

SYNTHESIS OF LEAD PYROSILICATE AND OTHER
BARYSILITE-LIKE COMPOUNDSH. W. BILLHARDT,¹ *Mineralogisches Institut der Universität
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ABSTRACT

In the binary system PbO-SiO₂ the compound Pb₃Si₂O₇ was synthesized. Indexed X-ray powder and single crystal data as well as optical and IR data show that Pb₃Si₂O₇ is the Pb-analogue of the mineral barysilite Pb₃Mn(Si₂O₇)₃. To elucidate the barysilite formula Pb in Pb₃Si₂O₇ has been partially replaced by Mn, Mg, Ca, Sr and Ba. A Pb-Sr-Ba-mixed crystal was synthesized which is isotypic but not isomorphic to natural barysilite. This Pb-Sr-Ba-"barysilite" probably has the formula Pb₃(Pb, Sr, Ba)(Si₂O₇)₃. The ternary compound 2PbO·MgO·2SiO₂ found by Argyle and Hummel (1965/66) in the system PbO-MgO-SiO₂ was shown to be a Mg-"barysilite" of the composition Pb₃Mg(Si₂O₇)₃.

INTRODUCTION

During the investigation of the ternary system PbO-SiO₂-SO₃ and the reexamination of the well known binary system PbO-SiO₂ the compound Pb₃Si₂O₇ was synthesized, probably in two modifications. This compound has often been searched for and has been discussed by many authors because it should correspond to the mineral barysilite. According to the mineral tables of Strunz (1966) barysilite has the formula Pb₃Si₂O₇ although in recent papers this formula has been considered as being too idealized. Thus Glasser (1964) suggested the formula Pb₄(Mn, etc)(Si₃O₁₁), but he failed to synthesize a barysilite of this composition. Lajzerowicz (1966) stated the barysilite formula as XPb₃·3(Si₂O₇); for natural barysilite X is mainly Mn. She prepared synthetic "barysilites" with X = Be, Mg, Ni, Co, Cu, Zn, Mn, Cd, Ca and Sr, but not a pure Pb-"barysilite." In 1967 Ito and Frondel suggested the formula MnPb₅(Si₂O₇)₂. Their efforts to get Pb₃Si₂O₇ even hydrothermally were unsuccessful.

In the system PbO-SiO₂ the compound Pb₃Si₂O₇ was first described by Krakau and Vakhrameev (1932), but in later investigations carried out by the same author and reported by Eitel (1965) it was not further mentioned. In 1939 Kordes reported the existence of Pb₃Si₂O₇ which he had obtained as hexagonal crystals and in 1962 Berezkina and Chizhikov gave a method of preparation for Pb₃Si₂O₇, and the first X-ray powder data which are in contradiction to the results presented here and discussed below. Without mentioning any details about Pb₃Si₂O₇ Argyle and Hummel (1965/66) accepted this compound in the system MgO-SiO₂-PbO. They also described a ternary compound 2PbO·MgO·2SiO₂

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which, according to our investigations, is a Mg-"barysilite" of the composition $Pb_8Mg(Si_2O_7)_3$.

All other authors (Geller *et al.*, 1934; McMurdie *et al.*, 1939; Paetsch *et al.*, 1965; Argyle *et al.*, 1960) investigating the system $PbO-SiO_2$ doubted the existence of $Pb_3Si_2O_7$ or neglected the compound altogether.

PREPARATION OF $Pb_3Si_2O_7$

Pure PbO and SiO_2 from E. Merck and R. de Haen were used for the preparation of $Pb_3Si_2O_7$. The oxides in stoichiometric relation were fused in Pt-crucibles at temperatures of about $950^\circ C$, taking into account the loss caused by evaporation. To protect the Pt-crucible from reaction with Pb a small amount of NH_4NO_3 was added to the sample in order to get an oxidizing atmosphere (Merker and Wondratschek 1967) and then the batch was heated very slowly. Glass of $Pb_3Si_2O_7$ composition was obtained by quenching the homogeneous melt.

