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THERMAL STUDY OF SYNTHESIS OF CRYPTOHALITE

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The present work represents a thermal study of synthesis of cryptohalite (Ammonium silicon hexafluoride) by sintering of quartz with ammonium fluoride using a derivatograph. The reaction products were identified microscopically and by using a Siemens Crystalloflex diffractometer. The DTA curves indicate that the intensive formation of cryptohalite takes place at 125°–155°C by an endothermic reaction. Cryptohalite is unstable and dissociates at 320°–335°C as represented by the sharp and large endothermic peaks at these temperatures.

The resulted cryptohalite is colorless in thin sections and crystallizes in cubic system, in the form of octahedral crystals with perfect (111) cleavage. The dimorph bararite is not detected in all runs.

Keywords: synthesis of cryptohalite, DTA, crystalloflex diffractometer

Introduction

Cryptohalite (Ammonium silicon hexafluoride) occurs as a sublimation product at Visuvius, Italy, admixed with salammoniac and bararite. Also, found as a sublimate crusts on the surface of the ground, above a burning coal seam at the Barari, Jahria coal field, India, associated with sulfur and bararite, and similarly at Libusin in the Kladno coal basin, Bohemia [10–12].

The thermal behaviour of the starting materials, namely quartz and ammonium fluoride is well known [1–7, 9]. Quartz is stable from ordianry temperature up to 870°C. It has two enantiotropic modifications, alpha and beta forms. The inversion of alpha-quartz to beta-form takes place at 573°C and is indicated by an endothermic peak on the DTA curve [4, 6, 9].

Ammonium fluoride has paid much attention as important fluorinating agent [1–5]. Its DTA curve shows two large and sharp endothermic peaks. The first at 158°–170°C corresponds to the liberation of ammonia and the formation of ammonium bifluoride. The second, at 225°–240°C represents

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the dissociation of the resulted ammonium bifluoride to hydrogen fluoride and ammonia vapours.

The reaction of silicon with ammonium bifluoride was reported to take place at 80°C [1]. The products of the reaction are ammonium silicon hexafluoride and a binary salt $(NH_4)_2SiF_6 \cdot NH_4F$.

This work represents a differential thermal analysis study of synthesis of cryptohalite by sintering of quartz with ammonium fluoride using derivatograph.

Experimental

This research 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 separated from quartz vein, and 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.

In thin sections, the processed quartz is colorless, low relief, visible twinning, no cleavage and weak birefringence. It crystallizes in trigonal system and is optically positive.

Quartz powder and ammonium 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 200 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 removel of evolved gases (namely, ammonia, silicon tetrafluoride, hydrogen fluoride), which resulted from sintering reaction. The temperature was regulated automatically with accuracy of ±5°C.

The thermal investigation of synthesis of cryptohalite by sintering of quartz with ammonium fluoride was studied by using the MOM derivatograph [8]. 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 the mix 0.5 g; temperature range, ambient up to 1200°C, sensitivities of DTA and DTG circuits 1/10; weight used in TG curve, 500 mg; heating rate, 10 deg·min^{-1}. The DTA and temperature measuring thermocouples were Pt-Pt/Rh wire. The atmosphere was air and the volatile silicon tetrafluoride and other gases were removed as formed.

Phase identification

X-ray procedure. The phases of the products of quartz sintering with ammonium fluoride were identified both microscopically and by X-ray diffraction analysis using a Siemens Crystalloflex diffractometer. The finely ground sintered material was mixed with sodium chloride as a standard. Its peaks occurring at 2θ = 31.38°C and 45.44°C were used for corrections. Nickel-filtered copper radiation was used. Exposure time was 1 h. Intensities were collected to maximum 2θ = 65°C. The sensitivity of the experiment was 4×10^4 impl/min and the statistical error was 1.5%.

Results and discussion

For studying the synthesis of cryptohalite, DTA experiments were carried out using mixes of quartz with different amounts of ammonium fluoride, ranging from 50 to 150% of the theoretical value. The obtained thermal analysis records were evaluated on the basis of literature data [1–7, 9], which were also repeated experimentally in order to explain the reactions which may be connected to certain peaks on the DTA curves.

The DTA of ammonium fluoride is shown in Fig. 1. It shows two large and sharp endothermic peaks. The first 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.

