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FORMATION OF MULLITE, TOPAZ AND CORUNDUM

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ABSTRACT

The influence of aluminium fluoride on the thermal behavior of quartz and the formation of topaz, mullite and corundum have been examined in the present work using the derivatograph. The products of sintering were identified microscopically and by using a Siemens Crystalloflex diffractometer. The DTA curves indicate the formation of topaz at 760°C and the formation of mullite at 1000°C using the theoretical amount of aluminium fluoride. The reaction between quartz and aluminium fluoride takes place in two distinct steps using 50% excess of aluminium fluoride. The first is marked by a large endothermic peak at 780°C, representing the formation of topaz and the second by a sharp endothermic peak at 960°C, representing its subsequent dissociation with the formation of corundum or alpha-aluminium oxide.

INTRODUCTION

It is well known that silica has three important modifications: quartz, tridymite and cristobalite. All three have two enantiotropic modifications alpha and beta. Beta-quartz is stable from ordinary temperature up to 573 to 870°C, alpha-tridymite from 870 to 1470°C, and alpha-cristobalite from 1470 to 1713°C. The inversion of beta-quartz to the alpha-form takes place at 573°C and is indicated by an endothermic peak on the DTA curve[3,4,6,8,9]. This inversion is independent of the condition of formation of the quartz crystal [3].

Little is known about the effect of aluminium fluoride on the thermal behavior of quartz and the products of its sintering. It is reported that the reaction of silica with aluminium fluoride takes place through an intermediate product of aluminium silicon fluoride in the temperature range from 600 to 900°C and that this intermediate decomposes to alpha-aluminium oxide and silicon tetrafluoride. A small exothermic peak at 510°C and an endothermic one at 880°C were observed on the DTA heating curve. The exothermic peak at 510°C may correspond to the formation of the aluminium silicon fluoride complex and the effect at 880°C may be its dissociation[1,5,7,10,11].

The present work includes a detailed study of differential thermal analysis and

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a thermogravimetric investigation of the effect of aluminium fluoride on the thermal behaviour of quartz under different conditions together with a study of the products of its sintering, namely, mullite, topaz and alpha-aluminium oxide.

EXPERIMENTAL

This work was carried out with quartz crystals, having X-ray powder diffraction data which agreed with those given in the ASTM index.

Starting materials

Starting materials usually consisted of quartz mixes. Quartz crystals were crushed in a percussion mortar and the product passed through an 80 mesh sieve. The powder was boiled with concentrated hydrochloric acid to remove iron and other impurities and then washed with hot water by decantation until free from acid. The resultant powder was dried at red heat in a silica crucible. Its purity was tested by evaporation of 1 g with 30 ml of 40% hydrofluoric acid and 0.5 ml concentrated sulphuric acid in a platinum crucible and then heat treatment to 900°C (ref. 14).

Quartz powder and aluminium fluoride in particular amounts were mixed together. Mixes were processed by repeated grinding in an automated agate mortar followed by sieving until all the powder passed through a 325 mesh sieve. The mixes were then ground with a pestle and mortar for 1 h to achieve homogenity.

Apparatus

Experiments were carried out using platinum crucibles, heated in an electrical furnace with the removal of the evolved silicon tetrafluoride which resulted from the reaction. The temperature was regulated automatically with an accuracy of ± 5°C.

The thermal investigation of the sintering of quartz with aluminium fluoride was studied by using the MOM derivatograph[12,13]. This apparatus records simultaneously four curves; the change of temperature of the sample (T), differential thermal analysis (DTA), thermogravimetric analysis (TG) quantitatively in mg and the derivative thermogravimetric curve (DTG) on a single sample under controlled conditions.

The parameters during the test were as follows: Platinum crucible, medium size; inert material, aluminium oxide. Weight of mix ranges from 0.5 to 1 g; temperature range, ambient up to 1200°C; sensitivity of DTA circuit, 1/3, 1/5; sensitivity of DTG circuit, 1/10; weight used in TG curve, 100–500 mg; heating rate, 10°C min^{-1}. The DTA and temperature measuring thermocouples were Pt–Pt/Rh wires. The atmosphere was air and the volatile silicon tetrafluoride was removed as formed.

Phase identification

X-Ray procedure. The phases of the products of quartz sintering with aluminium fluoride were identified both microscopically and by X-ray analysis using a Siemens

Crystalloflex diffractometer. Nickel filtered copper radiation was used. Exposure was one hour.

