

SOLID STATE FORMATION OF BARIUM, STRONTIUM AND LEAD FELDSPARS IN CLAY-SULFATE MIXTURES

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ABSTRACT

Mixtures of kaolin-type clays and sulfates with theoretical compositions of the barium, strontium, and lead feldspars were *x*-rayed continuously during heating to 1400° C. at a rate of 5° C. per minute.

Formation of the feldspars in the solid state is characterized by the appearance of a metastable phase with a structure similar to hexagonal celsian and hexagonal anorthite. The barium hexagonal phase is very persistent. Prolonged heating is necessary to convert it completely to the feldspar, the conversion proceeding more rapidly with increasing temperature. The strontium and lead hexagonal phases are, however, very unstable, having been detected only during continuous *x*-ray investigation. They also change to the feldspars, the change occurring more rapidly with increasing temperature.

The presence of small amounts of impurities has a marked effect on the formation temperatures and reaction rates. Titania tends to lower formation temperatures of the reaction products and to enhance the *x*-ray diffraction maxima. Potash tends to inhibit formation of the hexagonal phases and to promote formation of the feldspars in the barium and strontium compositions but has little effect on the lead phases.

INTRODUCTION

It has long been recognized that a number of univalent and divalent ions with suitable ionic radii can proxy for the potassium, sodium, and calcium ions which normally occupy interstitial positions in the silica-alumina tetrahedral framework structure of the common feldspars.

Celsian, the natural barium feldspar, is approximately isostructural with sanidine and has been shown to form a complete series with potash feldspar, with the coupled substitution of aluminum and barium for potassium and silicon, analogous to the substitution of calcium and aluminum for sodium and silicon in the plagioclase series.

Synthesis studies have shown that barium and strontium feldspars can be formed in the solid state and from melts; however a hexagonal phase with the theoretical composition of the barium feldspar has also been obtained and has been assumed to be a high-temperature polymorph of the feldspar. No lead aluminum silicate with the feldspar structure has been definitely identified.

Celsian was discovered by Sjögren (1895) in the manganese mines of Jakobsberg, Sweden. He established the composition of the mineral as $BaO \cdot Al_2O_3 \cdot 2SiO_2$ and considered it triclinic. Strandmark (1903, 1904) established the monoclinic symmetry. Taylor, Darbyshire, and Strunz (1934) investigated the feldspars, sanidine, adularia, and celsian, using *x*-ray techniques and indicated that celsian is isostructural with sanidine. More recently, Gay (1956) and Newnham and Megaw (1960) have done

detailed structural analyses of natural celsian and have determined that ordering of silicon and aluminum ions in tetrahedral positions results in formation of a super-lattice. The presence of a group of extremely weak layer reflections indicates a doubling of the unit cell in the c direction and body-centered symmetry.

The first synthesis experiments on these feldspar compositions were performed by Fouqué and Michel-Lévy (1880) who reported the formation of barium, strontium, and lead analogs of anorthite, oligoclase, and labradorite from melts of the oxides. The phases were not well crystallized and so could not be characterized optically. Dittler (1911) produced synthetic barium feldspar from a melt and showed that it was biaxial. However, Ginsberg (1915) obtained uniaxial positive crystals from a melt of barium feldspar composition and regarded the phase as a barium nepheline.

Eskola (1922) prepared both strontium and barium feldspars in the solid state by heating oxides to 1400° C. with $\text{Sr}(\text{VO}_3)_2$ and $\text{Ba}(\text{VO}_3)_2$ as fluxes. Eskola's work indicated that strontium feldspar forms solid solutions with anorthite and barium feldspar forms solid solutions with the potash feldspars.

Yoshiki and Matsumoto (1951) produced hexagonal, mica-like crystals up to 2 cm in width with perfect cleavage and lead-gray pearly luster by electrofusion of a mix of kaolinite and barium carbonate of the celsian composition. The crystal structure of the phase was determined by Ito (1950) and was found to consist of a double sheet of silica-alumina tetrahedra with common apices, held together by barium ions in 12-fold coordination (Fig. 1).

Geller and Bunting (1943) reported three lead aluminum silicates in the high lead portion of the system. Although they did not investigate the lead feldspar composition, they believed that other ternary compounds existed and published powder data for a lead aluminum silicate of unknown composition (A.S.T.M. 3-0373).

Davis and Tuttle (1952), during extensive studies of the hexagonal anorthite, synthesized the barium hexagonal phase by heating the oxides at 1500° C. for four days. Longer heating changed it to celsian.

The primary objective of this study was to determine the temperatures and rates of formation of barium, strontium, and lead feldspars from mixes of kaolinite-type clays and the sulfates and to investigate the stability relations between the hexagonal phases and the feldspars. In conjunction with this work it was necessary to study the effects of impurities, notably potash and titania, which are common constituents of clays, on the temperatures and extents of the reactions.