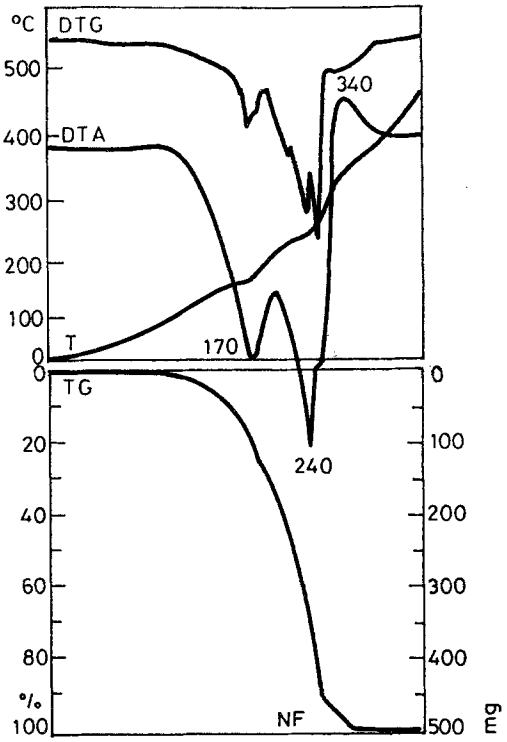

Fig. 1 DTA curve of Ammonium Fluoride

Using 50 to 125% of the theoretical amount of ammonium fluoride

The thermal analysis data of these mixes (Fig. 2, A, B, and C using 50, 100 and 125% of the theoretical amount of ammonium fluoride, respectively) show the formation of cryptohalite as represented by the wide and sharp endothermic peak at 125°–155°C. The samll endothermic peak at 230°C represents the dissociation of the resulted ammonium bifluoride. The large and sharp endothermic peak at 330°–335°C represents the intensive dissociation of cryptohalite. These processes are connected with a remarkable decrease in weight (TG curve) due to the volatilization of silicon tetrafluoride and removal of ammonia, hydrogen fluoride and water vapours.

The small endothermic peak at 570°–575°C represents the phase transformation of alpha-quartz to the beta-form.

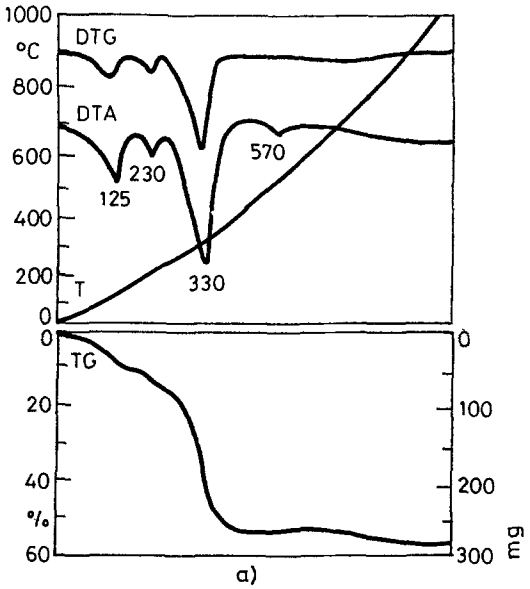

Fig. 2A DTA curves of synthesis of cryptohalite by sintering of quartz with ammonium fluoride of amount 50% of theoretical value

Microscopic and X-ray diffraction study

The products of the runs at 125°–155°C (using 50 to 125% of the theoretical amount of ammonium fluoride) were identified microscopically and by X-ray diffraction. Cryptohalite appears in thin sections as colorless crystals with large amount of quartz grains in the run at 125°C and using 50% of the theoretical amount of ammonium fluoride. This indicates the incompleteness of the reaction of formation of cryptohalite, due to the difficiency of the fluorinating agent.

At 150°C and amount of ammonium fluoride 125% of theoretical value, cryptohalite constitutes the main composition of the product of this run, together with few quartz grains.

At 335°C and using the theoretical amount of ammonium fluoride, unreacted relict quartz grains constitute the total composition of the product of the reaction.

The X-ray diffraction patterns of these products are shown in Fig. 3 (A, B, and C at 125°, 150° and 335°C respectively). Cryptohalite is present in large amount in the run at 150°C and its peaks completely disappeared in the run at 335°C, indicating its complete dissociation. Unreacted quartz constitutes the total composition of the run product at 335°C, due to the dis-

sociation of cryptohalite and the incompleteness of the reaction of quartz with ammonium fluoride.

