

# **ELECTRONEGATIVITY FORCE OF CATIONS AND THERMAL DECOMPOSITION OF COMPLEX FLUORIDES**

## **I. Thermal decomposition of fluorosilicates**

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### **Abstract**

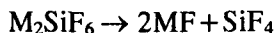
The thermal decompositions of anhydrous fluorosilicates  $M_2SiF_6$  ( $M=Li, Na, K, Rb, Cs$ ) and  $MSiF_6$  ( $M=Ca, Sr, Ba$ ) were investigated. The decompositions proceeded according to a simple acid-base mechanism with evolution of  $SiF_4$ . The influence of the cationic counter-ion acidity (expressed by means of the electronegativity force) on the course of thermal decomposition was estimated quantitatively.

**Keywords:** complex fluorides, electronegativity force, IR, thermal decomposition, X-ray

### **Introduction**

The wide-ranging practical application of fluorine compounds imposes the need for study of their physicochemical properties and the mechanisms of the chemical processes occurring on their heating. There are a number of papers [1-6] on the thermal decompositions of fluorosilicates and their hydrates. However, we have found no paper on the influence of the acidity of the cationic counter-ions on the course of thermal decomposition. Such an influence may be decisive as concerns the stability of the salts.

From the viewpoint of the general definition of acids, bases, oxidizers and reducers [7] the decomposition of fluorosilicates:



is a typical acid-base reaction, where  $SiF_6^{2-}$  is a base (donor of  $F^-$ ), and the metal cation is an acid (acceptor of  $F^-$ ). The anion-acceptor properties (acidity) of the cations may be characterized in terms to the 'acidity force' proposed by

Gontarz and Górski [8, 9]. This force has been defined as the ratio of the energy of that stage of the metal ionization reaction which results in formation of the cation  $M^{n+}$ , to the standard ionic radius (with coordination number 6):

$$E_f = \frac{-E_i}{r}$$

The electronegativity force is expressed in nanonewtons [nN]. Analyses of the thermal decomposition processes of whole classes of oxy compounds [9, 10] have confirmed the good usability of this quantity.

The thermal decompositions of fluoro salts of the main group elements are particularly convenient processes for studies of the effect of the acidity of the cation on the counter-ion, since in most cases they proceed according to simple acid-base mechanisms. In the present work the electronegativity force has been utilized as a quantitative parameter. For its application to fluorine compounds, it has been calculated from the ionic radii of fluorine compounds at various coordination numbers. Electronegativity forces calculated for 11 selected cations are compiled in Table 1. The values of ionic radii have been taken from the paper by Shannon and Prewitt [11].

The aim of the present work was to determine the course and the temperatures of thermal decomposition of anhydrous fluorosilicates under comparable experimental conditions, and to compare the obtained results with the electronegativity forces of the cations. The objects of study were systems containing the following cations:  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . The experimental techniques involved were thermal analysis, X-ray phase analysis and infrared spectroscopy.

## Experimental

Thermogravimetric analyses were carried out with the derivatograph produced by MOM, Budapest. Weighed samples of about 0.3 g were located in the platinum crucible, which was then placed in a quartz envelope in a continuous flow of purified nitrogen. The rate of heating was  $9 \text{ deg}\cdot\text{min}^{-1}$ , TG, DTG and DTA curves were recorded.

X-ray diffractograms were taken by the powder method with a TUR-M62 bicircular diffractometer and  $\text{CuK}\alpha$  radiation. The starting materials and the decomposition products were identified by comparison with X-ray standards published by the Joint Committee on Powder Diffraction Standards or with other literature data.

Infrared spectra of samples included in KBr tablets were recorded on a SPECORD 75IR spectrophotometer in the region  $2000\text{--}400 \text{ cm}^{-1}$ .