RESULTS AND DISCUSSION

For studying the influence of aluminium fluoride on the thermal behaviour of quartz and the products of its sintering, DTA experiments were carried out using different amounts of aluminium fluoride, ranging from 100 to 150% of the theoretical value. The derivatograms obtained were evaluated on the basis of literature data[1–9,15,17] which were also repeated experimentally in order to explain the reactions which may be connected to certain peaks on the DTA curves.

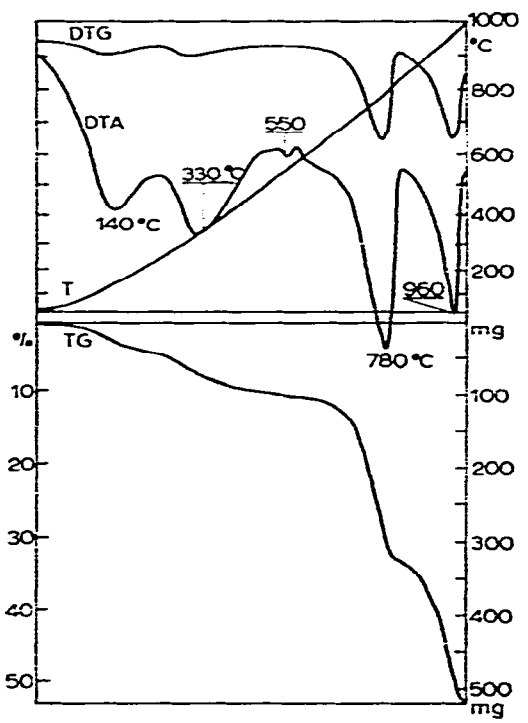

Fig. 1. Derivatogram of quartz sintering with aluminium fluoride using 150% of theoretical value. Weight of sample 1000 mg. Heating rate 10 °C min^{-1}. DTA-1/5.

Using 150% of the theoretical amount of aluminium fluoride

The derivatogram of quartz mix with 150% of the theoretical amount of aluminium fluoride is shown in Fig. 1. The first two wide endothermic peaks at 140 and 330°C are in good agreement with the thermal data of aluminium fluoride, representing its dehydration[1]. The weight of the sample continuously decreases during the test (TG), probably due to sublimation. The small endothermic peak at 550°C represents the transition of beta-quartz to the alpha-form and the beginning of the reaction between quartz and aluminium fluoride. The large and sharp endothermic

peak at 780°C indicates the formation of topaz. The process is connected with a remarkable decrease in weight (TG curves) due to the volatilization of silicon in the form of silicon tetrafluoride. The fifth endothermic peak at 960°C is large and sharp and represents the formation of alpha-aluminium oxide or corundum. This is accompanied by a sharp decrease of the sample weight due to the removal of silicon tetrafluoride and the loss of constitutional OH radicals.

The results obtained are consistent with the literature of the thermal behaviour of topaz as it looses silicon tetrafluoride at 827°C and at 960°C, aluminium oxide is formed and the character of the curve of weight loss is similar to that in Fig. 1[2,15,17].

The products of runs at 550, 780 and 960°C were identified both microscopically and by X-ray diffraction. By microscopic examination of thin sections of these products it is observed that a few topaz grains appear in the run at 550°C, representing the beginning of the sintering reaction between quartz and aluminium fluoride. At 780°C, the product consists mainly of topaz grains with few quartz grains and an excess of aluminium fluoride. The product obtained at 960°C consists mainly of corundum and aluminium fluoride with few topaz grains.

The X-ray powder diffraction patterns of these products are shown in Fig. 2 (A, B, and C at 550, 780 and 960°C, respectively). No peaks of aluminium silicon fluoride have been detected as reported earlier[5,7]. Topaz is present in large amounts in the run at 780°C and its peaks have completely disappeared in the run at 960°C.