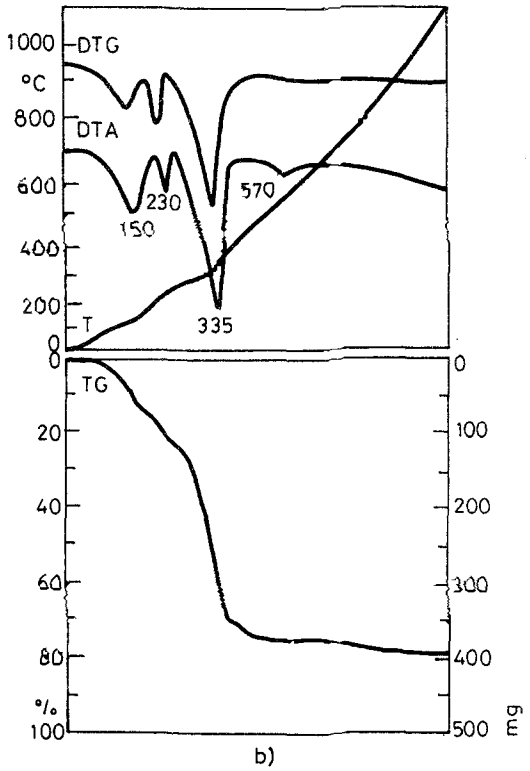

Fig. 2B DTA curves of synthesis of cryptohalite by sintering of quartz with ammonium fluoride of amount 100% of theoretical value

It is observed that the microscopic study of cryptohalite synthesis is well consistent with their X-ray diffraction patterns.

Using 150% of the theoretical amount of ammonium fluoride

The derivatogram of quartz mixed with 150% of the theoretical amount of ammonium fluoride is shown in Fig. 4. The DTA curve shows similar peaks at similar temperatures, as the DTA curves obtained by sintering quartz with 50 to 125% of the theoretical amount of ammonium fluoride, with the exception of disappearence of the wide and sharp endothermic peak at 125°–155°C. This may be attributed to the reaction of dissociation

of the resulted ammonium bifluoride covers the reaction of formation of cryptohalite.

The microscopic study of the products of runs at 150° and 200°C during 0.5 h shows that cryptohalite constitutes the total composition of the product at 150°C. Cryptohalite is colorless and crystallizes in the form of octahedral crystals. At 200°C, the product is composed mostly of cryptohalite together with a double compound $(NH_4)_2SiF_6 \cdot NH_4F$. No quartz grains were detected in these runs, indicating the complete reaction of cryptohalite synthesis.

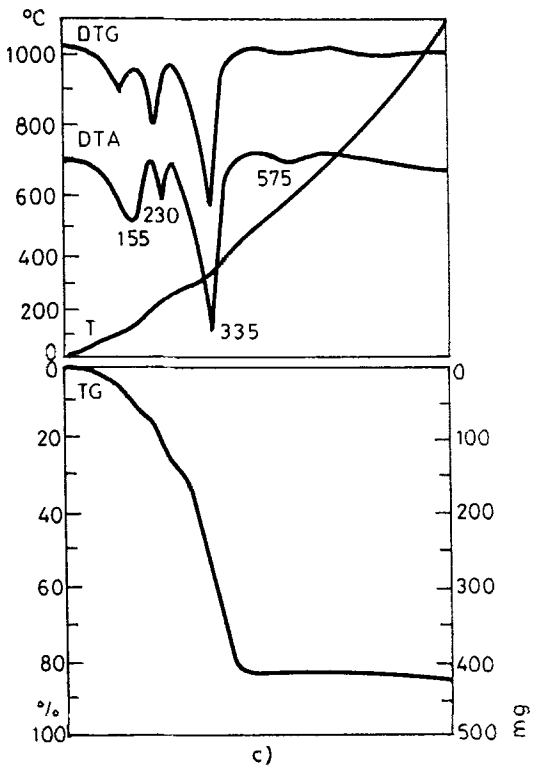

Fig. 2C DTA curves of synthesis of cryptohalite by sintering of quartz with ammonium fluoride of amount 125% of theoretical value

The X-ray diffraction patterns of these products at 150° and 200°C (Fig. 5A and B respectively) shows the the presence of cryptohalite at 150°C and its association with the double compound $(NH_4)_2SiF_6 \cdot NH_4F$ at 200°C. The cryptohalite peaks are well defined and intense, suggesting good crys-

tallinity. The X-ray study is in good agreement with the microscopic study of the thin sections of the sintering products.

