

PHASE TRANSFORMATIONS IN SILICA-ALUMINA-
MAGNESIA MIXTURES AS EXAMINED BY CONTINUOUS
X-RAY DIFFRACTION: I. TALC-KAOLINITE
COMPOSITIONS

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ABSTRACT

The phase transformations of natural and synthetic oxide mixtures of talc-kaolinite compositions were examined by continuous *x*-ray diffraction while heated to 1450° C. Diffraction intensity data show the enhanced development of protoenstatite within the sheet structure of talc, thus indicating that the growth of this mineral on firing is largely controlled by the structure of the talc. The formation temperature of cordierite, which was used as a measure of the reactivity of various starting materials, indicates that alumina in the form of mullite, rather than as corundum, is most effective in lowering the development temperature of this mineral. Additional cordierite formation, through recrystallization on cooling indicates the presence of an intermediate liquid phase in the formation of this mineral.

INTRODUCTION

General statement

Continuous high-temperature *x*-ray diffraction methods make it possible to observe high-temperature reactions as they occur (Wahl *et al.*, 1961). Previously, high-temperature *x*-ray diffraction has been used mainly for selected observations at some desired temperature and not for continuous observations of a sample as it is heated. The technique of continuous scanning was used in the present investigation for the study of high-temperature reactions in talc, kaolinite, talc:kaolinite mixtures, and mixtures of oxides with compositions corresponding to talc and kaolinite.

Influence of starting materials

Reaction rates between solids are known to be influenced by the nature of the starting materials. Significantly different results have been obtained by using different starting materials which have the same bulk composition. Thus, Fyfe (1960) has discussed the reactivity of oxides as opposed to glasses, and Roy (1956) has reported on the reactivity of coprecipitated gels. Reaction rates in the systems SiO₂ and Al₂O₃-SiO₂ with different starting materials have been investigated by Wahl *et al.* (1961a, 1961b) by means of continuous high-temperature *x*-ray diffraction.

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Continuous high-temperature x-ray diffraction

In the technique, as used in the present study, the sample was packed on a small platinum holder which was then placed in a small platinum-wound furnace. This furnace was mounted on a water-cooled base which, in turn, was mounted on a Philips recording x-ray diffractometer. The desired 2θ values were repeatedly scanned while the sample was heated at a constant rate. The intensities of the various diagnostic diffraction peaks were plotted against the temperatures at which they occurred. The curves obtained in this manner depict changes in the amounts (not absolute quantities) of crystalline materials as a function of temperature. Because the same sample was used throughout the run, differences in packing or preferred orientation were minimized and smaller changes in diffraction intensity could be detected.

Purpose of the investigation

A primary objective of the investigation was to determine the reaction rates of various starting materials which had the same bulk composition within the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system. Cordierite² was formed from most of these mixtures, and the formation temperature of cordierite was used as a measure of the reactivity of the starting materials. The transformations of kaolinite to mullite and cristobalite and of talc to protoenstatite³ and cristobalite, were briefly investigated.

EXPERIMENTAL PROCEDURE

Furnace and sample holder

The furnace used in this investigation was similar to that described by Grim and Kulbicki (1957). In the construction of the present furnace, however, the resistance winding (Pt—13% Rh) was coiled before it was wrapped on the alundum core. Five feet of .012-inch wire were used and coiled in such a manner that four evenly spaced wraps could be made on the alundum center piece. The base plate was grooved so as to insure reproducible alignment of the platinum sample holders, which were $1 \times 8 \times 14$ mm with a depression $0.5 \times 6 \times 10$ mm.

Temperature control and measurement

The power supplied to the furnace was controlled by two variacs, and a constant heating rate of 5.6° C. per minute was obtained. When the temperature of the furnace had reached the desired maximum (usually

² All of the cordierite which was synthesized in this study was apparently indialite, as discussed by Sorrell (1960).

