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SYNTHESIS OF SOME LEAD CALCIUM ZINC SILICATES[1]

JUN ITO, *Department of Geological Sciences, Harvard University, Cambridge, Massachusetts.*[2]

ABSTRACT

Compounds of the general formula $Pb_xCa_yZn_zSiO_{2+n}$ $(n=x+y+z;\ x<2;y\leq 1;\ z\leq 2)$ were synthesized both by heating in air and by hydrothermal crystallization of chemically precipitated gels.

Newly synthesized phases are larsenite $PbZnSiO_4$, barysilite $(Pb,Mn)_3Si_2O_7$, esperite $(Ca,Pb)_4Zn_4Si_4O_{16}$, margarosanite $Ca_2PbSi_3O_9$, phase X_1 $CaPb_2Zn_3Si_3O_{12}$, phase X_2 (possibly a high temperature polymorph of nasonite $Ca_2Pb_3Si_3O_{11}$) and phase X_3 (probable formula, $CaZnSi_2O_6\cdot H_2O$).

X-ray powder data of the new phases are recorded and unit-cell constants are given where known.

INTRODUCTION

My interest in the lead calcium zinc silicates arose largely from studies of silicate gel synthesis for the originally difficult syntheses of barysilite and larsenite (Ito and Frondel, 1967). Moreover, in 1964 while at the Mineralogical Institute of Tokyo University, I used the gel technique to synthesize alamosite and Pb_2SiO_4. Although the latter had been repeatedly synthesized, the rare mineral alamosite was for the first time easily synthesized in large crystals.

The work by Moore and Ribbe (1965) on natural esperite encouraged me to synthesize this mineral and to establish its relation to larsenite. I failed to synthesize larsenite and esperite with either lead or zinc replaced by other ions. A literature survey of all Pb-Zn-Ca silicates of similar composition occurring in nature led to syntheses of margarosanite ($Ca_2PbSi_3O_9$); but attempts on nasonite-ganomalite and clinohedrite failed.

EXPERIMENTAL

Preparation of the starting materials. Chemically precipitated hydrous silicate gels were used for both dry and hydrothermal syntheses. In their preparation, hot acid solutions containing exact amounts of lead nitrate, calcium nitrate, zinc nitrate and sodium silicate were neutralized by freshly prepared 7M NaOH solution until permanent precipitation occurred. The final pH was adjusted to 9.5. To avoid the formation of $CaCO_3$ from CO_2 in air, the solution was not stirred. Formation of $CaCO_3$ changes the ratio of reactive Ca/Pb, which affects the crystallization of the minerals of the desired composition. The precipitate was centrifuged

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[2] Present address: National Bureau of Standards, Washington, D. C. 20234.

and washed once by distilled water and dried in an evacuated oven at 110°C. Chemical analysis to determine the Ca and Pb content was necessary to ascertain the actual ratio of those elements in the gel. Remixing of two different gels was sometimes required to achieve the specific composition in this system.

Analysis of starting materials for CaO and PbO. A 100-mg portion of the sample was weighed in a platinum basin and decomposed by a mixture of HF and HNO_3. The solution was heated and evaporated to complete dryness on a hot plate. The dried residue was then dissolved by 0.2N of HNO_3 and transferred to a 50-ml measuring flask. Pb-diethyl dithiocarbamate was extracted using 10 ml aliquot, by chloroform at pH 3. The organic extract was heated with 10ml of 6N HNO_3 and evaporated to expel all the solvent and to destroy the organic compound. The dried residue was dissolved in water and Pb was titrated by 0.01 M EDTA standard solution at pH 10 with the buffer (NH_4OH & NH_4Cl, pH 10) using EBT indicator, and KCN as a masking agent for Zn.

CaO was determined using an aqueous phase of the above extraction. After the extraction, the nitric acid solution was heated and brought into complete dryness on a hot plate, expelling the remaining chloroform and destroying excess carbamate. The dried residue was dissolved by H_2O and titrated by 0.01 M EDTA solution at pH 10 in the presence of KCN with EBT indicator.

Syntheses. Approximately 100 mg of the finely ground gels were placed in a 10 ml porcelain crucible and heated in a box furnace at 300°C–1,000°C. A chromel-alumel type thermocouple was ordinarily used for temperature measurement. Temperatures were regularly checked by plantinum-rhodium thermocouple with highly sensitive potentiometer. Fluctuation in temperature was held to ± 10°C. Heating was usually limited to 24 hours. No improvement of the crystallinity was observed by longer heating.

