Thermal and XRD analysis of synthesis of fluoro-topaz

A.M. Abdel-Rehim[*]

Alexandria University, 69 Sultan Hussein Str, Shallalat, Alexandria, Egypt

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ABSTRACT

The present work deals with thermal and XRD analysis of fluoro-topaz synthesis by sintering of aluminium and silicon oxides (in the form of corundum and quartz) with ammonium fluoride and carried out in open Pt crucibles (for XRD studies) and a closed furnace of simultaneous DTA/TG thermoanalytical apparatus called MOM Derivatograph. The furnaces are connected to a gas suction device to remove gas decomposition products.

The study shows the endothermic peak at 125–155 °C, representing the formation of ammonium aluminium hexafluoride and cryptohalite. The endothermic peak at 220–240 °C represents the beginning of dissociation of ammonium aluminium hexafluoride to the more stable ammonium aluminium tetrafluoride. The endothermic peak at 340–350 °C represents the dissociation of cryptohalite and ammonium aluminium tetrafluoride with the formation of aluminium fluoride.

The formation of fluoro-topaz is represented by the wide endothermic peak at 770–800 °C. The medium wide or sharp endothermic peaks at 950 °C and 1000 °C represent the subsequent dissociation of fluoro-topaz to corundum or mullite, respectively.

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1. Introduction

Fluoro-topaz $Al_2(SiO_4)F_2$ is a fully fluorinated analogue of topaz $Al_2(SiO_4)[F_{0.9}, (OH)_{0.1}]_2$ which is a very popular gemstone, occurs as large, beautifully shaped and coloured crystals. It 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 [1–6].

The synthesis of fluoro-topaz is achieved by different methods. The methods are thermal hydrolysis of aluminium fluoride and silica between 750 and 850 °C, or heating a mixture of sodium silicon fluoride, aluminium oxide and water to 500 °C at pressure of 4000 bar, or sintering of kaolinite either with ammonium fluoride or aluminium fluoride at 750 °C [1–4,7–12].

The present work illustrates a differential thermal analysis of synthesis of fluoro-topaz by sintering of aluminium and silicon oxides (in the form of corundum and quartz) with ammonium fluoride. Also, it includes the study of the influence of ammonium fluoride on the thermal behaviour of corundum and quartz under different conditions together with a study of the products of sintering, namely, fluoro-topaz, mullite and corundum.

The thermal behaviour of the starting materials (quartz, corundum and ammonium fluoride) is well known [4,13–21]. Quartz is the stable form of silica at ordinary temperature up to 870 °C. It has two enantiotropic modifications, alpha and beta forms. The inversion of alpha-quartz to beta-form is represented by a very small sharp endothermic peak on the DTA curve at 573 °C. Corundum or alpha-aluminium oxide is thermally the most stable form of aluminium oxide.

The thermal behaviour of ammonium fluoride was reported in literature [14,17,18]. The DTA curve of ammonium fluoride [14] shows two large and sharp endothermic peaks. The first one at 170 °C corresponds to the formation of ammonium bifluoride and liberation of ammonia. The second, at 240 °C represents the dissociation of the resulted ammonium bifluoride into hydrogen fluoride and ammonia vapours. These processes are accompanied by remarkable decrease in mass (TG curve) in two distinct steps. The first is due to the liberation of ammonia and the second is due to the volatilization of ammonia and hydrogen fluoride from the dissociation of ammonium bifluoride.

The fluorinating action of fluorine, fluorides, hydrogen fluoride and silicon tetrafluoride are well known [1–3,7–10,13,14,16,19–22]. Ammonium fluoride is considered as an important fluorinating agent. The reaction of corundum or aluminium oxide with ammonium fluoride was reported to take place at 110–180 °C with the formation of ammonium aluminium hexafluoride, which dissociates at 300 °C to ammonium aluminium tetrafluoride. The latter one decomposes at 360 °C with the formation of aluminium fluoride [2,13]. The reaction of

[*] Tel.: +20 3 486 1356.
E-mail address: aabdelrehim@gmail.com

quartz or silicon dioxide with ammonium fluoride takes place at 125–155 °C by an endothermic reaction with the formation of cryptohalite (ammonium silicon hexafluoride). Cryptohalite is unstable and dissociates at 320–335 °C as represented by the sharp and large endothermic peak on the DTA curve, with the liberation of ammonia, silicon tetrafluoride and hydrogen fluoride [10,14]. At 200 °C and excess of ammonium fluoride, the product of the reaction is composed of cryptohalite and a double compound $(NH_4)_2SiF_6 \cdot NH_4F$.

Alumina or mullite reacts at 1 atm silicon tetrafluoride below 660 ± 7 °C to form aluminium fluoride and silica. At higher temperatures, the product is fluoro-topaz. Mixtures of fluoro-topaz and aluminium fluoride decompose in 1 atm of silicon tetrafluoride at 973 ± 8 °C and form tabular alpha-aluminium oxide. Fluoro-topaz itself decomposes at 1056 ± 5 °C in 1 atm silicon tetrafluoride to give acicular mullite $(2Al_2O_3 \cdot 1.07SiO_2)$. Mullite is stable in presence of 1 atm silicon tetrafluoride above 1056 °C [19,20].

