

# Isomorphous Substitution of Aluminium for Silicon in Tobermoritic Structure. II.

## The Mixtures Prepared from Different Starting Materials and from Gels Containing Aluminium Ion

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The samples with the molar ratio  $C/(S + A) = 0.8^*$  were prepared by hydrothermal synthesis at  $180^\circ\text{C}$ . The  $\text{SiO}_2$  gels, containing from 4.32—44.80% of  $\text{Al}_2\text{O}_3$ , as well as different forms of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  [1] were applied as starting materials. The samples were studied by X-ray diffraction method, differential thermal analysis, infrared spectroscopy and electron microscopy. It was found that tobermorite was formed in the samples prepared from the gels containing up to 15% of  $\text{Al}_2\text{O}_3$ . The hydrogarnet arose when the aluminium content was higher. It was found that the entering of aluminium into tobermoritic structure advanced the transformation of C—S—H I into tobermorite. This substitution had also effect on the morphologie shapes of tobermoritic crystals.

In the preceding paper [1], it was found that the degree of isomorphous substitution of aluminium for silicon in the tobermorite lattice was dependent on the starting materials. The gels of  $\text{SiO}_2$  with different content of aluminium were used as starting materials in this study. These gels were prepared by hydrolysis of the non-aqueous solutions of silicon tetrachloride and aluminium chloride. It was supposed that the results thus obtained would not be influenced by the choice of starting materials. For the comparison of the obtained results, different starting materials were used for the preparation of samples [1], in consideration of the results obtained by *Diamond et al.* [5].

### Experimental

#### *Preparation of gels*

Silicon tetrachloride (Lachema), anhydrous aluminium chloride (Merck, anal. grade) and acetone (Lachema, anal. grade) were employed for the preparation of gels. The solutions were made by using the acetone solution of silicon tetrachloride (0.5 volume %) as a basic solution in which various amount of aluminium chloride were dissolved. It was found that a white precipitate irreproducibly arose by the dissolution of aluminium chloride. But this precipitate did not arise when distilled water was added into acetone

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

The content aluminium that substitutes silicon in the mixtures as well as in tobermorite is expressed in the percentage of aluminium oxide.

in the amount of 0.5 volume %. The solutions thus prepared were used for a short time. The solution was allowed to drop from a separating funnel into hot (*ca.* 80°C), distilled water containing about 0.1% of ammonia. In this way, a simultaneous hydrolysis of aluminium chloride and silicon tetrachloride was assured. The obtained gels were washed up with hot, distilled water, dried at 60°C and analyzed. They contained from 14–25% of water and after converting to anhydrous gels, the  $\text{Al}_2\text{O}_3$  content was from 4.32–44.80%. It was found by means of X-ray diffraction that the gels were amorphous. Their DTA curves were characterized by an expressive peak at 900°C [2]. The infrared spectroscopy showed that the absorption band at 9.15  $\mu\text{m}$  (corresponding to a gel without aluminium) shifted to higher wavelengths with increasing content of aluminium (Fig. 1). The results obtained at 1000°C accorded to those of *Crofts* and *Marshall* [3].

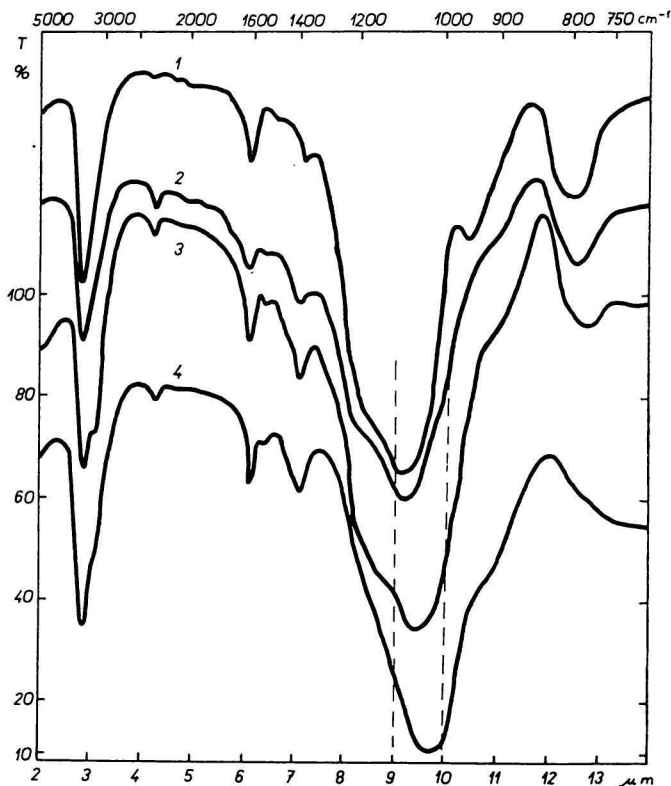


Fig. 1. Infrared spectra of the gels with different contents of aluminium.  
1. 0%; 2. 4.32%; 3. 10.48%; 4. 24.72%.

