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SODIUM FLUOROALUMINATES FORMED IN THE REACTION BETWEEN ALUMINUM FLUORIDE SOLUTION AND CRYSTALLINE SODIUM FLUORIDE

MARIAN GROBELNY

Institute of Inorganic Chemistry, Gliwice (Poland)

SUMMARY

The reaction of aluminum fluoride solution with crystalline sodium fluoride was investigated. Conditions for the formation of Na_3AlF_6 (cryolite) , $Na_5Al_3F_{14}$ (chiolite) and $NaAlF_4.H_2O$ were established. The hitherto presumed to be unstable $NaAlF_4.H_2O$ was isolated and its X-ray diffraction data as well as thermal behaviour were determined. The possibility to convert these compounds one into the other was outlined.

INTRODUCTION

The nature of sodium fluoroaluminates formed in the preparation of synthetic cryolite from aqueous solutions has not been yet explained sufficiently. Various authors consider the solution reaction between aluminum fluoride and sodium fluoride as proceeding with the formation of $NaAlF_4.H_2O$ or $Na_5Al_3F_{14}$ as intermediates.

The first information about $NaAlF_4.xH_2O$ phase was given by Cagliotti [1] in his short communication for the International Congress of Chemistry. He called it pseudo-cryolite and determined its structure as identical with that of natural cryolite, $Na_5Al_3F_{14}$ (?!) except for a slight widening perpendicular to the c axis. The precipitate corresponding to the formula $NaAlF_4.H_2O$ prepared by Yatlov [2] by partial neutralization of fluoroaluminic acid with sodium carbonate was then put into doubt by Cowley and Scott [3] who recognized it as a mixture of chiolite and aluminum fluoride, $AlF_3.3H_2O$. In 1949, Yatlov and Pinayevskaya reported [4] that adding natrium fluoride solution to a great excess of AlF_3 solution results in the precipitation of $NaAlF_4.H_2O$ which however does not crystallize in the form of stable solid phase. This was confirmed by Smirnov [5] who found by means of graphic-analytical method that $NaAlF_4.H_2O$ is the intermediate in the reaction between AlF_3 and NaF solutions, leading to cryolite of composition $Na_{11}Al_4F_{23}.H_2O$.

Variability in composition of sodium fluoroaluminates in the system $NaF-AlF_3-H_2O$ in the range of molar ratio NaF/AlF_3 from 0.6 to 2.7 was attributed by Yatlov and Pinayevskaya [4] to chiolite and its solid solutions with NaF or AlF_3. Frolkova and Dmitrevsky [6] have stated that indenpendently on molar ratio NaF/AlF_3, from unsaturated aluminum fluoride solutions always cryolite of composition $11NaF.4AlF_3.H_2O$ arises, while from supersaturated solutions the precipitates of composition varying from $1.2NaF.AlF_3$ to $2.2NaF.AlF_3$ and of chiolite structure are obtained. Kozlov et al. consider [7] the sodium fluoroaluminates having molar ratio NaF/AlF_3 greater than 1.67 as being consisted of chiolite and cryolite and those of lower molar ratio as mixtures of chiolite and aluminum fluoride trihydrate, the latter being undetectable by X-ray diffraction method at least in the range of NaF/AlF_3 from 0.8 to 1.3. The authors cited above [7] assume that from aqueous solutions crystal hydrates $Na_5Al_3F_{14}.H_2O$ and $Na_3AlF_6.0.5H_2O$ arise which decompose above 300°C while retaining their crystal structures. However, variation in intensity and appearance of new diffraction lines are observed.

It is noteworthy that $NaAlF_4.H_4O$ has not been hitherto isolated and its structural data are lacking, in contrast to well-known cryolite and chiolite.

An attempt was undertaken in this work to clarify the diverse literature data and to establish the conditions for the formation of individual phases during the reaction of AlF_3 solution with NaF crystals.

