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# Thermal analysis of topaz synthesis from kaolinite

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## Abstract

The present work represents a thermal analysis study of topaz synthesis from kaolinite by its sintering with aluminium fluoride using a derivatograph. Also, it includes the study of the influence of aluminium fluoride on the thermal behaviour of kaolinite. The products of sintering were identified microscopically and by using a Siemens Crystalloflex diffractometer.

The DTA and X-ray powder diffraction data show the beginning of the appearance of both topaz and mullite at 600°C and indicate that the reaction of kaolinite and aluminium fluoride of different amounts takes place in two distinct steps. The first is marked by a medium endothermic peak at 750–790°C, representing the intensive formation of topaz, and the second by a large and sharp or wide endothermic peak at 930–950°C, representing its subsequent dissociation with the formation of either mullite or (corundum and mullite) or corundum, depending on the amount of aluminium fluoride. This process is accompanied by a sharp decrease in weight, (TG curve), due to the volatilization of silicon tetrafluoride, water vapour and other gases.

The synthesized topaz is colourless in thin sections and crystallizes in orthorhombic system in the form of elongated prismatic crystals, with perfect basal (0 0 1) cleavage; it is optically positive. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Topaz synthesis; Derivatograph; ASTM; Kalabsha kaolinite

## 1. Introduction

Topaz  $\text{Al}_2(\text{SiO}_4)[\text{F}_{0.9}, (\text{OH})_{0.1}]_2$  is a characteristic mineral formed in pneumatolytic or hypothermal stages of igneous activity. It occurs chiefly in acid igneous rocks, such as granites, granite pegmatites and rhyolites. It is a common constituent of greisen, formed by fluorine-metasomatism. Minerals associated with topaz may include quartz, fluorite, tourmaline, beryl, cassiterite, muscovite and Li-minerals. Topaz is locally abundant as detrital grains in sedimentary rocks [1–4].

The synthesis of topaz is achieved by different methods [1,2,4–8]. These include, thermal hydrolysis of aluminium fluoride and silica or quartz at 750–

850°C, heating a mixture of sodium silicon fluoride, aluminium oxide and water at 500°C and pressure 4000 bar and sintering of kaolinite with ammonium fluoride at 750°C.

The present work represents a differential thermal analysis study of the synthesis of topaz by sintering kaolinite with aluminium fluoride using a derivatograph. Also, it includes the study of the influence of aluminium fluoride on the thermal behaviour of kaolinite under different conditions together with a study of the products of its sintering, namely, mullite, topaz and corundum.

The thermal behaviour of the starting materials, kaolinite and aluminium fluoride, is well known [2,5,6,9–12]. The DTA curve of kaolinite shows a

large and sharp endothermic peak between 530°C and 700°C, representing its dehydration and loss of constitutional OH groups and the decomposition of the structure. Also, it shows a sharp medium strong exothermic effect between 940°C and 1000°C, reflecting the crystallization of a spinel phase. The end products of decomposition may be mullite and cristoballite [6,9–11].

The fluorinating action of fluorine, fluorides and hydrogen fluoride are well known [2,5,6,8]. The solid fluorinating agents are very important since they have many advantages. 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°C to 900°C and which decomposes to alpha-aluminium oxide and silicon tetrafluoride [7]. The reaction of kaolinite with aluminium fluoride is reported to take place with the formation of mullite and topaz. Topaz loses silicon tetrafluoride at 827°C and liberates fluorine on heating to 850–900°C, and mullite is produced. The dissociation of topaz takes place at 960°C [2,4–6,12–14].

## 2. Experimental techniques

*Starting materials:* This research was carried out with kaolinite from the Kalabsha area near Aswan, Egypt; it was processed by the wet method: After degritting, the kaolinite fraction was washed many times with water by decantation until free from mineral impurities. The resultant kaolinite was filtered and dried. Its chemical composition is given in Table 1.

Table 1  
Chemical composition of Kalabsha kaolinite

Chemical component	Content (%)
SiO <sub>2</sub>	46.34
Al <sub>2</sub> O <sub>3</sub>	38.82
Fe <sub>2</sub> O <sub>3</sub>	00.18
FeO	00.10
MnO	00.00
TiO <sub>2</sub>	00.21
CaO	00.00
Na <sub>2</sub> O	00.04
H <sub>2</sub> O	14.26

The X-ray diffraction data of the processed Kalabsha kaolinite are consistent with the corresponding ASTM data of kaolinite. The pattern shows only the characteristic kaolinite peaks, which are sharp and intense, suggesting good crystallinity. No peaks of any mineral impurity were detected.

Starting materials were mixtures of kaolinite with aluminium fluoride in particular amounts. Mixes were processed by repeated grinding in an automated agate mortar followed by sieving until all the powder passed through a 200 mesh sieve. Finally, the mixtures were then ground with a pestle and mortar for 1 h to achieve homogeneity.

*Apparatus:* Heating experiments were carried out using platinum crucibles heated in an electrical furnace with the removal of the evolved silicon tetrafluoride and other gases which resulted from the reaction. The temperature was regulated automatically with an accuracy  $\pm 5^\circ\text{C}$ .