Acicular mullite is also produced by controlled decomposition of fluoro-topaz at 1000–1200 °C in presence of silicon tetrafluoride. Acicular mullite grains interlock forming an efficient filter used as a diesel particulate filter (DPF) [23].

Mixtures of alumina and silica react with silicon tetrafluoride above 600 °C to form fluoro-topaz. Pyrolysis of fluoro-topaz gives whiskers of mullite and silicon tetrafluoride [21,22].

2. Experimental techniques

2.1. Starting materials

This research was carried out with aluminium oxide and silicon dioxide in the form corundum and quartz, respectively. The chemical composition of corundum used: 99.3% Al_2O_3; 0.3% SiO_2; 0.1% Fe_2O_3; 0.06% MgO; and 0.1% CaO. The chemically processed quartz is composed of 99.99% SiO_2.

In thin sections, corundum is pale bluish white, has high relief, high birefringence, no cleavage and lamellar twinning (10$\bar{1}$1). It crystallizes in trigonal system and is optically negative. Quartz is colourless, visible twinning, low relief and weak birefringence. It crystallizes in trigonal system and is optically positive.

The X-ray diffraction data of the processed corundum and quartz are consistent with the corresponding ASTM data of these minerals. The patterns show only the characteristic corundum and quartz peaks, which are sharp and intense, suggesting good crystallinity. No peaks of any mineral impurity were detected.

Ammonium fluoride used in experiments is a white crystalline material having chemical composition: ammonium fluoride 98%, ammonium bifluoride 1%, residue after ignition 0.01%, hexafluorosilicate 0.1%, chloride measure 0.001%, sulphate measure 0.05%, iron measure 0.005% and heavy metal (as lead) 0.001%.

Starting materials were mixtures of corundum and quartz with ammonium 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.

2.2. Apparatus

Heating experiments were carried out using platinum crucibles heated in a muffle furnace. The furnace has abrasion resistance ceramic annealing chamber and operates up to 1100 °C. The evolved silicon tetrafluoride and other gases are removed using a gas suction device connected to the furnace chamber. The temperature was regulated automatically with an accuracy ± 5 °C.

The thermal analysis of synthesis of fluoro-topaz by sintering of corundum–quartz mixes with ammonium fluoride was conducted with DTA apparatus (MOM Derivatograph, system; Paulik et al.) [24]. 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 chamber of the closed derivatograph furnace is made of high alumina refractory material. There are porcelain suction tubes beside the tubes holding the thermocouples of the sample and inert material, reaching into the furnace chamber to remove the gas decompositions products. The tubes are connected to a gas adjustable suction device. The latter is composed of a gas washer cylinder, a pump and a needle valve. Gas products are sucked off through this device in order to prevent corrosion and entry into the furnace and balance during the measurement.

The parameters during the test were as follows: platinum crucible: medium size; inert material, aluminium oxide, mass of mix 500 mg, temperature range, ambient up to 1200 °C, sensitivity of DTA circuit, 1/5; sensitivity of DTG circuit, 1/10; mass used in TG curve 500 mg; heating rate 10 °C/min. 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.

2.3. Phase identification

X-ray procedure: The phases of the products of the reaction of sintering of corundum–quartz mix with ammonium fluoride were identified microscopically and by X-ray diffraction. The fine ground sintered material was mixed with sodium chloride as standard. Its peaks at $2\theta = 31.38°$ and $45.44°$ were used for corrections. Nickel-filtered copper radiation was used. The sensitivity of the experiment was 4×10^4 imp/min and the statistical error was 1.5%.

3. Results and discussion

For studying the synthesis of fluoro-topaz by sintering of corundum–quartz mix with ammonium fluoride, DTA experiments were carried out using different amounts of ammonium fluoride. Mixes of corundum–quartz and ammonium fluoride of molar ratios 1:1:12.5, 1:1:10 and 1:1:5 are used. The DTA curves obtained were evaluated on the basis of literature data [1–4,8,9,12–23,25,26] to explain the reactions, which may be connected to certain peaks on the DTA curves.

3.1. Using mixes of corundum–quartz and ammonium fluoride of molar ratio 1:1:12.5

The DTA, TG and DTG curves of corundum–quartz mix with ammonium fluoride of molar ratio1:1:12.5 is shown in Fig. 1. The first wide and large endothermic peak at 155 °C represents the formation of ammonium silicon hexafluoride (cryptohalite) and ammonium aluminium hexafluoride and the liberation of ammonia and water vapours. The very small endothermic peak at 240 °C may represent the dissociation of the resulted ammonium bifluoride and to some extent decomposition of the unstable ammonium aluminium hexafluoride, yielding the more stable ammonium aluminium tetrafluoride. The large and sharp endothermic peak at 345 °C represents the intensive dissociation of cryptohalite and ammonium aluminium tetrafluoride with the formation of aluminium fluoride.

