Thermochimica Acta, 72 (1984) 277–287
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

STUDIES ON THE THERMAL DECOMPOSITION OF THE SILVER GROUP OF ALKALI METAL NITRITOCOBALTATES(III)

A. FURMANIAK-SUWALSKA
Institute of Occupational Medicine, 90-950 Łódź (Poland)

A. CYGAŃSKI
Institute of General Chemistry, Technical University, 90-924 Łódź (Poland)

(Received 18 July 1983)

ABSTRACT

The thermal decomposition of nitritocobaltate(III) of the silver group of general formula $M_2Ag[Co(NO_2)_6]$ (where M = K^+, NH_4^+, Rb^+ or Cs^+) has been investigated. Based on the thermal curves of the investigated compounds and chemical and diffractometric analysis, the mechanism of thermal decomposition has been determined. The results obtained indicate that the decomposition proceeds in three stages. As a result of decomposition in the first stage (300°C), nitrates of alkali metals, metallic silver and Co_3O_4 are formed. In the second stage (500°C), a partial decomposition of nitrates to alkali metal oxides occurs, and in the third stage the products are alkali metal oxides, silver and Co_3O_4. This paper also presents the dependence of the decomposition temperature of nitritocobaltates(III) of the silver group on the ionic radius of the outer-sphere cation.

INTRODUCTION

Nitritocobaltates of alkali metals of general formula $M_2M'[Co(NO_2)_6]$ where M = K^+, NH_4^+, Rb^+ or Cs^+ and M′ = Na^+ or Ag^+ can, depending on the cation M′, be divided into the sodium group of formula $M_2Na[Co(NO_2)_6]$ and the silver group of formula $M_2Ag[Co(NO_2)_6]$. The characteristic feature of this division is the dependence $r_M > r_{M'}$, which means that the ionic radius of the cation M is always greater than the ionic radius of the cation M′. Nitritocobaltates(III) of the silver group show better analytic properties than nitritocobaltates(III) of the sodium group, since, generally, their dissolution is much more difficult, e.g., the limiting concentration of potassium ions needed for the formation of the precipitate $K_2Na[Co(NO_2)_6]$ is 1 : 27 000 [1], whereas for the formation of $K_2Ag[Co(NO_2)_6]$ it is 1 : 1 000 000 [2].

The thermal decomposition of nitritocobaltates(III) of the sodium group was investigated by Duval [3,4] and by Wendlandt and Suthern [5]. Data concerning the thermal decomposition of potassium–silver nitritocobaltates(III) are given by Duval [3]. He mentioned that the thermogravimetric curve of this compound falls gradually and is not used for analytical determinations. However, he did not investigate the thermal decomposition of nitritocobaltates(III) of other alkali metals from the silver group.

Nitritocobaltates(III) of the alkali metals from the silver group were obtained according to Fresenius and Jander [6].

The thermal decomposition of the compounds $K_2Ag[Co(NO_2)_6]$, $(NH_4)_2Ag[Co(NO_2)_6]$, $Rb_2Ag[Co(NO_2)_6]$ and $Cs_2Ag[Co(NO_2)_6]$ was investigated in this paper.

Derivatographic and diffractometric investigations, and chemical analysis of the decomposition products allowed determination of the mechanism of thermal decomposition of the investigated compounds.

EXPERIMENTAL

Thermal analysis

Thermal investigations on nitritocobaltates(III) of ammonium and alkali metals of the silver group were carried out using a thermal analyzer MOM