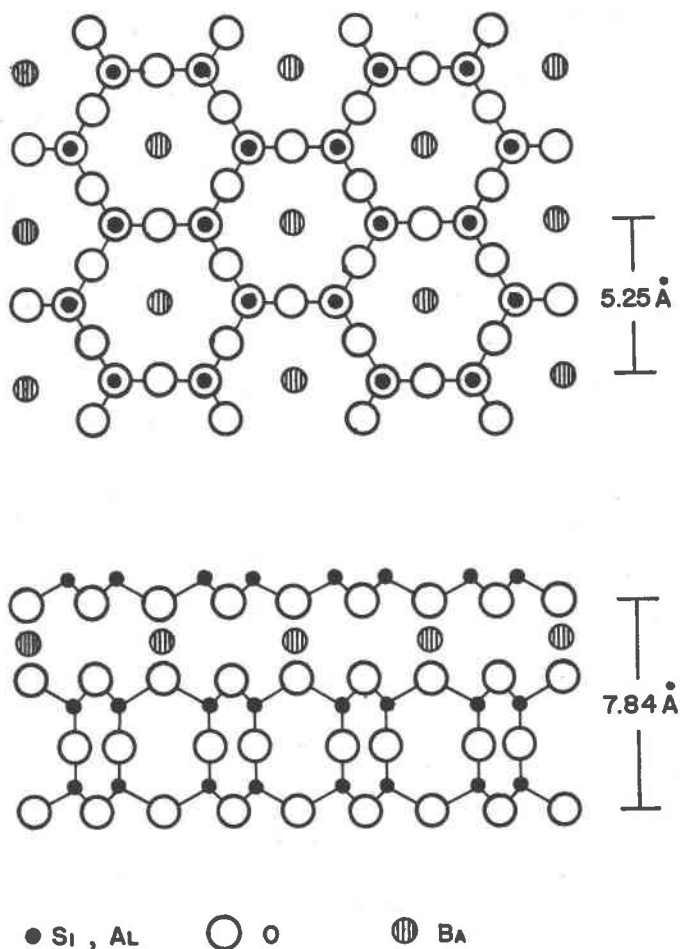


FIG. 1. The structure of the hexagonal barium aluminum silicate according to Ito (1950).

EXPERIMENTAL PROCEDURE

Characteristics of starting materials. Several factors were considered in the selection of starting materials. Oxides and gels are commonly used in solid state reaction studies of this type. However, clays of the kaolinite group were chosen as sources of silica and alumina and the sulfates were chosen as sources of barium, strontium, and lead primarily because of the fact that these materials are widely used as ceramic raw materials for reasons of availability in bulk at moderate cost. Clays of the kaolinite

TABLE 1. CHEMICAL COMPOSITIONS OF CLAYS

	Kaolin	Halloysite
SiO ₂	45.83	42.3
Al ₂ O ₃	38.60	30.4
K ₂ O	1.8	0.0
Na ₂ O	0.06	
CaO	0.05 ¹	0.0
Fe ₂ O ₃	0.64	2.3
FeO		0.1
TiO ₂	0.10	1.7
MgO	0.1-0.3 ¹	0.1
MnO ₂	0.05 ¹	
CuO	0.01	
B ₂ O ₃	0.08 ¹	
P ₂ O ₅		0.5
H ₂ O+		11.5
H ₂ O-	12.58	11.0

¹ Spectrographic analysis.

group occur with varying degrees of crystallinity and with significantly different thermal behaviors. Therefore, they provide an opportunity for the study of the effects of structural characteristics on the formation of high-temperature phases.

Two clays of greatly different crystallinity were used. As a representative of a typical commercial kaolin, Baker N.F. grade kaolin, containing approximately 5 per cent muscovite-type mica, was used. The outstanding chemical characteristic of this material is the relatively high potash content. The iron content is moderate and other impurities are present in very minor amounts (Table 1). Halloysite from Muswellbrook, New South Wales (Loughnan and Craig, 1960), was used because of the poorly crystalline nature of the material. It contains a moderate amount of coarse quartz and some anatase. The chemical analysis of Loughnan and Craig is given in Table 1 and reveals relatively high iron and titania contents. Reagent grade barium, strontium, and lead sulfates were used.

Compositions studied. Three basic compositions were studied. The compositions of the three feldspars, BaAl₂Si₂O₈, SrAl₂Si₂O₈, and PbAl₂Si₂O₈, are referred to throughout this study by the shorthand notations, BAS₂, SrAS₂, and PbAS₂, respectively.

All three feldspar compositions were prepared using the sulfates in combination with each of the clays, for the purpose of determining the basic reaction sequences and the effects of structural variations on phase formation. The molar ratio of silica to alumina in kaolin-type clays is

the same as that in theoretical feldspar, 2:1. Therefore, it was not necessary to add free silica or alumina to formulate the compositions.

For the study of the effects of titania and potash, TiO_2 (anatase) was added to the previously prepared kaolin-sulfate mixes in an amount equal to 2 per cent, by weight, of the kaolin content of the mixes. Potassium metasilicate (K_2SiO_3) was added to the halloysite-sulfate mixes to provide K_2O in an amount equal to 2 per cent, by weight, of the halloysite content of the mixes. The silicate was used because its melting point, 976°C ., is near the temperature at which mica dissociates. Potassium presumably would thus become available to the reacting materials in the same general temperature range as would potassium from the mica.

A series of mixes of the sulfates with a flint clay containing 2.5 per cent titania and 0.4 per cent iron was investigated but is not described here. Reactions in the flint-clay-sulfate mixes were nearly identical with those of the halloysite, indicating that the iron content of the halloysite (2.3 per cent) has little effect on the reactions. The effect of iron as an impurity was therefore not further investigated.

Preparation of samples. For calculations of the weight percentages of the starting materials to be used in formulation of the compositions, the available chemical analyses of the kaolin and halloysite (Table 1) and the theoretical compositions of the sulfates were used.