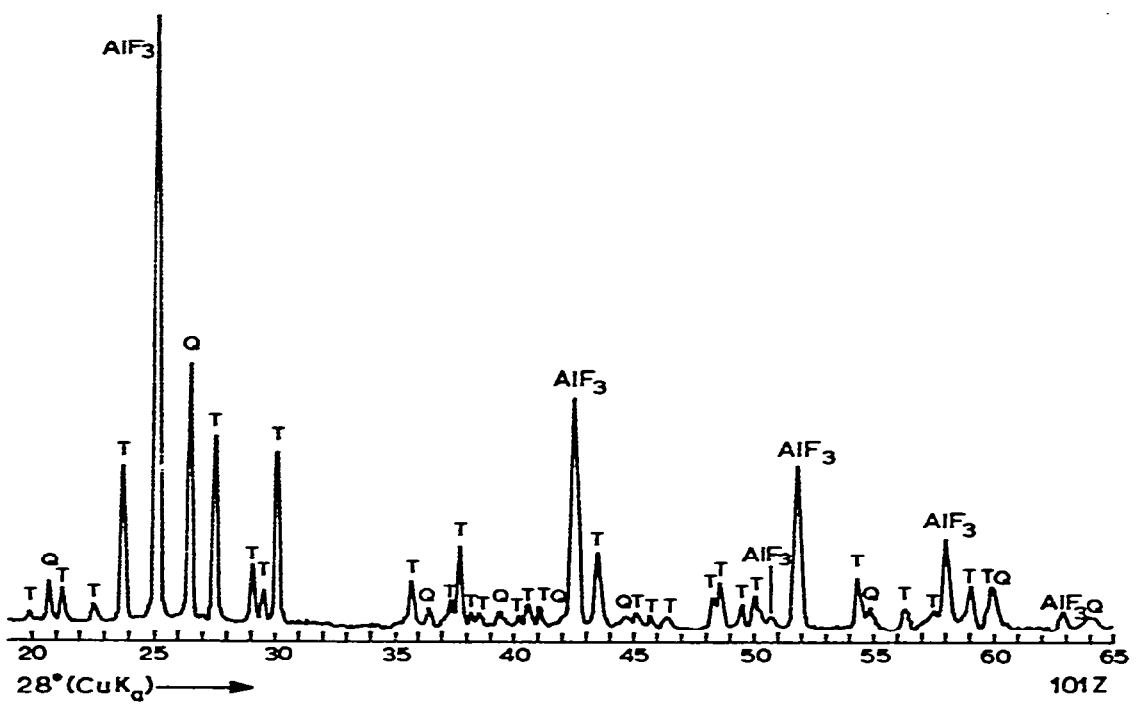

Fig. 2A

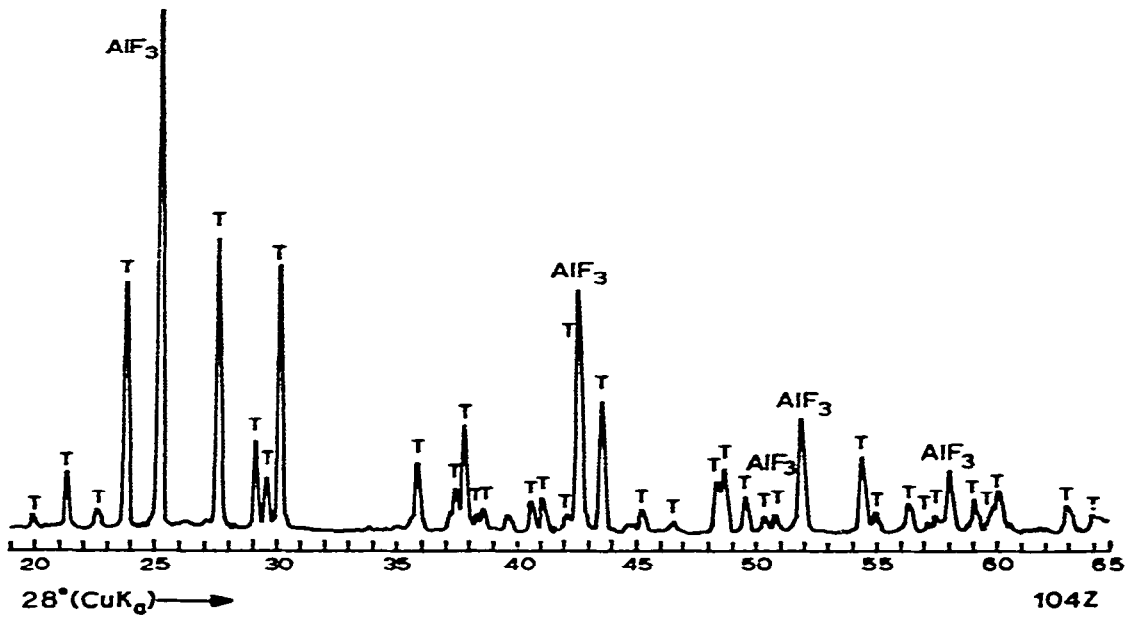

Fig. 2B

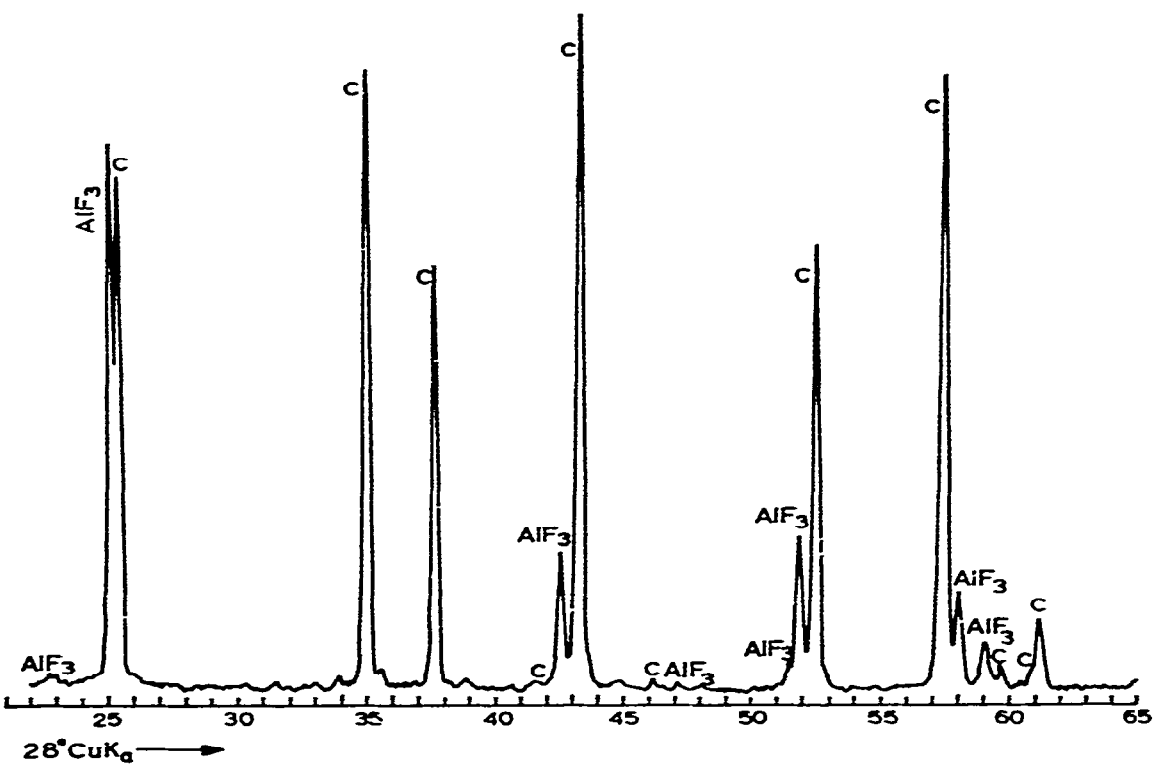

Fig. 2. X-ray powder diffraction patterns of quartz sintering with aluminium fluoride using 150% of theoretical value (A), (B), and (C) at temperatures 550, 780, and 960° C,respectively. T = topaz, C = corundum and Q = quartz.

The microscopic study of the products of quartz sintering with aluminium fluoride is well consistent with their X-ray powder diffraction patterns. No mullite was detected in this study.

Using the theoretical amount of aluminium fluoride

The derivatogram of quartz mixed with the theoretical amount of aluminium fluoride is shown in Fig. 3. The first two endothermic peaks at 70 and 310 °C represent the dehydration of aluminium fluoride. The small endothermic peak at 480 °C may be connected with its transition to another form. The temperature of transition of aluminium fluoride has been previously recorded[16] as 460 °C and the crystal structure is not firmly established. The second small endothermic peak at 560 °C indicates the transition of quartz. The endothermic peak at 760 °C is large and sharp and represents the formation of topaz. This is accompanied by a considerable decrease in weight due to the volatilization of silicon tetrafluoride. The sharp endothermic peak at 1000 °C represents the formation of mullite.