For hydrothermal syntheses, 100 mg of the gel was put into a silver liner and heated in a steel rod bomb with an exact amount of H_2O at temperatures from 300°C to 500°C under 2–3 kbars. After 20 to 48 hours of heating, the reactor was quenched to room temperature with compressed air. Margarosanite and alamosite were synthesized only hydrothermally. Natural esperite remained unchanged under the hydrothermal conditions (300°C, 2 kbars and 72 hours), but direct synthesis of esperite was not successful under the same conditions. The gels having the compositions of esperite and X_1 phase crystallized as larsenite +willemite and larsenite respectively at 300°C under 2 kbars. No other

phases were detected in X-ray powder diffraction diagrams. At temperatures below 250°C, reaction seemed sluggish. No further attempts were made.

Results

Efforts have been made to establish conditions for the syntheses of existing calcium, zinc and lead silicate minerals. Search was also made for possible new compounds having those constituents. The investigation was especially concentrated in the composition range between $CaZnSiO_4$ to $PbZnSiO_4$ in order to elucidate the relation of esperite with other

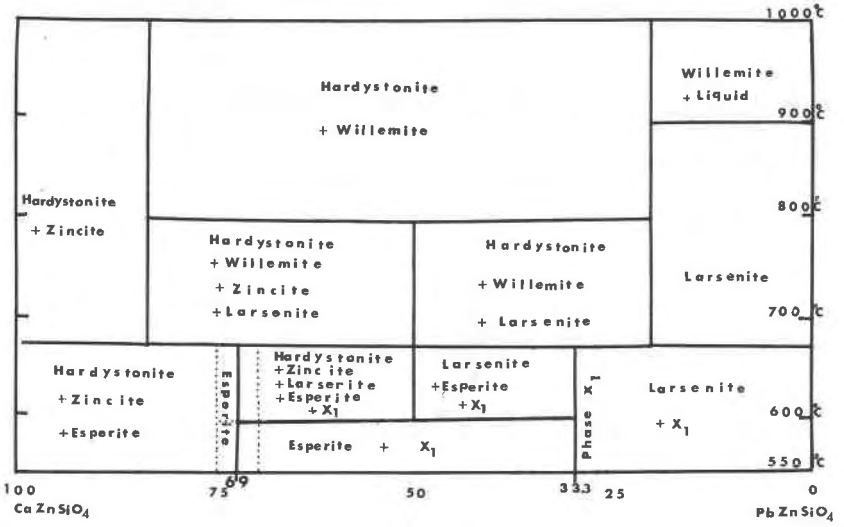

FIG. 1. Schematic representation of major phases identified after heating of gels having the compositions between $CaO\text{-}ZnO\text{-}SiO_2 \rightleftarrows PbO\text{-}ZnO\text{-}SiO_2$. Hardystonite $Ca_2ZnSi_2O_7$, larsenite $PbZnSiO_4$, willemite Zn_2SiO_4, esperite $(Pb,Ca)_4Zn_4Si_4O_{16}$, X_1: $(Pb_2Ca)ZnSiO_4$, and zincite ZnO.

phases. The major phases that were detected after heating the gels in air for 24 to 48 hours, have been summarized schematically in Figure 1. The data so far available are inadequate to construct even an approximate equilibrium diagram. It must be remembered that heating of chemically prereacted gels for a limited time may achieve slightly different results from those obtained by fully equilibrated phase study. The Pb:Ca ratio in esperite in Figure 1 (69:31) has been derived by analysis. It differs from the original ratio (75:25) given by Moore and Ribbe (1965). The true ratio could not be deduced from the author's synthesis because pure esperite phase was never obtained. It was always accompanied by small

