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*EFFECTS OF ISOMORPHOUS SUBSTITUTION
IN HYDROTHERMALLY-SYNTHESISED
TOBERMORITE*

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by
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Technical Paper

EFFECTS OF ISOMORPHOUS SUBSTITUTION IN HYDROTHERMALLY

SYNTHESIZED TOBERMORITE

TO: K. B. Woods, Director
Joint Highway Research Project

June 19, 1964

FROM: H. L. Michael, Assistant Director
Joint Highway Research Project

Project: C-36-47I
File: 4-6-9

Attached is a Technical Paper titled "Effects of Isomorphous Substitution in Hydrothermally Synthesized Tobermorite". This paper has been authored by Messrs. Sidney Diamond, J. L. White and W. L. Dolch. Much of the content of the paper was obtained from research project C-36-47I and from the Final Report on that project titled "Tobermorite and Tobermorite-Like Calcium Silicate Hydrates: Their Properties and Relationships to Clay Minerals."

This research was a cooperative project with the State Highway Commission and the Bureau of Public Roads and the paper will also be sent to them for their review and approval.

The paper is presented to the Board for approval of publication.

Respectfully submitted,

H. L. Michael

H. L. Michael, Secretary

HLM:bc

Attachment

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Technical Paper

EFFECTS OF ISOMORPHOUS SUBSTITUTION IN HYDROTHERMALLY
SYNTHESIZED TOBERMORITE

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EFFECTS OF ISOMORPHOUS SUBSTITUTION IN HYDROTHERMALLY

SYNTHESIZED TOBERMORITE^{1/}

by

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ABSTRACT

Tobermorite and substituted tobermorites incorporating various contents of aluminum, iron, or magnesium were prepared by hydrothermal synthesis. Earlier observations of Kalousek on the effects of aluminum substitution were confirmed. The presumed location of aluminum in tetrahedral sites was demonstrated by x-ray fluorescence spectroscopy. X-ray diffraction disclosed several specific effects of the substituting ions, most prominent of which were marked reductions in intensity of the strong (002) and (222) reflections in iron- and magnesium-bearing tobermorites. Electron microscopy revealed thin, platy crystals with sharp edges; iron-bearing tobermorite particles were distinctly elongated. A strong high-temperature exothermic response occurred in the DTA of aluminum-bearing tobermorite, but not with the other varieties, and is attributed to the probable formation of an amorphous aluminosilicate (spinel?) accompanying the conversion of tobermorite to wollastonite. Infrared spectra of tobermorite showed distinct bands at 1207, 922, and 745 cm^{-1} in addition to the strong Si-O lattice vibration band at 965 cm^{-1} and other bands attributed to water and adsorbed carbonate. Substitution of aluminum induced a progressive

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shift to lower wave numbers in the 1207 and 745 cm^{-1} bands. Iron and magnesium substitution had comparatively small effects. Only very weak and broad bands attributable to the hydroxyl stretching vibrations were observed.

INTRODUCTION

Tobermorite, a rare calcium silicate hydrate mineral described originally by Heddle (1880), has been found to be of considerable technical importance. This phase is produced on autoclaving concrete or sand-lime masonry blocks, and apparently serves as the principal binding agent in these building materials (Kalousek, 1954). Furthermore, there are several poorly-crystalline calcium silicate hydrates that seem to be closely related to tobermorite, the most notable among which is tobermorite gel, the basic cementing compound produced by the normal hydration of portland cement (Brunauer, 1962).

The crystal structure of tobermorite was determined by Megaw and Kelsey (1956), and involves a combination of layer and chain silicate structural features of considerable complexity. The basic unit consists of a central sheet comprising a double layer of calcium and oxygen ions, coupled with rows of $\text{SiO}_2(\text{OH})_2$ tetrahedra that are linked into chains running parallel to the b-axis direction. The chains occur on either side of the central sheet. The structural unit has been compared to a piece of double-sided corrugated cardboard, with the central sheet reinforced on each surface by the longitudinal ridges. Two of these structural units pack together with their ridges superposed vertically, i.e. not nested. This leaves channels parallel to the b-axis that are presumed to contain additional calcium not located by the structural determination. On heating tobermorite

 

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to several hundred degrees there is a loss of water accompanied by a reduction in the basal spacing from about 11.2 Å to about 9.5 Å; this has been interpreted as indicating the close approach of the structural units into intimate contact (Taylor, 1959). Further heating to temperatures of 800-900°C produces a phase change to wollastonite (β -CaSiO₃).