Annealing experiments on " $Pb_3Si_2O_7$ -glasses" showed no crystallization of $Pb_3Si_2O_7$ at $300^\circ C$ after 24 hours. At $400-500^\circ C$, however, a microcrystalline phase X crystallized which is probably a low-temperature modification of lead pyrosilicate. This compound is stable up to about $650^\circ C$ and decomposes at higher temperatures into lead orthosilicate Pb_2SiO_4 and lead metasilicate $PbSiO_3$. At $500-600^\circ C$ another binary phase Y crystallizes from under-cooled melts, together with small amounts of Pb_2SiO_4 and $PbSiO_3$. This phase Y has an X-ray powder pattern similar to natural barysilite. It seems to decompose incongruently at about $710^\circ C$ into Pb_2SiO_4 and melt. DTA-analyses show complete melting at $725 \pm 5^\circ C$.

Attempts to convert the high temperature phase Y into phase X by heating for 10 days at about $500^\circ C$ failed. This may be due to a kinetic effect and does not rule out the possibility that X and Y are two modifications of the same compound. The X-ray powder diffraction pattern of X, however, is not similar to Y, but to a compound of pyromorphite type. Many lines could be indexed with hexagonal $a=9.94 \pm 0.02 \text{ \AA}$. The cell constant c could not be determined. Further investigations for the phase X are planned.

PREPARATIONS OF SINGLE CRYSTALS

Crystals of phase Y suitable for X-ray single crystal techniques were prepared by the following two methods:

1. Heating the quenched melt for several hours at about $650^\circ C$.
2. Quenching a melt to $680^\circ C$. When this temperature is reached, the cooling rate is retarded to about $5^\circ C/min$ down to $650^\circ C$. At this temperature the sample is held for several hours. The cooling rate above $680^\circ C$ should be not too slow, otherwise Pb_2SiO_4 crystallizes primarily. Pb_2SiO_4 is very stable and (together with the residual melt) cannot be converted into another compound, so that the metasilicate $PbSiO_3$ is formed out of the residual melt.

The second method of preparation is more successful than the first one. The single crystals thus obtained have irregular shapes and a cross-section of about 0.1 mm. Berezkina *et al.* (1962) got crystals in a glass matrix by quenching an undercooled melt that had been heated for 24 hours close to or below the melting point. They believed these crystals to have the composition $Pb_3Si_2O_7$ and to exist only near the melting point. Slow cooling was supposed to lead to decomposition of $Pb_3Si_2O_7$ to lead orthosilicate and metasilicate. This statement is in contradiction to our results described above. Experiments carried out under the conditions mentioned by Berezkina *et al.*, revealed that these crystals are a high tem-

perature modification of Pb_2SiO_4 . The X-ray powder pattern, however, given by Berezkina *et al.* (FeK_α -radiation; 70–100 hours exposure time) could not be identified either with that of our phases X and Y or with any prepared PbSiO_3 or Pb_2SiO_4 modification (Billhardt, 1968).

X-RAY INVESTIGATIONS

Powder diffraction patterns of all compounds were made with an AEG-Guinier camera using pure Si-powder as an internal standard (Si, $a=5.431 \text{ \AA}$). Intensity measurements were made with a Zeiss-Jena photometer and the cell constants were refined and computed by the use of indexed powder diffraction patterns. In table 4 and 5 the d -values and intensities of phase X and Y are listed.

Oscillation and precession photographs of phase Y revealed hexagonal symmetry with the following conditions limiting possible reflexions:

$$\begin{aligned} hki\bar{l}: & \quad -h + k + l = 3n \\ (hk\bar{2}hl) & \quad \quad \quad l = 3n \\ (h\bar{l}0l) & \quad \quad \quad h + l = 3n \\ & \quad \quad \quad \text{and } l = 2n \end{aligned}$$

This leads to the probable space groups $R3c$ and $R\bar{3}c$. The cell constants in hexagonal setting are: $a=10.13(6)$, $c=38.70(3) \text{ \AA}$. By assuming $Z=18$ for $\text{Pb}_3\text{Si}_2\text{O}_7$ the calculated density $\rho_{(\text{calc})}=6.86_4 \text{ g/cm}^3$ is in good agreement with the measured value $\rho_{(\text{meas})}=6.84 \pm 0.05 \text{ g/cm}^3$.