All starting materials were dried at 60°C . for several hours prior to preparation of the mixes. Halloysite was heated to 300°C . for one hour to eliminate all interlayer water and thereby prevent excessive shrinkage during firing. The materials were passed through a 230 mesh screen prior to weighing and mixing. Thirty-gram batches of the materials were weighed to the nearest milligram and mixed by hand for at least ten minutes.

Methods of analysis. Differential thermal analysis and x -ray diffraction techniques were used in this study. Detailed powder data were obtained by conventional diffractometer methods, using nickel-filtered copper radiation at 45 Kvp. and 18 ma. with a scanning rate of one degree 2θ per minute.

The continuous x -ray heating method was used to follow the courses of high-temperature reactions. The furnace used was a platinum-wound electric furnace, powered through a motor-driven Variac arrangement programmed to increase the temperature at a rate of 5°C . per minute. The furnace was constructed on the principle developed by Kulbicki and described by Grim and Kulbicki (1957) and was adapted for use with a Phillips recording diffractometer. All high-temperature x -ray work was done with nickel-filtered copper radiation at 45 Kvp. and 18 ma. with a scanning rate of two degrees 2θ per minute.

Prepared mixes were placed in recessed platinum slides, packed firmly with a spatula, and placed in the furnace. A thermocouple was placed beneath the platinum slide for temperature determination. During heating, diagnostic diffraction maxima of the phases were scanned repeatedly and temperatures, obtained with a potentiometer, were recorded on the diffractogram. The normal procedure was to scan a wide 2θ range in order to detect all phase changes and then, with a new sample, to scan narrow 2θ ranges to obtain recorded intensity values of diagnostic peaks at small temperature intervals.

The recorded intensity of each diagnostic reflection was plotted versus the recorded temperature. These plots are referred to as continuous diffraction curves or continuous phase development curves. The intensity values provide an estimate of the amount of a phase present at various temperatures. Other variables are involved, however. The intensity of a given peak may vary with crystallite size, the absorption characteristics of other phases present, with crystallinity, and with the degree of ordering in the crystal lattice. The curves do not provide a quantitative estimate of the relative amounts of two or more reacting phases, but do indicate the temperatures at which an amount of a phase sufficient to be observed is developed and the temperature interval through which development occurs at that particular heating rate.

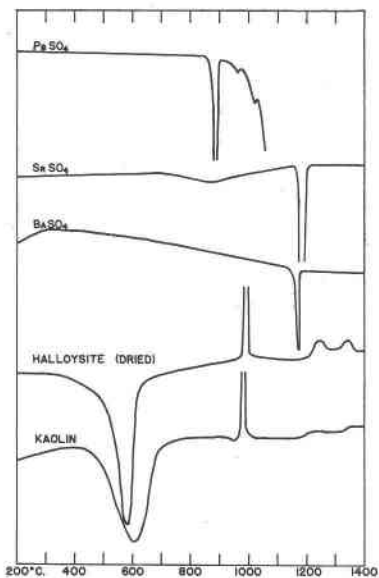
The differential thermal analysis apparatus used consists of a platinum-wound tube-type furnace heated through a motor-driven Variac at a rate of 10° C. per minute. Samples were placed in a platinum sample block and referred to an alpha-alumina standard. Differential temperature was recorded by an electric cell recorder activated by a reflecting galvanometer connected to the differential thermocouple circuit. Temperatures were read from a potentiometer and marked on the thermogram by the observer.

All observations by continuous x -ray methods and differential thermal analysis were made up to 1400° C. All temperatures reported are in degrees centigrade.

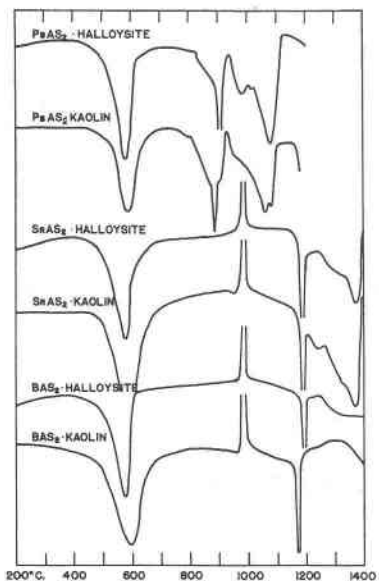
EXPERIMENTAL DATA AND RESULTS

Thermal behavior of the sulfates and clays. Thermograms of the sulfates are shown in Fig. 2. Hodgman (1953) listed barium sulfate as rhombohedral with transition to a monoclinic form at 1149° and a melting point of 1580° . Birch, Schairer, and Spicer (1942) gave the transition point as 1178° . The thermogram shows an intense endothermic effect with a sharp break at 1150° . Continuous x -ray examination indicates a rapid, reversible transition at approximately 1150° . Powder data for the high-temperature form are listed in Table 2.

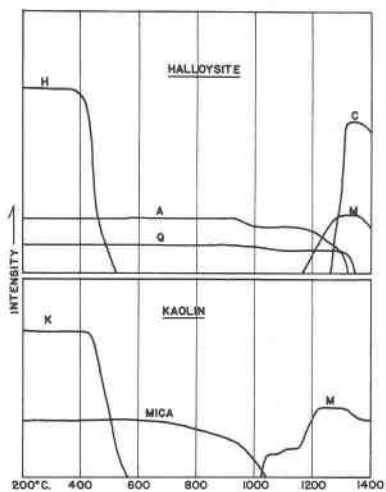
Hodgman (1953) gave the melting point of strontium sulfate as 1580°



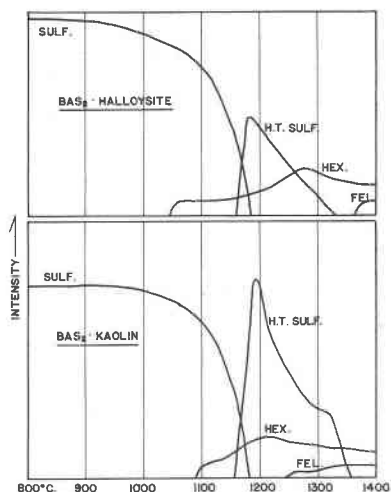
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FIG. 2. Thermograms of the clays and sulfates used as starting materials.