In general, the X-ray data of the resulted synthetic cryptohalite are consistent with those of the corresponding ASTM values of the natural one.

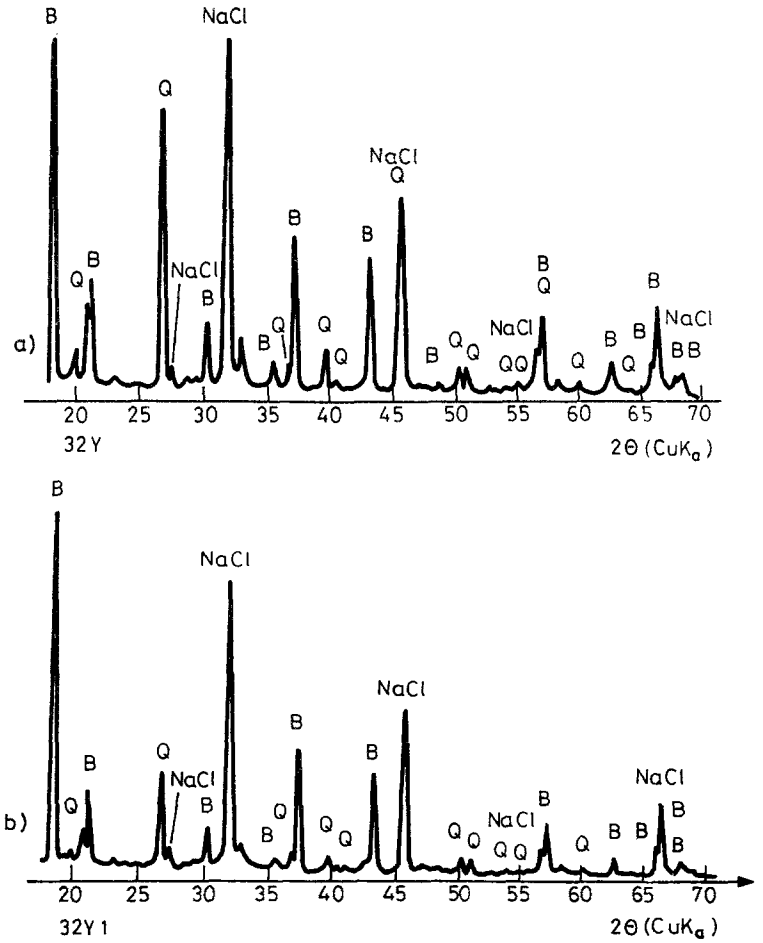

Fig. 3A–B X-ray powder diffraction patterns of the products of cryptohalite synthesis, using quartz mixed with different amounts of ammonium fluoride. (A and B at 125 and 150°C and 50 and 125% of the theoretical amount of ammonium fluoride B = Cryptohalite and Q = Quartz

The mechanism of the reaction of cryptohalite synthesis by sintering of quartz with ammonium fluoride can be considered as the following:

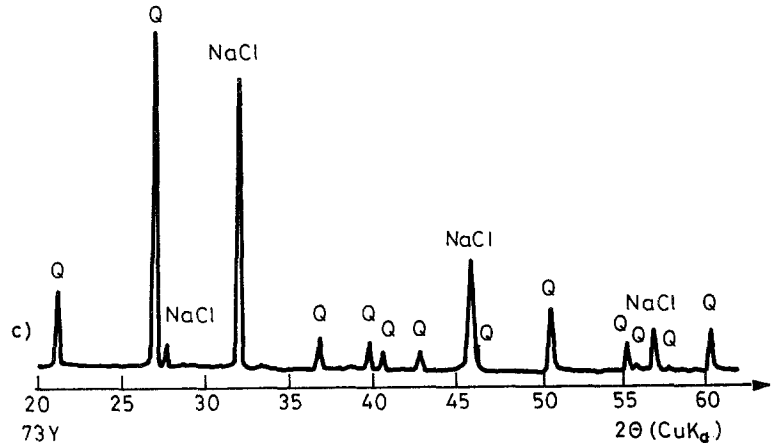

Fig. 3C X-ray powder diffraction patterns of the products of cryptohalite synthesis, using quartz mixed with different amounts of ammonium fluoride. (at 335°C and 100% of the theoretical amount of ammonium fluoride B = Cryptohalite and Q = Quartz