Little information exists on the range of isomorphous substitution possible in tobermorite. The subject is of interest since tobermorite arising in technical products may have considerable opportunity to incorporate foreign ions, notably iron and aluminum. Kalousek (1957) studied the incorporation of aluminum into synthetic tobermorite and noted changes in the x-ray diffraction and differential thermal analysis characteristics of the substituted phases. The present work confirms and extends these earlier observations on aluminum-bearing tobermorite and reports the results of a similar incorporation of iron and magnesium into the tobermorite lattice.

METHOD OF SYNTHESIS

Well-crystallized tobermorite is readily synthesized from calcium hydroxide and quartz at comparatively low temperatures under hydrothermal conditions. The method used in this study was patterned after that of Kalousek (1957). The quartz was "Special Silica" (Ottawa Silica Co.), that passed the No. 325 sieve. The calcium hydroxide was derived from reagent-grade calcium carbonate that was calcined at 1050°C for four hours. Exactly eight grams of the resulting calcium oxide were weighed, suspended in 32 ml of freshly-boiled distilled water, and stirred for three minutes. The newly-formed calcium hydroxide was transferred to a malted milk mixer with an additional 40 ml of water. A 10.3 gram portion of oven-dried quartz

was then added to the material and the resulting mixture was stirred at high speed for five minutes. The mixture, now of the consistency of heavy cream, was then transferred to hydrothermal vessels, sealed, and placed in an oven at 175°C. The reaction was allowed to proceed for 19 hours, after which the product was cooled, the bombs opened, and the sample immediately bottled.

The substituted tobermorites studied in this work were prepared in an identical manner except that an admixture bearing the substituting ions was mixed with the quartz in the dry state prior to the addition of the latter to the freshly-slaked lime.

DEGREE OF SUBSTITUTION ACHIEVED

Kalousek (1957) presented indirect chemical evidence suggesting that aluminum substituted for silicon in tetrahedral coordination in the silica chains of tobermorite. This conclusion is substantiated in the present work by evidence from x-ray fluorescence spectroscopy. Thus, rather than expressing substitution in terms of weight percent of Al_2O_3 incorporated into the tobermorite, as Kalousek did, it seems more pertinent to discuss the degree of substitution in terms of atomic percentage of the silicon ions replaced by substituent ions. One percent of Al_2O_3 on an ignited weight basis is equivalent to replacement of almost two percent of the silicon ions in tobermorite.

In the present report, for convenience, the degree of substitution of iron and magnesium is expressed in the same way as for aluminum. However, it should be remembered that the postulated assignment of these ions to the tetrahedrally-coordinated silicon sites in tobermorite is arbitrary, and no definite evidence is available.

Following Kalousek, a series of "Al-tobermorites" was prepared using kaolinite as the source of the aluminum. The kaolinite used was the "Hydrite 10" grade supplied by the Georgia Kaolin Co. It was added in amounts calculated to supply aluminum to substitute for 3, 5, 10, and 15% of the silicon ions in the resulting tobermorite product. The amount of quartz used was reduced by the calculated SiO_2 content of the added kaolinite.

Two additional Al-tobermorites were prepared using reagent grade $\text{Al}(\text{OH})_3$ (synthetic gibbsite) as the source of the aluminum. The amounts of silicon replaced in these preparations were calculated at 10 and 15%, respectively.

Examination of the resulting products suggested that, except for the nominally 15% Al-tobermorites, essentially all of the added aluminum had been incorporated into the lattice of the tobermorite. The 15% Al-tobermorites gave evidence of a small content of hydrogarnet formed as a separate phase. The only restriction on this general conclusion is that supplementary electron diffraction studies suggested that a portion of the finest particles may have been calcium silicate hydrate (I), a poorly crystallized phase of composition similar to tobermorite, but characteristically showing only a few of the strongest diffraction lines of that phase.