The thermal analysis study of synthesis of topaz by sintering of kaolinite with aluminium fluoride was conducted with the MOM derivatograph [15]. This apparatus records simultaneously four curves; the change of temperature of the sample ( $T$ ), differential thermal analysis (DTA), thermogravimetric analysis (TG) quantitatively in milligrams, 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 1000 mg, temperature range, ambient up to 1200°C; sensitivity of DTA circuit, 1/5; sensitivity of DTG circuit, 1/10; weight used in TG curve 500 mg; heating rate  $10^\circ\text{C min}^{-1}$ . The DTA and temperature measuring thermocouples were Pt–Pt/Rh wires. The atmosphere was air, and the volatile silicon tetrafluoride and other gases were removed as formed.

### 2.1. Phase identification

*X-ray procedure:* The phases of the reaction products of kaolinite sintering with aluminium fluoride were identified microscopically and by X-ray diffraction analyses using a Siemens Crystalloflex diffractometer. The finely ground sintered material was mixed with sodium chloride as a standard. Its peaks at  $2\theta = 31.38^\circ$  and  $45.44^\circ$  were used for corrections.

Nickel-filtered copper radiation was used. The sensitivity of the experiment was  $4 \times 10^4$  imp/min and the statistical error was 1.5%.

### 3. Results and discussion

Before studying the synthesis of topaz, the thermal behaviour of the starting materials, namely, kaolinite and aluminium fluoride was studied by DTA. The DTA curves obtained were evaluated on the basis of literature data [1,2,5–14].

The DTA curve of Kalabsha kaolinite (Fig. 1) shows the characteristic peaks of kaolinite [5,9–12]. The large and sharp endothermic peak at 575°C represents the dehydroxylation of kaolinite, and the TG curve shows the loss of constitutional OH groups. The large and sharp exothermic peak at 965°C represents the conversion of metakaolinite into the spinel phase and its crystallization.

The DTA curve of aluminium fluoride (Fig. 2) shows three large and sharp endothermic peaks and

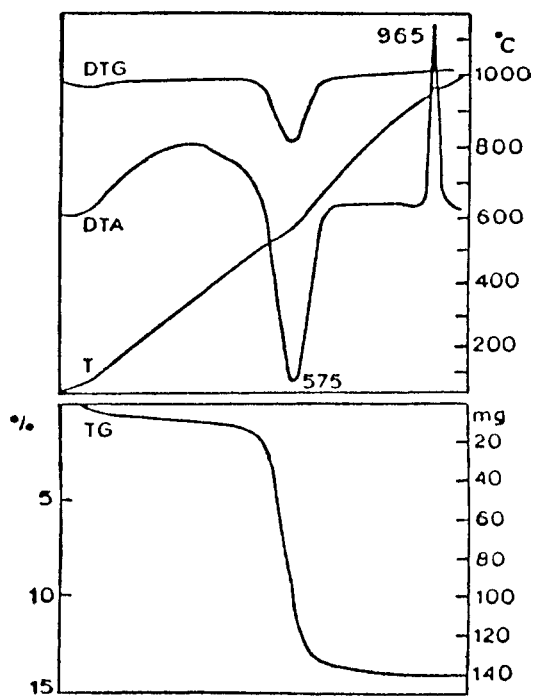


Fig. 1. DTA curve of Kalabsha kaolinite. Weight of sample 1000 mg. Heating rate 10°C/min.

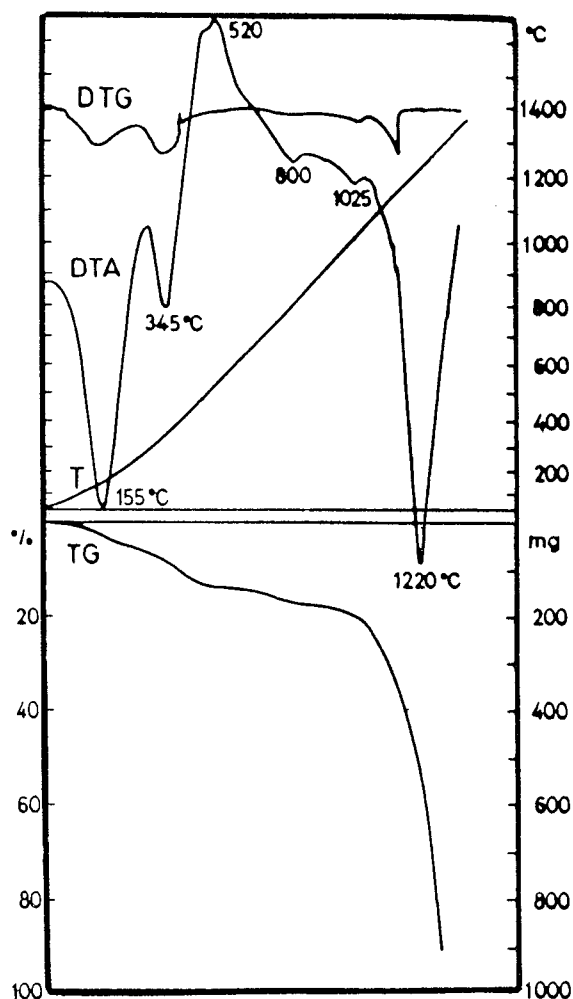


Fig. 2. DTA curve of aluminium fluoride. Weight of sample 1000 mg. Heating rate 10°C/min.

