

## SYNTHETIC CUSPIDINE

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## ABSTRACT

Cuspidine ( $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2$ ) can be synthesized hydrothermally, from crystallizing melts, and by solid state reactions. Efforts to substitute hydroxyl for fluoride ions in the cuspidine structure were not successful, and this suggested that custerite,  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{Ca}(\text{F},\text{OH})_2$  may not exist as a mineral. Synthetic cuspidine is monoclinic, optically positive with indices of refraction of  $\alpha=1.591$ ,  $\beta=1.596$ , and  $\gamma=1.602$  ( $\pm .003$ ). The extinction angle measured from the  $c$  axis is  $7^\circ$ . The specific gravity was determined as 3.05. Cuspidine melts congruently at approximately  $1410^\circ\text{C}$ . at atmospheric pressure. On prolonged heating cuspidine alters to  $\gamma\text{-}2\text{CaO} \cdot \text{SiO}_2$  with the escape of silicon tetrafluoride. Powder  $x$ -ray data, a differential thermal curve and an infrared spectrogram are given.

## INTRODUCTION

Cuspidine ( $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2$ ) was obtained as a hydrothermal reaction product in experiments designed to substitute fluoride for hydroxyl ions in a calcium hydro-garnet. The optical properties of this synthetic cuspidine corresponded to the natural mineral described by Scacchi in 1876. The material was found in ejected blocks of metamorphosed limestone at Vesuvius [1]. The natural crystals had a characteristic spear-shape and were referred to by Scacchi as *cuspidis*, the Latin word for spear, hence the name cuspidine. Figure 1 shows natural cuspidine crystals from Vesuvius having the characteristic spear outline. Cuspidine has been synthesized by V. V. Lapin [2] in 1944, who identified the material from reaction products formed in electric welding slags; by C. E. Tilley [3] in 1947, who sintered  $\text{CaCO}_3$ ,  $\text{SiO}_2$  and excess  $\text{CaF}_2$  at  $1140^\circ\text{C}$ .; and by McCaughey, Kautz and Wells [4] in 1948, from melts consisting of  $\text{CaO}$ ,  $\text{CaF}_2$  and  $\text{SiO}_2$ .

In 1913 Umpleby, Schaller and Larsen [5] described a mineral with essentially the same composition as cuspidine except that it contained some hydroxyl groups, and they named the mineral custerite. The optical indices reported for custerite were significantly lower than those found for cuspidine, and this seemed strange, for it is well-known with silicates that the indices of refraction increase when a hydroxyl replaces a fluoride ion. Tilley [3], in his excellent work on cuspidine, seriously doubted the existence of a hydroxyl-bearing cuspidine (custerite) as described by Umpleby et al., and he showed quite conclusively from  $x$ -ray, optical and chemical data that cuspidine and custerite were one and the same mineral. Through the courtesy of Dr. George Switzer of the U. S. National Museum, the authors obtained a specimen of custerite from Custer County, Idaho, and found that it had essentially the same  $x$ -ray

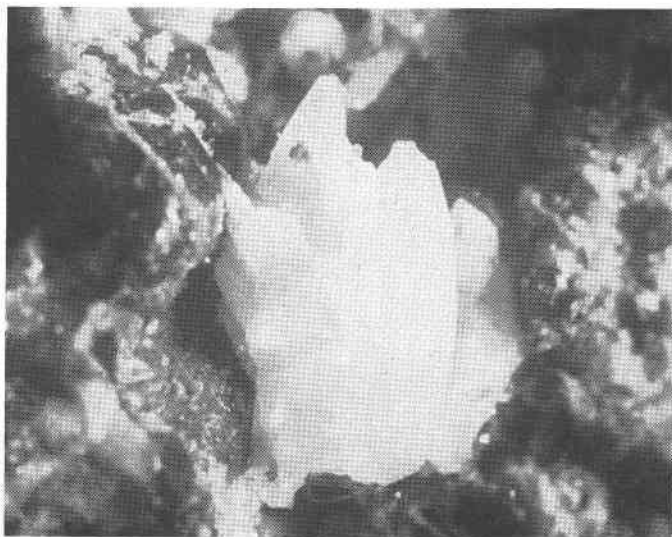


FIG. 1. Natural cuspidine from Vesuvius. Magnification 50X.