Attempts to incorporate iron into the tobermorite lattice using hematite as the iron source were only partially successful; even at low levels of substitution most of the hematite remained as a separate phase. Trials with goethite, however, were more satisfactory. Addition of goethite in an amount calculated to supply iron to replace 10% of the silicon ions in tobermorite yielded an off-white tobermorite product whose x-ray diffraction pattern showed no trace of goethite as a separate phase. Firing

of this material at $1,000^{\circ}\text{C}$ turned it faintly pink, and subsequent x-ray examination disclosed a small but definite hematite peak in addition to the expected wollastonite x-ray pattern. Standard mixtures of iron-free tobermorite and goethite were prepared and fired, and the size of the resulting hematite peaks were observed. Comparison with the peak obtained from the Fe-tobermorite suggested that about one-fifth of the goethite added was not incorporated into the tobermorite but remained as a separate phase and gave rise to hematite on firing. Consequently the nominally 10% iron-substituted tobermorite was concluded to have actually about 8% substitution, expressed on the basis of replacement of silicon ions.

An attempt to incorporate magnesium into the tobermorite lattice was also considered successful. The magnesium was supplied in the form of reagent grade MgO (synthetic periclase), in an amount calculated to replace 10% of the silicon ions of the resulting tobermorite. The product showed no x-ray peaks attributable to periclase, but a very small peak at $2.35\text{\AA}$ was attributed to a separate brucite phase formed under the hydrothermal reaction conditions. No periclase was observed in the fired product, so a method analagous to that previously employed for the estimation of unincorporated iron could not be used. However, differential thermal analysis of the Mg-tobermorite disclosed a small endothermic peak at about 435°C which is attributed to brucite. Standard mixtures of Mg-free tobermorite and brucite were prepared and subjected to differential thermal analysis under standard conditions. Comparison of the intensities of the resulting endothermic peaks suggested that an amount of brucite equivalent to about 30% of the MgO added originally was present in the Mg-tobermorite product as a separate phase. Thus the degree of replacement actually achieved was about 7% instead of the nominal 10%.

COORDINATION OF SUBSTITUTED ALUMINUM

It has been demonstrated by various workers (White, McKinstry, and Bates, 1959; Brindley and McKinstry, 1961; Day, 1963) that the wavelength of the K- α x-ray emission peak of aluminum is affected significantly by the coordination of the aluminum ion, and that the coordination can be unequivocally determined by observation of the angular displacement of the position of the peak for a specimen compared to that from metallic aluminum. The measurement is readily made on a diffractometer equipped with a flow proportional counter and a helium or vacuum path to minimize absorption of the long-wavelength emitted radiation. The displacement range, using an ethylene diamine ditartrate crystal is 0.04 - 0.06 degrees two-theta for tetrahedrally coordinated aluminum ions (coordinated to oxygen) and 0.08 - 0.12 degrees two-theta for octahedrally coordinated aluminum ions.

The angular displacement for the 15% Al-tobermorite specimen was measured using a suitably-equipped General Electric XRD-3 diffractometer. The goniometer was set successively at fixed angular settings at close intervals around the position of the aluminum K α peak (142.45 degrees two-theta), and the intensity of emitted x-rays determined at each position by direct counting. A plot of the resulting intensity vs. angular setting gave a profile of the peak, from which the center was determined to within 0.01 degree. A similar measurement of the position of the peak from aluminum metal was made, and the displacement was calculated as the angular difference between the centers of the two peaks.

The displacement recorded for the 15% Al-tobermorite was 0.05 degrees two-theta; the same result was recorded in repeated trials on successive

days. This result affords definitive evidence for the four-fold coordination of aluminum in Al-tobermorite, thus confirming Kalousek's assumption that the aluminum substitutes for silicon in the tetrahedral chains.

X-RAY DIFFRACTION CHARACTERISTICS OF SUBSTITUTED TOBERMORITES

X-ray diffractometer traces were secured from randomly-oriented powder mounts of unsubstituted tobermorite and the various substituted varieties. A General Electric XRD-5A instrument using nickel-filtered copper radiation was used throughout. All of the materials yielded patterns indicative of well-crystallized tobermorites with no observable impurities except as noted previously. The results are in excellent correspondence with published diffractometer traces of Kalousek (1957) and camera data of Heller and Taylor (1956).

Traces for the tobermorite and for the Al-tobermorites prepared from kaolinite admixtures are given in Figure 1. The findings of Kalousek with regard to the effect of aluminum substitution on the x-ray patterns are confirmed in detail as indicated below:

1. The basal spacing increases with increasing Al substitution, the spacing varying from 11.2 Å for the unsubstituted tobermorite to 11.5 Å for the nominally 15% Al-tobermorite.

2. A gradual decrease of the intensity of the (400) reflection at 2.81 Å with increasing aluminum content was noted. In the present work the intensity of this peak relative to that of the strongest tobermorite peak at 3.07 Å in each case was 55, 52, 44, 39, and 33% respectively, for samples containing zero, 3, 5, 10, and 15% replacement, respectively.

