

Isomorphous Substitution of Aluminium for Silicon in Tobermoritic Structure. I. The Mixtures of Different Forms of Silicon Dioxide and of Different Compounds of Aluminium

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The isomorphous substitution of Al(III) for Si(IV) in tobermoritic structure was examined by X-ray phase analysis and DTA. It has been found that the extent of the substitution depends on the materials used. The samples were prepared using different forms of silica—either β -quartz, quartz-glass, SiO₂-gel or aerosil. Gibbsite, boehmite, dehydrated kaolinite, kaolinite, corundum and γ -Al₂O₃ were used as sources of aluminium. The samples were heated in an autoclave at 150, 180 and 200°C for 10, 24 and in some cases for 48 hours.

Tobermorite can be synthesized from calcium oxide and silica under hydrothermal conditions. Up to temperatures of about 110°C it is stable, at higher temperatures and under hydrothermal conditions it is formed as an unstable compound. When the reaction is allowed to proceed for a longer time, or when it takes place at higher temperature, another stable calcium hydrosilicate arises. At lower temperature a calcium hydrosilicate with tobermoritic structure is formed. It has been found that tobermorite is produced on autoclaving building materials containing lime and some materials with high SiO₂ content. It is also formed from anhydrous dicalcium silicates in the course of setting of cement. Under different conditions, compounds with tobermoritic structure arise which, however, differ in the amount of lime and water in the molecule, as well as in the arrangement of the structure — *e.g.* in the set cement [1–4]. These compounds are usually designated as tobermoritic phases or tobermorite-like phases. Tobermorite forms sheets of colloidal size. Its phases are fibrous, sometimes forming tubular formations. *Megaw* and *Kelsey* studied the crystal structure of tobermorite [5].

Tobermorite and its phases (further tobermorite) arise under technological conditions in surroundings where different ions and compounds are present. We may assume that some of these ions are incorporated in the crystal structure of tobermorite. Aluminium is one of these elements which are abundant in the raw materials. Some authors [6, 7] studied the isomorphous substitution in tobermoritic structure. Different extent of substitution was attained when β -quartz or kaolinite were used for preparation of the mixtures. It has been proved [7] that aluminium has four-fold coordination in tobermoritic structure. Since aluminium occurs in different compounds, it was necessary to find in which way these compounds contribute to the formation of tobermoritic structure.

Experimental

Materials and the preparation of samples

Different forms of silica were used as starting materials. β -Quartz — 99.9% SiO_2 , that passed the 0.06 sieve was prepared by grinding a single crystal of brasil quartz, gel SiO_2 — 82% SiO_2 , 17.5% H_2O aerosil supplied by Degussa — 99.3% SiO_2 and quartz glass — 99.8% SiO_2 prepared by melting brasil quartz. As alumina bearing materials the following were used: gibbsite (aluminium hydroxide, reagent grade, supplied by Lachema), boehmite, prepared from gibbsite under hydrothermal conditions (300°C, 7 days), kaolinite (Sedlec), dehydrated kaolinite (700°C — 2 hours), corundum (derived from gibbsite that was calcined at 1200°C for 3 hours) and dehydrated gibbsite (γ - Al_2O_3 prepared on calcining gibbsite at 500°C for 2 hours). The calcium oxide was prepared from reagent-grade CaCO_3 that was calcined at 1000°C for 4 hours.

From the above materials mixtures with molar ratio of $\text{C/S} + \text{A}^* = 0.4-0.8$ were prepared so as to allow a part of SiO_2 to be substituted by aluminium. The amount of aluminium added is expressed in % of Al_2O_3 . When using kaolinite or dehydrated kaolinite, the kaolinic SiO_2 was added to the total amount of SiO_2 so as to maintain the ratio of $\text{C/S} + \text{A}$ constant.

The dry mixture of these components was first thoroughly homogenized. On addition of hot distilled water from which carbon dioxide had been removed by boiling, the mixture attained the consistency of a paste and subsequently this was well stirred. The samples were then put into silver crucibles, covered with lids and transferred into the autoclave. The carbon dioxide from the water in the autoclave was also removed by boiling. The autoclaving proceeded for 10 to 24 hours at 180°C. The reaction conditions were chosen with regard to the instability of tobermorite at this temperature. Another solution would be to let the reaction take place at lower temperature, only in this case, the reaction rate between calcium hydroxide and silica decreases very rapidly lowering of temperature. In some cases temperature between 150–200°C was used.

Hydrogarnet phase having composition C_3ASH_4 was prepared. For the preparation of it, oxides in equimolar ratio were used. Temperature used was 250°C, duration of the reaction, 7 days. The sample thus prepared confirms to data reported by Kalousek [6].

Aluminium compounds used as source materials were submitted to hydrothermal process at 180°C for 12 hours. It was found that under these conditions, about 80% of the originally present gibbsite is changed to boehmite, corundum is partially hydrated and a small quantity of boehmite is formed, γ - Al_2O_3 is transformed to boehmite and the dehydrated kaolinite is partly transformed to kaolinite of fireclay type.

Apparatus

X-ray phase analysis was used for the investigation of the above specimens (diffractograph URS 50). The phases which were formed in these mixtures were identified, or else transformations of the non-reacted source materials were studied.

A differential thermal analysis apparatus of our own construction, with thermocouples PdAuPt—PtRh and with mechanical recording with compensation recorder EZ 2 was used. The heating rate was 100°C/2 min. The sample size was about 300 mg. This being the arrangement of the experiment, the temperature of thermal effects are, when compared with the classical DTA, shifted towards higher values.

Data cited in literature [6, 8] were used for identification of the individual phases.