The comparison of these data with those of natural barysilite in Table 1 shows close agreement. The probable space group for barysilite of Långban/Sweden was determined as $R3c$ or $R\bar{3}c$, in agreement with J. Lajzerowicz, who assumed the space group $R\bar{3}c$ by investigating the systematic intensity distribution. The relationship between these two

TABLE 1. SINGLE CRYSTAL DATA OF BARYSILITE AND $\text{Pb}_3\text{Si}_2\text{O}_7$

Barysilite, Långban			Synthetic $\text{Pb}_3\text{Si}_2\text{O}_7$
This paper	J. Lajzerowicz	F. P. Glasser	This paper
$a = 9.80(1) \text{ \AA}$	$9.821(5) \text{ \AA}$	$^a 8.46(2) \text{ \AA}$	$10.13 \pm 0.006 \text{ \AA}$
$c = 38.35(5) \text{ \AA}$	$38.38(6) \text{ \AA}$	$38.3(2) \text{ \AA}$	$38.70 \pm 0.03 (\text{ \AA})$
$Z = 6$	6		18
$\rho_{(\text{calc})} = 6.91 \text{ g/cm}^3$	6.84 g/cm^3		6.86_4 g/cm^3
	$\rho_{(\text{meas})} = 6.72 \text{ g/cm}^3$	(Winchel, 1965)	$6.84 \pm 0.05 \text{ g/cm}^3$
	and $6.55\text{--}6.706 \text{ g/cm}^3$	(Flink, 1917; referred by Glasser)	

^a The deviation from the cell constant a presented by Glasser (1964) is apparent. Most probably he erroneously published the $(a^x)^{-1}$ -value, because $a = (a^x)^{-1} / \sin 60^\circ = 9.77 \text{ \AA}$ is in rather good agreement to the other values in Table 1.

compounds is also indicated by the same optical character (negative birefringence) and similar IR-data. But while the mica-like platelets of barysilite and synthetic Mn-"barysilite" have excellent cleavage parallel to (001) no characteristic cleavage of phase Y was observed.

All investigations of phase Y and barysilite revealed that these two compounds are isotypic. According to the statement of J. Lajzerowicz that the natural barysilite has the formula $Pb_8Mn(Si_2O_7)_3$ the newly prepared phase Y has the composition $Pb_8Pb(Si_2O_7)_3$ and is the Pb-"barysilite" of the ideal composition $Pb_3Si_2O_7$.

Comparing the cell dimensions of barysilite and $Pb_3Si_2O_7$ in Table 1 it is evident that the substitution of Mn^{2+} by Pb^{2+} causes a considerable enlargement of the barysilite lattice. The synthesis of mixed crystals of Mn-"barysilite" and $Pb_3Si_2O_7$ was not possible. There were always two phases of different "barysilites." The ionic radii of Pb^{2+} and Mn^{2+} are too different for an isomorphic replacement in this structure. Therefore barysilite and $Pb_3Si_2O_7$ are isotypic but not isomorphic.

INFRARED DATA

With a Beckman Infrared Spectrophotometer IR 10 infrared spectra were recorded at liquid nitrogen temperatures, using KBr- and CsBr-pellets. The absorption bands of phase X, $Pb_3Si_2O_7$ and barysilite are listed in Table 2. The absorption spectra of $Pb_3Si_2O_7$ and barysilite,

TABLE 2. IR-ABSORPTION SPECTRA OF X, Pb-"BARYSILITE" AND BARYSILITE

Phase X		Pb-"barysilite"		Barysilite	
258 cm^{-1}	st	258 cm^{-1}	st	260 cm^{-1}	st
328	vw				
360	vw	360	vw	378	w
400	vw	395		394	w
		420	b	418	m
438	w	432	m	448	m
		458	m	464	m
475	st b	476	w	480	m
		508	vw		
522	st b	526	st	530	st
		536	w	554	w
668	m				
700	vw	679	st	702	st
822	w	822	st	832	st
845	m	855	vw		
875-885	st b	882	st b	892	st b
				914	w
940	m	936	st b	934	st b
965	m			976	vw
1062	m				