3. Kalousek noted the appearance of hydrogarnet in samples having compositions corresponding to substitutions greater than about 11%. The pattern of the nominally 15% Al-tobermorite in Figure 1 lacks any definite pattern for hydrogarnet. However, a shift of the 2.81 Å peak toward the position of the strongest peak for hydrogarnet at 2.76 Å was observed, the actual position measured for this sample being 2.79 Å. The corresponding pattern for the 15% Al-tobermorite made with gibbsite had a more definite indication of the presence of hydrogarnet in a distinct peak at 5.07 Å; otherwise the patterns were essentially identical.

A comparison of the diffractometer traces for tobermorite and Al-Fe-, and Mg-tobermorites, each of nominally 10% substitution, is given in Figure 2. There are considerable differences in the relative intensities of some of the strongest peaks. Table 1 gives the intensities in counts per second above background for the four main tobermorite peaks. It is clear from the table that while aluminum substitution has only a modest effect, substitution of iron or magnesium to this extent approximately halves the relative intensities of the (002) and (222) reflections. In contrast, there is little effect on the reflections from planes entirely within the unit layer, the (220) and the (400) peaks. It appears that substitution of iron or magnesium, both of which have ionic radii substantially larger than silicon, results in some disorder in the c-axis direction.

Other changes in the tobermorite x-ray pattern are observed to result from the substitutions. The Fe- and Mg-tobermorites display new peaks at 1.94 - 1.95 Å and at 7.0 Å, and all three substituted varieties yield new peaks at about 2.7 Å and 4.2 Å. Also, the Al- and Mg-tobermorites show strongly-enhanced (h0l) peaks at about 3.3 Å and 3.6 Å. Despite these

changes in detail, both the basic structure and the degree of crystallinity of the tobermorites are substantially unaffected by the lattice substitutions.

MORPHOLOGY

Electron microscopic observation of the unsubstituted tobermorite and of the Al- and Fe-tobermorites with 10% nominal substitution was made using an RCA EMU-3A instrument operated at 50 kv. All the samples examined appeared to be composed of particles showing a thin, platy morphology, in agreement with results previously published by others. Particles of the unsubstituted tobermorite and of the Al-tobermorite showed a slight tendency toward elongation, but the Fe-tobermorite particles were more definitely lath-shaped. It is interesting that nontronite, the iron-substituted montmorillonite, also exhibits a lath-shaped morphology. (Grim, 1953, p. 116). Many of the particles of unsubstituted tobermorite and of the Al-tobermorite had unusually acute angles, and some were triangular, giving the appearance that one would associate with flat pieces broken from larger sheets. Some of the particles seemed to contain small inclusions. It was observed that the substituted tobermorites displayed a relatively greater content of small particles than did the unsubstituted variety, as was suggested previously by Kalousek (1957) for Al-tobermorites.

DIFFERENTIAL THERMAL ANALYSIS

Synthetic tobermorite is known to yield only a broad low-temperature endotherm at about 260°C and a weak and indefinite high-temperature exothermic response at about 850°C (Kalousek, 1954). The endotherm reflects a loss of water and reduction of the c-axis spacing to about 9.5 Å; the exotherm marks the transition to wollastonite.

The samples were examined by DTA using a portable unit (Eberbach Co., Ann Arbor, Michigan) that was modified by replacing the Transite insulating unit with a close-fitting sleeve of commercial pipe insulation. The apparatus so modified had a linear heating rate of 58°C per minute from room temperature to about 600°C , after which the rate fell gradually to about 5° per minute at about 1000°C . This equipment consequently yields low-temperature peaks at slightly higher temperatures and high-temperature peaks at slightly lower temperatures than units capable of maintaining a constant rate of temperature increase, but the differences are not large and the peak shapes appear to be well-preserved.

DTA patterns for unsubstituted tobermorite and the series of Al-tobermorites the x-ray diffraction patterns of which were given in Figure 1, are shown in Figure 3. It is obvious that, within this range of substitution, increases in the aluminum content led to increasing sharpness and intensity of the high-temperature exotherm, and also to increasing peak temperature. These effects have been observed by Kalousek (1957), who also noted a decrease in intensity of the exotherm for samples with still higher aluminum contents. The latter effect was attributed to increasing formation of hydrogarnet. In the present series the small endothermic response at 380° in the nominally 15%-substituted sample is presumably due to this phase.