EXPERIMENTAL

As the starting materials were used:

a) aluminum fluoride solutions of 21 and 75 g/l, having different pH values of 1.2 and 2.8 adjusted with fluorosilicic acid,

b) crystalline sodium fluoride, NaF p.a.,

c) chiolite $Na_5Al_3F_{14}$ obtained in the reaction of stoichiometric amounts of AlF_3, HF and NaCl at 50°C; it was used in experiments as a nucleating agent and as the X-ray standard.

Investigations included effects of initial concentration of AlF_3 solution(21 and 75 g/l), molar ratio of reactants NaF/AlF_3(covering the range 0.5-3.0), temperature(60, 80, 100°C), presence of added chiolite and pH values of 1.2 or 2.8 upon the phase composition of reaction products obtained.

The experiments were carried out as follows: into 1 liter of aluminum fluoride solution contained in a three-necked flask fitted with a thermometer, reflux condenser and a stirrer, and brought to the appropriate temperature, the calculated amount of solid NaF was introduced. The mixture was then stirred at constant temperature for 2 hours. Samples were removed at intervals for analysis. After filtering, the AlF_3 content in solution was determined by the EDTA method, whereas the solids were identified by X-ray method. The X-ray analysis was made in a MUR-61 analyzer with copper radiation and a nickel filter. The results of experiments are shown in Fig.1 giving the relations between AlF_3 concentration and reaction time. Owing to the very low solubility of precipitates the overall reaction taking place might be followed on solute concentration curves.

RESULTS

The influence of temperature upon the reaction of solid sodium fluoride with unsaturated aluminum fluoride solution of 21 g/l, pH 1.2(in the presence of H_2SiF_6 10 g/l), with equimolar quantities of reactants is shown in Fig. 1a. From this figure it follows that at 100 and 80°C the reaction proceeds essentially to completion and only 2 g/l AlF_3 remains in the solution, whereas at 60°C the consumption of AlF_3 is markedly smaller. The X-ray diffraction analysis of samples taken at 60°C along the reaction curve show that in the 30th minute undissolved NaF still occurs together with cryolite Na_3AlF_6 and chiolite $Na_5Al_3F_{14}$. After some time, the lines of NaF and cryolite are no longer evident but only those of $Na_5Al_3F_{14}$ and a new phase which was believed to be $NaAlF_4.H_2O$. The admixture of $Na_5Al_3F_{14}$ may account for incomplete conversion of AlF_3 in solution. At 80°C no chiolite was observed but only $NaAlF_4.H_2O$ in its pure form. Initially some Na_3AlF_6 was also observed. At 100°C the reaction gives $NaAlF_4.H_2O$ as the sole product. X-ray diffraction pattern of this compound is shown in Fig.2 as compared with chiolite and cryolite.

Chemical analysis of the final product obtained at 80°C gives Al, 18.7; F, 51.4%; Na, 16.8 and H_2O 12.7% which is corresponding to the formula $Na_{1.05}AlF_{3.96}.H_2O_{1.02}$. Density of this material amounts to 2.53 g/cm^3. The solubility of $NaAlF_4.H_2O$ after stirring 100g of solid in 1 liter of water for 2 hours at 25°C was found to be 0.50 g/l, increasing in fluorosilicic acid of 50 and 100 g/l to 3.8 and 8.0 g/l, respectively. The aluminum concentration was used as a measure of the solubility of $NaAlF_4.H_2O$ and it was not ascertained if incongruent resolution takes place, or not.