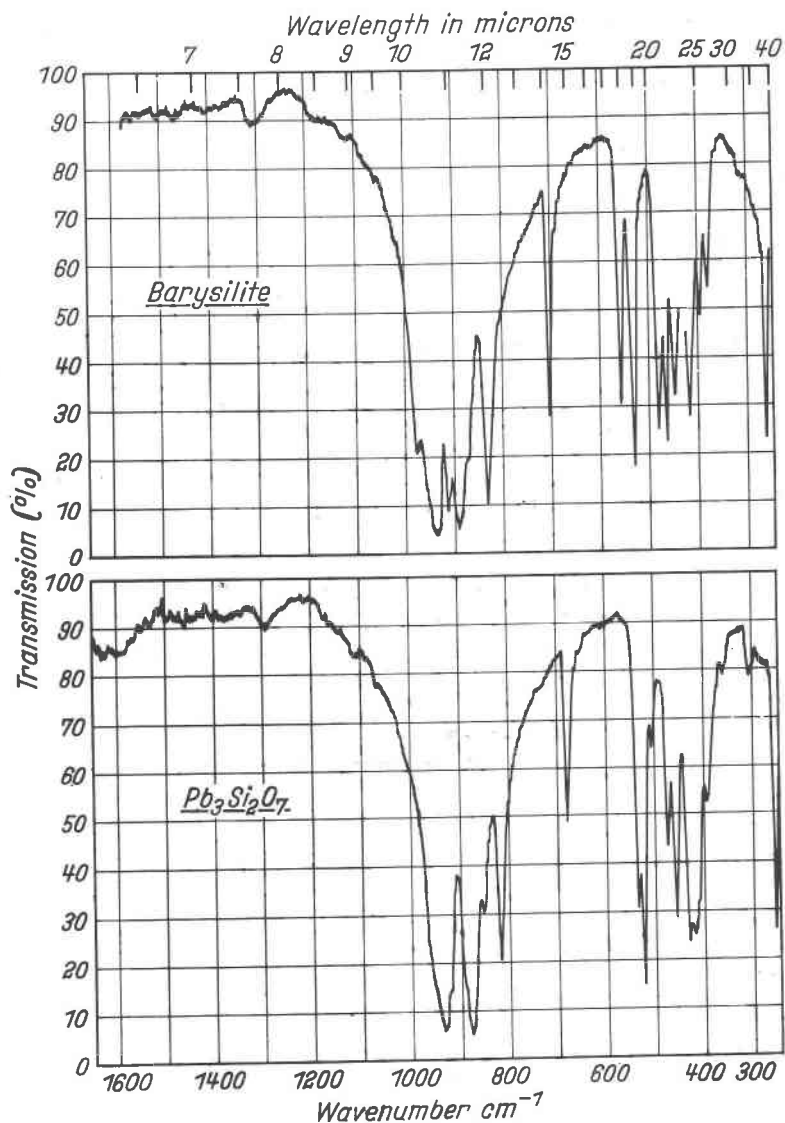


FIG. 1. Infrared absorption spectra of barysilite and $Pb_3Si_2O_7$.

compared in Figure 1, are very similar except for the band near 700 cm^{-1} . This absorption band is characteristic for all pyrosilicates as have been pointed out by Lazarev (1961) and Lajzerowicz (1965). According to these authors the position of this band depends on the Si-O-Si-valence angle in the pyrosilicate structure which is a function of the Me^{2+} -oxygen

