed with water, centrifuged, and air dried at room temperature. Samples were then heated together with water in steel rod bombs fitted with silver liners and connected by capillary tubing to a force pump and a Bourdon gauge for control of pressure. The crystals obtained were hexagonal plates ranging up to several millimeters in size (Figure 2). The X-ray powder diffraction pattern of the synthetic material is identical with that of natural barysilite from Franklin, New Jersey, except that the latter material very commonly contains weak extra lines caused by intimately intergrown nasonite. Our powder data agrees closely with that of Glasser (1964), obtained on Franklin material. His pattern apparently also contains nasonite lines. Nasonite breaks down readily to an unidentified anhydrous CaPb silicate at about 780°C (Ito and Frondel, 1966). The X-ray powder data given by Glasser for Franklin barysilite heated at 760°C appears to represent a mixture of barysilite, nasonite and the decomposition product of nasonite. We observed that synthetic barysilite is not irreversibly changed by heating in air to 800°C; the melting point is near 850°C.

The ferrous iron analogue of barysilite has been synthesized hydrothermally, by the same method, as yellow hexagonal plates 3 to 4 mm in width. The Co, Ni, Ca, Mg, Cd, Zn and Cu analogues also have been synthesized either hydrothermally or by heating gels in air at 1 atm. In all instances gels were used as the starting material. They were prepared as with barysilite but with the appropriate 0.2 molar nitrate or chloride solution used in place of manganous nitrate. The Fe^{2+} member was precipitated by NH_4OH to a final pH of 10 from a solution containing ascorbic acid. The results of these syntheses are listed in Table 3.

In some syntheses of Mn-barysilite and of Fe-barysilite small amounts of kentrolite, $Pb_2Mn_2Si_2O_9$, and of melanotekite, $Pb_2Fe_2Si_2O_9$, were formed. A study of the synthetic kentrolite-melanotekite solid solution series is given elsewhere (Ito and Frondel, 1966).

The X-ray patterns of all of these phases are identical with that of barysilite, aside from differences in spacings reflecting the sizes of the ions involved, and are listed in Table 4. The spacings of the natural Mn-barysilites examined by us and by Glasser (1964) are virtually identical with those of the synthetic material. Under the microscope, the materials

TABLE 2. X-RAY POWDER DATA FOR SYNTHETIC LARSENITE

d(Å)	I	hkl	Q Obs.	Q Calc.
7.591	10	110	0.0173	0.0175
6.231	5	120	0.0258	0.0258
4.875	80	011	0.0420	0.0419
4.751	20	040	0.0443	0.0443
4.191	60	111	0.0569	0.0566
4.111	50	200, 140	0.0591	0.0588, 0.0590
4.030	50	210	0.0616	0.0616
3.965	2	031	0.0636	0.0640
3.928	10	121	0.0648	0.0649
3.776	30	220	0.0701	0.0699
3.556	15	131	0.0791	0.0787
3.450	20	230, 150	0.0840	0.0837, 0.0840
3.193	100	201, 141	0.0981	0.0979, 0.0981
3.151	10	210	0.1007	0.1007
3.114	15	240	0.1031	0.1031
3.035	80	051, 221	0.1086	0.1084, 0.1090
2.955	5	160	0.1145	0.1144
2.854	90	151, 231	0.1228	0.1231, 0.1228
2.793	30	250	0.1282	0.1281
2.720	30	310	0.1352	0.1350
2.651	3	241	0.1423	0.1422
2.576	8	170	0.1507	0.1504
2.525	25	330, 002	0.1568	0.1572, 0.1564
2.442	1	251, 022	0.1677	0.1672, 0.1674
2.395	3	112, 071	0.1743	0.1739, 0.1741
2.376	5	080	0.1771	0.1773
2.341	3	122, 321	0.1825	0.1822, 0.1825
2.295	2	171	0.1899	0.1895
2.249	8	261	0.1977	0.1976
2.230	8	350, 042	0.2011	0.2016, 0.2007
2.150	10	212, 142	0.2163	0.2154, 0.2157
2.100	5	222	0.2268	0.2263
2.080	5	181	0.2311	0.2311
2.075	5	360	0.2323	0.2320
2.068	7	271	0.2338	0.2336
2.064	8	400	0.2347	0.2352
2.057	5	280	0.2363	0.2361
2.053	8	410	0.2373	0.2381
2.044	5	190	0.2394	0.2391
2.039	10	351, 152	0.2405	0.2404, 0.2407
2.014	5	420	0.2465	0.2462
1.975	5	062	0.2564	0.2561
1.961	10	430, 242	0.2600	0.2595, 0.2601
1.932	25	370	0.2679	0.2680
1.917	8	361	0.2721	0.2711
1.894	10	191	0.2788	0.2782