³ The enstatite in this investigation is apparently the protoenstatite for which a complete structure analysis was made by Smith (1959).

about 1475° C.), the power was turned off and the furnace was allowed to cool. Because the furnace has a small heat capacity, a rapid and uniform cooling rate was obtained. Temperatures were measured by using Pt-Pt 10% Rh thermocouples with a cold junction and a Minneapolis-Honeywell Model 2732 potentiometer. The accuracy of the thermocouples was checked several times during the investigation by using the inversion of BaSO₄ at 1149° C. The agreement was usually within about 5° C. and never greater than 10° C.

At least two runs were made for each sample. In the first run, 2θ values of 2° to 50° (the maximum range with this furnace) were repeatedly scanned as the samples were heated. In the second run, only the diagnostic diffraction peaks for each phase were measured, usually at temperature intervals of about 25° C. All of the data were obtained using nickel-filtered copper radiation generated at 45 kv and 18 ma.

Starting materials

The following materials were used as reactants: MgO, light powder, Allied Dye and Chemical Corporation; "silicic acid," Mallinckrodt Chemical Works; talc, Baker Chemical Company; kaolin, McIntyre, Georgia; and synthetic gibbsite, Al(OH)₃, Merck and Company. The kaolin was shown by x-ray diffraction to be substantially pure well-crystallized kaolinite. A small amount of mica was present and analyses of similar kaolins indicate that one or two per cent K₂O may be present. The "silicic acid" and synthetic gibbsite were of reagent grade. When the MgO was fired in a continuous run, it was at first characterized by very broad diffraction peaks which corresponded to those of periclase. These diffraction peaks became sharper as the firing was continued.

The mixtures were made according to mole per cent calculations in ratios of talc to kaolinite as follows; 4:1, 3:2, 1:1, 2:3, and 1:4. One of group of mixes was composed of natural talc and kaolinite in those proportions. Another group was composed of kaolinite and MgO-"silicic acid" which were mixed in proportions corresponding to talc. A third group consisted of talc and synthetic gibbsite-"silicic acid" corresponding to the composition of kaolinite. The mixtures of oxides corresponding to the natural minerals will be referred to as TC and KC, meaning respectively talc composition and kaolin composition. Thus, 4K:TC refers to a mixture in which MgO and "silicic acid" corresponding to the composition of talc are mixed with four times as much naturally occurring kaolinite (mole per cent). In this investigation, talc and kaolinite were compared to the mixtures of oxides as if they were anhydrous. However, the water content was considered in the weighing and mixing of the samples.

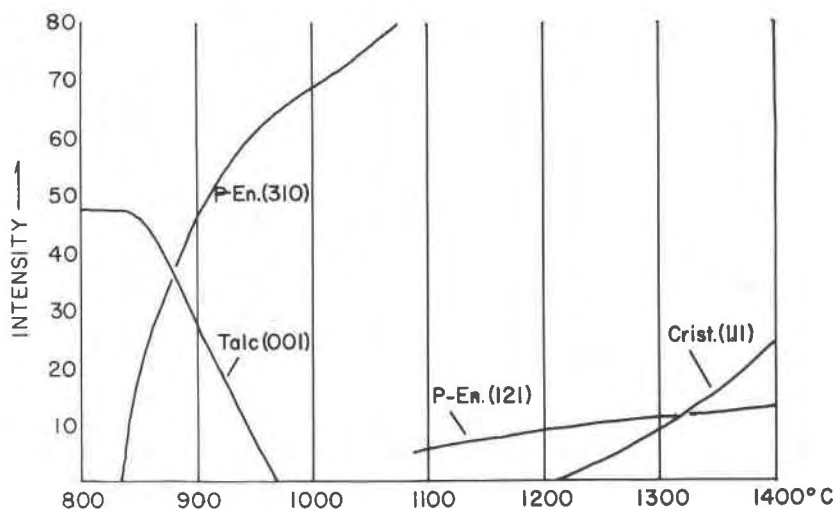


FIG. 1. Intensity of diffraction by high-temperature phases in heated talc.

The materials which were used in the various mixes were dried, weighed and mixed in the desired proportions, mixed further as a paste with distilled water, dried at 100° C. for about 8 hours, and then re-ground. An attempt was made to pack the same amount into the sample holder each time.