It is apparent that the reaction between AlF_3 and NaF when carried out under suitable conditions may have potential for producing three different compounds:

$$AlF_3 + NaF \begin{array}{l} \nearrow \; Na_3AlF_6 \qquad (1) \\ \longrightarrow \; Na_5Al_3F_{14} \qquad (2) \\ \searrow \; NaAlF_4.H_2O \qquad (3) \end{array}$$

When equimolar amounts of the reactants are used, the final product may be $NaAlF_4.H_2O$ and/or $Na_5Al_3F_{14}$, depending on temperature. Higher temperatures are favorable to the formation of $NaAlF_4.H_2O$ and lower ones to chiolite and cryolite. The disappearance of initially formed cryolite in further course of the reaction can be explained by its conversion with aluminum fluoride solution:

$$Na_3AlF_6 + 2\ AlF_3 \longrightarrow 3\ NaAlF_4.H_2O \qquad (4)$$

Observations made on supersaturated AlF_3 solution of 75 g/l, pH 2.8 at 60, 80 and 100°C lead to similar conclusions (Fig. 1b): Na_3AlF_6 is the intermediate and $NaAlF_4.H_2O$ the final product. Rapid decrease in AlF_3 contents during the first 10 minutes, especially at 60 and 80°C, may be attributed to the Na_3AlF_6 precipitation whereas the further slow drop is caused by its transformation according to the equation (4). Crystalline phases resulted at 80 and 100°C at pH 2.8 are very close to that of $NaAlF_4.H_2O$ show, however, varied intensity and decreased sharpness of the spectra (Fig. 2d). This is presumed to be caused by the formation of aluminum fluoride solid solution in the crystal lattice of $NaAlF_4.H_2O$ to give fluoroaluminates with NaF/AlF_3 ratio less than 1. This phenomenon was not observed at the same temperature 80°C but at lower pH (e.g., 1.9) or at lower temperatures (e.g., 60°C) and at the same pH value of 2.8, thus under conditions less favorable for spontaneous crystallization of aluminum fluoride trihydrate from supersaturated solution.

The influence of $Na_5Al_3F_{14}$ used as nucleating agent in amount of 10 g/l upon the reaction of equimolar amounts NaF and AlF_3 solution of 21 g/l, pH 2.0 and 3.4 at 60, 80 and 100°C is demonstrated by the isotherms in Fig. 1c. These plots are quite different from those given in Figure 1a. In this case, irrespective of reaction temperature, about 40% of unreacted AlF_3 remains in solution. Such behaviour may be ascribed to the chiolite formation in accordance with the equation:

$$5\ NaF + 3\ AlF_3 \xrightarrow{seed} Na_5Al_3F_{14} \qquad (5)$$

This was confirmed by X-ray diffraction patterns of the samples taken along the reaction curves.

Also in this case, as in the absence of chiolite, the formation of cryolite in the beginning of reaction could be observed, especially at lower temperatures (e.g., 60°C, pH 2.0) or at less acidic media (e.g., 80°C, pH 3.4) . Its further disappearance indicates on the following reaction:

$$5\ Na_3AlF_6 + 4\ AlF_3 \xrightarrow{seed} 3\ Na_5Al_3F_{14} \qquad (6)$$

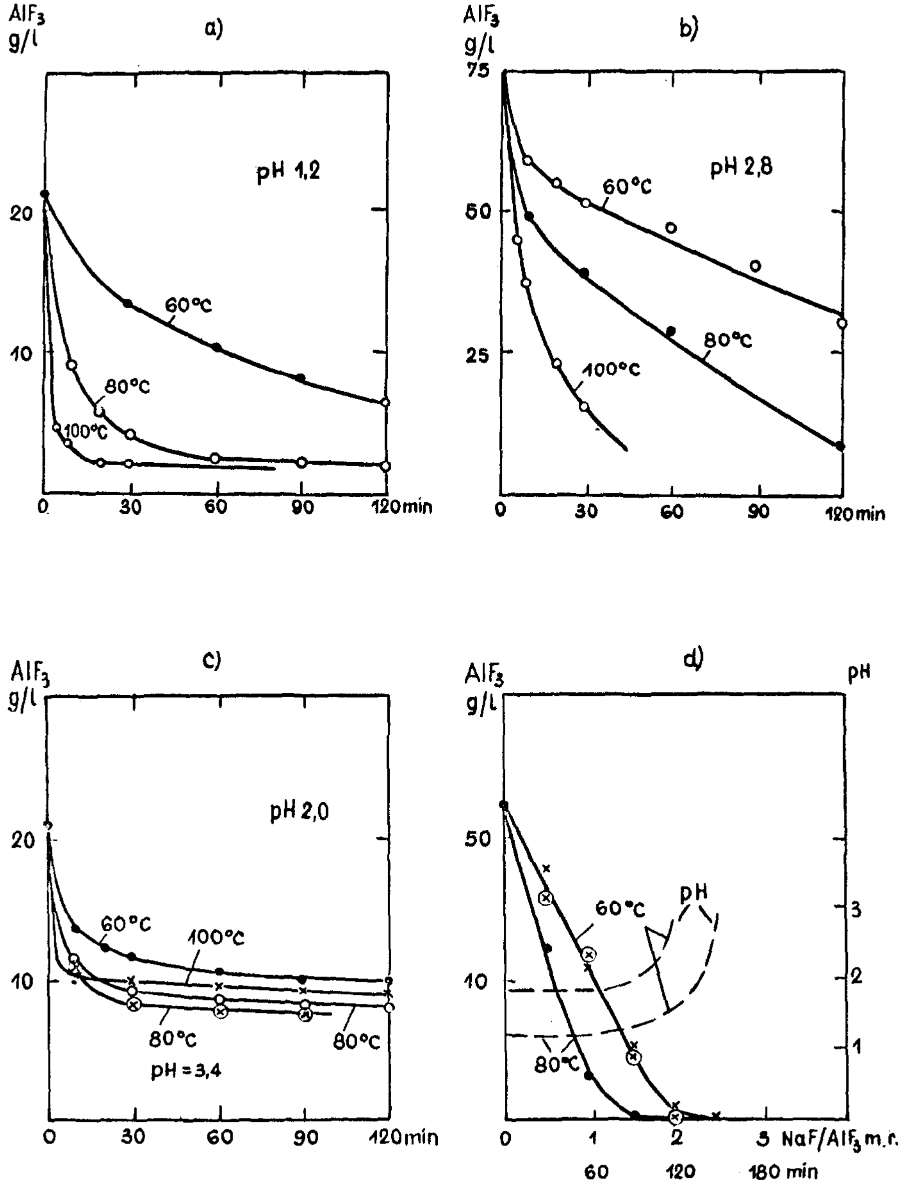


Fig. 1. Isotherms of AlF_3-concentration during the reaction with solid NaF at 60, 80 and 100°C.
Initial conditions: a) - c) mole ratio NaF : AlF_3 = 1:1; a) pH 1,2; b) pH 2,8; c) pH 2,0 (and 3,4 for 80°C), $Na_5Al_3F_{14}$ seed 10 g/l; d) pH 1,2 (and 1.8 for 60°C) , adding 0,5 m NaF per 1 mole AlF_3 at intervals of 30 min.

The influence of molar ratio NaF/AlF_3 upon the phase composition of reaction products was investigated at 60 and 80°C by adding to the AlF_3 solution of 22 g/l, pH 1.2 and 1.8 at intervals of 30 minutes equal portions of solid NaF, each increasing the molar ratio of reactants of 0.5. Prior to introducing every next portion of NaF, samples of suspension were taken and analyzed. The relation between AlF_3 content and pH values versus the NaF/AlF_3 molar ratio are shown in Figure 1d. The X-ray diffraction patterns of solid samples taken at 80°C, pH 1.3 indicate that at molar ratios of 0.5 and 1.0 only $NaAlF_4.H_2O$ exists whereas at 1.5 also chiolite does, and at 2.0 only chiolite. In compliance with this, the following reaction is to be assumed:

$$3\ NaAlF_4.H_2O + 2\ NaF \longrightarrow Na_5Al_3F_{14} + 3\ H_2O \qquad (7)$$

The isotherm at 60°C is the same for pH 1.3 and for 1.8. Despite that, the X-ray patterns reveal distinct differences in the composition of reaction products obtained. At pH 1.3 for the molar ratios of 0.5, 1.5 and 2.5 higher amounts of $NaAlF_4.H_2O$ together with Na_3AlF_6 and traces of chiolite are observed whereas at a pH value of 1.8 cryolite predominates all the time, along with minor amounts of $NaAlF_4.H_2O$ and no chiolite. The pH of suspension proved to be dependent upon the molar ratio at values greater than 1 raising from 1.3 to 2.8 when the NaF/AlF_3 attains a value of 2.5 and from 1.8 to the same value of 2.8 already at NaF/AlF_3 = 2.0.