The results obtained are consistent with literature data [2,7,8,10,13,14] as quartz reacts with ammonium fluoride at
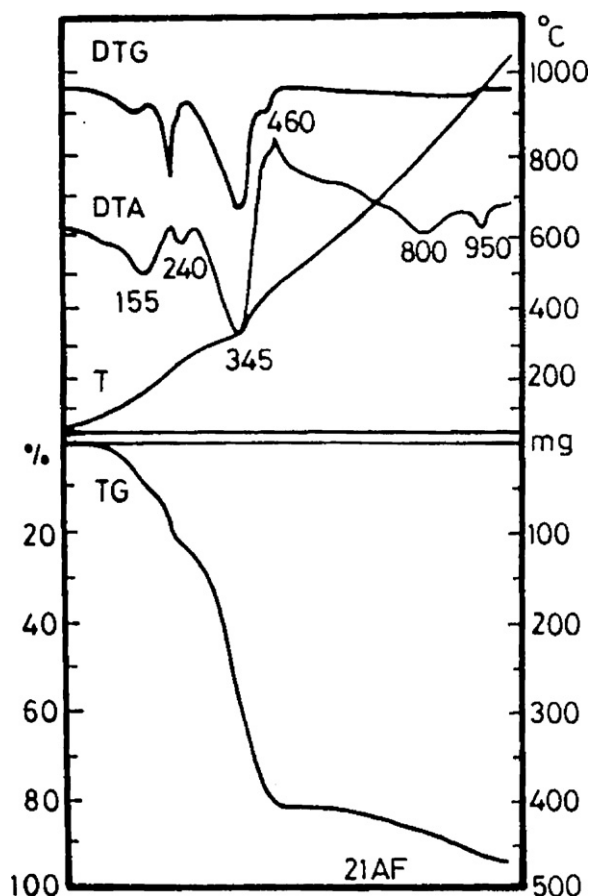
Fig. 1. DTA, TG and DTG curves of synthesis of fluoro-topaz using corundum–quartz–ammonium fluoride mix of molar ratio 1:1:12.5. Mass of sample 500 mg. Heating rate 10 °C/min.

125–155 °C with the formation of ammonium silicon hexafluoride (cryptohalite), which dissociates by an endothermic reaction at 330–335 °C. Corundum or alpha-aluminium oxide reacts with ammonium fluoride at 180 °C with the formation of ammonium aluminium hexafluoride, which dissociates at 300 °C to ammonium aluminium tetrafluoride. The last one dissociates at 360 °C with the formation of aluminium fluoride.

The wide endothermic peak at 800 °C indicates the reaction between the resulted aluminium fluoride and quartz with the formation of fluoro-topaz. It was previously reported that the formation of fluoro-topaz from sintering of quartz with aluminium fluoride takes place at 780 °C [2,7–19].

The endothermic peak at 950 °C represents the dissociation of fluoro-topaz. In presence of excess of aluminium fluoride, the dissociation of fluoro-topaz takes place simultaneously with its desilication, with the formation of corundum. The results obtained are in good agreement with literature data [1–4,7–9], as fluoro-topaz loses silicon tetrafluoride above 827 °C and its decomposition to corundum takes place at 950 °C.

The thermogravimetric curve (TG) shows the remarkable decrease in mass in five distinct steps:

1. The first step is the mass loss (about 13%), representing the volatilization of ammonia and water vapours from the reaction of corundum–quartz mix with ammonium fluoride at 155 °C and its dissociation.
2. The second step is the decrease of mass (about 10%), due to the volatilization of ammonia, hydrogen fluoride and water vapours at 240 °C from the dissociation of ammonium bifluoride resulted
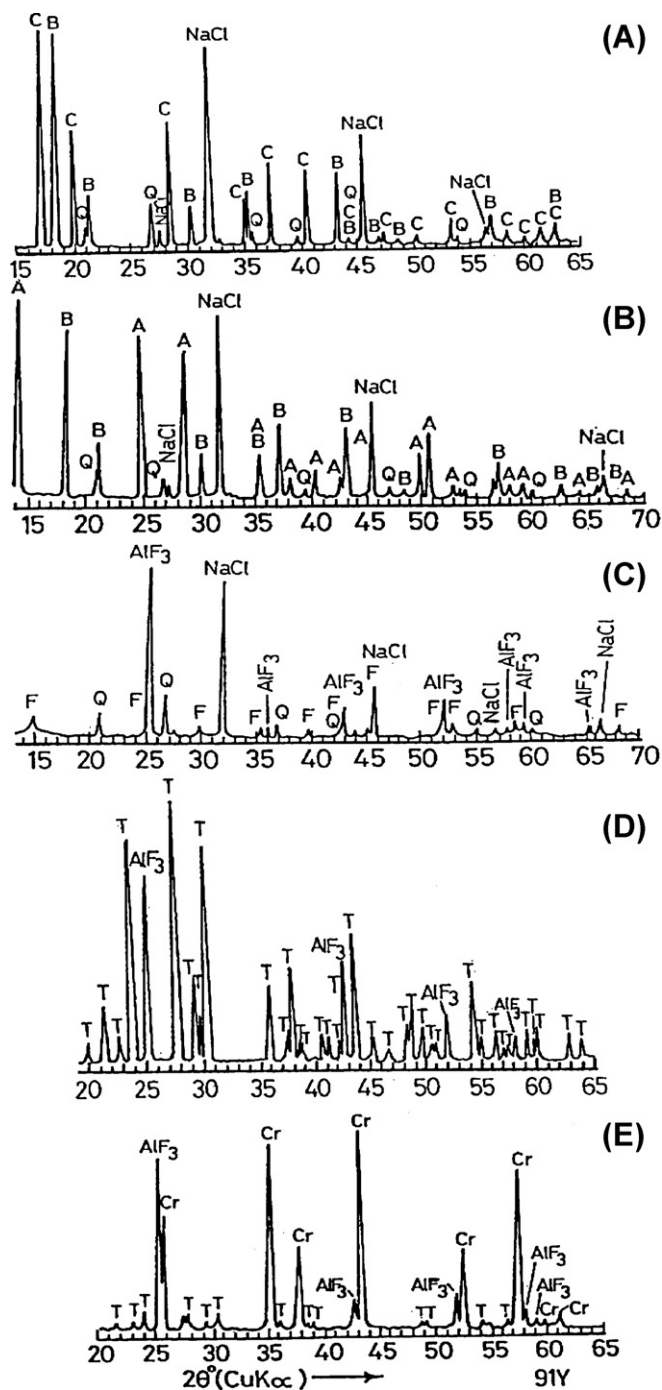

Fig. 2. X-ray diffraction patterns of the products of synthesis of fluoro-topaz using corundum–quartz–ammonium fluoride mix of molar ratio 1:1:12.5. (A) 155 °C, (B) 240 °C, (C) 345 °C, (D) 800 °C and (E) 950 °C. A: NH_4AlF_4 (JCPDS File No. 20-77); B: $(NH_4)_2SiF_6$ (cryptohalite) (JCPDS File No. 7-13); C: $(NH_4)_3AlF_6$ (JCPDS File No. 22-1036); F: γ-AlF_3 (JCPDS File No. 20-6); T: topaz (JCPDS File No. 12-765); Cr: corundum (JCPDS File No. 10-173); Q: quartz (JCPDS File No. 33-1161); and AlF_3 (JCPDS File No. 9-138).

and to some extent ammonium aluminium hexafluoride. That yields the more stable ammonium aluminium tetrafluoride. (Fig. 2B).
3. The third step is the large and sharp decrease of mass (about 58.5%) at 345 °C. This decrease is due to the volatilization of ammonia, silicon tetrafluoride and hydrogen fluoride from the dissociation of cryptohalite and ammonium aluminium tetrafluoride with the formation of aluminium fluoride. (Fig. 2C).

4. The fourth step is the mass loss (about 7.5%), representing the volatilization of silicon tetrafluoride from the reaction of aluminium fluoride and quartz at 800 °C with the formation of fluoro-topaz (Fig. 2D).

5. The fifth step is the small decrease of mass (about 2%) due to the dissociation of fluoro-topaz at 950 °C and liberation of silicon tetrafluoride and some sublimation of aluminium fluoride. Remarkable sublimation of aluminium fluoride is observed at 1000 °C and its intensive sublimation at 1256 °C without melting [1].

The total mass loss is 91% (stoichiometric loss 89.2%) and the residue remain at 1000 °C is about 9% of the initial mass of sample mix and is composed of corundum (Fig. 2E).

The products of the runs at 155, 240, 345, 800 and 950 °C were identified both microscopically and by X-ray diffraction. By microscopic examination of thin sections of these products, it is observed that few quartz grains appear in the products of the runs at 155 and 240 °C, indicating fluorination of these mixes with ammonium fluoride and the formation of cryptohalite and ammonium aluminium hexafluoride.

At 240 °C, the product consists of cryptohalite and ammonium aluminium tetrafluoride with few relict quartz grains. At 345 °C, aluminium fluoride constitutes the main composition of this product with unreacted relict quartz grains. At 800 °C, the product is composed mainly of fluoro-topaz and aluminium fluoride. At 950 °C, corundum constitutes the main composition of the end product with aluminium fluoride and few undissociated fluoro-topaz grains.