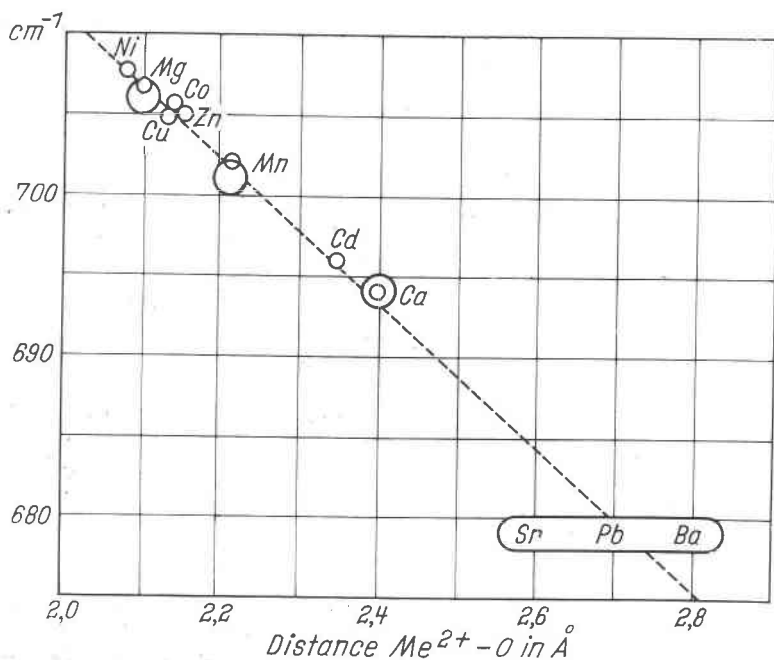


FIG. 2. The position of the "characteristic pyrosilicate absorption band" of different "barysilites" as a function of the cation-oxygen distance. Small circles represent measurements of J. Lajzerowicz, large circles our own measurements.

distance. Therefore this characteristic pyrosilicate-band has been measured for all our synthesized "barysilites" and is compared with the data of J. Lajzerowicz in Figure 2.

This figure shows a good fitting of the data of the new Pb-"barysilite" and of the later described "barysilites" with large cations as Sr and Ba on the elongated line given for "barysilites" by J. Lajzerowicz.

SYNTHESIS OF Sr-Pb-Ba-"BARYSILITE" MIXED CRYSTALS

After the Pb-"barysilite" synthesis had been successful, the next step was to find out whether it is possible to replace Pb^{2+} by other large cations like Sr^{2+} and Ba^{2+} in the barysilite structure of $Pb_3Si_2O_7$.

The method of preparing these compounds was the same as described above for $Pb_3Si_2O_7$. However a treatment at higher temperatures was chosen ($620-720^\circ C$). Besides pure PbO and SiO_2 the metal oxides SrO and BaO were used as reagents. These were obtained by thermal decomposition of their nitrates and carbonates under a nitrogen atmosphere (G. Brauer).

The partial replacement of Pb by Sr and Ba in the barysilite structure led to the following mixed crystals:

between Pb- and Sr-“barysilite”
 Pb- and Ba-“barysilite”
 Sr- and Ba-“barysilite”

The cell dimensions of these “barysilites” are tabulated in Table 3 and compared with the data of other “barysilites” in Figure 3.

TABLE 3. CELL DIMENSIONS OF Pb-Sr-Ba-“BARYSILITES”

Composition ^a	a_{hex} Å	c_{hex} Å
Pb ₈ Sr(Si ₂ O ₇) ₃	10.091 ± 0.006	38.72 ± 0.03
Pb _{8.5} Sr _{0.5} (Si ₂ O ₇) ₃	10.110	38.71
Pb ₉ (Si ₂ O ₇) ₃	10.130	38.70
Pb ₈ Sr _{0.5} Ba _{0.5} (Si ₂ O ₇) ₃	10.130	38.84
Pb _{8.5} Ba _{0.5} (Si ₂ O ₇) ₃	10.155	38.84
Pb ₈ Ba(Si ₂ O ₇) ₃	10.166	38.91

^a The tabulated chemical composition is that of the weighed-in material. Losses by evaporation can be neglected. Chemical analyses are difficult because it is not certain whether the samples were homogenous or whether there were also some small relicts of glass.

The synthesis of Ba-“barysilite” proved to be more difficult than that of Pb- and Sr-“barysilite.” This may be due to the larger cation-radius of Ba²⁺. The synthesis of Mg- and Mn-“barysilite” (with small cations) is quite uncomplicated. This fact may explain why Pb-“barysilite” has never been found in nature up to now.