Then the mixtures of different starting materials were prepared in which different aluminium compound were substituted for 15% of  $\text{SiO}_2$ . The preparation or procedure have been described in the preceding paper [1]. The prepared mixtures were subjected to a hydrothermal process for 24 hours at 180°C. In some cases, the hydrothermal process was prolonged up to 48 hours. After drying (105°C) the samples were studied.

### Equipment used

The X-ray diffractograph and DTA apparatus have been described in the preceding paper. In some cases, the X-ray diffractograph Müller Mikro 111 was used. (In both cases the radiation  $\text{CuK}_\alpha$  and Ni filter were applied.) The infrared spectroscopic measurements were carried out by means of Perkin—Elmer 221 and the investigated samples were made up according to the usual KBr method (0.4 mg/300 mg KBr). The preparations for electron microscopic observations, performed by means of the instrument Tesla BS 242, were prepared in water suspensions.

### Results and Discussion

The results obtained by DTA indicate that only tobermorite is formed in the mixtures, prepared from the gels the  $\text{Al}_2\text{O}_3$  content of which does not exceed 15% (Fig. 2). The DTA curve of a sample without aluminium is characterized by an intense exothermic peak that correspond to C—S—H I [4]. The DTA curves of the samples with the substituted  $\text{Al}_2\text{O}_3$  up to 10.48% are characterized by an intense exothermic peak. The samples with a higher  $\text{Al}_2\text{O}_3$  content are characterized by exothermic peaks the intensity of which fall and the deflections get broader and shift to higher temperatures. These results are not conform to those of *Diamond et al.* [5]. These authors applied the mixtures of microcrystalline quartz and the sample without aluminium contained tobermorite the DTA curve of which was characterized by a weak exothermic peak. The differences found may be due to the use of different starting materials. The samples containing more than 15% substituted  $\text{Al}_2\text{O}_3$  do contain no more tobermorite but hydrogarnet or further components, resp. (Fig. 3). The DTA curves of hydrogarnet are characterized by an endothermic deflection

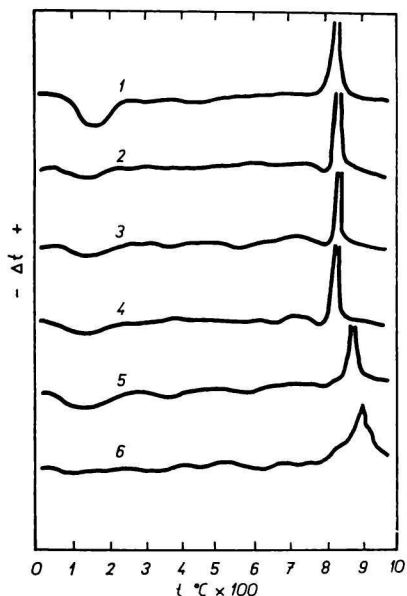


Fig. 2. DTA curves of the samples prepared from the gels containing substituted  $\text{Al}_2\text{O}_3$  up to 15%.

1. 0%; 2. 4.23%; 3. 8.58%; 4. 10.48%;  
5. 13.18%; 6. 15.05%.

starting at about 350°C. With increasing aluminium content, gibbsite arises in the samples with an endothermic deflection starting at about 300°C as well as böhmite with an endothermic deflection at 500°C.

The DTA curves of samples, prepared from different starting materials by 24 hours' heating, are characterized by an exothermic peak belonging to tobermorite

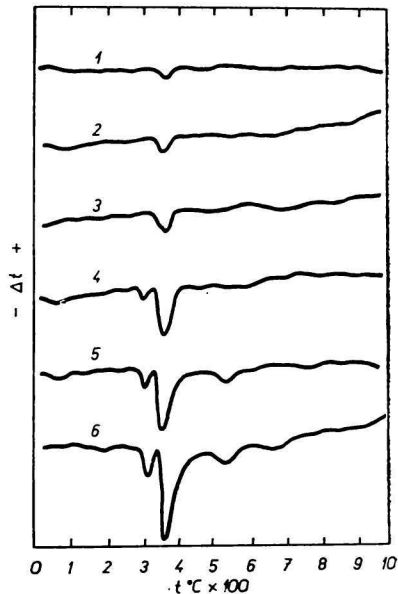


Fig. 3. DTA curves of the samples prepared from the gels containing from 17.30–44.80%  $\text{Al}_2\text{O}_3$ .