Table 1 Electronegativity force  $E_t$  of some cations

Cation	$E_i/eV$	Coordination number											
		4		6		8		9		12			
		$r_j/pm$	$E_t/nN$	$r_j/pm$	$E_t/nN$	$r_j/pm$	$E_t/nN$	$r_j/pm$	$E_t/nN$	$r_j/pm$	$E_t/nN$	$r_j/pm$	$E_t/nN$
Li <sup>+</sup>	5.39	73	11.8	88	9.8	-	-	-	-	-	-	-	-
Na <sup>+</sup>	5.14	113	7.3	116	7.1	130	6.3	146	5.6	-	-	-	-
K <sup>+</sup>	4.34	-	-	152	4.6	165	4.2	169	4.1	174	4.0	174	4.0
Rb <sup>+</sup>	4.18	-	-	163	4.1	174	3.8	-	-	187	3.6	187	3.6
Cs <sup>+</sup>	3.89	-	-	184	3.4	-	-	192	3.2	202	3.1	202	3.1
Ca <sup>2+</sup>	11.87	-	-	114	16.7	126	15.1	132	14.4	149	12.8	149	12.8
Sr <sup>2+</sup>	11.03	-	-	130	13.6	139	12.7	-	-	158	11.2	158	11.2
Ba <sup>2+</sup>	10.00	-	-	150	10.7	156	10.3	161	10.0	174	9.2	174	9.2
Mg <sup>2+</sup>	15.04	63	38.2	66	36.5	-	-	-	-	103	23.4	103	23.4
Zn <sup>2+</sup>	17.96	74	38.9	88.5	32.5	-	-	-	-	-	-	-	-
Cd <sup>2+</sup>	16.91	98	27.6	109	24.9	121	22.4	-	-	145	18.7	145	18.7

Fluorosilicates of the alkali metals were prepared by crystallization from aqueous solutions of samples obtained in reactions of aqueous solutions of the corresponding hydroxides (Li, Na, K) or carbonates (Rb, Cs) with 40% fluorosilicic acid. Fluorosilicates of Ca and Sr were crystallized in the form of dihydrates  $\text{MSiF}_6 \cdot 2\text{H}_2\text{O}$  from aqueous solutions obtained by dissolving the carbonates in 40%  $\text{H}_2\text{SiF}_6$ , after separation of small amounts of fluorides and concentration under reduced pressure at room temperature.  $\text{BaSiF}_6$  was precipitated from an aqueous solution of  $\text{Ba}(\text{NO}_2)_2$  by means of 40%  $\text{H}_2\text{SiF}_6$ . The products were dried in air at  $80^\circ\text{C}$ . Anhydrous  $\text{CaSiF}_6$  and  $\text{SrSiF}_6$  were obtained by drying the hydrates at 160 and  $140^\circ\text{C}$ , respectively, in dry  $\text{N}_2$ . The powder diffrac-