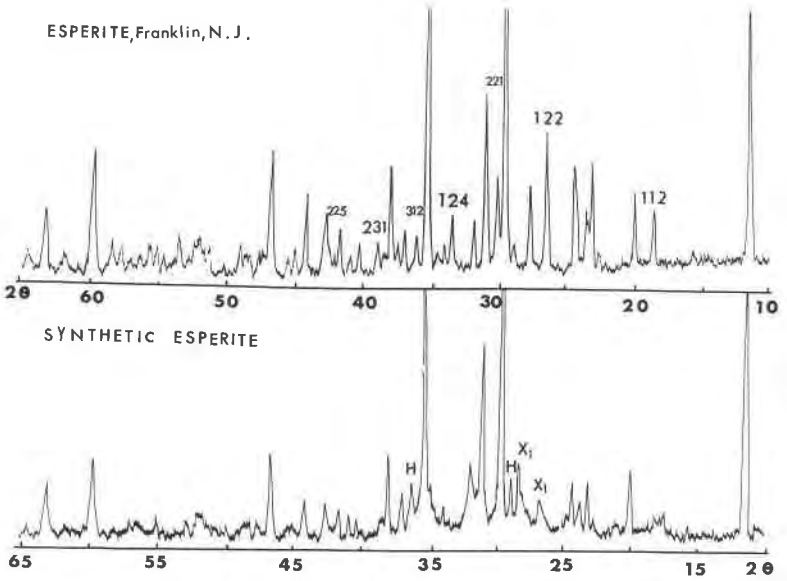

FIG. 2. X-ray powder diffraction diagrams of natural and synthetic esperites. Indexed reflexions ($h+l=$ odd) in natural esperite are absent in synthetic esperite. Extra reflections in synthetic esperites were identified as belonging to other phases and noted in the diagram as $H=$ hardystonite and $X_1=$ new phase (cf. Table 2).

TABLE 1. X-RAY POWDER DATA FOR SYNTHETIC ESPERITE (Ca, Pb)$_4$Zn$_4$Si$_4$O$_{12}$
(580°C, 1 bar, 24 hrs.)(CuKα Ni filter)
Pseudo-orthorhomic $a=8.79$ Å, $b=8.29$Å, $c=15.25$Å; $h+l=$odd are absent

hkl	*d*, Å	I. (Visual)	*hkl*	*d*, Å	I. (Visual)
002	7.64	80	412	2.047	8
012	5.61	1	330, 140	2.017	30
003	5.023	5	331, 420	1.992	1
200, 103	4.423	30	226	1.943	30
020	4.187	2	043	1.920	1
210	3.900	3	404	1.909	2
004, 202	3.818	25	422	1.883	1
022, 121	3.642	25	242	1.826	2
212	3.477	2	208	1.754	2
220	3.023	100	424	1.735	1
204, 105	2.879	60	137	1.677	1
222	2.810	10	406	1.665	5
214	2.727	1	416	1.632	2
130	2.644	3	426	1.546	35
006	2.545	90	600	1.470	20
016, 313	2.428	10	602	1.445	3
224	2.366	30	604	1.370	2
034	2.236	30	428	1.362	1
206, 400	2.200	5	260	1.324	1
026, 323	2.166	8	446	1.300	2
216	2.133	5	606	1.274	3
402	2.119	10		1.172	2

TABLE 2. X-RAY POWDER DATA FOR PHASE X_1 $Pb_2CaZn_3Si_3O_{12}$ STABLE AT 550–680°C, 1 BAR. (CuKα Ni FILTER)

d, Å	*I*. (Visual)	*d*, Å	*I*. (Visual)	*d*, Å	*I*. (Visual)	*d*, Å	*I*. (Visual)
5.34	3	3.153	100	2.261	10	1.758	5
5.14	10	3.083	8	2.215	1	1.727	1
5.035	5	2.982	30	2.166	3	1.714	5
4.865	20	2.908	20	2.141	15	1.672	8
4.562	10	2.875	80	2.120	2	1.660	1
4.427	20	2.825	40	2.081	3	1.654	3
4.259	1	2.773	20	2.046	3	1.630	1
4.164	8	2.699	1	2.021	5	1.598	3
4.088	15	2.680	1	2.005	3	1.577	5
4.040	8	2.645	50	1.955	10	1.550	8
3.904	5	2.567	3	1.940	25	1.538	8
3.705	10	2.518	40	1.922	3	1.529	8
3.593	5	2.477	1	1.894	1	1.515	5
3.493	5	2.430	1	1.879	3	1.500	1
3.409	3	2.370	10	1.824	20	1.472	1
3.326	25	2.331	15	1.812	15		
3.250	8	2.286	3	1.794	10		

amounts of X_1 or hardystonite phase (Fig. 2). Pure single phase of X_1 was obtained from the gels having a Ca:Pb ratio 1:2.