FIG. 3. Thermograms of the feldspar compositions prepared with the sulfates and clays.

FIG. 4. Continuous diffraction curves showing high-temperature reactions in the clays. (H) halloysite (02, 11) peak; (K) kaolinite (11 $\bar{1}$) peak; (M) mullite 5.40 Å peak; (C) cristobalite (111) peak; (A) anatase (101) peak; (Q) quartz (alpha-beta undifferentiated) (101) peak; (Mica) muscovite-type mica 10 Å peak.

FIG. 5. Continuous diffraction curves showing phase development in barium feldspar mixes. Sulfate (211) peak; high-temperature sulfate 3.77 Å peak; barium hexagonal phase (001) peak; barium feldspar (020) peak.

but did not mention a transition point. Birch *et al.* (1942), however, indicated a melting point of 1605° with a transition at 1166°. The thermogram (Fig. 2) shows a very intense endothermic effect beginning at approximately 1165°. Continuous *x*-ray examination indicates a rapid, reversible transition at approximately 1165°. Powder data are in Table 2.

Hodgman (1953) listed lead sulfate as monoclinic or rhombohedral with decomposition at 1000°. However, that temperature is well above the melting point of the decomposition product, PbO, which Hodgman indicated melts at 888°. Birch *et al.* (1942) listed a rhombic to monoclinic inversion at 865°. The thermogram is characterized by a very intense endothermic effect beginning at approximately 830° with a sharp break at 865°. Continuous *x*-ray investigation was complicated by the fact that

TABLE 2. POWDER DATA FOR HIGH-TEMPERATURE Ba AND Sr SULFATES

H.T. BaSO ₄ ¹		H.T. SrSO ₄ ²	
d(Å)	I/I ₁	d(Å)	I/I ₁
4.35	31	4.15	4
4.31	30		
3.77	100	3.62	100
		2.87	6
2.65	64	2.54	41
2.26	30	2.17	13
2.17	12	2.08	9

¹ Data obtained at 1234° C. Reversible transition at approximately 1150° C.

² Data obtained at 1182° C. Reversible transition at approximately 1165° C.

marked bloating of the sample accompanied the endothermic effect at 865°. Bloating was followed almost immediately by fusion. The nature of the endothermic effect has not, therefore, been satisfactorily determined. *X*-ray data indicate that the formation of PbO occurs in conjunction with the endotherm. Bloating, moreover, would suggest that loss of SO₃, rather than inversion, is the cause of the effect. The observed melting temperature is in agreement with that of PbO.

The continuous diffraction curves of both clays show loss of hydroxyls beginning at approximately 400° with loss of structure and disappearance of diffraction characteristics between 500° and 575°.

In the kaolin (Fig. 4) mullite appears between 1000° and 1050°, slightly above the temperature of the exotherm. Mullite content increases rapidly between 1150° and 1200° and decreases slightly above 1300°. The ten angstrom peak of mica decreases gradually over a large temperature

range and disappears near 1000°. No cristobalite forms within the range of temperatures investigated. Both the lack of cristobalite and the slight decrease of the mullite near 1400° are interpreted as the result of the relatively high potash content. The well-sintered character of the kaolin after firing indicates formation of an appreciable quantity of glass. The thermogram shows no large heat effect in the high-temperature range.

Mullite appears in halloysite (Fig. 4) at 1180°, develops rapidly, and decreases slightly above 1350°. Cristobalite appears at about 1250°, reaches a maximum at 1300°, and decreases slightly above 1350°. It is noted that quartz persists over a temperature range of some 40° after the formation of cristobalite as a dissociation product of kaolinite. Anatase disappears above 1300°. The delayed appearance of mullite is interpreted as a result of the poorly crystalline nature of the halloysite, with higher temperatures required for crystal growth from nuclei. The decreases in the intensities of mullite and cristobalite peaks near 1400° may be connected with the high iron and titania content. The initial decrease of anatase is approximately coincidental with the nucleation of mullite and the disappearance is coincidental with rapid mullite development. It might reasonably be assumed, therefore, that titania is incorporated into the mullite lattice.

X-ray characteristics of the feldspars. Preliminary studies of fired kaolin-sulfate mixes indicated that barium, strontium, and lead feldspars, with *x*-ray characteristics quite similar to those of sanidine, can be formed in the solid state. Firing at 1400° for at least twelve hours was required for complete formation of barium feldspar. The strontium mix, however, converted completely to strontium feldspar in less than one hour at 1400°. Lead feldspar formed after a very short time at 1000°. Melting of the lead mix occurred above 1200°.

Table 3 summarizes the *x*-ray powder data for all three feldspars formed under the conditions described above. Data for sanidine, calculated from Weissenberg data of Taylor, Darbyshire, and Strunz (1934), are included. The *d*-values for celsian have been calculated, using the unit cell dimensions of Taylor et al. ($a=8.63 \text{ \AA}$, $b=13.10 \text{ \AA}$, $c=7.29 \text{ \AA}$, $\beta=116^\circ$), for comparison with observed values of celsian and the other two feldspars.