Figure 4 contains DTA results for the nominally 10% substituted Al-, Fe-, and Mg-tobermorites of Figure 2. The aluminum-bearing sample here is that derived from gibbsite; its DTA pattern is similar to that for the corresponding sample in the series in which aluminum was derived from kaolinite admixtures. The cause of the 635°C endotherm is unknown. In

the Fe-tobermorite, the small endotherm at 365°C is due to a small content of unreacted goethite, and in the Mg-tobermorite the endotherm at 435°C is due to brucite, as previously mentioned.

The Fe- and Mg-tobermorites do not undergo the high-temperature recrystallization exotherm characteristic of Al-tobermorite, but display only a weak response similar to that of unsubstituted tobermorite. The following experimental observations were recorded in attempts to determine the nature of the unique response for Al-tobermorites:

1. At about 775°C the Al-tobermorite samples started to undergo a remarkable shrinkage that was completed by about 800°C . The volume change was estimated of the order of 50%. The resulting product was at least partially fused. It was hard and tenacious, and could be removed from the sample well of the DTA unit only with difficulty. By contrast, unsubstituted tobermorite and the other substituted varieties did not fuse or undergo any noticeable volume change and were recovered as friable powders after completion of the run.

2. The shrinkage is definitely not associated with delayed conversion of the 11 Å Al-tobermorite to the 9.5 Å dehydrated state: experiments indicated that this conversion was complete by about 350°C for all the varieties of tobermorite discussed in this report.

3. X-ray diffraction of all samples after the DTA runs showed only wollastonite, except, as previously mentioned, a small amount of hematite in the Fe-tobermorite sample. The wollastonite pattern for the heated Al-tobermorite was identical with those derived from the other tobermorite varieties.

Both the exothermic response and the shrinkage observed for Al-tobermorites may be associated with the formation of an amorphous alumin-

silicate, possibly an Al-Si spinel. As pointed out by Taylor (1959), the wollastonite produced on heating tobermorite probably has the normal Ca:Si ratio of 1.0. Because this ratio in the parent tobermorite is only 0.83, excess silica must also be produced along with the wollastonite. In normal tobermorite samples this silica is presumed to be present in an amorphous state not detectable by x-ray methods. It seems to the present writers that this free silica might readily react with some or all of the aluminum in the decomposed Al-tobermorite to produce an aluminosilicate of such poor crystallinity that it also escapes detection. Formation of such a quasi-amorphous compound, an Al-Si spinel, is held to be responsible for the similar strong DTA exotherm of kaolinite at about 980°C (Brindley and Nakahira, 1959).

It should be noted that the poorly-crystalline phase known as calcium silicate hydrate(I) also displays a strong high-temperature exothermic response, in this case in the absence of aluminum. However, this appears to be due to a different cause, since virtually no shrinkage occurs, and samples remain friable after the DTA run.

INFRARED SPECTRA

Infrared absorption spectra of the tobermorites were secured with a Perkin-Elmer 421 dual-grating spectrometer. The specimens consisted of thin films of the tobermorites deposited on potassium bromide plates. The dried tobermorite was suspended in spectral-grade carbon tetrachloride; then several drops of the suspension were pipetted so as to cover the surface of the previously oven-dried plates, which were retained in the drying oven. Immediate evaporation of the carbon tetrachloride left an incomplete but satisfactory deposit of the tobermorite on the plate surface. Each specimen was quickly transferred to the instrument and its spectrum

obtained. These precautions were taken with a view toward minimizing any possible effects of adsorbed water.

Kalousek and Roy (1957) and Hunt (1962) published spectra of synthetic tobermorites showing OH stretching vibration bands with amplitudes on the order of 50 - 75% of those of the corresponding main Si-O lattice vibration bands. These authors used the conventional KBr pellet technique of sample preparation, in which a minute amount of sample is mixed with a large excess of powdered potassium bromide and formed into a transparent pellet under pressure in an evacuated die. Potassium bromide in powder form is hygroscopic, and it may be that these authors were unsuccessful in eliminating all traces of water despite their considerable efforts to do so. At any rate, in the present spectra only a weak band was found in the region characteristic of the stretching vibrations of OH groups, the location being between 3400 and 3000 cm^{-1} . The band was uniformly broad and indistinct, with its maximum amplitude only about 10-15% of that for the main Si-O lattice vibration band at about 965 cm^{-1} .