EXPERIMENTAL RESULTS

When talc was fired in a continuous run (Fig. 1), it began to decompose at about 830° C. and protoenstatite was formed immediately. When the temperature reached approximately 1220° C., cristobalite⁴ also was formed. The most prominent feature of the formation of protoenstatite was the enhanced intensity of the (310) as compared to the (121) reflection. Such intensity relationships have been used by Kulbicki (1959) to explain the structural relationships of the transformations of sepiolite, attapulgite, and saponite to enstatite. He considered the formation of enstatite to be favored by the fibrous nature of sepiolite and attapulgite, and stated that enstatite would form with less intensity and rapidity from a mineral with a layer-type structure. In the present investigation, however, protoenstatite formed rapidly and in considerable abundance from talc. Using the (310) and (121) reflections it is possible to compare the intensities of reflections from planes parallel to the *c* axis (310) with those from planes which intersect the *c* axis (121). The intensity differ-

⁴ The cristobalite formed at elevated temperatures is beta cristobalite in every case.

ences indicate that protoenstatite is preferentially grown with the c axis in the plane of the silica sheets of the original talc. The sheets must therefore be partitioned into chains to afford the protoenstatite nucleations, with consequent expulsion of one-fourth of the silica, which later forms cristobalite. Therefore, it is considered that the protoenstatite has grown preferentially within the talc and its development is influenced by the talc structure.

Protoenstatite was also synthesized from a mixture of MgO-"silicic acid" with a MgO:SiO₂ ratio equivalent to talc (Fig. 2), the mineral first appearing at 750° C. The (310) of the newly formed protoenstatite again

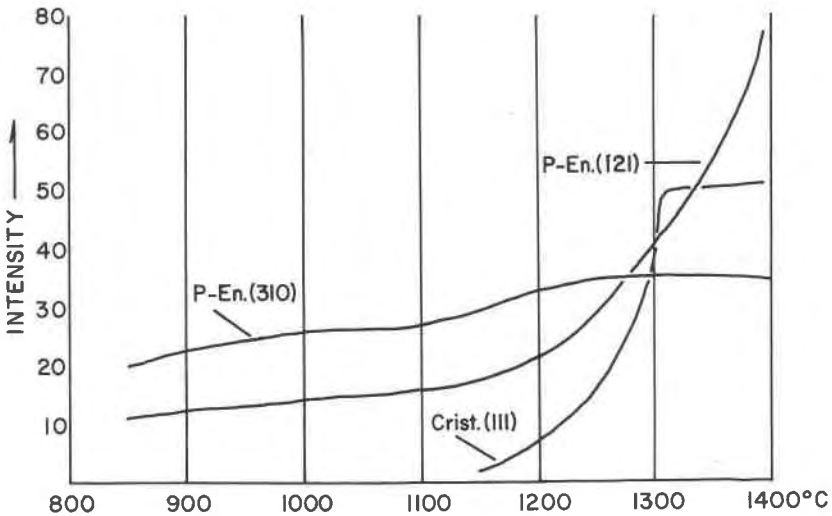


FIG. 2. Intensity of diffraction by high-temperature phases in a heated talc composition mixture prepared from MgO-silicic acid.

had a higher initial intensity than the (121), but the difference was much smaller than in talc. At 1275° C. the intensities were equal, and at 1400° C. the (121) was considerably more intense than the (310), which is the proper relationship when no preferential growth has occurred. Protoenstatite which was formed in the firing of MgO-"silicic acid":kaolinite mixtures had the same relative diffraction intensities that were observed when the MgO-"silicic acid" was fired separately (Fig. 2). In the talc:kaolinite mixtures (Fig. 3), protoenstatite formed at the same temperature and had the same intensity relationships that were recorded when the talc was fired separately.