The (220) line, prominent in all three feldspars, was not listed by Taylor, Darbyshire, and Strunz (1934) but was listed as a strong line by Taylor in an earlier study (1933). The (130) line of celsian is a single peak at 3.82 Å but the same line is a well defined doublet in the strontium and lead feldspars, suggesting that celsian is monoclinic and the other two synthetic feldspars are triclinic.

The powder data for the lead feldspar are virtually identical with those

TABLE 3. POWDER DATA FOR FELDSPARS

Sanidine Taylor <i>et al.</i>		Celsian Calc.	Celsian Obs.		Sr Feldspar Obs.		Pb Feldspar Obs.	
hkl	d(Å)	d(Å)	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁
020, 001	6.37	6.55	6.56	64	6.56	35	6.62	79
11 $\bar{1}$	5.85	5.92	5.88	18	5.83	15	5.98	40
021	4.59	4.63	4.63	40	4.60	17	4.64	30
200	3.86	3.88	3.92	21	4.15	12	3.97	14
130	3.74	3.81	3.82	47	3.82	15	3.83	40
13 $\bar{1}$	3.59	3.65	3.63	27	3.77	39	3.80	35
			3.56	40	3.62	20	3.63	26
11 $\bar{2}$	3.49	3.51	3.48	77	3.50	20	3.52	35
220		3.35	3.36	100	3.45	71	3.48	95
040, 002	3.24	3.28	3.28	33	3.29	94	3.31	100
131	3.00	3.02	3.03	60	3.24	100	3.25	56
22 $\bar{2}$	2.96	2.96	2.97	8	2.99	39	3.02	40
022	2.92							
041	2.88	2.93	2.92	34	2.90	24	2.93	19
13 $\bar{2}$	2.77	2.80	2.78	39	2.75	36	2.78	38
241	2.61	2.60	2.59	73	2.56	61	2.57	74
240	2.52	2.50			2.49	9	2.50	9
15 $\bar{1}$	2.44	2.44	2.42	10	2.41	11	2.42	12
11 $\bar{3}$	2.34	2.36	2.40	7	2.36	12	2.37	12
042	2.30	2.32	2.33	14	2.32	9	2.33	9
151	2.21	2.22	2.22	17	2.23	11	2.25	19
					2.20	12	2.22	12
060, 003	2.18	2.18	2.18		2.17	17	2.18	12
15 $\bar{2}$	2.12	2.13	2.13	11	2.12	9		
15 $\bar{3}$	2.09	2.10	2.09	18	2.10	8	2.09	9
					2.07	11		
061, 023	2.06	2.07	2.06	7	2.05	15	2.07	19
					2.07	11		
400, 351	1.93	1.94	1.95	11	1.97	15	1.98	16
					1.90	15	1.91	9
26 $\bar{2}$	1.82	1.83	1.85	10	1.88	11	1.88	9
06 $\bar{2}$, 043	1.81	1.82	1.81	13	1.84	9	1.85	7
17 $\bar{1}$	1.80	1.80	1.80	19	1.79	23	1.80	14
171	1.70	1.71			1.75	8	1.76	9
440		1.67	1.68	7	1.66	8	1.67	9
080, 004	1.64	1.64	1.65	11	1.63	9	1.63	5
13 $\bar{4}$	1.63							
081	1.59							
024	1.57	1.59	1.58	13	1.59	11	1.58	14

TABLE 4. POWDER DATA FOR BARIUM HEXAGONAL PHASE¹

hkl	d(Calc.) ²	d(Obs.)	I/I ₁
001	7.84	7.83	29
100, 010	4.54	4.59	7 ³
101, 011	3.93		
002	3.92	3.97	97 ³
102, 012	2.97	2.98	100
110	2.63		
003	2.61	2.65	49
111	2.49	2.51	9
200, 020			
103, 013	2.27	2.26	36 ³
201, 021			
112	2.18	2.20	29
202, 022	1.98		
004	1.96	1.95	24 ³
113	1.85	1.86	31 ³
104, 014	1.80	1.79	11 ³
203, 023			
210, 120	1.72		
212, 122			
114, 005	1.57	1.58	24 ³
300, 030	1.51	1.53	9 ³

¹ BAS₂·Kaolin oriented aggregate; 1135° C., 12 hours.

² Calculated with unit cell dimensions of Ito (1950): $a=5.25 \text{ \AA}$, $c=7.84 \text{ \AA}$.

³ Enhanced slightly by diffraction maxima of Ba feldspar.

of the unidentified lead aluminum silicate of Geller and Bunting (1943).

X-ray characteristics of the hexagonal phases. BAS₂ mixes fired at temperatures somewhat below 1400° or for times less than twelve hours contained, in addition to varying amounts of barium feldspar, a phase with diffraction lines which indicate a crystal identical with, or quite similar to, the hexagonal barium aluminum silicate described by Ito (1950). The powder data listed in Table 4 were obtained from an oriented aggregate fired at 1135° for twelve hours, after which time the hexagonal phase was at maximum development and the feldspar was present in a very minor amount. Observed d-values agree well with those calculated from the unit cell dimensions of Ito.