Another important feature of Figure 1 is the incongruent melting of larsenite to willemite and lead silicate liquid above 900°C. Flux growth of willemite from PbO flux is therefore possible by slow cooling or evaporation of flux. Attempts were made to obtain manganese activated willemite single crystals from the melt having the composition of MnO: $PbO:ZnO:SiO_2=0.1:1:1:1$ by slow cooling at the rate of 5°C per hour after soaking for 72 hours. Single crystals up to 2 mm of fluorescent willemite (yellowish green under mercury discharge excitation) were obtained. Larsenite single crystals 2–3 mm parallel to the *c* axis also crystallized but at later stages of cooling. Mixed flux of PbO and PbF 1:1 was

TABLE 3. X-RAY POWDER DATA FOR CALCIUM LEAD SILICATE (CLOSE TO $Ca_2Pb_3Si_3O_{11}$), HIGH TEMPERATURE X_2 PHASE. STABLE OVER 300°C, 2 KBARS (CuKα Ni FILTER)

d, Å	*I*. (Visual)	*d*, Å	*I*. (Visual)	*d*, Å	*I*. (Visual)	*d*, Å	*I*. (Visual)
4.940	80	2.730	70	1.943	20	1.565	2
4.440	70	2.467	5	1.926	20	1.534	5
4.271	40	2.367	10	1.883	10	1.516	5
3.545	80	2.339	10	1.864	3	1.502	3
3.393	50	2.302	5	1.832	20	1.468	8
3.229	50	2.263	5	1.808	30	1.458	5
3.153	10	2.222	3	1.721	10	1.414	5
3.078	100	2.180	8	1.705	8	1.400	3
2.976	5	2.136	20	1.700	5		
2.850	80	1.999	30	1.642	1		
2.801	70	1.961	8	1.615	2		

TABLE 4. X-RAY POWDER DATA OF X_3 PHASE, HYDROUS CALCIUM ZINC SILICATE, CLOSE TO ($CaZnSi_2O_6 \cdot H_2O$) SYNTHESIZED AT 200°C, 2 KBARS AND 6 DAYS

d, Å	*I*. (Visual)	*d*, Å	*I*. (Visual)	*d*, Å	*I*. (Visual)	*d*, Å	*I*. (Visual)
6.29	50	2.545	80	1.972	10	1.611	5
4.71	30	2.531	80	1.874	5	1.579	5
4.28	30	2.354	30	1.835	3	1.564	3
3.534	100	2.247	10	1.770	10	1.541	20
3.227	50	2.207	5	1.741	10	1.494	3
3.131	10	2.088	3	1.703	5		
2.822	70	2.022	20	1.674	5		

also useful for willemite growth but crystals obtained from this flux did not fluoresce on manganese doping. The fluorine perhaps combines preferentially with manganese. It may be helpful to remark that the flux can be washed out from the synthetic willemite and larsenite by prolonged soaking in warm 5 percent NaOH solution and subsequent rapid washing by dilute acetic acid.

The synthetic products were examined by X-ray diffractometry and identification was made by comparison with known standard minerals. X-ray powder data for newly crystallized synthetic compounds esperite, phase X_1, phase X_2, phase X_3 and margarosanite are cited in Tables 1, 2, 3, 4, and 5, respectively.

In nature esperite and larsenite occur with zincite and willemite but not with each other. From the results, larsenite and esperite could be coexisting phases under certain conditions and compositions.

From the X-ray powder data (Table 1) for synthetic esperite indexed according to the cell dimensions by Moore and Ribbe, the following cell constants were obtained which are in close agreement with those of nat-

TABLE 5. X-RAY POWDER DATA FOR SYNTHETIC MARGAROSANITE (350°C, 2 KBARS FOR 48 HOURS) $Ca_2PbSi_3O_9$ (CuKα, Ni FILTER)

d in Å	*I* (Visual)	*d* in Å	*I*. (Visual)	*d* in Å	*I*. (Visual)	*d* in Å	*I*. (Visual)
6.59	8	3.234	25	2.460	2	1.857	1
6.15	8	3.186	40	2.421	2	1.833	3
5.19	10	3.087	30	2.367	3	1.813	2
5.217	10	3.048	80	2.330	5	1.773	1
5.063	10	2.986	100	2.279	1	1.748	3
4.440	10	2.930	30	2.254	3	1.682	5
4.388	15	2.794	2	2.217	10	1.646	1
4.110	3	2.713	15	2.160	8	1.603	3
3.917	2	2.690	20	2.093	8	1.577	2
3.786	5	2.654	10	2.043	5	1.541	3
3.490	10	2.642	10	1.972	3		
3.366	10	2.627	10	1.897	1		
3.341	10	2.567	8	1.875	1		