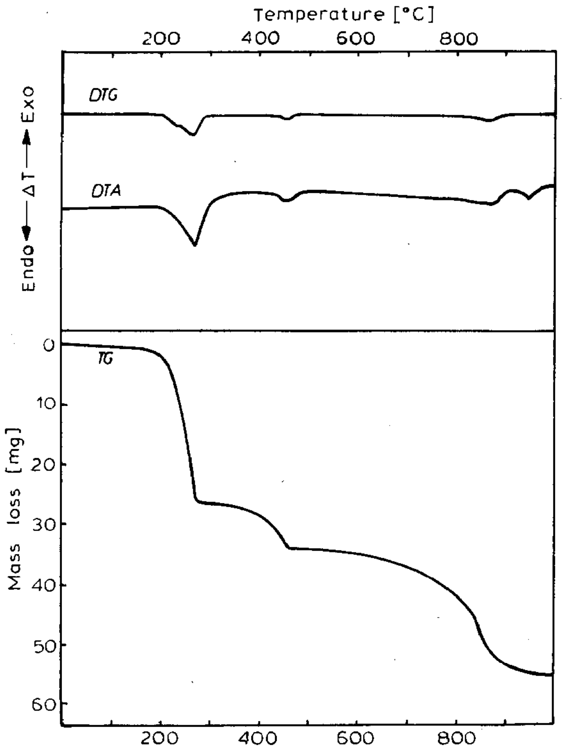

Fig. 1. Thermal analysis curves of potassium–silver nitritocobaltate(III).

Budapest type OD-102/1500°C. The measurements were made in air, in the temperature range 20–1000°C, at a heating rate of 5°C min^{-1}. The sensitivity of the galvanometer for the DTA curve was 1/15 and for the DTG curve 1/20. TG sensitivity was 200 mg. α-Al_2O_3 was used as the reference material. The weight of the samples used for investigation was 250 mg.

Thermal curves of potassium–silver nitritocobaltate(III) and ammonium–silver nitritocobaltate(III) are presented in Figs. 1 and 2. From the thermal curves it follows that, during the heating of $K_2Ag[Co(NO_2)_6]$, four thermal processes take place. The first one starts at 180°C and reaches a maximum rate at 230°C. This is an endothermic process (a sharp peak on the DTA curve). The second process is also an endothermic one and is connected with a decrease in the mass of the sample. The maximum rate of this process is observed at 430°C (peaks on the DTA and DTG curves). The third endothermic peak on the DTA curve at 850°C also corresponds to a considerable loss in mass of the sample. The endothermic peak on the DTA curve at 960°C corresponds to the melting point of silver.

Similar processes are observed for the thermal curves of $Rb_2Ag[Co(NO_2)_6]$

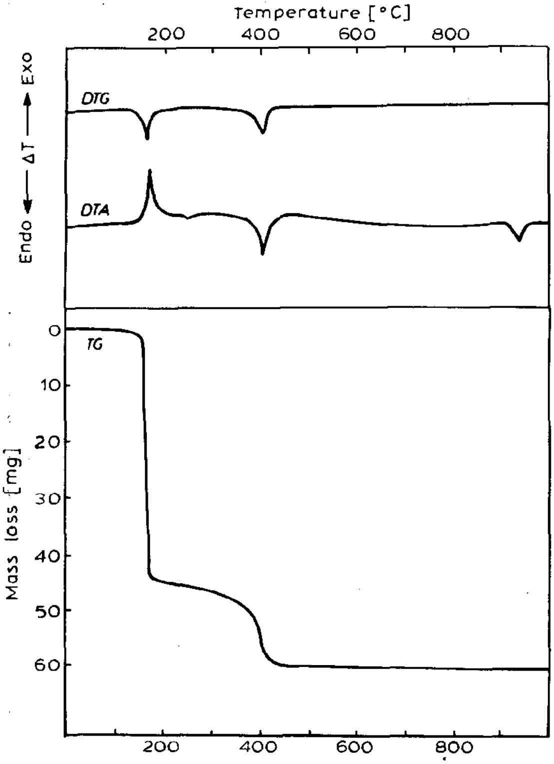

Fig. 2. Thermal analysis curves of ammonium–silver nitritocobaltate(III).