Mg-“BARYSILITE” IN THE SYSTEM PbO-MgO-SiO₂

Only one ternary compound was synthesized by Argyle and Hummel (1965/66) during their investigation of the system PbO-MgO-SiO₂. They supposed that this compound 2PbO·MgO·2SiO₂ has the “unusual ability to take 2PbO·SiO₂, 3PbO·2SiO₂, PbOSiO₂, MgO·SiO₂ and SiO₂ into solid solution.” They assumed that this was especially evident in the systems 2PbO·SiO₂—2PbO·MgO·2SiO₂ and PbO·SiO₂—2PbO·MgO·2SiO₂. No change in the spacings of the “mixed crystals” was found. Therefore they explained this feature as caused by a “cation defect.”

Now it was interesting to see whether the compound 2PbO·MgO·2SiO₂ has the barysilite structure or not. A comparison of the diffraction pattern of this “mixed crystal” given by Argyle and Hummel and of our natural barysilite shows good agreement in Table 6. We indexed the powder pattern of “2PbO·MgO·2SiO₂” with the lattice spacing of our

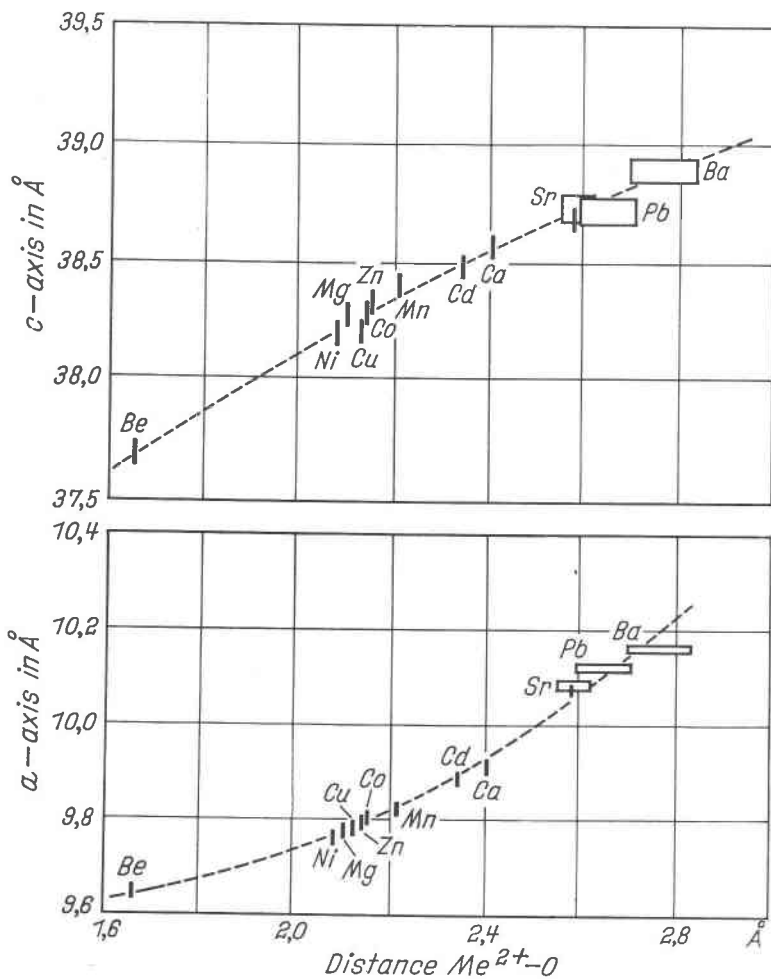


FIG. 3. Cell dimensions of different "barysilites" as a function of the cation-oxygen distance. This figure of J. Lajzerowicz was extended with the data of Pb-Sr-Ba-"barysilites". Because there are no definite values of the cation-oxygen distance in the literature, these values are indicated as wide rectangles (compare also Fig. 2).

barysilite and calculated the cell dimensions $a_{\text{hex}} = 9.73(\pm 0.05)$, $c_{\text{hex}} = 38.24 \pm 0.1$ Å.