TABLE 2—(*continued*)

d(Å)	*I*	*hkl*	*Q* Obs.	*Q* Calc.
1.872	15	421	0.2854	0.2853
1.850	10	1.10.0	0.2922	0.2917
1.828	8	322, 431	0.2993	0.2991, 0.2998
1.802	3	371	0.3080	0.3071
1.779	3	262	0.3160	0.3149
1.770	5	441	0.3192	0.3186
1.760	3	291	0.3228	0.3223
1.737	8	1.10.1	0.3314	0.3308
1.731	8	342, 082	0.3337	0.3330, 0.3337
1.705	2	451	0.3440	0.3436
1.687	5	272	0.3514	0.3509
1.672	8	352	0.3577	0.3580
1.640	5	470, 510	0.3718	0.3702, 0.3709
1.630	8	033	0.3764	0.3768
1.587	15	391	0.3971	0.3958
1.558	20	480, 540	0.4120	0.4118, 0.4125
1.534	10	372	0.4250	0.4244
1.513	10	550, 442	0.4368	0.4368, 0.4359
1.487	5	121, 481	0.4522	0.4516, 0.4527
1.474	3	452	0.4603	0.4609

Cu radiation, Ni filter, in Ångstrom units. Relative line intensities in arbitrary chart units. Indexing for cell with *a* 8.24 Å, *b* 19.00, *c* 5.05.

synthesized by heating gels in air were found to be microcrystalline. The hydrothermal syntheses afforded distinct hexagonal plates in most instances. Optically, all of the phases were uniaxial negative with indices of refraction over 1.97. Mg-barysilite fluoresced a pale buff color in short-wave ultraviolet radiation and the other preparations did not fluoresce.

Composition of Barysilite. Barysilite, originally described by Sjögren and Lundström (1888) from the Harstig mine, Pajsberg, Sweden, and later described from Långban and Jacobsberg, Sweden, and from Franklin, New Jersey,* has been generally considered to have the ideal composition $Pb_3Si_2O_7$. We have failed in efforts to synthesize $Pb_3Si_2O_7$, and this phase

* Barysilite has been ranked among the rarest minerals at Franklin, and is known only from the brief description by Bauer and Berman (1930). In 1954, it was found abundantly when supporting pillars in the old Parker shaft area were removed prior to closing the mine. This material formed lamellar or interlocking aggregates of anhedral plates up to 3 cm across and 3 mm thick. It was colorless to white with a faint pink tint in direct sunlight. The crystals are uniaxial negative, with ω well over 1.97. Twinning parallel (0001) was observed in a few instances. The barysilite is closely associated with nasonite, as in the original finds. Margarosanite occurs locally and may have formed from barysilite.

TABLE 3. SYNTHESES OF BARYSILITE AND ANALOGUES

	Gel Compositions	Temp. (°C)	Pressure (bars)	Time	Phase
1.	$Pb_{2.5}Mn_{0.5}Si_2O_7$	550	2000	7 days	Barysilite
2.	$Pb_4Mn_{7/11}Si_3O_x$	500	2000	20 hours	Barysilite, alamosite
3.	$Pb_3Mn_1Si_2O_8$	500	1800	20 hours	Barysilite, alamosite
4.	$Pb_4Mn_1Si_3O_{11}$	500	1500	20 hours	Barysilite, alamosite
5.	$PbMnSiO_4$	380	1500	3 weeks	Barysilite, pyroxmangite
6.	$Pb_{2.5}Fe_{0.5}Si_2O_7$	450	3000	24 hours	Fe-barysilite
7.	$Pb_{2.5}Fe_{0.5}Si_2O_7$	380	1500	3 weeks	Fe-barysilite
8.	$PbCdSiO_4$	700	1	20 hours	Cd-barysilite, unident.
9.	$Pb_4Cd_1Si_3O_{11}$	700	1	20 hours	Cd-barysilite, unident.
10.	$Pb_2Cd_1Si_2O_7$	800	1	20 hours	Cd-barysilite, unident.
11.	$Pb_2Cd_1Si_2O_7$	500	2000	72 hours	Cd-barysilite, unident.
12.	$Pb_3Cd_1Si_3O_{10}$	800	1	20 hours	Cd-barysilite, unident.
13.	$Pb_{2.5}Ca_{0.5}Si_2O_7$	750	1	20 hours	Ca-barysilite
14.	$Pb_1Ca_2Si_3O_{11}$	350	2000	72 hours	Ca-barysilite, margarosanite, Pb-Ca silicate
15.	$PbCuSiO_4$	700	1	30 hours	Cu-barysilite, unident.
16.	$Pb_4CuSi_3O_{11}$	700	1	20 hours	Cu-barysilite, unident.
17.	$PbCoSiO_4$	700	1	20 hours	Co-barysilite, unident.
18.	$Pb_4CoSi_3O_{11}$	700	1	20 hours	Co-barysilite, unident.
19.	$Pb_3MgSi_2O_8$	750	1	20 hours	Mg-barysilite unident.
20.	$PbNiSiO_4$	700	1	20 hours	Ni-barysilite, unident.
21.	$Pb_4Ni_1Si_3O_{11}$	700	1	20 hours	Ni-barysilite, unident.
22.	$Pb_{2.5}Zn_{0.5}Si_2O_7$	600	1	20 hours	Zn-barysilite
23.	$Pb_{2.5}Zn_{0.5}Si_2O_7$	500	2000	72 hours	Zn-barysilite
24.	$Pb_3Si_2O_7$	480	3000	72 hours	Pb_2SiO_4, alamosite
25.	$Pb_3Si_2O_7$	350	2000	24 hours	Pb_2SiO_4, alamosite