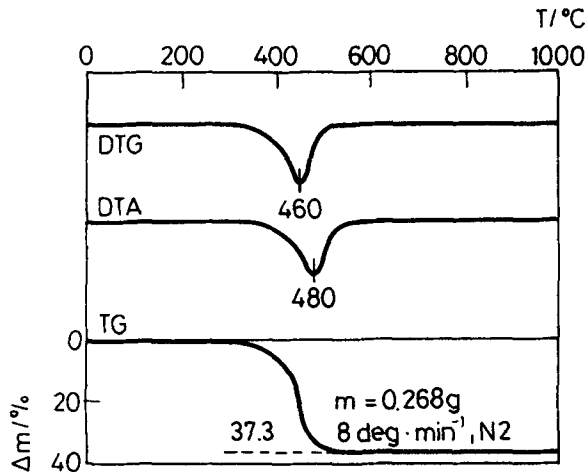


Fig. 1 TG, DTG and DTA curves of  $\text{BaSiF}_6$

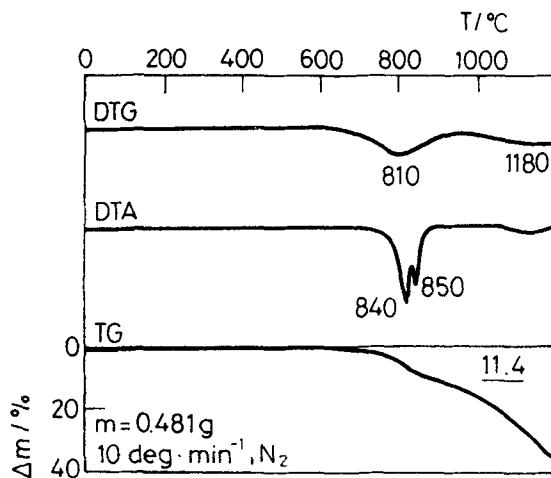


Fig. 2 TG, DTG and DTA curves of  $\text{Rb}_2\text{SiF}_6$

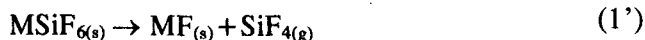
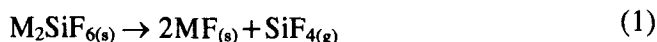
tograms obtained were in agreement with the ASTM standards:  $\text{Li}_2\text{SiF}_6$  16-307,  $\text{Na}_2\text{SiF}_6$  8-36,  $\text{K}_2\text{SiF}_6$  7-217,  $\text{Rb}_2\text{SiF}_6$  7-207,  $\text{Cs}_2\text{SiF}_6$  7-6,  $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$  1-227,  $\text{CaSiF}_6$  1-482,  $\text{BaSiF}_6$  15-736, and with literature data [4] in the cases of  $\text{SrSiF}_6$  and  $\text{SrSiF}_6 \cdot 2\text{H}_2\text{O}$ . The products of thermal decomposition were identified by X-ray diffraction and infrared spectroscopy in samples obtained by heating the corresponding salts in a tubular furnace in dry,  $\text{O}_2$ -free nitrogen at temperatures determined by means of the thermoanalytical curves.

## Results and discussion

The results of thermogravimetric analysis are presented in Table 1. Figures 1 and 2 show thermal curves of  $\text{BaSiF}_6$  and  $\text{Rb}_2\text{SiF}_6$ , which represent the two types of decomposition distinguished in the course of the studies.

### *Thermal decompositions of $\text{Li}_2\text{SiF}_6$ , $\text{Na}_2\text{SiF}_6$ , $\text{CaSiF}_6$ , $\text{SrSiF}_6$ and $\text{BaSiF}_6$*

The results of thermogravimetric analysis demonstrated that the decompositions of these salts lead to the emission of  $\text{SiF}_4$  and the formation of simple metal fluoride according to the following equations:



This was confirmed by X-ray diffraction of the solid products. Except for the thermogram of  $\text{Na}_2\text{SiF}_6$ , no effects were observed that would be accounted for by polymorphic transformations below the decomposition temperature. All decompositions were accompanied by strong endothermic effects.

The temperatures corresponding to the minimum in the DTA curves are given in Table 2. In the case of  $\text{Na}_2\text{SiF}_6$ , a strong endothermic effect was observed at about  $520^\circ\text{C}$ . As shown by X-ray analysis,  $\text{Na}_2\text{SiF}_6$  samples heated to  $530^\circ\text{C}$  and cooled did not reveal any new phase in addition to undecomposed starting material and small amounts of  $\text{NaF}$ . This indicates that the endothermic effect is due to a polymorphic transformation of  $\text{Na}_2\text{SiF}_6$ , which confirms literature observations [3]. In all cases, the observed losses in mass conformed to those obtained by calculation (Table 2).

### *Thermal decompositions of $\text{K}_2\text{SiF}_6$ , $\text{Rb}_2\text{SiF}_6$ and $\text{Cs}_2\text{SiF}_6$*

The decomposition scheme for these three salts is different from the preceding one. The TG curves point to the presence of two stages of decomposition. The losses in mass and analysis of the products following the first step of de-