From all these observations it is clear that hydrogen ions interfere with the formation of cryolite in favour of $NaAlF_4.H_2O$ and $Na_5Al_3F_{14}$. This is probably due to shifting equilibrium

$$AlF_6^{3-} + 2\ H^+ \rightleftharpoons AlF_4^- + 2\ HF \qquad (8)$$

to the right side when H^+-ions concentration is increased. It results from the difference between the dissociation constant of HF (pK 3.2) and the instability constant of AlF_6^{3-} in relation to AlF_4^-, being pK 2.1 [8].

Temperature exerts probably similar influence on the above equilibrium as H^+-ions. Under the same acidic conditions, lower temperatures are presumably more favorable to the formation of chiolite than $NaAlF_4.H_2O$.

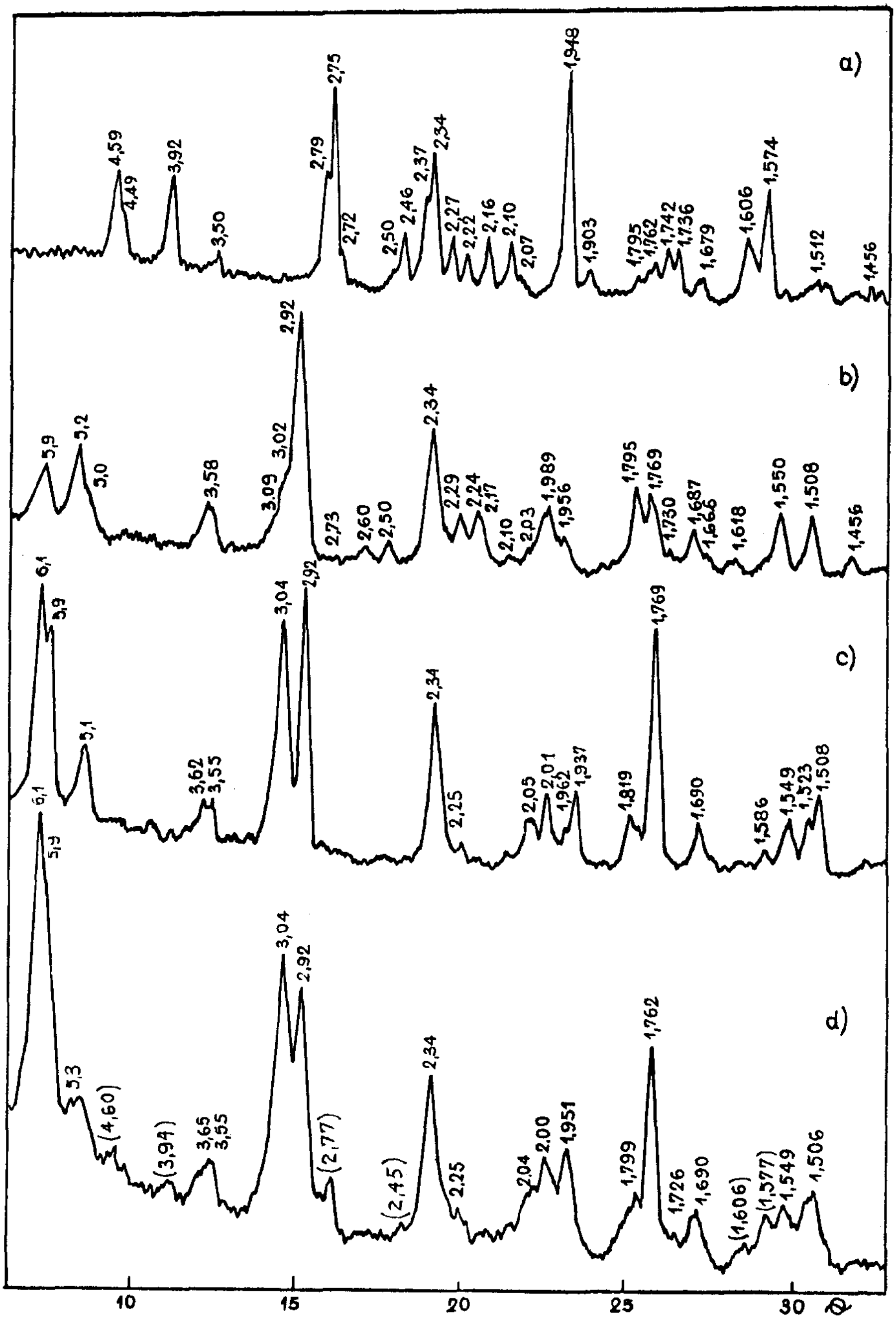


Fig. 2. X-ray diffraction patterns of sodium fluoroaluminates. a) Na_3AlF_6 (cryolite) , b) $Na_5Al_3F_{14}$ (chiolite), c) $NaAlF_4 \cdot H_2O$, d) $Na_{(1-x)}AlF_{(4-x)} \cdot yH_2O$ ($x < 1$; $y > 1$).

TABLE 1
X-ray diffraction comparison of sodium fluoroaluminates precipitated from aqueous solutions

Na_3AlF_6		$Na_5Al_3F_{14}$		$NaAlF_4 \cdot H_2O$		$Na_{(1-x)}AlF_{(4-x)} \cdot yH_2O$	
d	I	d	I	d	I	d	I
				6.1	87	6.1	130
		5.9	32	5.9	74	5.9	107
		5.2	40	5.1	29	5.3	25