1. 17.30%; 2. 19.36%; 3. 24.72%;  
4. 34.67%; 5. 39.24%; 6. 44.80%.

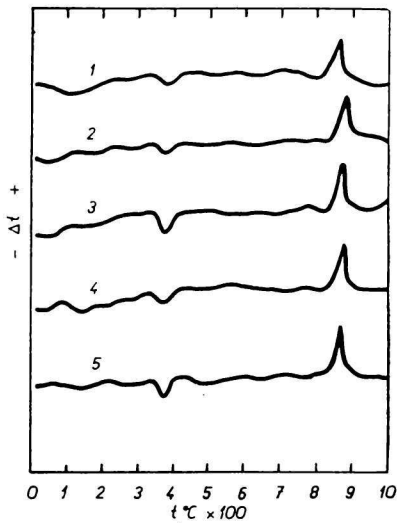


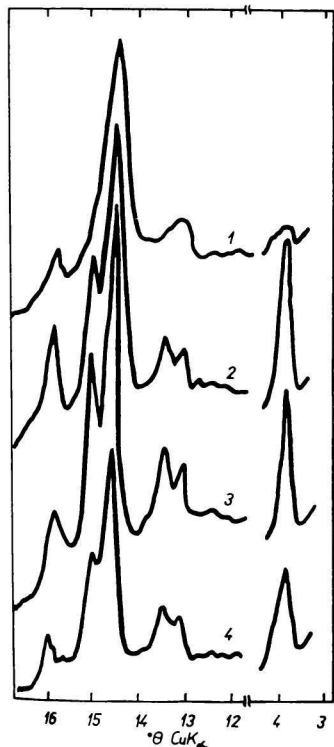
Fig. 4. DTA curves of the mixtures prepared from different starting materials after 48 hours' treatment.

1. silica glass – corundum; 2. silica glass – kaolinite; 3. silica glass – dehydrated kaolinite; 4. silica – kaolinite; 5. silica – dehydrated kaolinite.

and by an endothermic deflection of hydrogarnet (Fig. 4). The exothermic peak remains relatively intense even after 48 hours' hydrothermal process. These results are conform to the data of *Diamond et al.*

The results obtained show that the starting materials have a decisive influence on the degree of substitution. In case of the samples prepared from gels, the hydrogarnet is formed only in the mixtures containing more than 15% of substituted  $\text{Al}_2\text{O}_3$ . In the samples prepared from different starting materials, a lower degree of substitution has been reached and the samples have contained both tobermorite and hydrogarnet. The gels used behave as a single phase in this case and may represent a molecular mixture of both components, as stated by *Crofts and Marshall* [3].

It has been found by X-ray phase analysis that the sample prepared from the gel without aluminium contains C-S-H I. The samples with the content up to 15% of substituted  $\text{Al}_2\text{O}_3$  contain tobermorite. The entrance of  $\text{Al}^{3+}$  ions into tobermoritic structure has speeded up the transformation of C-S-H I into tobermorite (diffraction lines 2.97 and 2.80 Å) (Fig. 5). When the  $\text{SiO}_2$  gel is employed as starting material, the stability of C-S-H I is relatively high under given experimental conditions [4]. Tobermorite arises in a relatively short time if a gel containing  $\text{Al}^{3+}$  is used. The diffraction lines of tobermorite with 15.05% of substituted  $\text{Al}_2\text{O}_3$  show an intensity decrease in comparison to the tobermorite with a lower content of



*Fig. 5.* X-ray diffraction patterns of the tobermorites with different amounts of substituted  $\text{Al}_2\text{O}_3$ .

1. 0%; 2. 4.32%; 3. 10.48%; 4. 15.05%.

aluminium. The precise measurements of the position of the basal diffraction line has shown that its position changes in case of different aluminium contents, but these changes are irregular. *Diamond et al.* [5] as well as *Kalousek* [6] have stated a certain though different dependence on the aluminium content. The tobermorites have had these values of  $d_{002}$ : without aluminium 11.31 Å; 4.32%  $\text{Al}_2\text{O}_3$ , 11.78 Å; 10.48%  $\text{Al}_2\text{O}_3$ , 11.66 Å, and 15.05%  $\text{Al}_2\text{O}_3$ , 11.75 Å.