The X-ray diffraction patterns of these products are shown in Fig. 2A–E at 155, 240, 345, 800 and 950 °C, respectively. The product at 155 °C (Fig. 2A) consists of ammonium aluminium hexafluoride $(NH_4)_3AlF_6$ and cryptohalite $(NH_4)_3SiF_6$ with small peaks of quartz. The product of the run at 240 °C (Fig. 2B) consists mainly of ammonium aluminium tetrafluoride NH_4AlF_4 and cryptohalite. At 345 °C (Fig. 2C), aluminium fluoride constitutes the total composition of this product with quartz. Fluoro-topaz constitutes the total composition of the product at 800 °C (Fig. 2D) with aluminium fluoride. Fluoro-topaz peaks are sharp and intense, suggesting good crystallinity. Corundum constitutes the total composition of the end product at 950 °C (Fig. 2E) with aluminium fluoride.

The microscopic study of the products of sintering of corundum–quartz and ammonium fluoride mix of molar ratio 1:1:12.5 is consistent with their X-ray diffraction patterns.

3.2. Using corundum–quartz–ammonium fluoride mixes of molar ratios 1:1:10 and 1:1:5

The DTA, TG and DTG curves of corundum–quartz and ammonium fluoride mixes of molar ratios 1:1:10 and 1:1:5 are shown in Figs. 3 and 4, respectively. They show the first three endothermic peaks at relatively close temperatures and the same reaction products similar to those obtained for DTA curve of mix of molar ratio 1:1:12.5. The very small endothermic peak at 560 °C may represent phase transformation of quartz. The exceptions here are firstly, fluoro-topaz formation takes place at a slightly lower temperature than the previously recorded for mix 1:1:12.5, as represented by the endothermic peaks at 790 and 770 °C. This process is accompanied by gradual decrease in mass (TG curve) due to the volatilization of silicon tetrafluoride. The second exception is the sharp endothermic peak at 1000 °C, which represents the dissociation of fluoro-topaz to mullite due to the deficiency of aluminium fluoride produced.

The TG curves of both mixes of molar ratios 1:1:10 and 1:1:5 show decrease of mass in five distinct steps similar to that for mix of molar ratio 1:1:12.5. The total mass loss on ignition for mix of molar
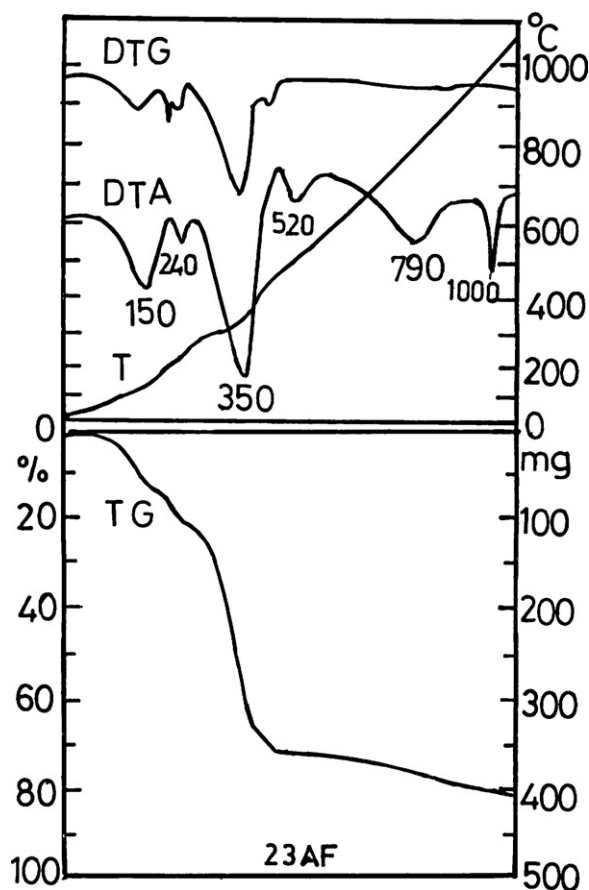

Fig. 3. DTA, TG and DTG curves of synthesis of fluoro-topaz using corundum–quartz–ammonium fluoride mix of molar ratio 1:1:10. Mass of sample 500 mg. Heating rate 10 °C/min.

ratio 1:1:10 is 79% and residue 21%, whereas the stoichiometric mass loss is 77.7%. The total mass loss on ignition of the other mix of molar ratio 1:1:5 is about 60.5% and the residue 39.5%, whereas the stoichiometric mass loss is 58.9%. The residue obtained after sintering of mix of molar ratio 1:1:10 is composed of mullite and corundum, while that obtained from mix of molar ratio 1:1:5 is composed of mullite and unreacted corundum and quartz.

The products of the runs at 770 and 1000 °C using corundum–quartz–ammonium fluoride mix of molar ratio 1:1:5 were examined microscopically. At 770 °C, the product of sintering consists of fluoro-topaz and unreacted corundum and quartz due to the deficiency of fluoride ions. The end product at 1000 °C consists mainly of mullite with unreacted corundum and quartz grains. No fluoro-topaz grains are detected in this product, indicating complete dissociation of fluoro-topaz in absence of aluminium fluoride and the formation of mullite.