The density as measured by Argyle and Hummel is $\rho(\text{exp}) = 6.15$ g/cm³. With this value the number of formula weights in the unit cell is $Z = 19.12$, whereas the theoretical value of Z for a barysilite is 18.

To elucidate this discrepancy we tried to synthesize a Mg-"barysilite." In the course of these efforts we observed two types of Mg-"barysilites":

TABLE 4. X-RAY POWDER DIFFRACTION OF PHASE X

I/I_0	$d, \text{\AA}$	I/I_0	$d, \text{\AA}$	I/I_0	$d, \text{\AA}$
10	8.62	90	2.855	15	1.929
10	4.97	50	2.827	30	1.875
20	4.39	3	2.743	20	1.863
50	4.30	1	2.579	35	1.840
30	3.75	5	2.483	15	1.820
7	3.561	4	2.292	10	1.781
30	3.287	3	2.257	4	1.722
55	3.250	5	2.232	4	1.717
15	3.220	10	2.147	4	1.679
4	3.173	45	2.034	10	1.660
40	3.068	25	1.979		
100	2.896	15	1.971		

TABLE 5. X-RAY POWDER DIFFRACTION OF Pb-"BARYSILITE"

I/I_0	d (meas), \AA	d (comp), \AA	hkl	I/I_0	d (meas), \AA	d (comp), \AA	hkl
15	8.02	7.99	102	15	2.637	2.637	10.14
15	6.54	6.50	014	5	2.533	2.532	220
15	6.50	6.45	006	10	2.518	2.518	12.10
50	4.99	5.06	110	25	2.429	2.428	311
40	4.28	4.28	022	20	2.412	2.413	21.11
		3.99	204	5	2.357	2.359	314
30b	4.00	3.98	116			2.357	226
40	3.54	3.54	01.10	20	2.333	2.332	01.16
85b	3.29	3.28	119	10	2.320	2.321	135
	3.27	3.27	212	10	2.299	2.299	11.15
		3.27	10.11	5	2.225	2.226	317
30	3.25	3.25	028	15	2.182	2.182	229
40	3.23	3.23	00.12	10	2.141	2.139	044
90	3.05	3.05	215	10	2.118	2.118	20.16
70	2.926	2.924	300	30	2.061	2.060	31.10
30	2.903	2.902	20.10	20	2.010	2.010	231
65	2.845	2.851	303	20	2.002	2.002	322
		2.843	127	40	1.992	1.991	22.12
100b	2.736	2.735	218	10	1.975	1.979	11.18
	2.722	2.721	11.12	15	1.968	1.969	234
5	2.663	2.663	306	30	1.948	1.948	325

TABLE 6. X-RAY POWDER DIFFRACTION OF BARYSILITE AND Mg-"BARYSILITE"
COMPARED WITH "Pb₂MgSi₂O₇"

Barysilite		"Pb ₂ MgSi ₂ O ₇ " Argyle <i>et al.</i> (1965/66)		Mg-"barysilite"	
I/I_0	$d, \text{Å}$	I/I_0	$k, \text{Å}$	$d, \text{Å}$	hkl
15	6.39	18	6.33	6.39	006
		3	5.04		
5	4.90	5	4.85	4.87	110
50	4.57	54	4.53	4.56	113
20				4.17	201; 108
25	4.14	13	4.13	4.12	022
60	3.88	66	3.85	3.87	116; 204
35	3.50	29	3.48	3.46	01.10
50	3.22			3.21	10.11; 119
50	3.21	48	3.19	3.19	121; 00.12
60	3.16	62	3.14	3.15	212
15	3.04	10	3.02	3.03	124
100	2.957	100	2.94	2.947	215
		3	2.87		
50	2.829	35	2.81	2.816	300
80	2.765	67	2.75	2.757	127; 303
80	2.675	63	2.67	2.670	11.12
20	2.605	7	2.60	2.603	10.14
20	2.586	15	2.57	2.505	306
5				2.453	220; 12.10
5				2.393	223
15	2.358	11	2.35	2.353	309; 21.11
20	2.347	13	2.34	2.339	311
25	2.305	15	2.30	2.305	01.16; 02.14
10	2.285	11	2.28	2.277	226; 314
20	2.266	11	2.26	2.261	11.15
30 b	2.109	15	2.09	2.099	138; 402
10	2.083	7	2.08	2.076	20.16; 21.14
7	2.070				044
25	2.004	9	1.994	1.998	31.10
15	1.954			1.951	11.18
40 b	1.943	25	1.929	1.938	231; 408
					22.12
25	1.901	9	1.895	1.898	30.15
30	1.886			1.877	325
50	1.856	42	1.838	1.849	04.10
40	1.850			1.842	410
45	1.844				21.17
30	1.834	18	1.824	1.825	237; 143
10	1.784	6	1.774	1.778	13.14
20	1.777	10	1.768	1.770	146