At 125°–155°C: The reaction of quartz with ammonium fluoride takes place with the formation of cryptohalite.

$$\underset{\text{Quartz}}{SiO_2} + 6NH_4F \rightarrow \underset{\text{Cryptohalite}}{(NH_4)_2SiF_6} + 4NH_3 + 2H_2O$$

At 200°C and excess ammonium fluoride: The reaction of quartz with ammonium fluoride takes place with the formation of cryptohalite and a double compound.

$$2SiO_2 + 13NH_4F \rightarrow \underset{\text{Cryptohalite}}{(NH_4)_2SiF_6} + \underset{\text{Quartz}}{(NH_4)_2SiF_6 \cdot NH_4F} + 8NH_3 + 4H_2O$$

At 320°–335°C: Cryptohalite and the double compound $(NH_4)_2SiF_6 \cdot NH_4F$ are unstable and dissociate according to

$$\underset{\text{Cryptohalite}}{(NH_4)_2SiF_6} \rightarrow SiF_4 + 2NH_3 + 2HF$$

$$(NH_4)_2SiF_6 \cdot NH_4F \rightarrow SiF_4 + 3NH_3 + 3HF$$

or the reaction of quartz with ammonium fluoride takes place at such temperatures, according to

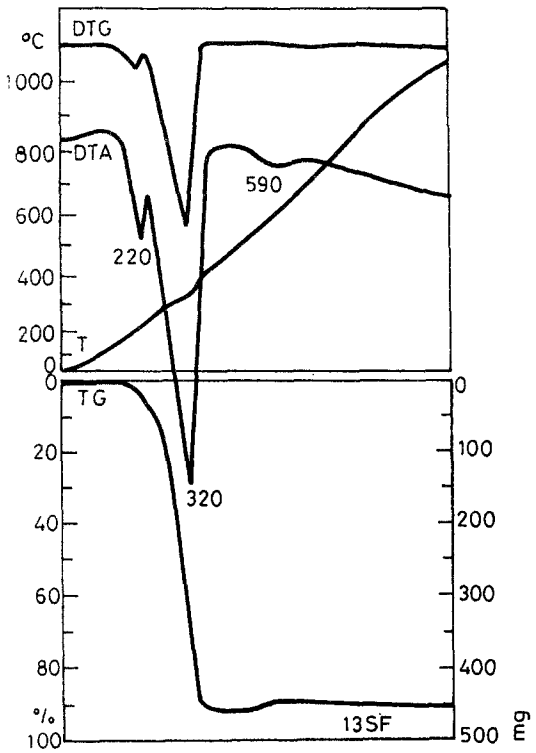

Fig. 4 DTA curve of synthesis of cryptohalite using quartz mixed with ammonium fluoride of amount 150% of theoretical value

$$SiO_2 + 6NH_4F \rightarrow SiF_4 + 6NH_3 + 2HF + 2H_2O$$
Quartz

The resulted cryptohalite is colorless in thin sections and crystallizes in cubic system, in the form of octahedral crystals with perfect (111) cleavage. The dimorph bararite (hexagonal) is not detected in all experiments. It has the following chemical composition: 20.31% NH_4, 15.82% Si and 63.84% F.

The studied conditions of formation of cryptohalite and its thermal behaviour gives a well evidence about its occurrence as a sublimation product near volcanoes.