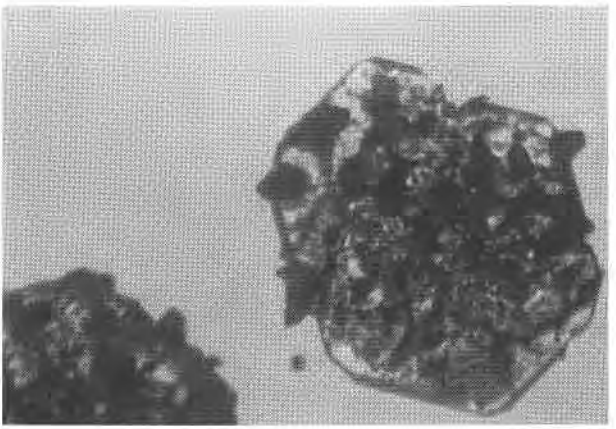

FIG. 2. Hexagonal tablet of synthetic barysilite, intergrown with kentrolite. ×50.

was not observed by Geller, Creamer and Bunting (1934) in their study of the system PbO-SiO_2. Gels with the composition of $Pb_3Si_2O_7$ recrystallized to a mixture of $PbSiO_3$, Pb_2SiO_4 and unidentified material. The present work indicates that the presence of Mn or of some other ion substituting therefor, in addition to Pb, is essential to the formation of the barysilite structure type. The ratio of (Mn, etc.) to Pb is not certain but is in the neighborhood of 1:5. The reported analyses of natural material all contain significant amounts of Mn, Mg, Ca and Fe in addition to Pb. Most of the analyses approach the idealized formula (Mn, Mg, Ca, etc.): $Pb_5(Si_2O_7)$ as is seen from the following tabulation, but one is very close to the formula (Mn, Mg, Ca, etc.) $_1Pb_4Si_3O_{11}$. We re-examined the original sample of the latter material and have verified the identification as barysilite.

TABLE 4. X-RAY POWDER DATA FOR SYNTHETIC BARYSILITE AND ANALOGUES

	d (*I*)					
Ni-barysilite	3.206 (65)	3.146 (70)	2.949 (100)	2.812 (40)	2.758 (65)	2.668 (70)
Co-barysilite	3.206 (50)	3.157 (60)	2.955 (100)	2.824 (30)	2.761 (70)	2.676 (65)
Cu-barysilite	3.197 (55)	3.162 (70)	2.957 (100)	2.825 (60)	2.763 (70)	2.674 (75)
Mg-barysilite	3.204 (80)	3.153 (65)	2.957 (100)	2.825 (40)	2.766 (60)	2.679 (95)
Fe-barysilite	3.206 (100)	3.160 (100)	2.957 (60)	2.827 (15)	2.763 (15)	2.680 (60)
Mn-barysilite	3.224 (80)	3.206 (100)	2.978 (35)	2.855 (30)	2.779 (30)	2.685 (40)
Zn-barysilite	3.213 (60)	3.166 (80)	2.963 (100)	2.827 (50)	2.773 (80)	2.679 (85)
Cd-barysilite	3.231 (60)	3.195 (70)	2.982 (100)	2.852 (60)	2.788 (70)	2.693 (75)
Ca-barysilite	3.231 (80)	3.222 (70)	2.986 (70)	2.855 (100)	2.789 (70)	2.690 (50)

Copper radiation, nickel filter, in Angstrom units. Spacing and intensity data given only for the six strongest lines.