and optical properties as cuspidine. Since no one had attempted experimentally to replace fluorine by hydroxyl in the cuspidine structure, it was decided to study the hydrothermal reactions of mixes corresponding to cuspidine, with and without fluorine. The investigation was carried on at the National Bureau of Standards as part of a larger program of fluorine substitution in hydroxyl silicates under the sponsorship of the Office of Naval Research.

#### EXPERIMENTAL WORK

##### *Crystallizations from Melt*

Cuspidine can be readily synthesized from a melt having the composition in weight per cent of  $\text{CaO} = 45.9$ ,  $\text{SiO}_2 = 32.8$  and  $\text{CaF}_2 = 21.3$ . This composition corresponds to the formula proportions and it melts congruently under a vapor pressure of fluorine. Platinum crucibles were used in all experiments to avoid contamination of the charge as fluoride melts are quite corrosive with refractory materials. For practical considerations cuspidine can be crystallized from a melt in air, as the vapor pressure of the fluorine melt is quite low at elevated temperatures. Usually a platinum cover is placed over the crucible to lessen the escape of volatile constituents. Synthetic cuspidine melts at  $1410^\circ \text{C.} \pm 10^\circ$  as determined by the well-known quench technique. A variation of this technique was employed to obtain reproducible results. The quench technique requires

the use of small samples of 0.1 gram or less to ensure quick freezing when the sample is dropped from the furnace into the quenching medium. This technique does not work well when a volatile constituent is present, as slight losses greatly change the bulk composition of small samples. Consequently, large errors are introduced in determining the melting temperature. With the use of large samples of a gram, or more, one can minimize this difficulty and slight losses do not appear to alter the bulk composition. The quenching of a large sample, however, will not produce uniform conditions of freezing within the charge. For example, a melt

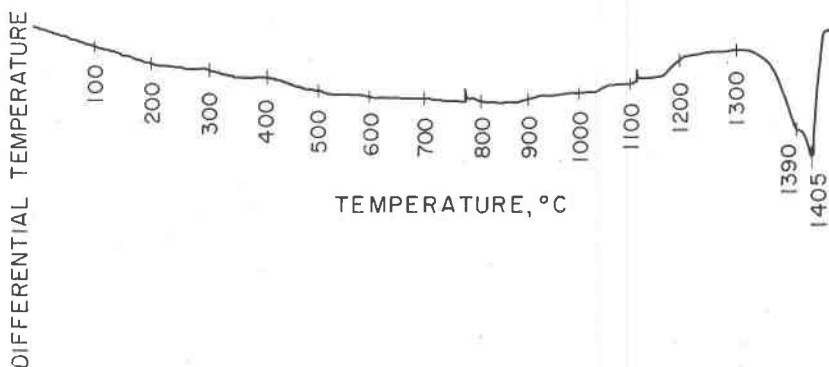


FIG. 2. Differential thermal curve of synthetic cuspidine.

when quenched will form a glass at the interface of the container and the glass will grade to crystalline material towards the center, where cooling is slower. Quenching at successively lower temperatures will decrease the proportion of glass to crystalline material, and by carefully analyzing the frozen surface adjacent to the container wall by means of a petrographic microscope, one can establish the temperature of crystallization within one or two degrees centigrade.

A differential thermal analysis of synthetic cuspidine crystallized from a melt was made to determine the possible existence of high temperature polymorphic forms. Figure 2 is the differential thermal curve which was made at a heating rate of 12° per minute in a conventional apparatus. The temperatures indicated in this figure and elsewhere are all given in degrees centigrade. There is no indication of a phase change occurring before the endothermic break at 1405°, which agrees satisfactorily with the melting temperature obtained by quenching.