When kaolinite was fired in a continuous run, mullite was detected first at 1180° C. and cristobalite at 1350° C. (Fig. 4). The diffraction

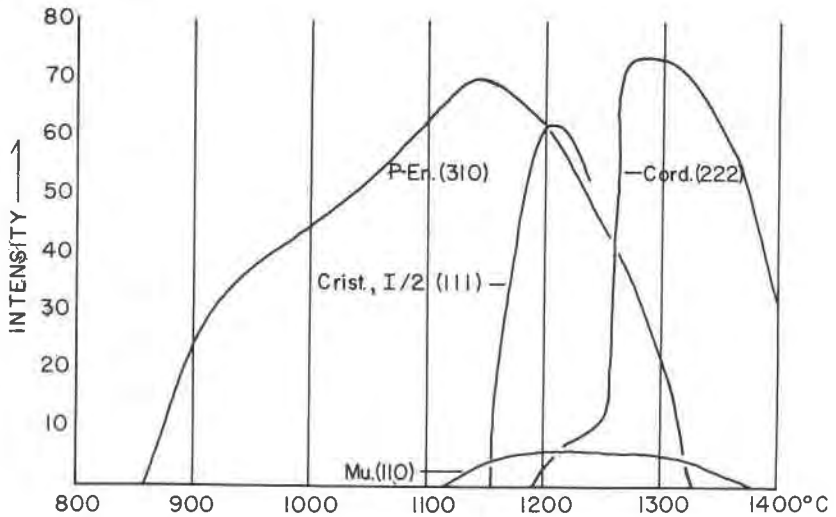


Fig. 3. Intensity of diffraction by high-temperature phases in a heated mixture of talc-kaolinite in the ratio of 1:1.

intensities of the (120) and the (210) peaks of mullite had a relatively uniform increase from 1180° C. to about 1300° C., at which temperature the intensities remained relatively constant as the temperature was further increased up to about 1435° C. The cristobalite diffraction intensity also increased in amount up to a temperature of about 1435° C. Fusion began at higher temperatures and the diffraction intensity of both minerals decreased.

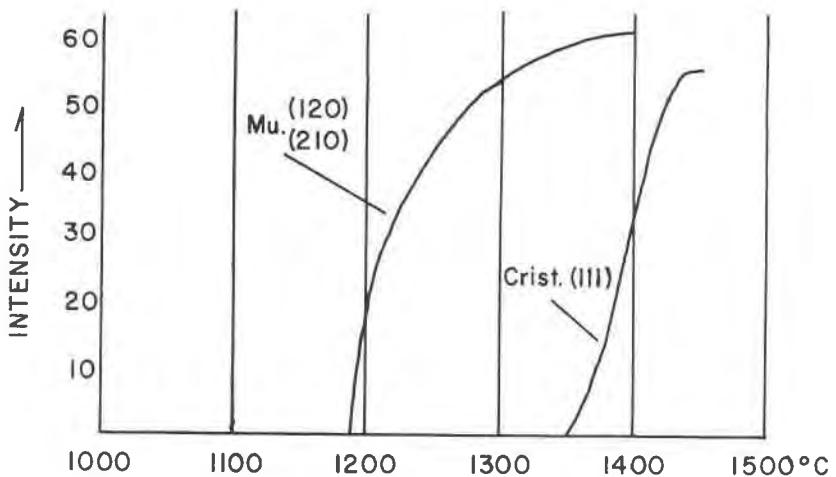


Fig. 4. Intensity of diffraction by high-temperature phases in heated kaolinite.

When talc was mixed with kaolinite and fired, protoenstatite, mullite, and cristobalite were formed. These phases then reacted together to form cordierite. Figure 3 illustrates the general pattern of the reactions for all of the talc:kaolinite mixes studied. In the talc:kaolinite mixtures, cordierite was formed at about 1195° C. regardless of the talc:kaolinite ratio. However, the temperature at which cordierite begins to fuse does depend to some extent upon the talc:kaolinite ratio. The fusion temperature was found to be relatively higher in those mixes containing more kaolinite than talc. Thus, the cordierite in the 4T:K mix began to fuse at about 1295° C., whereas in the T:4K mix the diffraction intensity of cordierite began to decrease at 1350° C. Further, cristobalite is formed at temperatures 50 to 100 degrees lower in the mixtures than when either talc or kaolin are fired separately. On the other hand mullite is formed at a higher temperature (usually about 50° higher) in mixtures than when kaolinite is fired alone.