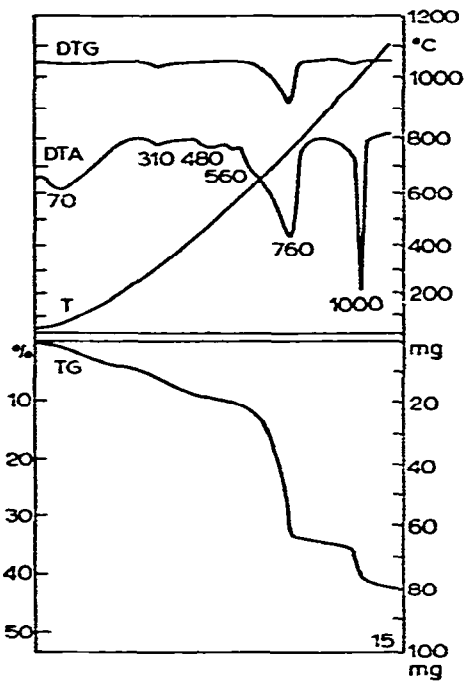

Fig. 3. Derivatogram of quartz sintering with theoretical amount of aluminium fluoride. Weight of sample 184 mg. Heating rate 10 °C min^{-1}. DTA-1/3.

The product of the run at 560 °C consists mainly of quartz with a few grains of topaz. At 760 °C, topaz constitutes the major component of the sintering product with a few quartz grains. The end product at 1000 °C consists mostly of mullite with a few quartz grains. The presence of quartz grains shows that the reaction is not complete.

The X-ray powder diffraction pattern of the end product at 1000 °C is shown in

Fig. 4. The peaks of mullite are well defined and intense. This is in good agreement with the microscopic study of its thin section. No peaks of aluminium silicon fluoride or alpha-aluminium oxide have been detected at any temperature, indicating their absence. Therefore, the products of sintering of quartz with the theoretical amount of aluminium fluoride at 760 and 1000 °C are topaz and mullite, respectively. The end product of sintering is mullite due to the deficiency of fluoride ion.

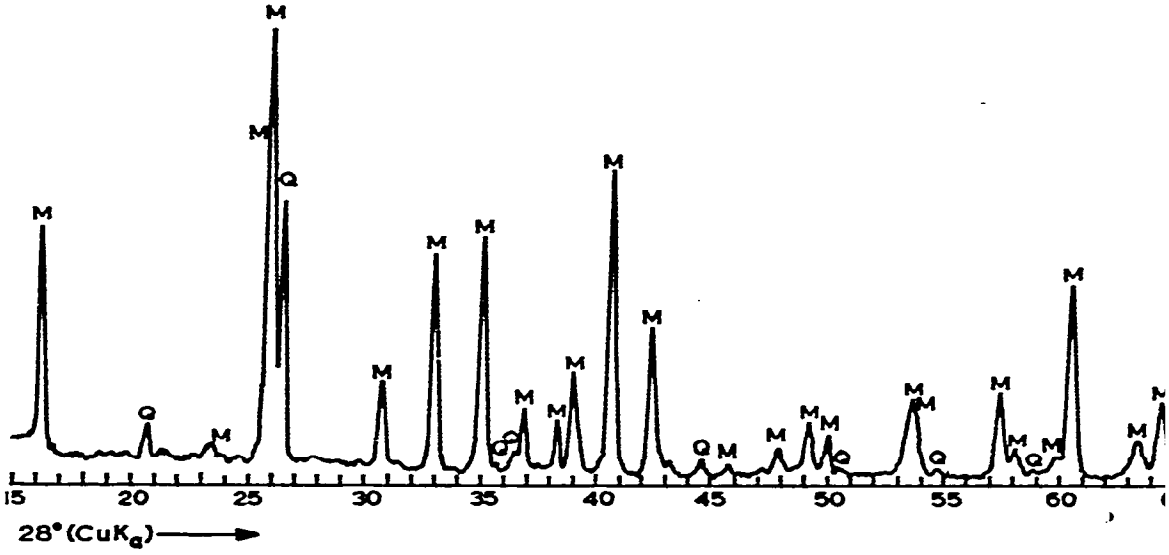

Fig. 4. X-raypowder diffraction pattern of the product of quartz sintering with theoretical amount of aluminium fluoride at 1000 °C. M = mullite and Q = quartz.