Figure 3 is an infrared transmission spectrogram of synthetic cuspidine crystallized from a melt. The spectrogram was made by pressing powdered cuspidine with powdered potassium bromide into a clear

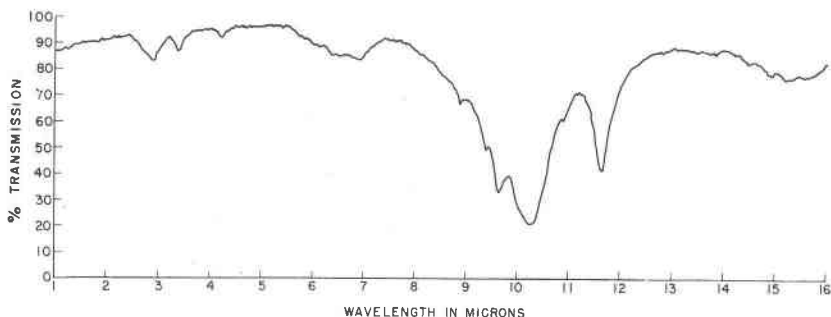


FIG. 3. Infrared spectrogram of synthetic cuspidine.

transparent pellet. The scanning instrument was a double beam spectrometer. The major absorption peak occurs at a wavelength of 10.3 microns and it is attributed to the stretching moments of the Si-O bonds. The second absorption peak occurring at 11.7 microns has not been identified.

#### *Hydrothermal Synthesis*

A series of hydrothermal experiments were made to synthesize cuspidine in the presence of water vapor to determine the possibility of substituting hydroxyl for fluoride ions. The apparatus used in these experiments was of the "cold seal type" developed by personnel of the Geophysical Laboratory. The reaction products were identified by *x*-ray and microscopic techniques. The raw batch materials consisted of calcium carbonate, silicic acid and calcium fluoride of reagent grade compounded in formula proportions. Compositions corresponding to cuspidine were prepared by mixing and grinding together the above constituents in stoichiometric proportions. Cuspidine has the molar ratio of Ca:Si:F=8:4:4. The ratios were 8:4:4, 8:4:3, 8:4:2, 8:4:1, and 8:4:0, with the last being equivalent to a hypothetical hydrous end member of the series. These mixtures were treated in the presence of five to ten per cent of water in sealed platinum capsules at temperatures from 500° to 700° C. at 20,000 psi. The experiments lasted from 3 to 7 days. The results are summarized in Table 1. The major phase in compositions 8:4:4, 8:4:3, and 8:4:2 was cuspidine with secondary phases of  $\beta$ -CaO·SiO<sub>2</sub> and 6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O. Small amounts of calcite were observed in the composition 8:4:2 at 500° and 600°C. and probably represent uncombined material. The major phase in composition 8:4:1 was 6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O with cuspidine next in abundance. Small amounts of CaF<sub>2</sub> were also observed in this composition. In composition 8:4:0 the compound 6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O constituted the major phase with minor amounts of  $\gamma$ -2CaO·SiO<sub>2</sub> present. It was observed that when the fluorine

content of the batches was reduced, as in compositions 8:4:3, 8:4:2 and 8:4:1, there was a reduction in the amount of cuspidine and  $\beta$ -CaO·SiO<sub>2</sub> and a corresponding increase in the amounts of 6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O. A synthetic cuspidine prepared from a melt, when treated at 800° C. and 20,000 psi in the presence of water vapor for four days, produced a large percentage of CaO·SiO<sub>2</sub> and CaF<sub>2</sub>. This indicates that the upper hydrothermal stability range is near 800° C. at 20,000 psi. In all the experi-