ural esperite. Synthetic esperite: $a=8.79$ Å, $b=8.29$ Å, $c=15.25$ Å. Esperite from Franklin, New Jersey,: $a=8.814$ Å$\times 2$, $b=8.270$ Å, $c=15.26$ Å$\times 2$, $\beta=90°$ (Moore and Ribbe 1965). Comparison of the X-ray powder patterns for natural and synthetic esperite in Figure 2 show excellent agreement between major peaks. It is noted, however, that several medium strong reflections having indices of hkl: $(h+l)=$ odd, possibly belonging to the superlattice structure according to Moore (private communication), are missing in synthetic esperite. Single crystallographic

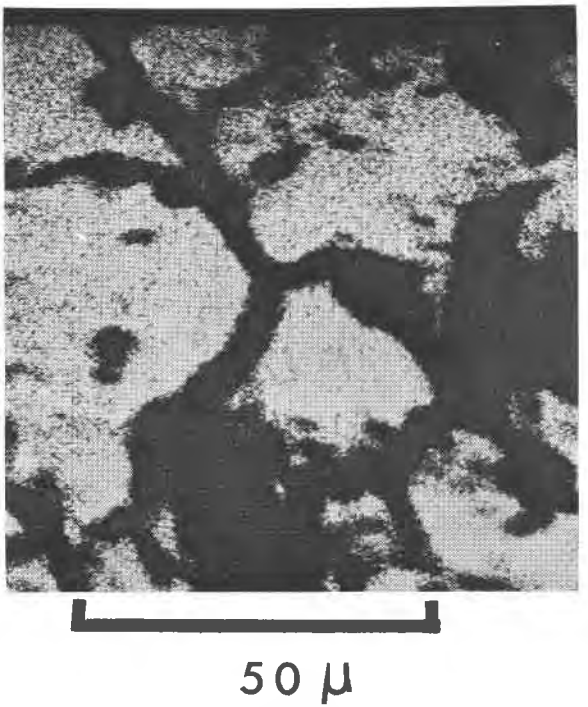

FIG. 3. Backscatter electron presentation. × 1,000. Minerals of highest average atomic number give the brightest image. The bright areas are esperite, dark areas are the altered phase analyzed. (20 kV, 0.06 μ amp.)

investigation of synthetic esperite is desirable, since the superlattice reflections noted by Moore and Ribbe did not appear in the power diffraction diagram. Synthetic esperite came out as a colorless fine crystalline mass and is stable at 550°C–680°C in air for periods of 48–72 hours but it decomposes rapidly to another phase at 700°C. Synthetic esperite does not fluoresce because it does not contain minor elements such as Mn to activate its luminescence efficiency. Microscopic examination of

TABLE 6. X-RAY POWDER DATA FOR SYNTHETIC ALAMOSITE, AT 500°C/2KB 20 HOURS AND NATURAL ALAMOSITE (FROM ALAMOS, SONORA, MEXICO, HARVARD MUSUEM 85510)

Synthetic		Natural		Synthetic		Natural	
d in Å	*I* (Vis.)	*d* in Å	*I* (Vis.)	*d* in Å	*I* (Vis.)	*d* in Å	*I* (Vis.)
6.50	10	6.49	15	2.379	10	2.380	3
5.832	60	5.832	40	2.348	60	2.348	10
5.734	50	5.734	20	2.300	100	2.297	50
5.175	8	5.157	10	2.209	20	2.207	8
4.771	5	4.792	1	2.168	5	2.068	2
4.410	8	4.414	8	2.140	10	2.140	10
4.183	3	4.267	15	2.056	10	2.058	10
4.081	2	4.077	2	2.036	10	2.039	10
3.562	80	3.559	60	2.030	40	2.029	10
3.528	40	3.504	20	2.002	3	2.004	3
3.341	100	3.343	100	1.990	2	1.979	5
3.243	10	3.297	20	1.962	10	1.958	2
3.229	40	3.231	30	1.940	15	1.940	10
3.157	10	3.160	2	1.900	10	1.901	3
3.095	50	3.095	20	1.847	15	1.844	10
3.046	55	3.046	50	1.804	10	1.796	8
3.025	5	3.019	10	1.789	8	1.789	8
2.986	60	2.984	60	1.763	20	1.760	10
2.934	5	—	—	1.742	20	1.738	10
2.913	30	2.913	20	1.734	30	1.732	10
2.880	8	2.880	10	1.691	20	1.691	10
2.859	5	—	—	1.682	10	1.682	5
2.813	20	2.813	8	1.654	5	1.655	8
2.801	10	2.794	10	1.620	20	1.620	5
2.741	20	2.743	8	1.594	10	1.589	3
2.725	40	2.718	20	1.575	8	1.574	8
2.680	10	—	—	1.569	15	1.567	10
2.667	30	2.668	10	1.554	20	1.555	10
2.597	10	2.592	8	1.547	5	1.550	5
2.532	20	2.527	10	1.524	3	1.524	3
2.465	8	2.462	5	1.491	3	1.491	2
2.422	3	2.424	1	1.466	2	1.454	2