In all mixtures the (111) of cristobalite, the (110) of mullite, and the (310) of protoenstatite decrease in intensity as cordierite is formed. The mixtures always contain more silica than does cordierite. The amount of cordierite that can form is dependent upon the abundance of the MgO and Al₂O₃ phases which are present in the mix and on the relative reactivity of these components. In the mixture with 4 talc:1 kaolinite the mullite is used up and its diffraction lines disappear at 1290° C., whereas in the 1 talc:4 kaolinite mix, the mullite persists to 1420° C. In both cases the cordierite intensity increases as the mullite intensity decreases up to the temperature of the disappearance of the mullite. Similarly, protoenstatite disappears at 1315° C. in 1 talc:4 kaolinite mixture and is still present up to the fusion point in 4 talc:1 kaolinite mixture with comparable variation in the development of cordierite.

When kaolinite is mixed with MgO-"silicic acid" (Fig. 5) in proportions corresponding to talc, cordierite is formed at temperatures about 25° C. lower than in the natural talc:kaolinite mixes with the corresponding compositions. Mullite is also formed at lower temperatures, below 1000° C. in the talc composition:kaolinite mixtures with high proportions of kaolinite. Protoenstatite is formed at temperatures ranging from 810° C. to 840° C., which is a higher temperature than for MgO and "silicic acid" alone. The diffraction intensity of the (310) reflection of protoenstatite in the TC:K mixes is much less than in the talc:kaolin mixes because of the previously mentioned lack of preferential growth. The disappearance of the protoenstatite and mullite with the development of cordierite follow the same reaction sequence as in the talc:kaolin mixtures.

The results obtained by firing the talc:synthetic gibbsite-"silicic acid" mixtures (Fig. 6) differ greatly from the talc:kaolin and the talc com-

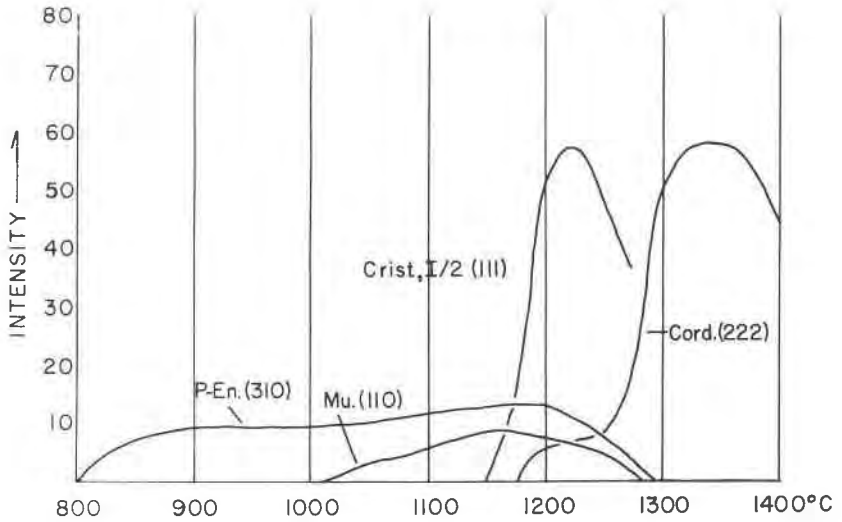


FIG. 5. Intensity of diffraction by high-temperature phases in a heated mixture of kaolin:talc composition in the ratio of 1:1.

position:kaolin mixes, because corundum is formed from the $\text{Al}(\text{OH})_3$, and it is much less reactive than mullite. Not only is a higher temperature necessary to form cordierite, but smaller amounts are formed. The cordierite begins to fuse at higher temperatures in those mixes which have