		5.0	25				
4.59	35					(4.60)	
4.49	21						
3.92	38					(3.94)	
				3.62	13	3.65	14
3.50	7	3.58	25	3.55	13	3.55	21
		3.09	18				
		3.02	34	3.04	84	3.04	114
		2.92	100	2.92	100	2.92	100
2.79	44						
2.75	86					(2.77)	
2.72	17	2.73	1				
		2.60	3				
2.50	7	2.50	6				
2.46	23					(2.45)	
2.37	40						
2.34	68	2.34	64	2.34	61	2.34	68
2.27	26	2.29	20	2.25	6	2.25	14
2.22	14	2.24	22				
2.16	26	2.17	22				
2.10	24	2.10	5				
2.07	7	2.03	12	2.05	19	2.04	25
		1.989	25	2.01	29	2.00	39
1.948	100	1.956	16	1.962	13	1.951	46
				1.937	29		
1.903	10						
1.795	8	1.795	40	1.819	23	1.799	28
1.762	14	1.769	40	1.769	93	1.762	90
1.742	19						
1.736	24	1.730	10			1.726	11
		1.687	16	1.690	16	1.690	25
1.679	10	1.666	10				
		1.618	5				
1.606	30					(1.606)	
1.574	47			1.586	6	(1.577)	
		1.550	23	1.549	19	1.549	25
				1.523	23		
1.512	5	1.508	26	1.508	32	1.506	32

In brackets: spacings of cryolite.

Thermal behaviour of $NaAlF_4.H_2O$

The X-ray diffraction data of sodium fluoroaluminates are listed in Table 1. There is a great resemblance in the interplanar distances between $NaAlF_4.H_2O$ and chiolite but there are also significant differences in intensities of corresponding lines, e.g., for d = 6.0, 3.0, 2.9 and 1.8.