one exothermic peak. The endothermic peaks at 155°C and 354°C may represent the dehydration of aluminium fluoride. The weight of the sample decreases in two overlapping steps. The third endothermic peak is remarkably large and sharp, indicating sublimation of aluminium fluoride as represented by the large loss in weight (TG). The results obtained are consistent with literature data of the stability of aluminium fluoride at red heat and its sublimation at 1256°C without melting [9,16]. The process of sublimation takes place rapidly and implies large heat absorption as indicated by the relatively large peak area. The exothermic peak at 520°C represents some decomposition of aluminium

fluoride with the formation of alpha-aluminium oxide or corundum. The total loss of ignition of aluminium fluoride is about 80%. The end product of ignition is composed mainly of corundum with some aluminium fluoride.

For studying the synthesis of topaz by sintering of kaolinite with aluminium fluoride, DTA experiments were carried out using different amounts of aluminium fluoride. Mixtures of kaolinite and aluminium fluoride of ratios 1 : 0.5, 1 : 0.7, 1 : 1 and 1 : 1.3 are used. The DTA curves obtained were evaluated on the basis of literature data [1,2,4–8,12–14] to explain the reactions which may be connected to certain peaks on the DTA curves.

### 3.1. Using mixes of kaolinite and aluminium fluoride of ratio 1 : 1.3

The DTA curve of the kaolinite mix of ratio 1 : 1.3 is shown in Fig. 3. The first two wide and large endothermic peaks at 130°C and 320°C are in good agreement with the thermal data of aluminium fluoride, representing its dehydration. The weight of the sample continuously decreases during the test (TG),

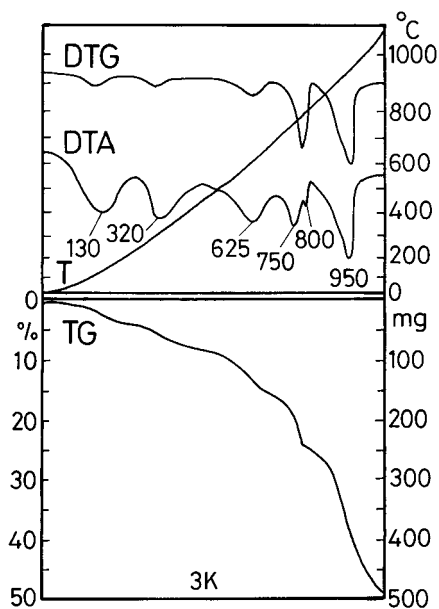


Fig. 3. DTA curve of synthesis of topaz using kaolinite-aluminium fluoride mix of ratio 1 : 1.3. Weight of sample 1000 mg. Heating rate 10°C/min.

probably due to sublimation. The wide endothermic peak at 625°C represents the dehydration of kaolinite and its reaction with aluminium fluoride with the formation of topaz and mullite. The medium and sharp endothermic peak at 750°C represents the intensive formation of topaz. The process is connected with a remarkable decrease in weight (TG curve) due to the volatilization of silicon in the form of silicon tetrafluoride and the loss of constitutional OH groups. The very small endothermic peak at 800°C represents the property of topaz to lose silicon tetrafluoride. The fifth endothermic peak at 950°C is large and sharp and represents the dissociation of topaz and its desilication in presence of excess aluminium fluoride with the formation of corundum or alpha-aluminium oxide. This is accompanied by a sharp decrease of the sample weight due to the removal of silicon tetrafluoride and the loss of constitutional OH groups and other gases.

The results obtained are consistent with the literature data of the thermal behaviour of topaz [2,4,7,12] as it loses silicon tetrafluoride at 827°C and its decomposition to corundum takes place at 950°C and the character of the curve of weight loss is similar to that in Fig. 3.

The products of the runs at 600°C, 750°C, 950°C and 1000°C were identified microscopically and by X-ray diffraction. By microscopic examination of thin sections of these products, it is observed that topaz with aluminium fluoride constitute the main composition of the product at 600°C with a few mullite grains. This represents the beginning of the reaction between kaolinite and aluminium fluoride. At 750°C, the product consists mainly of topaz with very few mullite grains and an excess of aluminium fluoride. The product obtained at 950°C is composed mainly of corundum with a few topaz and mullite grains. At 1000°C, corundum constitutes the total composition of the end product.