The results obtained by infrared spectroscopy are presented in Fig. 6. The spectra of substituted and non-substituted tobermorites are very similar. The spectra of substituted tobermorites have further weak absorption at different wavelengths. The tobermorite containing 4.32% of  $\text{Al}_2\text{O}_3$  shows a weak absorption at 11.22  $\mu\text{m}$  ( $891\text{ cm}^{-1}$ ). The sample with 10.48% of  $\text{Al}_2\text{O}_3$  has weak absorption bands at 11  $\mu\text{m}$  ( $909\text{ cm}^{-1}$ ) and 11.40  $\mu\text{m}$  ( $873\text{ cm}^{-1}$ ) as well as at 8.6  $\mu\text{m}$  ( $1162\text{ cm}^{-1}$ ). The tobermorite

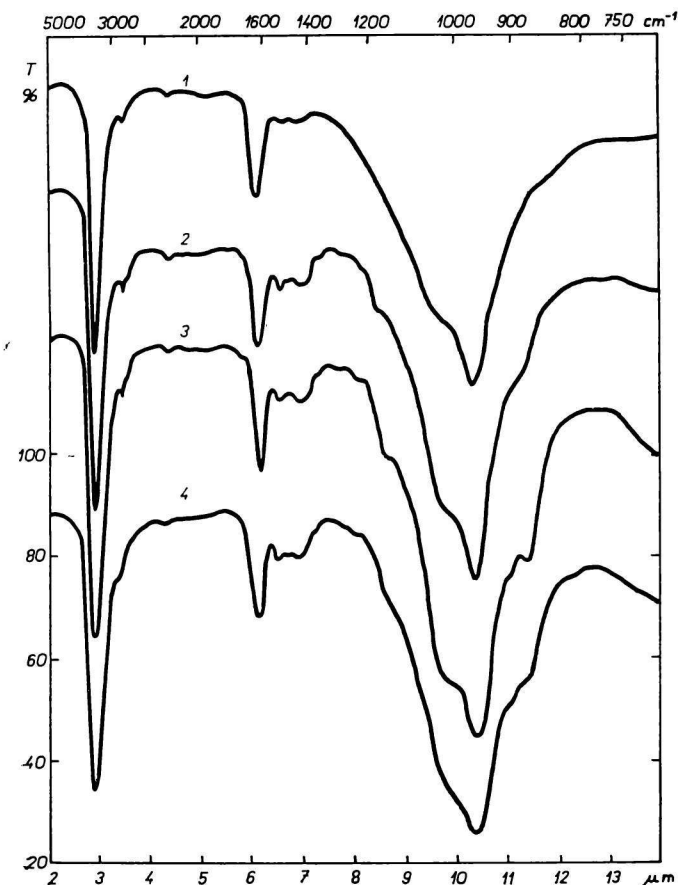
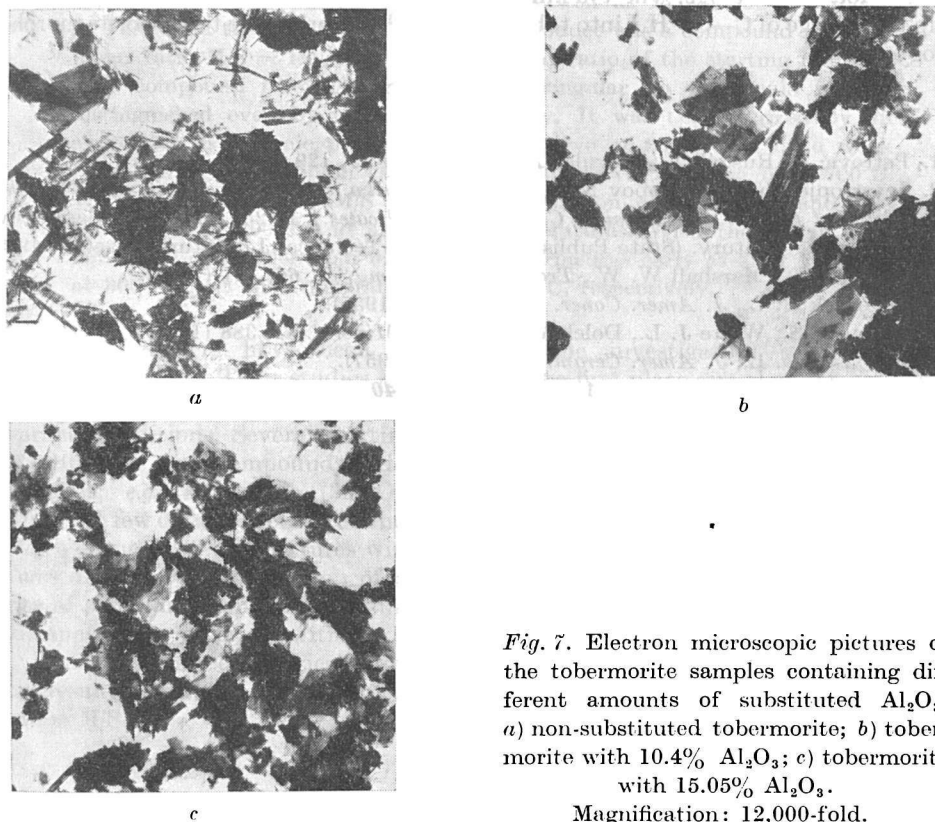