Tracings of the spectra of unsubstituted tobermorite and the nominally 10% substituted Al-, Fe-, and Mg-tobermorites are given in Figure 5 for the region from 1800 to 600 cm^{-1} . The 5x scale expansion feature of the instrument was used to enhance the definition of the various bands. The band at 1610-1620 cm^{-1} is attributed to the bending vibration of water molecules, presumably water located in the channels of the tobermorite structure. Bands at 1450 cm^{-1} , 890 cm^{-1} , and 660 cm^{-1} are attributed to the presence of carbonate ions as an impurity derived from atmospheric carbonation in preparation and handling of the tobermorite. The remaining features are attributed to the tobermorite itself.

Published assignments of infrared absorption features of complicated silicate structures to particular vibrational modes are still largely empirical. Stubican and Roy (1961, 1961a) have allocated various bands in layer silicates to certain vibrational modes on the basis of shifts in position and intensity observed to occur with varying composition in a series of specially-synthesized compounds. Roy (1962) tabulated these assignments specifically to assist in interpreting spectra of tobermorite-like calcium silicate hydrates, but the features observed in the present spectra appear to have no obvious correspondence to those noted by him for layer-lattice silicates. Aside from the main Si-O lattice vibration band, which is the strong feature at $965\text{--}970\text{ cm}^{-1}$, no definite assignment of the features attributed to the tobermorite can be offered here.

Figure 5 suggests that only moderate shifts occur in the tobermorite pattern with the degree of lattice substitution involved here. With aluminum substitution the sharp band at about 1205 cm^{-1} in tobermorite was decreased in wave number and reduced in intensity. Figure 6 is a tracing of this particular feature recorded for the series of Al-tobermorites prepared with quartz. A regular shift occurred from a measured position of 1207 cm^{-1} for unsubstituted tobermorite to one of 1172 cm^{-1} for the nominally 15%-substituted sample. It was also observed that the band at 745 cm^{-1} in unsubstituted tobermorite also shifted to lower wave numbers with increasing aluminum substitution, but the shift was irregular. The 3% Al-tobermorite showed a large shift from 745 cm^{-1} to 720 cm^{-1} , while additional increments of aluminum did not shift the position below 700 cm^{-1} . Finally, it was observed that Al-tobermorites did not display the small feature observed at about 822 cm^{-1} for unsubstituted tobermorite.

The spectra for the Fe- and Mg-tobermorites were similar to that of unsubstituted tobermorite. The 1207 cm^{-1} feature, which shifted and weakened with aluminum substitution, remained strong and at a nearly constant position at 1200 cm^{-1} for both Fe- and Mg-tobermorites. The 745 cm^{-1} feature shifted only slightly, to 735 and 730 cm^{-1} , respectively. The spectrum for the Mg-tobermorite contained a band at about 1070 cm^{-1} that was not apparent with the other tobermorites. This may be due to the small content of brucite in this sample, since brucite has a distinct band at this position.

In general, it seems that while the spectra are basically similar, Al-tobermorites are marked by comparatively large shifts in the bands originally at 1207 cm^{-1} and 745 cm^{-1} , while Fe- and Mg-tobermorites display smaller shifts.

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Table 1. Intensities* of Four Strongest X-Ray Peaks of Tobermorites

Sample	(002) 11 Å	(220) 3.07 Å	(222) 2.97 Å	(400) 2.81 Å
Unsubstituted tobermorite	61	90	58	49
10% Al-tobermorite (from kaolinite)	71	98	64	38
10% Al-tobermorite (from gibbsite)	72	91	60	42
10% Fe-tobermorite	33	92	32	43
10% Mg-tobermorite	30	102	31	44

* Intensity values are net peak heights in counts per second above background, as scaled from the x-ray diffractometer charts.

Fig. 1. X-ray Diffractometer Traces of Unsubstituted and Al-Substituted Tobermorites.

Fig. 2. X-ray Diffractometer Traces of Unsubstituted and 10% Substituted Tobermorites.

Figure 3. DTA Results for Tobermorite and Substituted Al-Tobermorites.

Figure 4. DTA Results for Tobermorite and for 10% Substituted Al-, Fe-, and Mg-Tobermorites.

Fig. 5. Infrared Absorption Spectra of Unsubstituted and 10% Substituted Tobermorites.

Fig. 6. Shift of Infrared Absorption Band at 1207 cm^{-1} with Increasing Al-Substitution.