The X-ray diffraction patterns of these products are shown in Fig. 4A–D at 600°C, 750°C, 950°C and 1000°C respectively. The product at 600°C is composed mainly of topaz with some mullite. Topaz constitutes the total composition of the product at 750°C and its peaks have completely disappeared in the run at 950°C. Corundum constitutes the main composition of the run product at 950°C and the total composition of the end product at 1000°C with excess of aluminium fluoride.

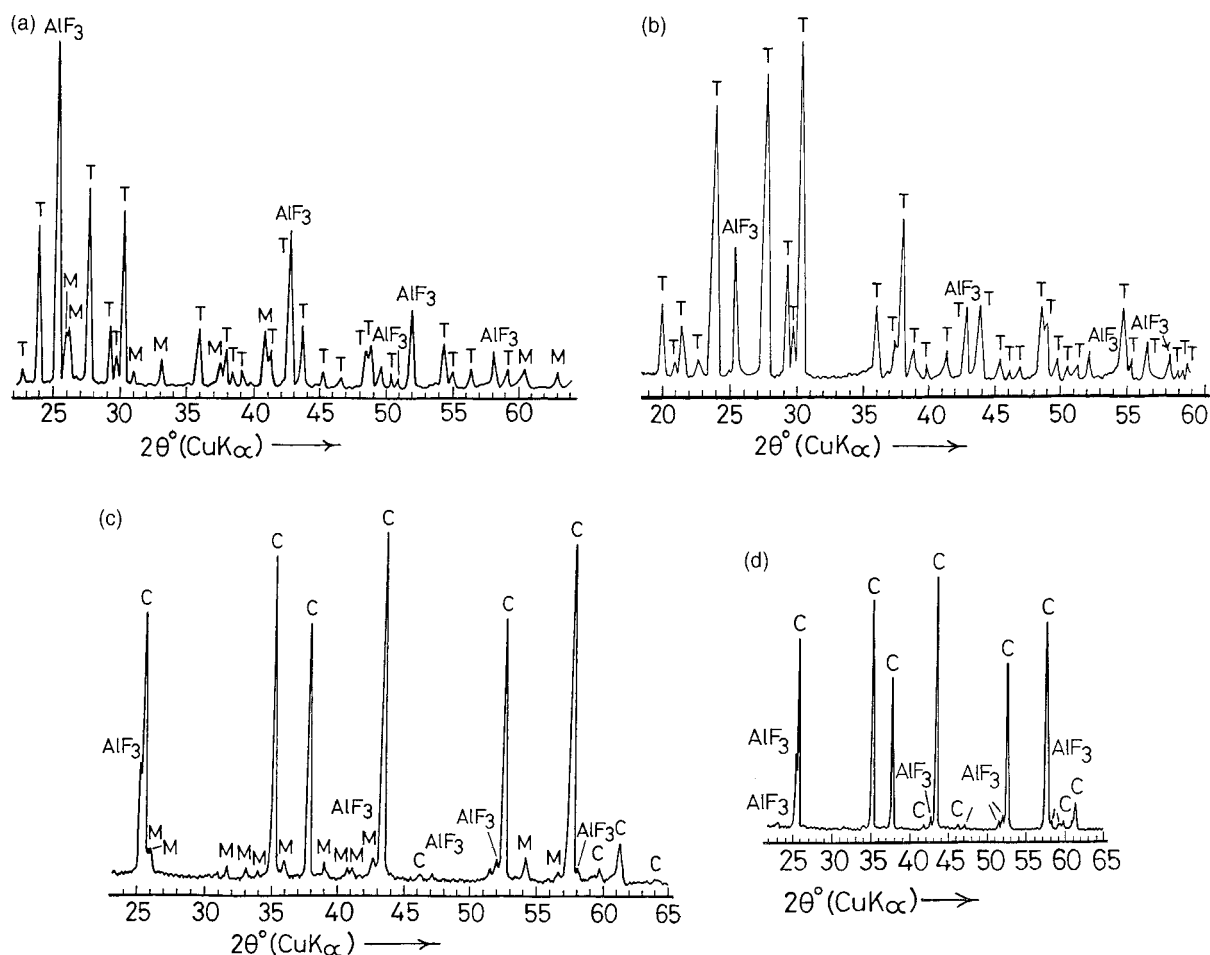


Fig. 4. X-ray diffraction patterns of the products of synthesis of topaz using kaolinite–aluminium fluoride mix of ratio 1 : 1.3 at temperatures (A) 600°C, (B) 750°C, (C) 950°C and (D) 1000°C. T: topaz; M: mullite; C: corundum.

The microscopic study of the products of kaolinite sintering with aluminium fluoride is consistent with their X-ray powder diffraction patterns. No peaks of aluminium silicon fluoride have been detected as reported earlier [7,12].

### 3.2. Using mixes of kaolinite and aluminium fluoride of ratio 1 : 1

The DTA curve of mix 1 : 1 (Fig. 5) shows similar peaks at slightly shifted temperatures as that obtained using mixes of kaolinite and aluminium fluoride 1 : 1.3, but here both topaz and mullite have been identified microscopically in the products of

sintering at 760°C. At the higher temperature 945°C, the product of sintering is composed mainly of corundum and mullite together with some topaz grains (Fig. 6).