Mg-"barysilite" of type I is microcrystalline with broad and diffuse lines on the Guinier-X-Ray pattern and is obtained by quenching the melt. The cell dimensions are intermediate between those of $\text{Pb}_8\text{Si}_2\text{O}_7$ and type II described below. Probably Pb^{2+} replaces Mg^{2+} in the Mg-"barysilite" and enlarges the lattice constants.

Mg-"barysilite" of type II crystallizes by annealing type I at about 600–700°C or by cooling a melt slowly. Type II forms crystals which give sharp and distinct X-ray patterns. The characteristic IR absorption band for pyrosilicates moves from 703 cm^{-1} for type I to 706 cm^{-1} for type II.

In the hexagonal setting the cell constants of well-crystallized Mg-"barysilite" (type II) are: $a = 9.75(3)$, $c = 38.28(6)$ Å.

The density $\rho(\text{exp}) = 6.83(\pm 0.1)$ g/cm^3 is in good agreement with the calculated density $\rho(\text{calc}) = 6.91$ g/cm^3 assuming $Z = 6$ for $\text{Pb}_8\text{Mg}(\text{Si}_2\text{O}_7)_3$.

Efforts to replace more than one of the nine Pb^{2+} by Mg^{2+} failed. Therefore the formula of the ternary compound $2\text{PbO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ in the system $\text{PbO}-\text{MgO}-\text{SiO}_2$ investigated by Argyle and Hummel (1965/66) could not be confirmed and is probably $\text{Pb}_8\text{Mg}(\text{Si}_2\text{O}_7)_3$.

DISCUSSION OF THE BARYSILITE FORMULA

According to their investigations of barysilite Ito and Frondel (1967) suggested the formula $\text{Pb}_5\text{X}(\text{Si}_2\text{O}_7)_2$. The number of formula weights per unit cell would then be $Z = 9$. This would only be in agreement with the space group $R3c$ or $R\bar{3}c$ determined by J. Lajzerowicz (1965) and given in this paper under the condition that X and Pb of Pb_8 are isomorphous. We never observed an isomorphous exchange of X and Pb of Pb_8 . Therefore the formula $\text{Pb}_5\text{X}(\text{Si}_2\text{O}_7)_2$ is probably incorrect.

Chemical analyses of barysilite made by Bauer and Berman (1930) and G. Flink (reported by Glasser, 1964) have a Pb:X-ratio (X = Fe, Mn, Zn, Ca, Mg, K, Na) of about 4–5:1. Glasser interpreted these analyses as indicating the formula $3[\text{Pb}_4(\text{Mn, etc})\text{Si}_3\text{O}_{11}]$. But even this formula is inconsistent with the single crystal data. Probably unpure barysilite was taken for these chemical analyses. As Ito and Frondel already pointed out, the barysilite X-ray powder diagram of Glasser contained nasonite $\text{Pb}_6\text{Ca}_4[\text{Cl}_2/(\text{Si}_2\text{O}_7)_3]$.

Our experiments to replace more than one of the nine Pb cations by Sr, Ba and any other cation in "barysilite" failed. X-ray diffraction patterns and observations under the microscope always revealed some additional phases besides "barysilite." Therefore the proposed formula of Lajzerowicz $\text{Pb}_8\text{X}(\text{Si}_2\text{O}_7)_3$ is confirmed and the substituted cation X should occupy a special position in the barysilite structure.

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