Although the strontium and lead analogs of the hexagonal phase were not observed during preliminary firings of the mixes, they were observed during continuous x-ray investigation. The very unstable nature of the phase required that they be fired in the x-ray furnace. In this way the phases could be quenched for detailed x-ray investigation. The c axis dimensions were calculated from the observed (004) values and the a axis

TABLE 5. POWDER DATA FOR STRONTIUM HEXAGONAL PHASE¹

hkl	d ^(Calc.) ²	d ^(Obs.) ³	I/I ₁
001	7.56	7.56	7
100, 010	4.54	4.54	4
101, 011	3.90	3.87	54 ³
002	3.78	3.77	39 ³
102, 012	2.91	2.92	100 ³
110	2.63	2.66	54 ³
003	2.52	2.53	24
111	2.48	2.48	13
200, 020	2.27	2.29	13
201, 021	2.18		
112	2.16	2.15	22 ³
202, 022	1.95	1.94	17
004	1.89	1.89	13
113	1.82	1.84	9
104, 014	1.75	1.78	9
203, 023	1.73		
210, 120	1.72		
211, 121	1.68	1.68	13 ³
212, 122	1.56	1.55	22
144	1.53		
005			
300, 030	1.51	1.51	6

¹ SrAS₂-Flint Clay oriented aggregate; 1160° C., 30 minutes.

² Assumed unit cell dimensions: $a = 5.25 \text{ \AA}$, $c = 7.56 \text{ \AA}$.

³ Coincident with diffraction maxima of SrSO₄ or Sr feldspar.

dimensions from observed (100,010) values. The complete sets of d-spacings were then calculated with the assumed unit cell dimensions. Powder data for the strontium hexagonal phase are listed in Table 5 and those for the lead hexagonal phase in Table 6. The three hexagonal phases are apparently isostructural, with the major difference being in the c axis dimensions.

Barium feldspar formation. Continuous diffraction curves for the barium feldspar mixes (Fig. 5) show that the sequence of reactions is the same in both clays. However, there are considerable differences in the temperatures at which the high-temperature phases appear.

Although some evidence of the formation of a very minor amount of mullite in the barium and strontium feldspar mixes was present, the diffraction maxima were not sufficiently well developed to allow accurate or consistent measurement of the intensities. It must be assumed, therefore, that mullite formation is quite limited and of minor importance. The mica, quartz, and anatase reflections were, in all cases, very weak

or coincident with reflections of the other phases. Therefore no continuous curves were obtained for these constituents.

The hexagonal barium phase forms between 1050° and 1100° at this heating rate with a corresponding decrease in the sulfate content. The inversion of the sulfate at approximately 1149° appears to have little effect on the silicate phase development. The high-temperature sulfate disappears rapidly with increasing temperature. The barium feldspar appears at approximately 1250° in the kaolin mix, but becomes evident only near 1400° in the halloysite mix. The formation of the feldspar is clearly at the expense of the hexagonal phase.

The results immediately suggest that the hexagonal phase is not a high-temperature polymorph of the feldspar, but rather a metastable form produced as a result of rapid crystal growth.

The differences between the reaction temperatures suggest that the effects of structural differences in the clays are small and that impurities are a major factor in phase development. Reactions in flint clay-sulfate

TABLE 6. POWDER DATA FOR LEAD HEXAGONAL PHASE¹

hkl	d(Calc.) ²	d(Obs.)	I/I ₁
001	7.60	7.62	68
100, 010	4.54	4.53	16
101, 011	3.90	3.89	84
002	3.80	3.80	32 ³
102, 012	2.92	2.92	100 ³
110	2.63	2.61	37
003	2.53	2.54	68 ³
111	2.48	2.48	20 ³
200, 020	2.27	2.27	10
103, 013	2.21	2.21	20
201, 021	2.18	2.17	31 ³
112	2.16	2.16	20 ³
202, 022	1.95	1.95	10
004	1.90	1.90	36 ³
113	1.82	1.82	20
104, 014	1.75	1.75	
203, 023	1.73		
210, 120	1.72		
211, 121	1.68		
212, 122	1.56	1.56	18
114	1.54		

¹ PbAS₂·Kaolin oriented aggregate; 790° C., 30 minutes.

² Assumed unit cell dimensions: $a = 5.25 \text{ \AA}$, $c = 7.60 \text{ \AA}$.

³ Coincident with diffraction maxima of Pb Feldspar.

mixtures, not described in this report, were essentially identical with those of the halloysite-sulfate mixtures, thus substantiating this conclusion. The flint clay used was structurally similar to the kaolin but chemically similar to the halloysite.

The thermograms of the barium feldspar mixes (Fig. 3) show no pronounced heat effects other than those observed in the components. A slight endothermic trend is noted between 980° and 1150° , approximately correlative with growth of the hexagonal phase. The trends above 1200° are not well defined or consistent.

Strontium feldspar formation. The continuous diffraction curves for the strontium feldspar mixes (Fig. 6) show that the strontium feldspar forms in the same general manner as barium feldspar. The hexagonal phase, however, is not observed in the kaolin mix and is very unstable in the halloysite mix. The feldspar forms rapidly above 1150° to 1200° and is the only detectable phase above 1350° .