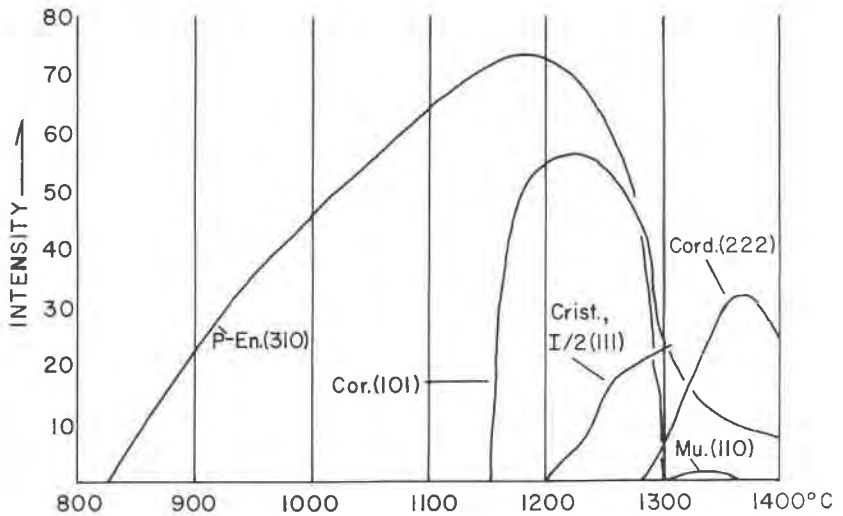


FIG. 6. Intensity of diffraction by high-temperature phases in a heated mixture of talc:kaolin composition in the ratio of 1:1.

a higher Al_2O_3 content. No cordierite was formed in the 4T:KC mix, while in the other mixes it forms at 1300°C . regardless of the $\text{MgO}:\text{Al}_2\text{O}_3$ ratio. In the 4T:KC sample the diffraction intensities of corundum, protoenstatite, and cristobalite, begin to decrease at approximately 1200°C ., just as in the other mixes, but apparently more Al_2O_3 must be present to form cordierite at the rate of firing used in the experiments. Mullite is formed in the 1:1, 2:3, and 1:4 talc:kaolinite composition mixtures in amounts which are proportional to the Al_2O_3 content of the samples. The formation of protoenstatite from talc is the same as in talc:kaolinite mixes. The disappearance of the protoenstatite also follows the same pattern as the reaction proceeds, but with greater variability in this group of mixes (*i.e.*, protoenstatite persists to a higher temperature in the mixes which contain greater amounts of this mineral). Also cristobalite is usually formed at a higher temperature in talc:synthetic gibbsite-"silicic acid" mixtures than in the other mixtures. The transformation to cristobalite takes place more readily in natural kaolinite than in synthetic mixes.

DISCUSSION OF RESULTS

The formation temperatures of cordierite within each group of mixes appear to be dependent largely on the nature of the reactants and independent of the $\text{MgO}-\text{Al}_2\text{O}_3$ ratio of the sample. Thus, whenever corundum was a reactant, cordierite was formed at about 1300°C . When mullite was the source of alumina, cordierite was first detected at temperatures ranging from 1150°C . to 1225°C .

In certain of the samples, a glassy phase could be observed after the samples were cooled. The samples with the highest MgO contents fused more easily and when cooled, they consisted of a colorless transparent bead of glass. The amounts of glass decreased as the Al_2O_3 content of the sample increased. The fired samples which contained more Al_2O_3 consisted of the glass and mullite, and in some cases, corundum.

Some indication of the composition of the glassy material is given by the fact that when the sample was cooled and then x -rayed, the diffraction intensity of cordierite was considerably enhanced as compared to the intensity measured at the higher temperature. When a 2 talc:3 kaolinite mixture was fired to the temperature at which the cordierite began to fuse (about 1400°C .) and then quickly cooled (from 1400°C . to 1000°C . in about 70 seconds and more slowly thereafter), the increase in the diffraction intensity of cordierite was about 60 per cent. When the sample was cooled quickly from a temperature of only 1300°C and then x -rayed, the increase in the diffraction intensity of cordierite was much smaller, usually about 10 per cent or less. This indicates that cordierite crystal-

lized from the glassy material on cooling—to a greater degree if the cooling is slow.

The mechanism which may be operative in the reactions in this investigation is that of differential melting. In this mechanism adjacent grains of enstatite (from the talc) and mullite (from the kaolinite) react with cristobalite (from both talc and kaolinite) to form a liquid which has a composition corresponding to that which has the lowest melting point in the phase diagram. It is possible that because this point is adjacent to the stability field of cordierite, cordierite is formed from the liquid. As the temperature is increased, more material can react and the composition of the liquid can change toward that of the original bulk composition of the sample. Therefore, the reaction rates which were measured were probably the tendencies of the materials to react to form the initial liquid. This would explain why the nature of the reactants was apparently more important than variations in the $MgO:Al_2O_3$ ratios of the samples.