The X-ray diffraction patterns of the products of sintering of mix of molar ratio 1:1:5 at 770 and 1000 °C are shown in Fig. 5A and B, respectively. The product at 770 °C (Fig. 5A) is composed mostly of fluoro-topaz with unreacted corundum and quartz. Fluoro-topaz peaks are well defined, sharp and intense. Aluminium fluoride peaks disappear completely in this run, indicating its absence. This means that all aluminium fluoride is consumed in the formation of fluoro-topaz.

The X-ray diffraction pattern of the product of sintering of mix of molar ratio 1:1:5 at 1000 °C (Fig. 5B) shows the intense, sharp and well defined peaks of mullite with small peaks of unreacted corundum and quartz. The fluoro-topaz peaks disappear completely in this run, indicating the complete dissociation of
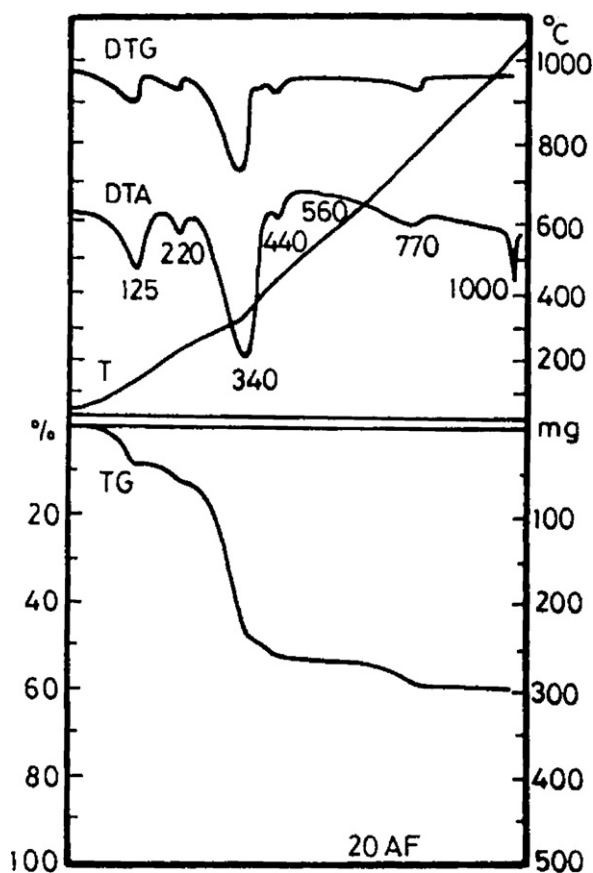
Fig. 4. DTA, TG and DTG curves of synthesis of fluoro-topaz using corundum–quartz–ammonium fluoride mix of molar ratio 1:1:5. Mass of sample 500 mg. Heating rate 10 °C/min.

Fig. 5. X-ray diffraction patterns of the products of synthesis of fluoro-topaz using corundum–quartz–ammonium fluoride mix of molar ratio 1:1:5 at temperature (A) 770 °C and (B) 1000 °C. T: topaz (JCPDS File No. 12-765); M: mullite (JCPDS File No. 15-776); Cr: corundum (JCPDS File No. 10-173) and Q: quartz (JCPDS File No. 33-1161).

fluoro-topaz produced to mullite. This means that the dissociation of fluoro-topaz in absence of aluminium fluoride takes place with the formation of mullite. This is in good agreement with the data in literature, as fluoro-topaz liberates fluorine when heated to 900 °C and mullite is produced [2–4,7–9].

In general, the X-ray peaks of the products of sintering of different mixes of corundum–quartz and ammonium fluoride, namely fluoro-topaz, aluminium fluoride, mullite and corundum are narrow, sharp and intense, suggesting good crystallinity. The X-ray diffraction data of these synthetic minerals is consistent with the corresponding ASTM values of natural minerals.

3.3. General characteristics of the synthesized fluoro-topaz

Mineralogy: The synthesized fluoro-topaz is colourless in thin sections and is characterized by high relief, perfect basal cleavage (0 0 1), weak birefringence and it is optically positive. It crystallizes in an orthorhombic system in the form of elongated prismatic crystals.