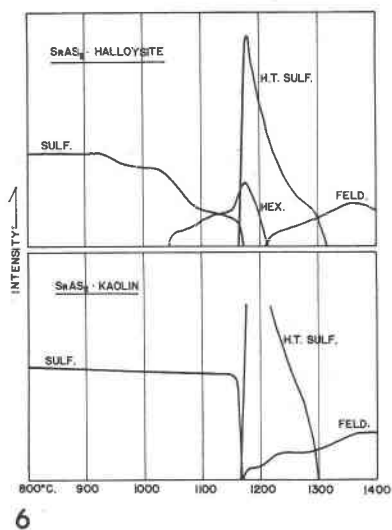
Thermograms of the strontium feldspar mixes (Fig. 2) indicate that feldspar formation is accompanied by a strong endothermic effect with a peak at approximately 1375° . The beginning of the reaction is difficult to detect. The development of the hexagonal phase apparently produces no large heat exchange.

Lead feldspar formation. The formation of lead feldspar from the kaolin mix occurs at approximately 800° simultaneously with the formation of the hexagonal phase and with a correlative decrease in the lead sulfate (Fig. 7). The hexagonal phase is very unstable, disappearing at about 930° . Rapid melting is preceded by a gradual decrease in peak intensity and so the melting point is not well defined.

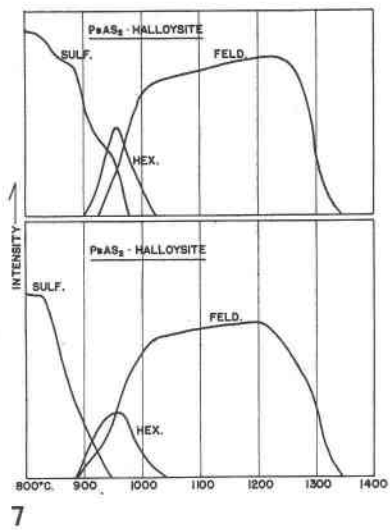
Feldspar formation in the halloysite mix occurs approximately 40° higher than in the kaolin mix and the range of the hexagonal phase is slightly less.

The thermograms of the lead feldspar mixes (Fig. 3) show that formation of the feldspar is accompanied by a moderately strong endothermic effect beginning at approximately 800° and continuing past the temperature range of the strong endotherm of the sulfate. The complex endotherm between 935° and 1100° cannot be correlated with data shown in the continuous curves. The beginning of the endotherm corresponds to the melting point of lead oxide and thus may be related to melting of residual oxide and to further reaction not indicated by the continuous diffraction curves. Melting of the feldspar is shown by endothermic trends beginning between 1100° and 1200° .

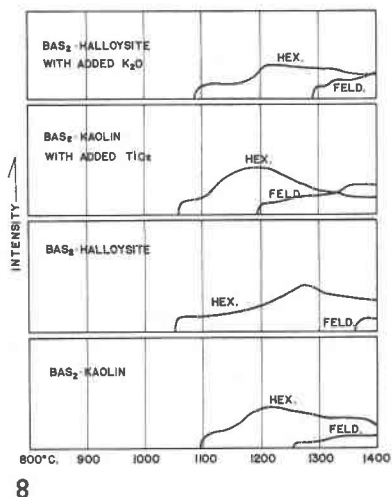
Effects of impurities on phase development. As stated previously, the continuous diffraction curves for phase development in the clay-sulfate mixtures indicate that the differences noted are the result of chemical



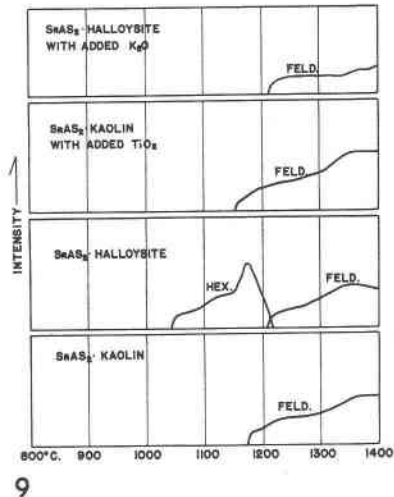
6



7



8



9

FIG. 6. Continuous diffraction curves showing phase development in strontium feldspar mixes. Sulfate (111) peak; high-temperature sulfate 3.62 \AA peak; strontium hexagonal phase (001) peak; strontium feldspar (020) peak.

FIG. 7. Continuous diffraction curves showing phase development in lead feldspar mixes. Sulfate (001) peak; lead hexagonal phase (001) peak; lead feldspar (020) peak.

FIG. 8. Continuous diffraction curves showing effects of added potash and titania on development of the barium hexagonal phase and barium feldspar. Barium hexagonal phase (001) peak; barium feldspar (020) peak.

FIG. 9. Continuous diffraction curves showing effects of added titania and potash on development of the strontium hexagonal phase and strontium feldspar. Strontium hexagonal phase (001) peak; strontium feldspar (020) peak.

differences in the clays. The kaolin has a very low titania content and relatively high potash content. Conversely, the halloysite has no potash and a high titania content. Therefore, potash was added to the halloysite-sulfate mixes and titania was added to the kaolin-sulfate mixes in approximately the same amounts as were present in the original mixes.

Figure 8 shows continuous phase development curves of barium feldspar and the hexagonal phase with and without added impurities. Addition of titania to the kaolin mix serves to lower the temperatures at which both the feldspar and the hexagonal phase are first recorded. The intensity of the (020) reflection of the feldspar is slightly increased. Addition of potash to the halloysite mix lowers the formation temperature of the barium feldspar by nearly 100° and retards formation of the hexagonal phase.

In general, titania appears to have a mineralizing effect on the reactions. It is not the presence of titania, but rather the absence of potash, which retards formation of the feldspar in the halloysite mix. Potash tends to inhibit development of the hexagonal phase and to markedly promote feldspar development.