In a consideration of the talc:4 kaolinite mix, the intensities of mullite and protoenstatite began to decrease at $1200^\circ C.$ and cordierite began to form at $1215^\circ C.$ As the temperature was increased, cristobalite began to decrease in intensity at about $1275^\circ C.$ However, cordierite continued to increase to $1350^\circ C.$, *i.e.*, even after the mullite, protoenstatite and cristobalite began to decrease. Because of the increase in temperature, the composition of the liquid could change toward that of the original bulk composition of the mix. At about $1300^\circ C.$ the enstatite was used up, at $1350^\circ C.$ the cordierite began to decrease in intensity, and at $1415^\circ C.$ mullite and a liquid remained. The protoenstatite which was reacted by $1310^\circ C.$ in this mix was observed to persist to successively higher temperatures in the mixes with higher contents of protoenstatite. Conversely, it was observed that in the mixes with more protoenstatite than mullite, the formation of a liquid phase used up the mullite first and that enstatite was present until fusion.

SUMMARY

The formation of protoenstatite from talc was characterized by the enhanced growth of the protoenstatite in the "c" direction indicating that the growth of the mineral was controlled by the structure of the talc.

When mixtures of talc, kaolinite, and oxides (corresponding to the compositions of talc and kaolinite) were fired, cordierite was formed at temperatures ranging from $1150^\circ C.$ to $1300^\circ C.$ The nature of the reactants was apparently more important in the reactions than the mole per cent variations in the compositions of the mixes. Thus, when the alumina is present in corundum rather than mullite, cordierite forms at the higher

temperature. It is suggested that the crystalline materials reacted to form a liquid which had a composition corresponding to the lowest melting point in the system. Such a liquid would have a composition in or near the stability field of cordierite. When some of the samples were cooled and *x*-rayed, additional cordierite had recrystallized. At the lower temperatures, when cordierite was first beginning to form, only small amounts of cordierite were formed through recrystallization upon cooling the samples.

The samples with the highest MgO contents could be fused to a clear glass bead. The fired mixtures containing greater amounts of Al_2O_3 consisted of glassy material, mullite, and in some cases, corundum. The cordierite began to fuse at higher temperatures in the mixes which had the higher contents of Al_2O_3 . This indicates that the composition of the liquid was changing toward the Al_2O_3 - SiO_2 side of the diagram, an area in which the liquid and cordierite can coexist at higher temperatures.

ACKNOWLEDGMENTS

This work forms part of a series of high-temperature *x*-ray diffraction studies made possible through a research grant from the National Science Foundation.

REFERENCES

- FYFE, W. S. (1960) Hydrothermal synthesis and determination of equilibrium between minerals in the sub-liquidus region. *Jour. Geol.*, **68**, 553-566.
- GRIM, R. E., AND G. KULBICKI (1957) Etude aux rayons X des reactions des mineraux argileux a haute temperature. *Bull. Soc. Franc. Ceram.* 21-27.
- KULBICKI, G. (1959) High temperature phases in sepiolite, attapulgite, and saponite. *Am. Mineral.* **44**, 752-764.
- ROY, R. (1956) Aids in hydrothermal experimentation: II, Methods of making mixtures for both "dry" and "wet" phase equilibrium studies. *Jour. Am. Cer. Soc.*, **39**, 145-146.
- SORRELL, C. A. (1960) Reaction sequence and structural changes in cordierite refractories. *Jour. Am. Ceram. Soc.* **43**, 337-343.
- SMITH, J. V. (1959) The crystal structure of protoenstatite, MgSiO_3 . *Acta. Crystall.* **12**, 515-519.
- WAHL, F. M., R. E. GRIM AND R. B. GRAF (1961a) Phase transformations in silica as examined by continuous *x*-ray diffraction. *Am. Mineral.* **46**, 196-208.
- (1961b) Phase transformations in silica-alumina mixtures as examined by continuous *x*-ray diffraction. *Am. Mineral.* **46**, 1064-1076.

Manuscript received, April 9, 1962.