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SYNTHESIS OF THE BERZELIITE ($Ca_2NaMg_2As_3O_{22}$)—MANGANESE BERZELITE ($Ca_2NaMn_2As_3O_{12}$) SERIES (ARSENATE GARNET)[1]

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Previous studies of the mineral berzeliite, $Ca_2Na(Mg, Mn)_2As_3O_{12}$, have been summarized by Blix and Wickman (1959). In their paper, new chemical and optical data as well as paragenetic observations were given on over one hundred specimens from Langbån, Sjogruvan and other localities.

As a part of the present author's investigation of compounds having the garnet structure, the synthesis of berzeliite ($Ca_2NaMg_2As_3O_{12}$) and manganese berzeliite ($Ca_2NaMn_2As_3O_{12}$) was studied. The end members and compounds of three intermediate compositions in the solid solution series have been synthesized hydrothermally.

The starting materials were prepared by pouring stoichiometric amounts of manganese carbonate, magnesium hydroxide and calcium hydroxide into solutions containing corresponding amounts of sodium arsenate and arsenic acid. The resulting white milky mixtures were agitated with a magnetic stirrer for 30 minutes, dried in an evacuated oven, pulverized and mixed thoroughly.

Samples of approximately 100 mg were placed in a silver liner made of 0.03 mm thick silver foil and heated in a 25 ml hydrothermal bomb at 450°C–480°C for a period of 24 to 72 hours. The bomb was filled with sufficient distilled water to maintain approximately 1.5 kilobars.

The products came out as fairly homogeneous small cubic crystals up to 30 μ in diameter. The crystals displayed no birefringence under crossed Nicols. Synthetic Mg berzeliite appeared colorless and under the microscope it occurred as aggregates of faintly bluish transparent crystals. Mn berzeliite formed small brownish particles which under the microscope appeared as slightly yellowish single crystals which probably are dodecahedra. The intermediate compounds showed a light brown to greyish appearance. The color changes progressively with Mn content.

The X-ray powder diffraction patterns were indexed and the spacings for the synthetic end compositions are given in Table 1. Very strong reflections at (211) and (321) are quite similar to those of hydrogarnet and rare earth garnet. The cell dimensions calculated from sharp reflections of (800), (640), 642), (422), (420) and (400) for the end compositions and

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TABLE 1. X-RAY POWDER DATA OF SYNTHETIC BERZELIITE, MANGANESE BERZELIITE AND NATURAL BERZELIITE. (Cu Kα, Ni FILTER.) SPACE GROUP *Ia3d*

a_0	Synthetic $Ca_2NaMg_2As_3O_{12}$		Berzeliite from Langbån (Matchatschki)		Synthetic $Ca_2NaMn_2As_3O_{12}$	
	12.33		12.38		12.52	
hkl	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
211	5.02	50	5.05	20	5.10	40
220	4.35	25	—	—	—	—
321	3.290	30	3.31	30	3.339	30
400	3.081	50	3.10	70	3.129	50
411	—	—	2.92	10	—	—
420	2.754	100	2.77	100	2.800	100
332	2.627	40	2.65	30	2.666	35
422	2.516	40	2.53	50	2.556	90
431	2.416	15	2.42	30	2.452	15
440	2.178	10	2.19	10	2.212	2
611	1.997	3	2.00	20	2.030	5
620	—	—	—	—	1.978	3
541	—	—	1.91	30	—	—
631	1.819	8	1.82	60	1.846	5
444	1.780	25	1.78	60	1.806	15
622	1.742	5	—	—	1.769	2
640	1.711	40	1.71	90	1.736	40
710	1.678	5	1.68	10	1.703	2
642	1.649	45	1.65	100	1.673	80
732	1.567	8	1.57	10	1.590	5
800	1.541	15	1.55	60	1.565	10
653	1.475	5	1.48	20	1.496	3
752	1.397	5	1.40	10	1.419	5
840	1.380	10	1.38	60	1.400	10
842	1.346	20	1.35	100	1.367	30