### 3.3. Using mixes of kaolinite and aluminium fluoride of ratio 1 : 0.7

The DTA curve of kaolinite mixed with aluminium fluoride of ratio 1 : 0.7 (Fig. 7) shows endothermic peaks at 160°C, 320°C and 625°C similar to those obtained before. Topaz formation takes place at somewhat higher temperature than that previously recorded, as represented by the endothermic peak at

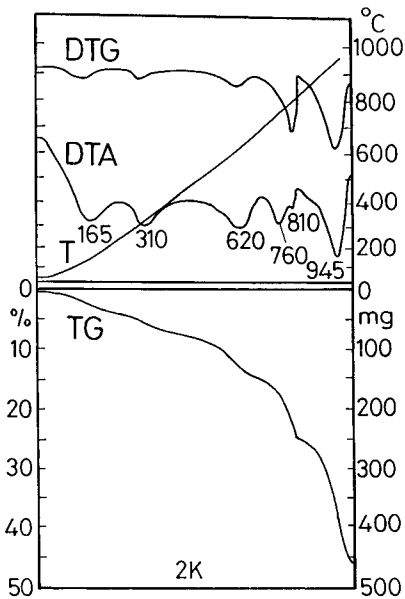


Fig. 5. DTA curve of synthesis of topaz using kaolinite–aluminium fluoride mix of ratio 1 : 1. Weight of sample 1000 mg. Heating rate 10°C/min.

790°C. This process is accompanied by a sharp decrease in weight (TG) due to the volatilization of silicon tetrafluoride. Topaz loses silicon tetrafluoride, as represented by the small endothermic peak at 810°C. The wide and large endothermic peak at 930°C represents the dissociation of topaz and the formation of mullite.

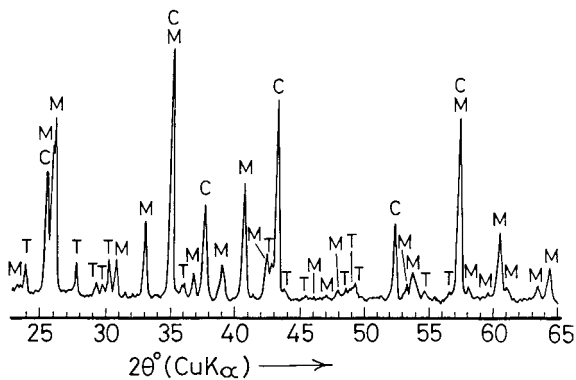


Fig. 6. X-ray diffraction pattern of the end product of topaz synthesis using kaolinite–aluminium fluoride mix of ratio 1 : 1 at 945°C. T: topaz, M: mullite and C the Corundum.

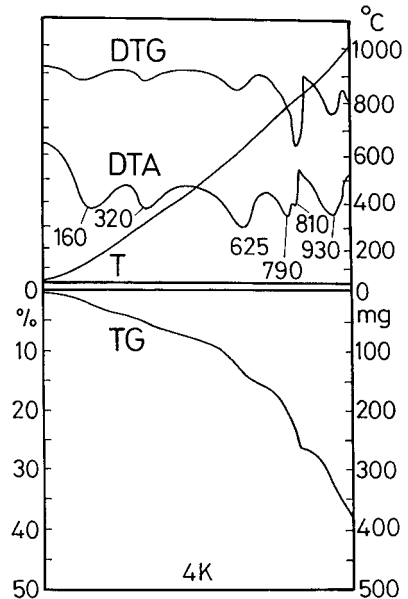


Fig. 7. DTA curve of synthesis of topaz using kaolinite–aluminium fluoride mix of ratio 1 : 0.7. Weight of sample 1000 mg. Heating rate 10°C/min.

The products of the runs at 790°C and 930°C were examined microscopically. At 790°C, topaz constitutes the major component of the sintering product with some mullite grains. The end product at 930°C consists mainly of mullite with a few topaz grains.

The X-ray diffraction patterns of the products at 790°C and 930°C are shown in Fig. 8A and B respectively. The product at 790°C is composed mainly of topaz with a few mullite grains. The topaz peaks are well defined and intense. Aluminium fluoride peaks disappeared completely in this run, indicating its absence. This means that all aluminium fluoride is consumed in the formation of topaz.

The X-ray diffraction pattern of the end product at 930°C shows mainly the mullite peaks, which are well defined and intense together with small peaks of topaz. No peaks of aluminium silicon fluoride have been detected in all runs. The X-ray diffraction study of the products of sintering are in good agreement with microscopic study of their thin sections.