TABLE 1. HYDROTHERMAL CUSPIDINE EXPERIMENTS AT  
20,000 PSI FOR 3-7 DAYS

Composition Ca:Si:F	Temperatures		
	500°	600°	700°
8:4:4	<u>Cuspidine*</u> $\beta$ CaO·SiO <sub>2</sub> 6CaO·3SiO <sub>2</sub> ·2H <sub>2</sub> O	<u>Cuspidine</u> $\beta$ CaO·SiO <sub>2</sub>	<u>Cuspidine</u> $\beta$ CaO·SiO <sub>2</sub>
8:4:3	<u>Cuspidine</u> $\beta$ CaO·SiO <sub>2</sub> 6CaO·3SiO <sub>2</sub> ·2H <sub>2</sub> O	<u>Cuspidine</u> $\beta$ CaO·SiO <sub>2</sub>	<u>Cuspidine</u> $\beta$ CaO·SiO <sub>2</sub>
8:4:2	<u>Cuspidine</u> $\beta$ CaO·SiO <sub>2</sub> CaCO <sub>3</sub>	<u>Cuspidine</u> $\beta$ CaO·SiO <sub>2</sub> CaCO <sub>3</sub>	<u>Cuspidine</u> $\beta$ CaO·SiO <sub>2</sub> 6CaO·3SiO <sub>2</sub> ·2H <sub>2</sub> O
8:4:1	<u>6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O</u> Unidentified Phase CaF <sub>2</sub>	<u>6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O</u> Cuspidine $\beta$ CaO·SiO <sub>2</sub> CaF <sub>2</sub>	<u>6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O</u> Cuspidine CaF <sub>2</sub>
8:4:0	<u>6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O</u> $\gamma$ -2CaO·SiO <sub>2</sub>	<u>6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O</u> $\gamma$ -2CaO·SiO <sub>2</sub>	<u>6CaO·3SiO<sub>2</sub>·2H<sub>2</sub>O</u> $\gamma$ -2CaO·SiO <sub>2</sub>

\* Underlined item indicates major phase.

ments where cuspidine formed in the presence of water vapor, the x-ray powder patterns and the indices of refraction for this compound remained constant and were identical to cuspidine crystallized from melts. These results appear to confirm Tilley's observations that hydroxyl groups are not a constituent part of the cuspidine structure; and the authors wish to join with him in discrediting the mineral name custerite, and they suggest the name be dropped from the literature.

#### Solid State Synthesis

Three compositions, 8:4:4, 8:4:3, and 8:4:2, were heated in a crimped platinum envelope in the absence of water at 1000° C. and

atmospheric pressure for 22 days. Solid state reactions occurred. The 8:4:4 composition resulted in the formation of cuspidine with minor amounts of  $\beta$ -CaO·SiO<sub>2</sub> and  $\gamma$ -2CaO·SiO<sub>2</sub>. Decreasing the amount of fluorine in these experiments resulted in increased formation of  $\gamma$ -2CaO·SiO<sub>2</sub>. Cuspidine was also synthesized by solid state reactions using a hot press technique. The raw ingredients were first compressed into a wafer of about 1" in diameter by  $\frac{1}{4}$ " thick. The wafer was then placed between two opposing carbon pistons enclosed in a carbon cylinder. Heat was obtained by the internal electrical resistance of the carbon cylinder. Cuspidine formed readily at 900° C. and 2,000 psi when left for  $\frac{1}{2}$  hour. At 1150° C. and 2,000 psi, the cuspidine batch extruded along the cylinder walls acting as if it were a fluid phase. When synthetic cuspidine is heated in air at 1200° C. for 12 hours or longer, it is converted into fine polycrystalline aggregates of  $\gamma$ -2CaO·SiO<sub>2</sub>.

#### PROPERTIES OF SYNTHETIC CUSPIDINE

The optical properties of the synthetic cuspidine were measured by oil immersion techniques on crystals grown hydrothermally, from melts, and by solid state reactions. The mineral has monoclinic symmetry and is biaxially positive in character. The extinction angle, measured from the *c* axis, is about 7°. The indices of refraction are  $\alpha=1.591$ ,  $\beta=1.595$  and  $\gamma=1.602 \pm 0.003$ . The optic angle  $2V=76^\circ$  (estimated).