TABLE 2. RESULTS OF BERZELIITE AND MANGANESE BERZELIITE SYNTHESIZED AT 1.5 KBARS

Composition	Temperature (C°)	Time (hour)	Unit-cell constants, (Å)	Refractive indices
$Ca_2NaMg_2As_3O_{12}$ Berz. 100	480	48	12.33	1.710
Berz. 75 Mn-berz. 25	450	24	12.37	1.73(5)
Berz. 50 Mn-berz. 50	450	24	12.43	1.755
Berz. 25 Mn-berz. 75	450	24	12.48	1.765
$Ca_2NaMn_2As_3O_{12}$ Mn-berz. 100	480	72	12.52	1.777

three intermediate compositions are given in Table 2 with the refractive indices measured by the immersion method. The unit-cell constants vary linearly to the precision of these data as a function of the chemical composition; the values obtained are compared in Figure 2 with those given by Blix and Wickman from natural specimens. The agreement of the two sets of data, shown in the diagram, seems reasonable except for slight departure toward the Mn end, probably due to extraneous ions such as Pb, in the solid solution in the natural specimens. The solubility gap suspected in much earlier studies of natural samples, referred to Blix and Wickman, could not be investigated successfully because of the very small difference in the unit cell constants between the end compositions and because of the inferior crystal quality of synthetic berzeliites formed at 1.5 kbars and at temperatures below 350°C, at which conditions the phase gap would be expected to become more prominent. It may still be safely stated that no real indication of a gap in the solid-solution series exists; if a gap exists, it must be very small as previously stated by Blix and Wickman (1959).

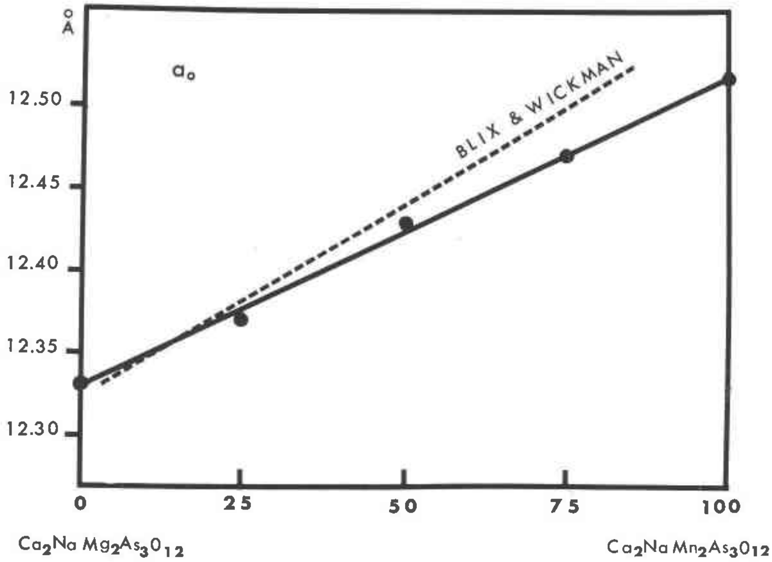

FIG. 1. Unit-cell constant a_0 of berzeliite and manganese berzeliite series.

At temperatures higher than 550°C with 1.5 kbars, Mg berzeliite decomposed to adelite, $CaMgAsO_4$, plus an amorphous phase, and Mn berzeliite decomposed to two crystalline compounds for which no match was found in the ASTM X-ray Powder Data File. Attempts to synthesize

Fe^{2+}, Co, Ni, Zn and Cu analogues of berzeliite failed under the corresponding conditions. The products all came out as minerals of the adelite group, namely conichalcite $CaCuAsO_4$, austinite $CaZnAsO_4$, and the Fe^{2+}, Co and Ni analogues of adelite, $CaFeAsO_4$, $CaCoAsO_4$ and $CaNiAsO_4$. Adelite occurs frequently in the localities where berzeliite is found. The absence of Fe^{2+}-berzeliite in nature may not necessarily be due to the low concentration of Fe^{2+} ions in the environment, as was suspected by Blix and Wickman (1959).

The synthesis of berzeliite in air was not achieved. The starting materials for Mg berzeliite did not react in air up to around 800°C. An unidentified single phase was obtained by heating these starting materials at 900°C.

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AN ELECTRON MICROSCOPIC STUDY OF SOIL ALLOPHANE WITH AN ORDERED STRUCTURE

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Allophane is known to possess different degrees of structural order. In the course of a study of soil allophane, Yoshinaga and Aomine (1962a, b) separated a low crystalline clay component, which they called "imogolite," from some volcanic ash soils. It was differentiated from coexisting X-ray amorphous component, "allophane," with a similar chemical composition ($SiO_2/Al_2O_3 \doteqdot 1$) in the following points: In an air-dry state, its parallel orientation specimen exhibited broad and relatively intense X-ray diffraction bands at about 14.5 Å and 7.5 Å and a weak one at