$(Mn_{0.74}Mg_{0.20}Ca_{0.06}Fe_{0.02})Pb_{4.94}Si_{3.98}O_{14}$ (Harstig; Sjögren and Lundström, 1888) $(Mn_{0.61}Ca_{0.44}Mg_{0.14}Fe_{0.02})Pb_{4.96}Si_{3.91}O_{14}$ (Jacobsberg; Flink, 1917) $(Mn_{0.68}Ca_{0.16}Mg_{0.01}Fe_{0.01}Ma_{0.04})Pb_{5.17}Si_{3.97}O_{14}$ (Långban; Sjögren, 1905) $(Mn_{0.66}Mg_{0.27}Ca_{0.05}Zn_{0.05}Fe_{0.04}Al_{0.16})Pb_{4.88}Si_{3.92}O_{14}$ (Franklin; Bauer and Berman, 1930) $(Mn_{0.62}Mg_{0.21}Ca_{0.04}Fe_{0.04}Zn_{0.04}Al_{0.13})$ $Pb_{3.81}Si_{3.08}O_{11}$ (same as above).

Samples adequate for chemical analysis were not obtained in the course of the present work. Support for the ratio (Mn, etc.): Pb = 1:5 also is found in our study of a portion of the system PbO-ZnO-SiO_2, cited in Table 3. Here gels of the composition $ZnO \cdot 5PbO \cdot 4SiO_2$ and $ZnO \cdot PbO \cdot SiO_2$ when heated in air crystallized to Zn-barysilite and to larsenite, respectively, whereas the compositions $ZnO \cdot 4PbO \cdot 3SiO_2$ and $ZnO \cdot 3PbO \cdot 2SiO_2$ both yielded mixtures of Zn-barysilite and larsenite.

Glasser (1964) has given the idealized unit-cell contents of natural barysilite from Franklin as 3 $[MnPb_4Si_3O_{11}]$ from the values a 8.46 ± 0.02 A, c 38.3 ± 0.02 (hexagonal coordinates), using the analysis of Bauer and Berman (1930) and the value 6.70 for the density. The calculated density using this formula, with (Mn, Mg, Ca, Zn, Fe, Al) taken in the ratio of

the analysis of Bauer and Berman, is 8.6. This value is not in satisfactory agreement with the measured value, 6.70, and an even higher value, 10.6, is obtained from the formula (Mn, etc.)$Pb_5Si_4O_{14}$. We suspect that the unit-cell dimensions employed in the computation may represent a pseudo-cell rather than the true cell. Efforts to index our X-ray powder data for the synthetic material on the basis of the stated cell failed.

After our work was in manuscript our attention came to a study by Lajzerowicz (1964), who determined the structure of synthetic barysilite. The cell dimensions found are a 9.821 Å $\pm$ 0.005, c 38.38 $\pm$ 0.05, correcting the work of Glasser (1964), and the space group is $R\bar{3}c$. The cell contents are given as $Mn_6Pb_{48}(Si_2O_7)_{18}$. The Mn:Pb ratio of 1:8 is based on a microprobe analysis of synthetic material. This formula can be restated as $(Mn_{0.66}Pb_{0.33})Pb_5(Si_2O_7)_2$. It then agrees with the analyses of the natural Swedish barysilite, in which roughly a third of the Mn position is occupied by Mg, Ca and, in the case of Sjögren's analysis, possibly also by Pb.

References

Bauer, L. H. and H. Berman (1930) Notes on some Franklin minerals. *Amer. Mineral.* **15** 340–348.

Flink, G. (1917) Bidrag till Sveriges Mineralogi. *Arkiv. Kemi. Mineral. Geol.* **6,** 1–149.

Geller, R. F., A. S. Creamer and E. N. Bunting (1934) *J. Res. Bur. Stds.* **13,** 243.

Glasser, F. P. (1964) New data on barysilite. *Amer. Mineral.* **49,** 1485–1488.

Ito, J. and C. Frondel (1966) The system CaO-ZnO-PbO-SiO_2 (in preparation).

Ito, J. and C. Frondel (1966) Synthesis of the kentrolite-melanotekite series. *Arkiv. Mineral. Geol.* **4,** no. 14, 387.

Lajzerowicz, J. (1964) Structure of barysilite. *C. R. Acad. Sci. Paris,* **259,** 4248–4250.

Layman, F. (1957) Unit cell and space group of larsenite, $PbZnSiO_4$, *Amer. Mineral.*, **42,** 910.

Palache, C. (1935) The minerals of Franklin and Sterling Hill, New Jersey, *U. S. Geol. Surv., Prof. Pap.* **180,** 80–81.

Palache, C., L. H. Bauer and H. Berman (1928) Larsenite, Ca-larsenite and the associated minerals at Franklin, New Jersey, *Amer. Mineral.* **13,** 142, 334.

Manuscript received, August 15, 1966; accepted for publication, September 22, 1966.