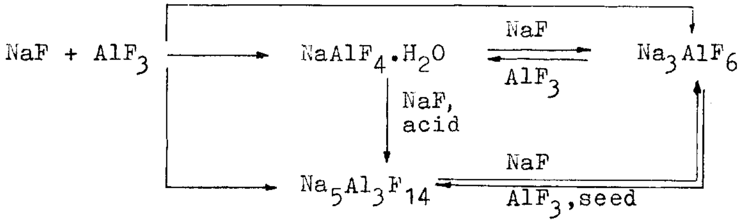
The X-ray diffraction pattern of $NaAlF_4.H_2O$ heated to various temperatures in the interval 200-600°C is gradually replaced by lines due to chiolite and anhydrous aluminum fluoride. At 300°C the compound almost completely loses its hydration water (more than 10% of total weight). At 500°C some amounts of $NaAlF_4.H_2O$ still occur, whereas at 600°C only chiolite and aluminum fluoride exist. Thus, the thermal decomposition of $NaAlF_4.H_2O$ may be expressed by the equation:

$$5\ NaAlF_4.H_2O \xrightarrow{200-600^\circ C} Na_5Al_3F_{14} + 2\ AlF_3 + 5\ H_2O \quad (9)$$

In contrast, chiolite precipitated from solution does not change its crystal structure pattern and its ignition losses at 600°C amounted to about 5 per cent.

DISCUSSION

The reaction of aluminum fluoride solution with crystalline sodium fluoride may lead to sodium fluoroaluminates of the formulae $NaAlF_4.H_2O$, $Na_5Al_3F_{14}$ and Na_3AlF_6. Under suitable conditions defined by molar ratio NaF/AlF_3 of reactants, temperature, time, manner of adding NaF, presence of nucleating agent, if any, there is a possibility to produce one or more of the above compounds directly or by conversion of one phase to another. This can be summarized in the following scheme:



Cryolite may be the final product of the reaction between AlF_3 and NaF directly or through $NaAlF_4.H_2O$ and/or $Na_5Al_3F_{14}$. Its formation is favoured by lower temperatures and higher pH values. In contrast, the precipitation of chiolite requires rather lower temperatures and lower pH values, especially the presence of seed crystals. On the other hand, increased temperatures possibly coupled with decreased pH values are the best conditions for the formation of $NaAlF_4.H_2O$ directly from equimolar amounts of AlF_3 and NaF or through cryolite with AlF_3. The conversion of $NaAlF_4.H_2O$ with NaF to chiolite takes place in more acidic media than to cryolite.

Crystal structure of $NaAlF_4.H_2O$ shows a great similarity to that of chiolite but differs in its thermal low stability. Contrary to chiolite, heating $NaAlF_4.H_2O$ make it lose its crystal water at about 300°C and decompose progressively to form a mixture of $Na_5Al_3F_{14}$ with AlF_3, between 500-600°C.

Results obtained in this work enable us to shed more light on the problem involving the nature of sodium fluoroaluminates of variable composition. The precipitates having NaF/AlF_3 molar ratio over the range 1.0-1.67 may now be considered not only as consisting of chiolite and $AlF_3.3H_2O$ as suggested hitherto by various authors [3,6,7] but also, if not exclusively, as being mixtures of chiolite (if not cryolite) with $NaAlF_4.H_2O$. By the presence of the latter, there can be explained both changes in diffraction line patterns of precipitates after ignition, and the increase in water content when sodium - aluminum ratio decreases.

Although chiolite and cryolite contain some combined water being rather incorporated in holes of the crystal lattice than occupying lattice points [3] , there seems to be little probably that these compounds might be responsible for the above-mentioned variations in X-ray diffraction patterns. The existence of crystal hydrates $Na_5Al_3F_{14}.H_2O$ and $Na_3AlF_6.0.5H_2O$ suggested by Kozlov et al. [7] for the explanation of thermal phenomena in the field of sodium fluoroaluminates seems to be doubtful in view of the results presented in this paper. As it can be concluded from above, such behaviour of samples could be caused by admixture of $NaAlF_4.H_2O$ in chiolite and cryolite.

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