3.4. X-ray diffraction study

The X-ray diffraction data of the produced fluoro-topaz is consistent with those of the corresponding values of the natural one. The unit cell dimensions and constants of the synthetic fluoro-topaz are given in Table 1. It is observed that the calculated cell dimensions, constants and optic axial angles of the synthesized fluoro-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 sintering of corundum–quartz mix with ammonium
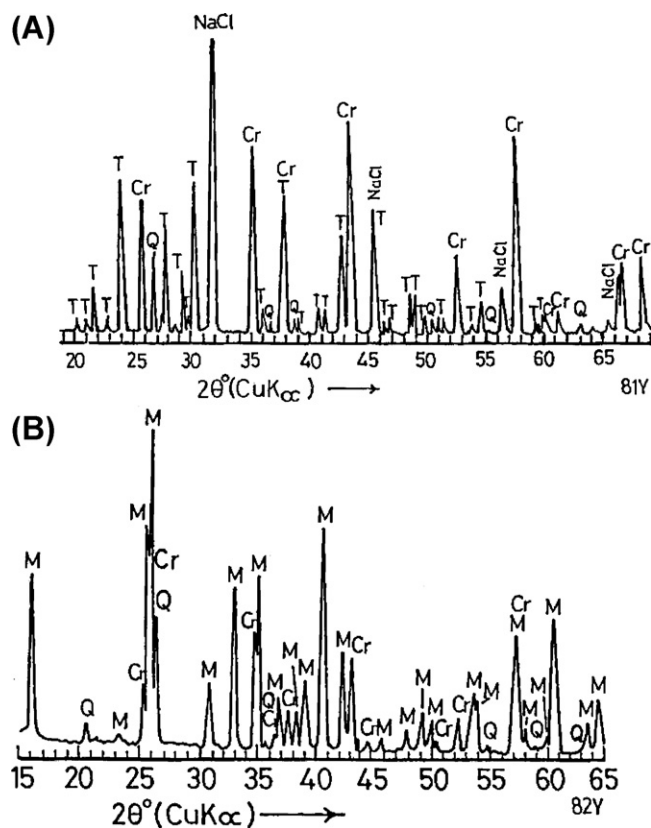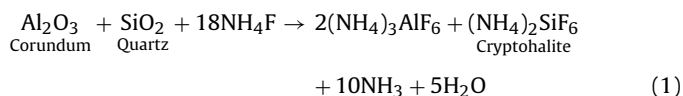
fluoride are different, depending upon the temperature of sintering and the amount of ammonium fluoride used.

3.5. Mechanism of reaction

The mechanism of the reaction of fluoro-topaz synthesis by sintering of corundum–quartz mix with ammonium fluoride is a complicated one and can be considered as the following:

At 125–155 °C: The reaction of corundum and quartz with ammonium fluoride for all mixes takes place with the formation of ammonium aluminium hexafluoride and cryptohalite (Fig. 2A), according to:

$$\underset{\text{Corundum}}{Al_2O_3} + \underset{\text{Quartz}}{SiO_2} + 18NH_4F \rightarrow 2(NH_4)_3AlF_6 + \underset{\text{Cryptohalite}}{(NH_4)_2SiF_6}$$

$$+ 10NH_3 + 5H_2O \qquad (1)$$

At 220–240 °C: Ammonium aluminium hexafluoride is unstable and begins to decompose at such temperature, yielding the more stable ammonium aluminium tetrafluoride, according to:

$$(NH_4)_3AlF_6 \rightarrow NH_4AlF_4 + 2NH_3 + 2HF \qquad (2)$$
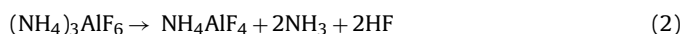
or the reaction of corundum and quartz with ammonium fluoride for all mixes takes place at 220–240 °C and the phases resulted are ammonium aluminium tetrafluoride and cryptohalite (Fig. 2B) according to:
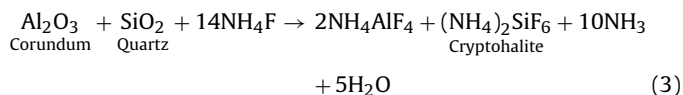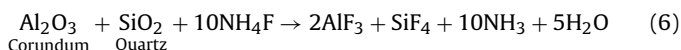
$$\underset{\text{Corundum}}{Al_2O_3} + \underset{\text{Quartz}}{SiO_2} + 14NH_4F \rightarrow 2NH_4AlF_4 + \underset{\text{Cryptohalite}}{(NH_4)_2SiF_6} + 10NH_3$$

$$+ 5H_2O \qquad (3)$$

Table 1
Unit cell dimensions and axial angles of fluoro-topaz.

Mineral	a (Å)	b (Å)	c (Å)	α (°, min)	β (°, min)	γ (°, min)	V (Å^3)
Topaz	Orthorhombic						
Synthetic	4.643	8.774	8.381	90.00	90.00	90.00	341.423
Standard	4.646	8.792	8.394	90	90	90	343.096

At 340–350 °C: Ammonium aluminium tetrafluoride and cryptohalite are unstable and dissociate according to:

$$NH_4AlF_4 \rightarrow AlF_3 + NH_3 + HF \qquad (4)$$

$$(NH_4)_2SiF_6 \rightarrow SiF_4 + 2NH_3 + 2HF \qquad (5)$$

or the reaction of corundum and quartz with ammonium fluoride for all mixes takes place at 340–350 °C with the formation of aluminium fluoride (Fig. 2C) according to:

$$\underset{\text{Corundum}}{Al_2O_3} + \underset{\text{Quartz}}{SiO_2} + 10NH_4F \rightarrow 2AlF_3 + SiF_4 + 10NH_3 + 5H_2O \qquad (6)$$
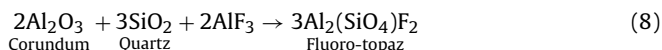
3.6. Fluoro-topaz formation