Figure 9 shows the continuous phase development curves of strontium feldspar and the hexagonal phase in the mixes with and without added impurities. Addition of titania to the kaolin-sulfate mix lowers the formation temperature of the feldspar approximately 20° and tends to increase the intensity of the (020) reflection. The amount of potash added to the halloysite-sulfate mix completely prohibits formation of the hexagonal phase and apparently decreases the intensity of the (020) reflection of the feldspar.

The effects of added impurities on phase development in the lead feldspar mixes were slight. Therefore, continuous diffraction curves are not included. Titania retarded development of the feldspar and the hexagonal phase slightly and increased the intensities of the diagnostic reflections. Added potash had no visible effect on the reactions in the halloysite-sulfate mix.

DISCUSSION

One of the most important factors in a solid state reaction study is the crystalline form of the starting materials. It would be expected that the feldspars investigated would form from mixes of oxides or other compounds of the cations, but that the temperatures of formation, the reaction rates, and stabilities of the intermediate compounds would be considerably different from those reported here. Synthesis of the barium hexagonal phase from a dry mix of the oxides, for example, was reported by Davis and Tuttle (1952) to require heating at 1500° for four days and

even longer heating was required to convert it to the feldspar. In the present study the hexagonal phase formed in clay-sulfate mixes at 1400° in a matter of minutes and conversion to the feldspar was immediately detectable. Therefore, it would appear that clays are among the more reactive of possible sources of silica and alumina.

The presence of small amounts of impurities has been shown to influence the formation temperatures and reaction rates. This factor, in addition to the effects of varying cooling rates, may explain why some earlier investigators obtained the barium feldspar from melts and others obtained the barium hexagonal phase.

The powder data for the synthesized feldspars appear to be sufficient to establish the basic crystal structure as that of the feldspar type. The barium feldspar is monoclinic and the strontium and lead feldspars are probably triclinic. In all probability, the phases formed by rapid crystallization in the solid state are disordered. No information as to the rates of ordering was obtained. For these reasons the barium feldspar was indexed according to the unit cell dimensions of Taylor *et al.*, (1934) rather than those of an ordered cell with a super-lattice as given by Newnham and Megaw (1960).

Structural and thermodynamic similarities of the barium and strontium sulfates suggest that formation of the feldspars in mixes with the same clay would occur in the same temperature range at approximately the same rates. This has been shown to be the case, with the stability of the hexagonal phase being the complicating factor. Reactions in the two mixes begin in the same general temperature range and the formation of the strontium feldspar and the barium hexagonal phase occurs at approximately the same rate. The important difference appears to be the stability of the hexagonal phases, the barium phase being very persistent and the strontium phase being extremely unstable or nonexistent.

The powder data of the hexagonal phases are sufficient to establish the basic structure of the crystals and their similarity to the hexagonal barium phase described by Ito (1950). The formation of large crystals, however, presupposes ordering in the Si-Al tetrahedra, a condition probably not attained by relatively short heating cycles.

The presence of a relatively small amount of potassium has been shown to markedly inhibit development of the hexagonal phases and to enhance development of the feldspars. The structure of the hexagonal phase requires the presence of a divalent ion in each of the 12-fold coordination positions. The univalent potassium ion, although nearly the same size as the barium ion, would have a tendency to weaken the structure when present between the Si-Al sheets of the barium hexagonal phase. In the strontium hexagonal phase the potassium ion would not only be unable

to satisfy valency requirements but would also tend to hold the sheets apart so that the electrostatic influence of the smaller strontium ion would be insufficient to maintain the structure. The tendency for potassium to retard development of the hexagonal phase and to enhance development of the feldspar, therefore, appears to have some geometric basis.

The presence of potassium in the lead feldspar composition has little effect on the stability of the hexagonal phase. Geometric considerations do not provide a ready explanation of this fact. The high reactivity of the composition at a relatively low temperature suggests that the formation of lead feldspar might be largely independent of those ions whose activities are low at that temperature.

The occurrence of barium, strontium, and lead in lattice positions of natural feldspars is well known. Numerous determinations of the barium contents of hyalophanes have led to the recognition of a complete series between potash feldspar and celsian and there is evidence that a similar series exists between strontium feldspar and the plagioclases.

The present study suggests that the presence of lead in the potash feldspar lattice may be more common than previously realized. The structural and thermal similarities between the lead feldspar and the potash feldspars also suggests that a complete isomorphous series might exist between these phases. It might be expected that lead-bearing feldspars or nearly pure lead feldspars would occur in the zones of alteration of many ore deposits.

The feldspar compositions studied could have numerous ceramic applications. Barium and strontium feldspars qualify as refractory materials. The lead feldspar is particularly interesting from a ceramic standpoint in view of the numerous applications of lead compounds for electrical purposes. The melting point of the feldspar is substantially higher than any of the lead silicates, the lead aluminates, or the lead aluminum silicates reported in the ceramic literature.

An extensive series of time-temperature studies, not included in this report, indicate that reaction rates are a function of temperature and are unaffected by the inversions of the sulfates. The true formation temperature of the barium and strontium feldspars and of the barium hexagonal phase prepared from the kaolin-sulfate mix is 1090° C. This indicates that the hexagonal phase has no stability range under the conditions of this experimental technique and therefore the name *alpha-celsian* is inappropriate.

A limited study of mixed crystal compositions, also not reported here, indicates that extensive substitution among the three types of feldspars is possible. The extent of substitution has not, however, been completely determined.

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