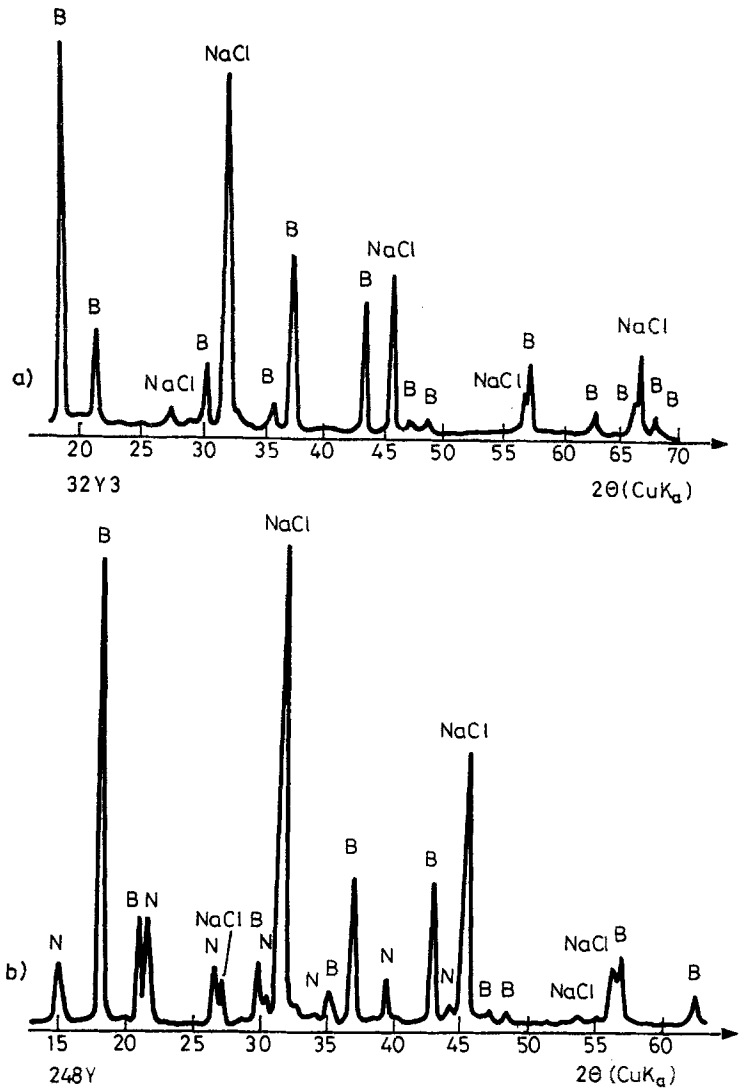

Fig. 5 X-ray powder diffraction patterns of the products of cryptohalite synthesis, using quartz mixed with ammonium fluoride of amount 150% of theoretical values. (A) and (B) at 150 and 200°C respectively. B = Cryptohalite, N = $(NH_4)_2SiF_6 \cdot NH_4F$

Conclusions

The thermal analysis study of synthesis of cryptohalite by sintering of quartz with different amounts of ammonium fluoride has revealed that the intensive formation of cryptohalite takes place at 125°–155°C by an en-

dothermic reaction. Cryptohalite is unstable and dissociates at 320°–335°C as represented by the sharp and large endothermic peaks at these temperatures, with the liberation of ammonia, silicon tetrafluoride and hydrogen fluoride.

At 200°C and excess of ammonium fluoride, the product of the reaction is composed of cryptohalite and a double compound $(NH_4)_2SiF_6 \cdot NH_4F$.

The resulted synthetic cryptohalite is colorless in thin sections and crystallizes in cubic system, in the form of octahedral crystals with perfect (111) cleavage. The hexagonal dimorph bararite is not detected in all runs.

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Zusammenfassung — Mittels eines Derivatographen wurde die Synthese von Kryptohalit (Ammoniumsiliziumhexafluorid) durch Sintern von Quarz mit Ammoniumfluorid thermisch untersucht. Die Reaktionsprodukte wurden mikroskopisch und mit Hilfe eines Siemens-Crystalloflex Diffraktometers identifiziert. Die DTA-Kurven zeigen, daß die intensive Bildung von Kryptohalit in einer endothermen Reaktion bei 125°–155°C abläuft. Wie durch die scharfen und intensiven endothermen Peaks bei 320°–335°C gezeigt wird, ist Kryptohalit bei dieser Temperatur instabil und dissoziiert.
Das erhaltene Kryptohalit ist in dünnen Schnitten farblos und kristallisiert im kubischen System in der Form von oktaedrischen Kristallen mit perfekter (111) Spaltbarkeit. Das dimorphe Bararit konnte in keinem der Versuche beobachtet werden.