Table 2 Results of thermogravimetric analysis of fluorosilicates

Salt	Decomposition products	Temperature range / °C	TG		DTG $T_{\max}$ / °C	DTA* $T_{\max}$ / °C
			observed	theoretical		
$\text{Li}_2\text{SiF}_6$	$\text{LiF}$ , $\text{SiF}_4$ (g)	240 - 350	66.6	66.74	340	350 d
$\text{Na}_2\text{SiF}_6$	$\text{NaF}$ , $\text{SiF}_4$ (g)	400 - 650	55.2	55.34	620	520 p 630 d
$\text{K}_2\text{SiF}_6$	$\text{K}_3\text{SiF}_7$ , $\text{SiF}_4$ (g)	560 - 830	18.7	15.75	800	790 m, d 840 c (exo) 860 m
$\text{Rb}_2\text{SiF}_6$	$\text{Rb}_3\text{SiF}_7$ , $\text{SiF}_4$ (g)	560 - 850	11.4	11.08	810	840 d 850 m
$\text{Cs}_2\text{SiF}_6$	$\text{Cs}_3\text{SiF}_7$ , $\text{SiF}_4$ (g)	670 - 800	9.1	8.51	760	760 d, m
$\text{CaSiF}_6$	$\text{CaF}_2$ , $\text{SiF}_4$ (g)	200 - 320	55.9	57.14	310	330 d
$\text{SrSiF}_6$	$\text{SrF}_2$ , $\text{SiF}_4$ (g)	260 - 410	45.2	45.31	390	400 d
$\text{BaSiF}_6$	$\text{BaF}_2$ , $\text{SiF}_4$ (g)	320 - 480	37.3	37.25	460	480 d

\* Abbreviations used in DTA column:

c - crystallization

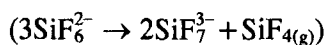
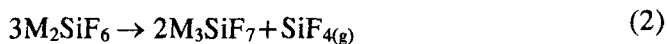
d - decomposition

m - melting

p - polymorphic transformation

All effects were endothermic except crystallization (noted exo)

composition show that the decomposition proceeds according to the following scheme:



X-ray diffraction analysis showed the presence of  $K_3SiF_7$  (ASTM 17-885) and  $Rb_3SiF_7$  (own standard, Table 3) in  $K_2SiF_6$  and  $Rb_2SiF_6$  samples heated at 830 and 850°C, respectively.

**Table 3** X-ray standard of  $Rb_3SiF_7$

<i>d</i> / pm	<i>I</i> / <i>I</i> <sub>0</sub>
413	20
402	20
352	20
338	60
327	10
302	40
289	60
280	60
250	30
231	20
224	60
218	30
201	60
193	30
190	20
183	20
182	20
174	20
170	20
163	20
160	10

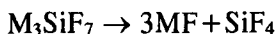
We did not succeed in  $Cs_3SiF_7$  because of its complete decomposition at lower temperatures. The obtained results obtained conform to the literature data concerning the phase systems  $KF-K_2SiF_6$  [12],  $CsF-Cs_2SiF_6$  and  $RbF-Rb_2SiF_6$  [13]. It should be noted that, despite the stoichiometry of the salts, the coordination number of silicon is not 7 but 6, and the structure of the salts involves

the anions  $\text{SiF}_6^{2-}$  and  $\text{F}^-$  [14]. Proof of this is provided by the infrared spectra of  $\text{K}_3\text{SiF}_7$  and  $\text{Rb}_3\text{SiF}_7$ , where absorption bands due to vibrations in  $\text{SiF}_6^{2-}$  occupy the same positions as in  $\text{K}_2\text{SiF}_6$  and  $\text{Rb}_2\text{SiF}_6$  (Figs 3 and 4).



Fig. 3 Infrared spectra of  $\text{K}_2\text{SiF}_6$  and  $\text{K}_3\text{SiF}_7$

Further decomposition of the fluorosilicates  $\text{M}_3\text{SiF}_7$  proceeds in the liquid phase. Thermal decompositions carried out in a tubular furnace showed that the emission of  $\text{SiF}_4$  is accompanied by salt evaporation. Hence, the mass losses recorded in the thermoanalytical curves are greater than those calculated for the reaction:



#### *Thermal decomposition and electronegativity force*

Analysis of the results in Table 2 shows a very good correlation between the temperature of the maximum rate of loss in mass, as registered in the TG, DTG



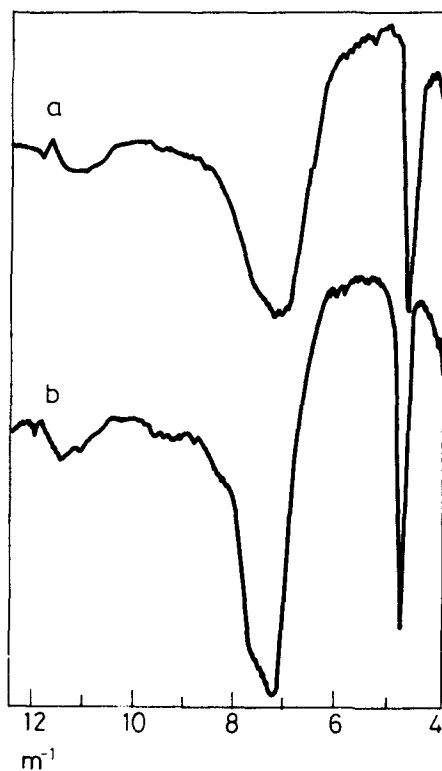


Fig. 4 Infrared spectra of  $\text{Rb}_2\text{SiF}_6$  and  $\text{Rb}_3\text{SiF}_7$