thin sections of the natural esperite failed to prove the presence of an appreciable amount of a second phase, but electron probe analysis showed (Fig. 3) that considerable areas of an unidentified, chemically different phase, are scattered within the esperite crystals. Under the microscope, the main mass of esperite shows a very intricate anastomosing pattern of cracks. The second phase occurs mostly as very fine linings (1–5 microns thick) (Fig. 3) along the fracture pattern. Results and conditions of

electron probe analyses for both esperite and this phase are given in Table 7.

The PbO:CaO ratio obtained from this analysis of the natural mineral from Franklin, New Jersey, is 31:69. That obtained from the middle of the narrow composition range of the synthetic material is 30:70. Both differ slightly from the ratio given by Moore and Ribbe 25:75. Unsuccessful attempts were made to synthesize this second phase hydrothermally (200°C–500°C, 1–2 kbars). Only a new phase X_3 was obtained at 200°C and 1 kbars (Table 4). Therefore, it is not yet clear whether this chemically distinguished phase possesses the extra reflections mentioned above. Higher temperature phases with esperite composition found in

TABLE 7. ELECTRON PROBE ANALYSIS OF ESPERITE AND SECOND PHASE
(20 kV., 0.06 mÅ. beam current; beam size approx. 2 microns)

	Esperite, Franklin, N. J. Harvard Museum 105492	Second phase
ZnO	34.5	25.6
PbO	26.1	1.4
CaO	14.3	19.1
SiO_2	27.1	53.4
Total	102.0	99.5

Analyst: C. Klein (1966).

this study (Fig. 1) are essentially identical with the findings by Moore and Ribbe.

Phase X_1 is a compound having the composition of $Pb_2CaZn_3Si_3O_{12}$ and is stable at about the same temperature as esperite (550–680°C). This X_1 phase developed in crystals too small for microscopic examination. It appeared in a very wide range of Figure 1, and gave a single-phase X-ray pattern at the Pb/Ca ratio 2:1. The presence of this mineral at Franklin seems possible.

Phase X_2 is a high temperature lead calcium compound of unknown formula stable up to 800°C. Nasonite and margarosanite change to this phase above 700°C. Under hydrothermal conditions, it crystallizes at a temperature as low as 280°C under 2 kilobars H_2O pressure.

Margarosanite was obtained only under hydrothermal conditions at 350°C and 2 kbars and developed fine acicular crystals up to 50 μ in length. The X-ray powder pattern is identical to that obtained from the natural material from Franklin, New Jersey. A slight increase of spacings due to the absence of smaller divalent ions in the synthetic mineral has been noted.

Synthetic alamosite formed in surprisingly large single crystals (about 5 mm) in a hydrothermal run at 500°C, 1.4–1.8 kb, for 24 hours.

X-ray powder diffraction data of both synthetic alamosite and natural specimens (Table 6) preserved at Harvard Mineralogical Museum showed complete agreement in both spacings and intensities. The X-ray powder pattern of $PbSiO_3$, synthesized by Aargyl and Hummel (1960) in air at 750°C, is different from that of alamosite and probably is a low pressure polymorph.

Synthetic larsenite (orthorhombic $a=8.24$ Å, $b=19.00$ Å, $c=5.05$ Å), synthetic hardystonite (tetragonal $a=7.83$ Å, $c=5.02$ Å) and synthetic barysilite have been described in separate papers (Ito and Frondel, 1967).

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