The X-ray diffraction pattern of the product of sintering of the kaolinite–aluminium fluoride mix of ratio 1 : 0.5 at 1000°C (Fig. 9) shows only the intense and sharp peaks of mullite. Topaz and corundum peaks disappear completely, indicating the complete disso-

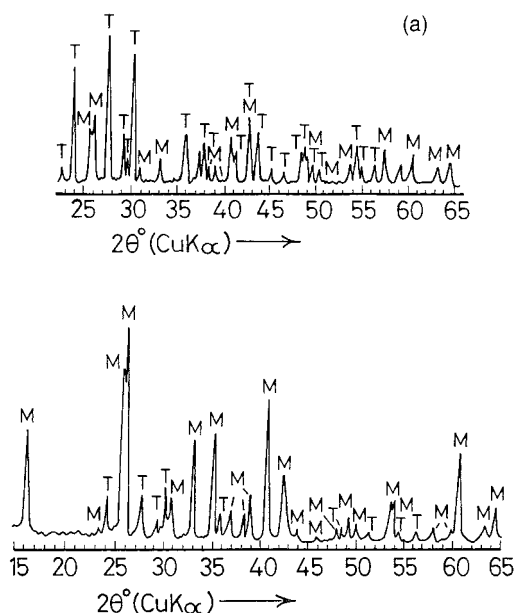


Fig. 8. X-ray diffraction patterns of the products of topaz synthesis using kaolinite–aluminium fluoride mix of ratio 1 : 0.7. A and B at temperatures 790°C and 930°C respectively. T: topaz and M: mullite

ciation of the produced topaz to mullite, due to the deficiency of fluorine. This means that the dissociation of topaz in absence of aluminium fluoride takes place with the formation of mullite. This is in good agreement with data in the literature, as topaz liberates fluorine on heating to 900°C and mullite is produced [2,4–7,12].

In general, the X-ray peaks of the products of kaolinite sintering with aluminium fluoride, namely, topaz, mullite and corundum are narrow and intense,

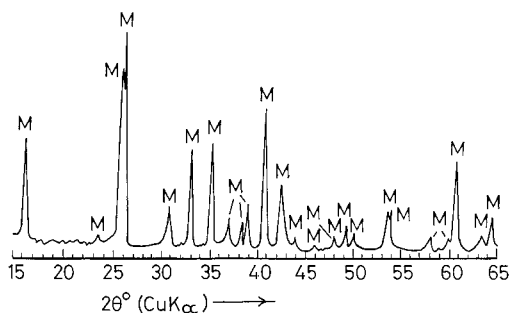


Fig. 9. X-ray diffraction pattern of the end product of topaz synthesis using kaolinite–aluminium fluoride mix of ratio 1 : 0.5 at 1000°C. M: mullite.

suggesting good crystallinity. The X-ray data of these synthetic minerals are consistent with those of the corresponding ASTM values of the natural minerals.

### 3.4. General characteristics of the synthesized topaz

**Mineralogy:** The synthetic topaz is colourless in thin sections and crystallizes in an orthorhombic system in the form of elongated prismatic crystals. It is characterized by high relief, perfect basal (0 0 1) cleavage, weak birefringence, and is optically positive. The refractive indices  $n_x = 1.610$ ,  $n_y = 1.612$  and  $n_z = 1.62$ .

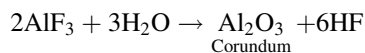
### 3.5. X-ray diffraction study

The X-ray diffraction data of the produced synthetic topaz are consistent with those of the corresponding values of the natural one (Table 2). The unit cell dimensions and constants of the synthetic topaz are given in Table 3. It is observed that the calculated cell dimensions, constants and optic axial angles of the synthesized topaz are consistent with the corresponding data of the natural mineral.

It is concluded from the results obtained that the products of the reaction of kaolinite with aluminium fluoride are different, depending upon the temperature of sintering and the amount of aluminium fluoride. The mechanism of the reaction is a complicated one.

### 3.6. Topaz formation

Aluminium fluoride may react with kaolinite in a hydrolysis-like manner or with the water produced by dehydroxylation of kaolinite. Above 300°C, aluminium fluoride will hydrolyse even under the effect of atmospheric moisture [6,12].



Topaz may be formed in different ways:

Firstly by the reaction of kaolinite with aluminium fluoride according to the following equation:

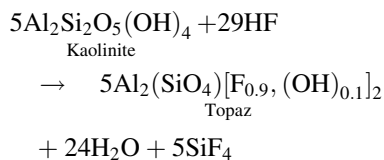
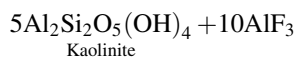
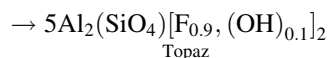