Fluoro-topaz may be formed in different ways for all mixes at temperature range 770–800 °C:

- Quartz may react with aluminium fluoride produced with the formation of fluoro-topaz (Figs. 2D and 5A), according to the following equation:

$$\underset{\text{Quartz}}{2SiO_2} + 2AlF_3 \rightarrow \underset{\text{Fluoro-topaz}}{Al_2SiO_4F_2} + SiF_4 \qquad (7)$$
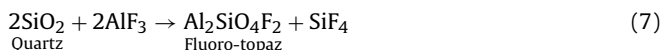
- Corundum and quartz may react with aluminium fluoride with the formation of fluoro-topaz (Figs. 2D and 5A), according to:

$$\underset{\text{Corundum}}{2Al_2O_3} + \underset{\text{Quartz}}{3SiO_2} + 2AlF_3 \rightarrow \underset{\text{Fluoro-topaz}}{3Al_2(SiO_4)F_2} \qquad (8)$$

The beginning of the reaction of fluoro-topaz formation is observed to take place at 600 °C. The intensive formation of fluoro-topaz by sintering of corundum–quartz mix with ammonium fluoride (for all molar ratios) takes place at 770–800 °C
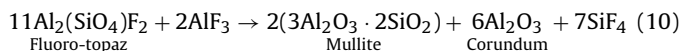
3.7. Fluoro-topaz dissociation

Fluoro-topaz is unstable at temperature higher than 850 °C. It has the property of losing silicon tetrafluoride at 827 °C as represented by the small endothermic peak at such temperature [2–4,7]. Fluoro-topaz liberates fluorine on heating to 850–900 °C and mullite is produced.

In the present work, the products of fluoro-topaz dissociation are either mullite or corundum depending on the amount of ammonium fluoride in the initial mix, temperature and aluminium fluoride produced.

In presence of excess of aluminium fluoride produced from mix of molar ratio 1:1:12.5, dissociation of fluoro-topaz together with its desilication take place at 950 °C with the formation of corundum (Fig. 2E), according to:

$$\underset{\text{Fluoro-topaz}}{6Al_2(SiO_4)F_2} + 4AlF_3 \rightarrow \underset{\text{Corundum}}{8Al_2O_3} + 6SiF_4 \qquad (9)$$
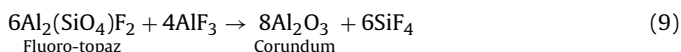
In presence of deficient amount of aluminium fluoride produced from mix of molar ratio 1:1:10, the products of fluoro-topaz dissociation at 1000 °C are mullite and corundum, according to:

$$\underset{\text{Fluoro-topaz}}{11Al_2(SiO_4)F_2} + 2AlF_3 \rightarrow \underset{\text{Mullite}}{2(3Al_2O_3 \cdot 2SiO_2)} + \underset{\text{Corundum}}{6Al_2O_3} + 7SiF_4 \qquad (10)$$

In absence of aluminium fluoride, fluoro-topaz dissociates at 1000 °C with the formation of mullite as end product (Fig. 5B) for mix of molar ratio 1:1:5.

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

4. Conclusions

The thermal analysis of synthesis of fluoro-topaz by sintering of corundum–quartz mixes with ammonium fluoride shows that the reaction mechanism is a complicated one. Different products of sintering are obtained, depending on the temperature and amount of ammonium fluoride.

The DTA curves, microscopic and X-ray diffraction study of the products of sintering show that the wide endothermic peak at 125–155 °C represents the formation of ammonium aluminium hexafluoride and cryptohalite. The endothermic peak at 220–240 °C represents the dissociation of ammonium bifluoride resulted and the unstable ammonium aluminium hexafluoride, yielding the more stable ammonium aluminium tetrafluoride. The large and sharp endothermic peak at 340–350 °C represents the intensive dissociation of cryptohalite and ammonium aluminium tetrafluoride with the formation of aluminium fluoride. These processes are connected with a sharp decrease in mass due to the volatilization of silicon tetrafluoride and liberation of ammonia and water vapour.

The DTA curves show the beginning of the reaction between aluminium fluoride produced and quartz at 600 °C with the formation of fluoro-topaz. The intensive formation of fluoro-topaz takes place at 770–800 °C, as represented by the wide endothermic peaks at such temperatures. The medium wide or sharp endothermic peaks at 950 and 1000 °C represent the subsequent dissociation of fluoro-topaz to corundum or mullite, respectively, depending on the amount of ammonium fluoride in the initial mix.

1. Using corundum–quartz and ammonium fluoride mix of molar ratio 1:1:12.5, fluoro-topaz constitutes the main composition of the product at 800 °C with aluminium fluoride.
2. Using mixes of molar ratios 1:1:10 and 1:1:5, the product at 770–790 °C is composed of fluoro-topaz with unreacted corundum and quartz and no aluminium fluoride is detected. All aluminium fluoride resulted, is consumed in the formation of fluoro-topaz.

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

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