

Metastable Rubidium Aluminum Silicate with a Hexagonal Sheet Structure

Abstract. *A compound of composition $RbAlSi_3O_8$, with a structure of double sheets of silica-alumina tetrahedra with common apices held together by rubidium ions in 12-fold coordination, may be crystallized from a melt by rapid cooling. The compound is an analog of the metastable forms of the calcium, barium, strontium, and lead feldspars.*

The synthetic hexagonal modification of the barium feldspar, celsian, was reported in 1915 by Ginsberg (1). The structure, determined by Ito and reported by Yoshiki and Matsumoto in 1951 (2), consists of double sheets of silica-alumina tetrahedra with common apices and barium ions situated in 12-fold coordination positions between the sheets. This structure requires that one-half the tetrahedral positions be occupied by aluminum ions and one-half by silicon ions. The compound is structurally unique since each tetrahedron shares all four oxygen atoms with adjacent tetrahedra, as is normally the case in the framework silicates. The structure is similar to that of the micas except that it is anhydrous and the octahedral layer is absent. Structural diagrams have been presented by several authors (2-4). A calcium analog of the compound was reported by Davis and Tuttle (5) and by Goldsmith and Ehlers

(6) from hydrothermally treated mixes of the oxides. Sorrell (4) reported strontium and lead analogs of the compound from fired mixes of kaolinite and the sulfates. The chemical analogs reported previously, because of the unique sheet structures, should provide a basis for profitable study of structural characteristics and thermal behavior of all sheet silicates.

The interlayer cations of these metastable phases are all divalent. The ratio of silicon to aluminum is therefore 1:1. No analogous phases have been reported in which the interlayer cation is univalent and in which this ratio is necessarily 3:1. The common occurrence of Ca, Ba, Sr, Pb, Rb, and Cs in the feldspar structure is well known. It seems reasonable to expect, therefore, that metastable modifications of Rb and Cs aluminosilicates can be formed, even though the total electrostatic force available for maintenance of the sheet structure would be approximately one-half that in the Ca, Ba, Sr, and Pb analogs. Barrer and McCallum (7) performed an extensive series of hydrothermal synthesis experiments with Rb and Cs aluminosilicate compositions, including those of the theoretical feldspars, $RbAlSi_3O_8$ and $CsAlSi_3O_8$. They reported several anhydrous phases, including a rubidium feldspar, but did not obtain hexagonal modifications.

For investigation of the possible existence of hexagonal modifications of the theoretical compositions, mixtures of kaolinite, silicic acid, and the appropriate alkali sulfates were prepared. Heating and quenching techniques were used to determine phases formed by solid-state reaction, by crystallization from the melt, and by devitrification of the glasses. In nearly all cases the results were similar to those reported by Barrer and McCallum (7). The compositions fused completely at a temperature near 1700°C.

The $RbAlSi_3O_8$ composition, when cooled rapidly from 1710°C, however, contained a substantial percentage of a phase in which x-ray and optical characteristics indicate the hexagonal modification of the feldspar. Attempts to form the phase by solid-state reaction and by devitrification were unsuccessful. An analogous Cs aluminosilicate was not obtained. The phase is extremely unstable. If the melt is quenched only slightly more slowly, a phase similar to the Rb analcite (7) is obtained. If it is quenched only slightly more rapidly, glass is the only phase.

X-ray data for the phase are shown



Fig. 1. Aggregates of crystals of the metastable hexagonal modification of $RbAlSi_3O_8$. Polarized light, Nicol prisms crossed.

in Table 1. Unit-cell dimensions were calculated from observed (30.0) and (00.5) lines as determined by comparison with the lines of barium, strontium, and lead analogs. Interplanar spacings were calculated from these assumed unit cell dimensions. Agreement between calculated and observed spacings is excellent. Optically, the phase is well crystallized, with moderate birefringence, and it has the appearance of shredded mica flakes (Fig. 1) with a suggestion of twinning.

In view of the observed stability of Cs in 12-fold positions in other crystals, our failure to synthesize a Cs analog of the hexagonal phase is surprising. The extreme instability of the Rb phase makes it very difficult to quench, however. The Cs analog would be expected to be equally as unstable, or even more so (8).

CHARLES A. SORRELL
TAKI NEGAS

Department of Geology,
Miami University, Oxford, Ohio

References and Notes

1. A. S. Ginsberg, *Ann. Inst. Polytech. Petrograd* 23, 39 (1915).
2. B. Yoshiki and K. Matsumoto, *J. Am. Ceram. Soc.* 34, 283 (1951).
3. T. Ito, *X-Ray Studies on Polymorphism* (Maruzen, Tokyo, 1950), pp. 19-29; W. Eitel, *Physical Chemistry of the Silicates* (Univ. of Chicago Press, Chicago, 1954), pp. 49-50.
4. C. A. Sorrell, *Am. Mineralogist* 47, 291 (1962).
5. G. L. Davis and O. F. Tuttle, in *The Bowen Volume* (American Journal of Science, New Haven, 1952), pp. 107-114.
6. J. R. Goldsmith and E. G. Ehlers, *J. Geol.* 60, 386 (1952).
7. R. M. Barrer and N. McCallum, *J. Chem. Soc. (London)* 1953, 4029 (1953).
8. We thank Miami University for funds for construction of equipment used in this study.

16 May 1963

Table 1. Data obtained by the method of powder x-ray diffraction for the hexagonal $RbAlSi_3O_8$ phase. Assumed unit cell dimensions: $a = 5.30$ Å, $c = 7.84$ Å. d is interplanar spacing of designated hkl plane. I/I_1 is line height compared with the most intense line.

hkl	d (Å)		I/I_1
	Calc.	Obs.	
001	7.84	7.86	100
100	4.58	—	—
101	3.96	3.97	47
002	3.92	3.92	6
102	2.98	2.98	47
110	2.65	2.65	15
003	2.61	2.61	6
111	2.51	2.51	2
200	2.29	2.30	3
103	2.27	2.26	13
201,112	2.20	2.20	10
202	1.98	1.98	2
004	1.96	1.95	14
113	1.86	1.86	9
104	1.80	1.79	2
210	1.74	—	—
203	1.72	—	—
211	1.69	1.70	5
212,114	1.59	1.59	5
005	1.57	1.57	6
300	1.53	1.53	2