Table 2  
X-ray powder diffraction data of synthetic topaz

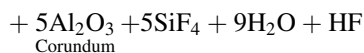
<i>d</i> (Å)		<i>I</i>		<i>h k l</i>
ASTM	Observed	ASTM	Observed	
4.400	4.403	6	25	0 2 0
4.190	4.226	4	5	0 0 2
4.111	4.129	12	14	1 1 0
3.896	3.914	6	8	0 2 1
3.693	3.707	60	80	1 1 1
3.195	3.211	65	82	1 2 0
3.037	3.044	35	40	0 2 2
2.985	3.002	25	25	1 2 1
2.937	2.946	100	100	1 1 2
2.480	2.493	20	27	1 3 0
2.397	2.402	10	13	1 0 3
2.378	2.384	25	36	1 3 1
2.361	2.365	45	55	0 2 3
2.325	2.318	8	13	2 0 0
2.313	2.306	10	12	1 1 3
2.247	2.252	6	5	2 1 0
2.199	2.189	10	13	0 4 0
2.141	2.140	12	15	2 1 1
2.127	2.113	8	16	0 4 1
2.105	2.103	45	54	1 2 3
2.056	2.065	25	28	2 2 5
2.987	2.988	8	9	1 4 0
1.982	1.984	10	11	2 1 2
1.947	1.941	4	5	0 4 2
1.934	1.931	6	5	1 4 1
1.869	1.875	25	31	1 1 4
1.853	1.875	25	25	1 3 3
1.821	1.831	12	11	2 3 0
1.797	1.802	8	7	1 4 2
1.779	1.781	6	6	2 3 1
1.671	1.676	25	32	2 3 2
1.656	1.661	8	25	2 2 3
1.620	1.627	12	15	1 4 3
1.601	1.605	2	4	1 3 4
1.597	1.594	4	7	2 4 0
1.568	1.564	4	5	2 4 1, 0 2 5
1.557	1.559	1	3	2 0 4
1.554	1.551	2	6	1 1 5



Kaolinite

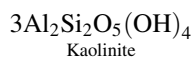


Topaz

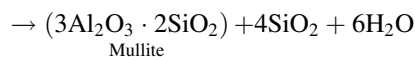


Corundum

Secondly by the reaction of the resulted mullite with aluminium fluoride according to



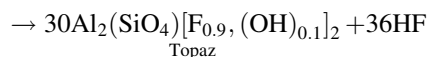
Kaolinite



Mullite



Mullite



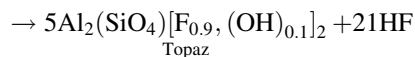
Topaz

Thirdly at the expense of the produced aluminium oxide and silica and their reactions with aluminium fluoride.

- The silica reacts with aluminium fluoride in presence of water vapour at 780°C with the formation of topaz.

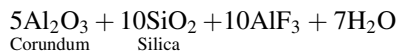


Silica



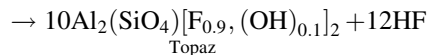
Topaz

- The aluminium oxide and silica react with aluminium fluoride in presence of water vapour at 800°C with the formation of topaz.



Corundum

Silica



Topaz

The beginning of the reaction of topaz formation is observed to take place at 600°C. The intensive formation of topaz takes place at 750–790°C.

Table 3  
Unit cell dimensions and axial angles of topaz

Mineral	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\alpha$ (°, minute)	$\beta$ (°, minute)	$\gamma$ (°, minute)	<i>V</i> (Å <sup>3</sup> )
Topaz	Orthorhombic						
Synthetic	4.638±0.0154	8.767±0.0313	8.378±0.0251	90, 00.00	90, 00.00	90, 00.00	340.661±0.004
Standard	4.649	8.792	8.394	90	90	90	343.096

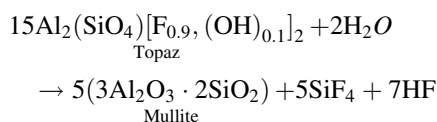


### 3.7. Topaz dissociation

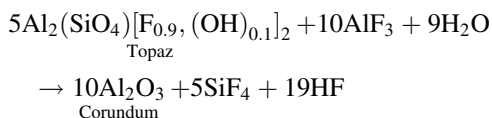
Topaz is unstable at higher temperature than 800°C. It has the property of losing silicon tetrafluoride at 800–810°C as represented by the small endothermic peak at such temperature and which is consistent with data in the literature [2,4,5]. Topaz liberates fluorine on heating to 850–900°C and mullite is produced.

In the present work, the products of topaz dissociation are either mullite or corundum depending on the amount of aluminium fluoride and the temperature.

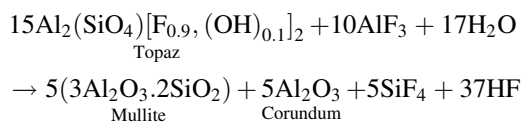
In absence of aluminium fluoride, topaz dissociates with the formation of mullite.



In presence of excess aluminium fluoride, dissociation of topaz together with its desilication takes place with the formation of corundum according to:



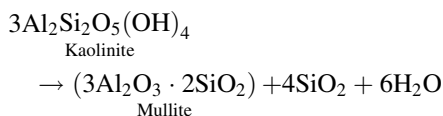
In presence of deficient amount of aluminium fluoride, the products of topaz dissociation are mullite and corundum, according to:



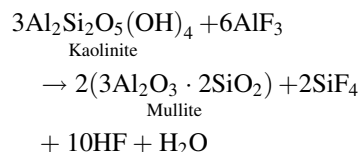
### 3.8. Mullite Formation

Under dynamical conditions, mullite formation takes place in two ways:

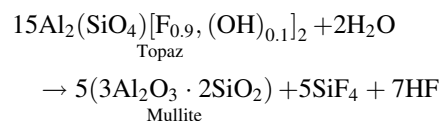
One starts from kaolinite, due to the deficiency of fluoride ions and the dehydration of kaolinite and decomposition of its structure, according to:



or,

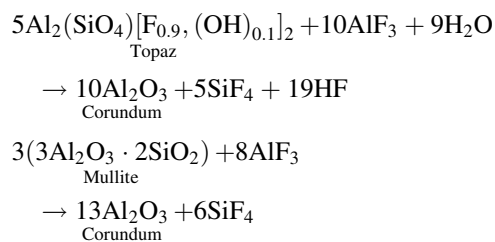


Secondly, mullite is formed by the dissociation of topaz, according to:

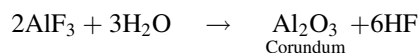


### 3.9. Corundum formation

Corundum may be formed in different ways: One from the desilication of topaz or mullite with aluminium fluoride at 930–950°C according to:



The second from the hydrolysis of aluminium fluoride above 800°C



The studied conditions of formation of topaz and its thermal stability give good evidence about its association with late-stage pneumatolytic action, its existence as a common constituent of greisen and its occurrence in high temperature quartz veins, pegmatites, granites and contact zone.

## 4. Conclusions

The thermal analysis study of topaz synthesis from kaolinite by its sintering with aluminium fluoride has revealed that the reaction mechanism is a complicated one. Different products of sintering are obtained, depending on the temperature and the amount of aluminium fluoride.

The DTA curves, microscopic and X-ray diffraction studies show the beginning of the reaction of topaz formation at 600°C. The reaction of kaolinite with aluminium fluoride of different amounts is observed to take place in two distinct steps. The first is marked by medium endothermic peak at 750–790°C, representing the intensive formation of topaz, and the second by the large sharp or wide endothermic peak at 930–950°C, representing its subsequent dissociation with the formation of mullite or (mullite and corundum) or corundum, depending on the amount of aluminium fluoride.

1. Using mixes of ratio 1 : 1.3, topaz constitutes the total composition of the product at 750°C, indicating completion of the reaction of topaz formation. The endothermic peak at 950°C represents the dissociation of topaz in presence of excess of aluminium fluoride together with its desilication, giving rise to corundum.
2. Using mixes of ratio 1 : 1, topaz and mullite constitute the total composition of the product at 760°C. The end product of sintering at 945°C is composed mainly of corundum and mullite.
3. Using mixes of ratio 1 : 0.5, mullite and topaz constitute the total composition of the product at 790°C. The end product at 930°C is composed totally of mullite, and no corundum grains have been detected due to the deficiency of fluorine. Topaz dissociates in absence of aluminium fluoride with the formation of mullite.

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

The produced synthetic topaz is colourless in thin sections and crystallizes in orthorhombic systems, in the form of prismatic crystals, with perfect basal (0 0 1) cleavage and is optically positive.

## References

- [1] A.M. Abdel-Rehim, Proc. 7th. Inter Conf. Therm. Anal., Kingston, Ont., 1982.
- [2] A.M. Abdel-Rehim, Acta Geologica Acad. Sci. Hung. 19(3-4) (1975) 287.
- [3] Wm.R. Phillips, D.T. Griffen, Optical Mineralogy. The Non-opaque Minerals, W.H. Freeman, 1981.
- [4] W.A. Deer, R.A. Howie, J. Zussman, An Introduction to Rock Forming Minerals, Longman, London, 1971.
- [5] A.M. Abdel-Rehim, in: W. Smykatz-Kioss, S.St. Warne (Eds.), Application of Thermal Analysis in Geoscience, vol. 38, Springer, Berlin, 1991, p. 188.
- [6] A.M. Abdel-Rehim, Thermochimica Acta 30 (1979) 127.
- [7] A.M. Abdel-Rehim, Thermochimica Acta 13 (1975) 231.
- [8] A.A. Opalovsky, V.E. Fedorov, T.D. Fedotova, J. Thermal Analysis 5 (1973) 475.
- [9] R.C. Mackenzie, 'Scifax' Differential Thermal Analysis Data Index, Cleaver-Hume Press, London, 1962.
- [10] R.C. Mackenzie, Differential Thermal Analysis, vol. 1, Fundamental Aspects, Academic Press, London, 1970.
- [11] W. Symkatz-Kloss, Differential Thermal Analysis, Application and Results in Mineralogy, Springer, Berlin, 1974.
- [12] B. Locsei, Proc. 9th silicate Industry, Acad. Sci., Budapest, 1968, p. 103.
- [13] A. Bien, W.L. De Keyser, Clay Min. Bull. 5 (1962) 80.
- [14] R.O. Donald, Econ. Geol. 66 (1971) 627.
- [15] F. Paulik, J. Paulik, L. Erdey, Talanta 13 (1966) 1405.
- [16] R.C. Weast et al., Handbook of Chemistry and Physics, The Chemical Rubber, 51st ed., 1971.