Using aluminium fluoride in amount 125% of theoretical value

The derivatogram of quartz mixed with aluminium fluoride in amount 125% of theoretical value shows similar peaks at the same temperature as that obtained by using 150% aluminium fluoride but here both topaz and mullite have been identified microscopically in the products of sintering at 780 °C. The X-ray powder diffraction pattern of such product (Fig. 5) shows the presence of both mullite and topaz. At the higher temperature 960 °C, corundum grains have been detected in the sintering product with some mullite and topaz grains (Fig. 6).

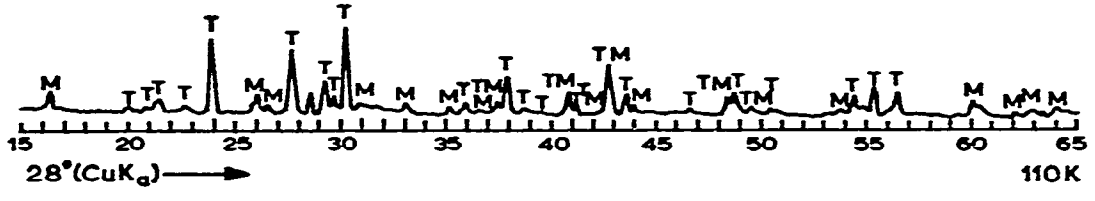

Fig. 5. X-ray powder diffraction pattern of product of sintering of quartz with aluminium fluoride using 125% of theoretical value at 780 °C. M = mullite and T = topaz.

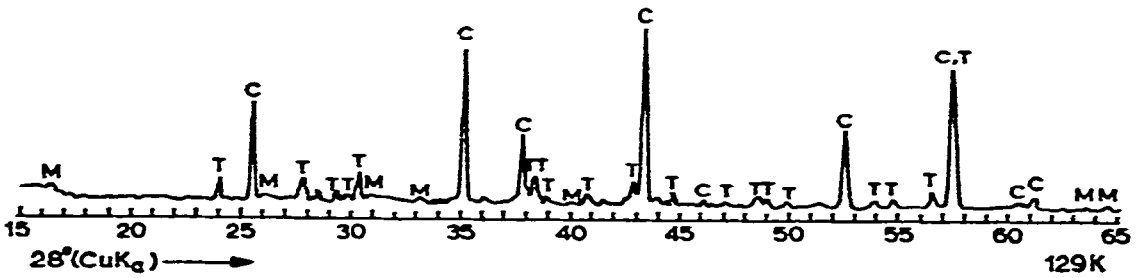

Fig. 6. X-ray powder diffraction pattern of the product of quartz sintering with aluminium fluoride using 125% of theoretical value at 960°C. C = corundum, M = mullite and T = topaz.

In general, the X-ray peaks of the products of sintering of quartz with aluminium fluoride, namely, topaz, mullite and alpha-aluminium oxide or corundum are narrow and intense, suggesting good crystallinity. The X-ray data of these synthetic minerals are consistent with those of the corresponding natural minerals.

CONCLUSIONS

The thermal investigation of the sintering of quartz with aluminium fluoride in different amounts with the formation of topaz, mullite and corundum have been studied under different temperatures. The following conclusions can be drawn:

(1) The product of quartz sintering with the theoretical amount of aluminium fluoride at 760°C is composed of topaz and unreacted quartz. The endothermic peak at 1000°C represents the formation of mullite as an end product due to the deficiency of fluorine.

(2) Using an excess of aluminium fluoride (25%) upon sintering, mullite and topaz have been formed at 780°C. Corundum has been detected in the sintering product at 960°C, together with some mullite grains.

(3) Using an excess of aluminium fluoride (50%) upon sintering, no mullite grains have been detected in the reaction products. Topaz formation takes place intensively at 780°C by an endothermic reaction. It looses silicon tetrafluoride and OH radicals at 825°C. The endothermic peak at 960°C represents the decomposition of topaz, giving rise to alpha-aluminium oxide or corundum.

In general, aluminium silicon fluoride has not been detected in the sintering product as reported earlier.

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