Fig. 6. Infrared spectra of the tobermorites with different amounts of substituted  $\text{Al}_2\text{O}_3$ .  
1. 0%; 2. 4.32%; 3. 10.48%; 4. 15.05%.

with 15% of  $\text{Al}_2\text{O}_3$  shows absorption at  $11.4 \mu\text{m}$  ( $873 \text{ cm}^{-1}$ ) as well as at  $11 \mu\text{m}$  ( $909 \text{ cm}^{-1}$ ). These absorption bands are weaker than those of the tobermorite with 10.48% of  $\text{Al}_2\text{O}_3$ . All samples have shown the absorption band between  $6.8\text{--}7.1 \mu\text{m}$  ( $1470\text{--}1408 \text{ cm}^{-1}$ ), which this type of tobermorite should not have according to the results of *Kalousek* [7]. The differences are probably due to the presence of aluminium in the tobermoritic structure. The position of SiO absorption band at  $10.3 \mu\text{m}$  ( $970 \text{ cm}^{-1}$ ) does not change owing to substitution. *Diamond et al.* [5] mention further absorption bands for the substituted and non-substituted tobermorite. It is probably due to the application of different starting materials. It can be seen on the basis of results thus obtained [5, 7] that the results got by infrared spectroscopy are diverse and do not give an explicit view. It is caused by the fact that the authors work under different experimental conditions and use different starting materials. Moreover, the problem is complicated by the fact that the tobermorites with different properties arise under different conditions.



*Fig. 7.* Electron microscopic pictures of the tobermorite samples containing different amounts of substituted  $\text{Al}_2\text{O}_3$ . a) non-substituted tobermorite; b) tobermorite with 10.4%  $\text{Al}_2\text{O}_3$ ; c) tobermorite with 15.05%  $\text{Al}_2\text{O}_3$ .

Magnification: 12,000-fold.

The electron microscopy has shown that the presence of aluminium in the tobermoritic structure influences the morphologic shapes of tobermorite (Fig. 7). The sample without aluminium is formed by the crystals of different shapes, the greater part of which are prolonged in one direction. The samples with aluminium are

characterized by sheet crystals and when the sample contains 15.05% of substituted  $\text{Al}_2\text{O}_3$  thin sheet crystals as well as crystals of irregular shapes are formed. The rod crystals as well as slab crystals are, however, absent.

From the results thus obtained, it follows that aluminium can be isomorphically substituted for silicon in the tobermoritic structure. The degree of substitution depends on starting materials. The maximum substitution is achieved when suitable starting materials have been applied. It has been found that the content of 15% of substituted  $\text{Al}_2\text{O}_3$  represents a boundary condition, as previously stated by *Diamond et al.* [5]. If the content of aluminium is greater, both hydrogarnet and tobermorite or only hydrogarnet is formed. In some cases, a certain view of substitution may be obtained by DTA [5, 6]. The position change of the basal diffraction line of tobermorite is not, however, a reliable criterion. It is also not possible to obtain the data on substitution by means of infrared spectroscopy because the results are dependent on the starting materials. The position of the main Si—O absorption band does not change. The aluminium coming into tobermoritic structure speeds up the change of C—S—H I into tobermorite and influences the tobermorite morphology.

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