Density measurements were made on a Berman Torsion Balance using toluene as the immersing medium, and an average value of  $3.05 \text{ g/cm}^3 \pm 1\%$  was obtained. This was thought to be high as the values reported in the literature were 2.9 or less. To check the accuracy of the density measurement against other known constants of cuspidine, the principle of Gladstone and Dale was employed. This principle is stated in the formula  $K=n-1/d$ , where  $n$ =mean index of refraction,  $d$ =density and  $K$ =the specific refraction of any substance.  $K$  was calculated for cuspidine from Larsen and Berman's table of specific refraction of the chief constituents of minerals [6]. Cuspidine's mean index of refraction was calculated using  $d=3.05$  and it was found to be 1.596, which is the same as the observed value of 1.596. If the value 2.9 is used for  $d$ , the mean index is found to be 1.586. The principle of Gladstone and Dale is an excellent tool for checking the accuracy of optical data and densities when the formula of a compound is known. The recent article by Jaffe [7] is an excellent example of the usefulness of this principle.

Table 2 contains the *x*-ray powder pattern data obtained from synthetic cuspidine made from a crystallizing melt. For comparison a natural cuspidine from Monte Somma, Italy, has been included. The patterns were made on an *x*-ray diffractometer using copper K $_{\alpha}$  radiation.

TABLE 2. CUSPIDINE

NBS Synthetic		Specimen from Monte Somma, Italy	
<i>d</i>	I	<i>d</i>	I
A	—	A	
—	—	10.11	13
7.36	4	7.36	9
7.11	3	7.12	3
5.27	3	5.28	3
5.13 <sup>d</sup>	4	5.14 <sup>d</sup>	4
4.62 <sup>d</sup>	3	4.62 <sup>d</sup>	1
4.55 <sup>d</sup>	3	4.55 <sup>d</sup>	4
4.23	3	4.23	3
3.68	7	3.68	9
3.42	4	3.43	4
3.361	21	3.363	14
3.257	7	3.259	32
3.064	100	3.062	100
—	—	3.034	26
2.944	16	2.943	37
2.930	14	—	—
2.898	17	2.900	28
2.871	40	2.873	29
2.819 <sup>d</sup>	4	—	—
2.568	4	2.569	6
2.550	7	2.550	7
2.520	1	2.521	4
2.493	8	2.493	8
2.477	<1	2.479	4
2.452	4	2.451	3
2.435	<1	2.435	<1
2.420	<1	2.421	2
2.307	8	2.307	6
2.292	14	2.289	10
2.159	3	2.158	3
2.089	3	2.089	4
2.063	8	2.063	9
2.047	7	2.047	7
2.016	16	2.018	17
1.995	4	1.994	4
1.985	4	1.984	4
1.959	1	1.959	8
1.884	27	1.883	9
1.832	7	1.832	14
1.821	10	1.821	11
1.809	6	1.809	8
1.787	3	1.787	3
1.770	1	1.770	2
1.733	7	1.733	11
1.691	3	1.691	4
1.658	1	1.658	3

<sup>d</sup> Indicates diffused.

TABLE 3. VALUES OF DIELECTRIC CONSTANT (K) AND THE QUALITY FACTOR (Q) WITH TEMPERATURE AT 1 MEGACYCLE

° C.	K	Q
25	5.8	160
50	5.8	400
75	5.8	310
100	5.9	270
125	5.9	210
150	5.9	170
200	6.0	110
300	6.3	53
400	6.7	19
500	7.3	10

Preliminary work on the electrical properties of synthetic cuspidine formed by solid state reactions indicate that the dielectric constant K increases with a rise in temperature, while the quality factor Q decreases. It was also found that with increasing frequency Q and K decrease in value. Table 3 gives the variation of K and Q at one megacycle with temperatures up to 500° C. The test specimen was not previously dried and the low Q value of 160 at 25° C. is probably the result of moisture contaminating the specimen surfaces.

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