* $\text{C} = \text{CaO}$, $\text{S} = \text{SiO}_2$, $\text{A} = \text{Al}_2\text{O}_3$, $\text{H} = \text{H}_2\text{O}$.

Results and Discussion

Mixtures prepared from aerosil in molar ratios of $C/S + A = 0.4$ and 0.6 , at temperatures 150 and 200°C , containing 4 and 10% Al_2O_3

Samples prepared at 150°C using gibbsite, the molar ratio being 0.4 , contained tobermorite and hydrogarnet after 24 hours. When the molar ratio was 0.6 , there was, apart from the above constituents, free calcium hydroxide in the sample. After 48 hours the samples contained tobermorite and hydrogarnet. In samples containing 10% Al_2O_3 , the molar ratio of $C/S + A$ being 0.4 and 0.6 , there was gibbsite, hydrogarnet and tobermorite after 24 hours of hydrothermal treatment at 150°C . After 24 hours at 200°C the phase composition did not practically change.

Results obtained at temperature of 180°C for 10 and 24 hours are shown in Tables 1, 2 and 3.

After 24 hours the phase composition of samples did not change. Only in mixtures which contained small amounts of calcium hydroxide this could not be identified after 24 hours. By prolongation of the hydrothermal procedure a better arrangement of tobermoritic structure was achieved.

Table 1

Composition of samples after 10 hours at 180°C (4% Al_2O_3)

Source of Al(III)

Gibbsite	□○	□○	□○●	□●
Boehmite	□▽	□▽	□▽	□●
Dehydrated kaolinite	□	□	□	□●
Kaolinite	□	□	□	□●
Corundum	□	□	□	□●
$\gamma\text{-Al}_2\text{O}_3$	□	□	□	□●
SiO_2	aerosil	gel	glass	β -quartz

- tobermorite
 ● hydrogarnet C_3ASH_4
 ○ gibbsite
 ▽ boehmite

Table 2

Composition of samples after 10 hours at 180°C (10% Al_2O_3)

Source of Al(III)

Gibbsite	□○	□○	□●○	□●○
Boehmite	□▽	□▽	□▽	□●▽
Dehydrated kaolinite	□	□	□●	□●
Kaolinite	□	□	□	□●
Corundum	□	□	□	□●
$\gamma\text{-Al}_2\text{O}_3$	□▽	□	□●	□●
SiO_2	aerosil	gel	glass	β -quartz

Table 3

Composition of samples after 24 hours at 180°C (10% Al₂O₃)

Source of Al(III)

Gibbsite	□○▽	□○▽	□●○	□●
Boehmite	□▽	□▽	□▽	□●▽
Dehydrated kaolinite	□	□	□●	□●
Kaolinite	□	□	□	□●
Corundum	□	□	□	□●
γ-Al ₂ O ₃	□▽	□	□●	□●
SiO ₂	aerosil	gel	glass	β-quartz

From the above results it follows that the extent of isomorphous substitution is not identical when different source materials are used. In mixtures in which Al(III) as gibbsite and boehmite was used, the hydrogarnet phase arises even when 4% of Al₂O₃ are present. Samples prepared with further compounds show similar results. Practically, they all contain tobermorite alone. Samples prepared using dehydrated kaolinite and γ-Al₂O₃ contain sometimes free boehmite or hydrogarnet. In samples made using β-quartz, the hydrogarnet phase was detected. In his work [6] Kalousek used microcrystalline quartz as source material which, under given conditions, reacts more readily so that after 24 hours of hydrothermal treatment tobermorite with perfectly developed structure was formed. When macrocrystalline quartz is used the reaction is slower, and though tobermoritic phase is formed after 24 hours, the structure is not so well ordered (Fig. 1). Hence it follows that the exotherm on the

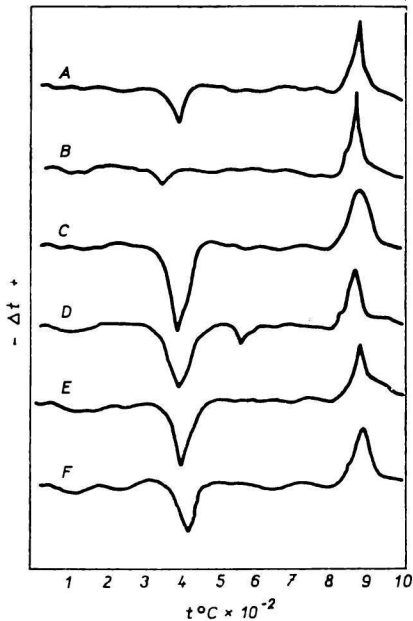


Fig. 1. DTA curves of samples prepared using β-quartz, C/S + A = 0.8, 180°C.

A.	4% Al ₂ O ₃	γ-Al ₂ O ₃	10 hours
B.	4% Al ₂ O ₃	gibbsite	10 hours
C.	10% Al ₂ O ₃	γ-Al ₂ O ₃	10 hours
D.	10% Al ₂ O ₃	boehmite	10 hours
E.	10% Al ₂ O ₃	kaolinite	24 hours
F.	10% Al ₂ O ₃	gibbsite	24 hours

DTA curve can not indicate the extent of the substitution. The same applies to the work of *Diamond et al.* [7]. Moreover, when macrocrystalline quartz was used, beside tobermorite the hydrogarnet phase is formed.

In order to be able to compare our results with those of the above authors, we prepared samples with molar ratio of $C/S + A = 0.5$. After 24 hours at 180°C they contained tobermorite and hydrogarnet phase. From the results we obtained we may see that the substitution in samples prepared using macrocrystalline quartz is lower than that reported by *Diamond* and *Kalousek*. As we see, the surface area of the starting materials is an important factor. Further we found that the solubility of the components as well as their interaction in solution are of importance [9].

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