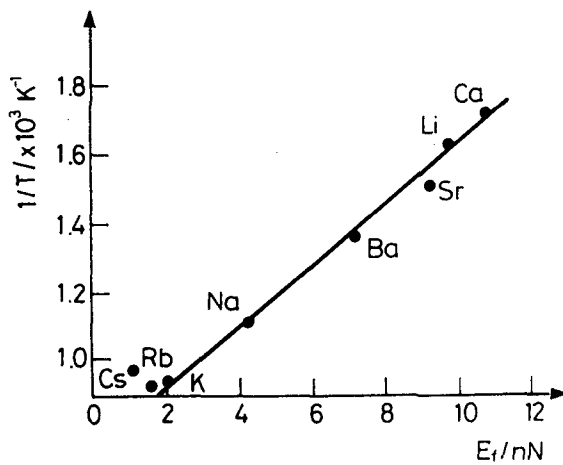


Fig. 5 Relationship between the reciprocal of  $T_{\text{max}}$  of decomposition of fluorosilicates and electronegativity force

and DTA curves, and the electronegativity force of the cationic counter-ions calculated for the following coordination numbers: Li-4; Na-8; K, Rb, Cs, Ca, Sr, Ba - 12. The linear relationship between the inverse of  $T_{\max}$  [in K] and  $E_f$  [in nN] is shown in Fig. 5.

**Table 4** Temperature of maximum mass loss in the course of decomposition of fluorosilicates - comparison of experimental and calculated values according to the equation:  
 $1/T_{\max} [\text{K}] = 1/1992\text{K} + 9.97 \cdot 10^{-5} \cdot E_f$

Cation	$E_f$ / nN	$T_{\max}$ / °C		$\Delta T$ / °C
		measured	calculated	
Li <sup>+</sup>	11.8	340	349	9
Na <sup>+</sup>	6.3	620	608	12
K <sup>+</sup>	4.0	800	797	3
Rb <sup>+</sup>	3.6	810	840	30
Cs <sup>+</sup>	3.1	760	894	134
Ba <sup>2+</sup>	9.2	460	451	9
Sr <sup>2+</sup>	11.2	390	372	18
Ca <sup>2+</sup>	12.8	310	320	10
Mg <sup>2+</sup>	36.5	-	- 4	-
Zn <sup>2+</sup>	32.5	-	23	-
Cd <sup>2+</sup>	22.4	-	125	-

There is a considerable divergence for the cesium salt. This may be accounted for by the strong volatility of Cs<sub>2</sub>SiF<sub>6</sub>. The high correlation factor  $R=0.993$  shows that the electronegativity force may be used as a quantitative parameter in the analysis of thermal decomposition processes. Extrapolation of the relationship to cations of higher electronegativity force (Cd<sup>2+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>) shows (Table 4) that one can expect the preparation of anhydrous CdSiF<sub>6</sub>, stable at ambient temperatures. This is the subject of investigations currently under way.

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**Zusammenfassung** — Es wurde die thermische Zersetzung der wasserfreien Fluorosilikate  $M_2SiF_6$  ( $M=Li, Na, K, Rb, Cs$ ) und  $MSiF_6$  ( $M=Ca, Sr, Ba$ ) untersucht. Die Zersetzungen zeigten eine Übereinstimmung mit einem einfachen Säure-Basen-Mechanismus, wobei  $SiF_4$  freigesetzt wird. Der Einfluß der Acidität des kationischen Gegeniones (ausgedrückt durch die Elektronegativitätskraft) auf den Verlauf der thermischen Zersetzung wurde quantitativ geschätzt.