TABLE 1

Results of the chemical analysis of sinters of the silver group alkali metal nitritocobaltates(III) prepared at 300°C

Compound	Determined (%)			Calculated (%)		
	Soluble fraction	Insoluble fraction	Percentage in the sinter	Soluble fraction	Insoluble fraction	Percentage in the sinter
$K_2Ag[Co(NO_2)_6]$ [a]	52.72	47.28	Co = 15.07 Ag = 26.1 K = 19.08	51.77	48.23	Co = 15.12 Ag = 27.63 K = 19.99
$(NH_4)_2Ag[Co(NO_2)_6]$ [b]	28.56 Ag = 62.3	71.44 Ag = 48.6	Co = 26.54 Ag = 52.53	27.11 Ag = 63.49	72.89 Ag = 47.22	Co = 28.26 Ag = 51.63
$Rb_2Ag[Co(NO_2)_6]$ [a]	59.93	40.07	Co = 12.7 Ag = 21.46 Rb = 35.04	61.06	38.94	Co = 12.47 Ag = 22.78 Rb = 35.39
$Cs_2Ag[Co(NO_2)_6]$ [a]	68.48	31.52	Co = 10.01 Ag = 18.2 Cs = 43.8	67.46	32.54	Co = 10.21 Ag = 18.65 Cs = 45.99

[a] Calculated values based on reaction 1.

[b] Calculated values based on reaction 6.

and $Cs_2Ag[Co(NO_2)_6]$. However, some differences are observed in the thermal curves for $(NH_4)_2Ag[Co(NO_2)_6]$ (Fig. 2). As the compound is heated, three thermal processes take place. The first of them is an exothermic process (a sharp peak on the DTA curve) connected with a considerable loss in mass. It starts at 140°C and reaches its maximum rate at 180°C. The second conversion, occurring at 420°C, corresponds to an endothermic peak on the DTA curve and a loss in mass on the TG curve. The third endothermic peak on the DTA curve corresponds to the melting point of silver.

After determining the decomposition temperature of a given compound we tried to define the products of the process. In order to achieve this, sinters of the investigated compounds were heated in an electric silite furnace at a heating rate of 5°C min^{-1}. For the control of the sinters' preparation, the mass loss of the sinters was determined and compared with the mass loss following from the TG curve.

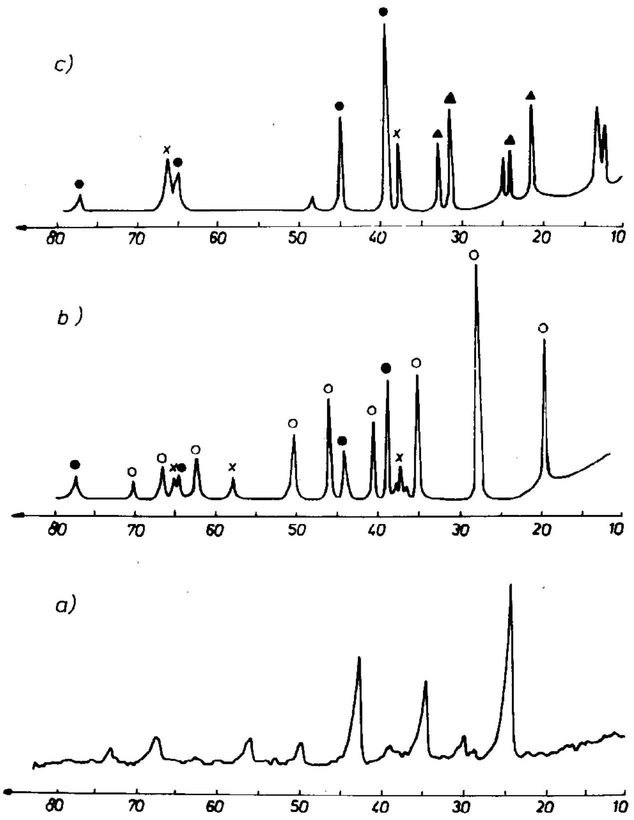

Fig. 3. X-Ray diffraction patterns of caesium–silver nitritocobaltate(III): (a), before sintering; (b), after sintering to 300°C; and (c), after sintering to 950°C. ○, $CsNO_3$; ▲, Cs_2O; ●, Ag; and ×, Co_3O_4.

Chemical analysis

The sinters prepared were divided into fractions: soluble and insoluble in water. In order to achieve this, the sinters were treated with hot water for several hours. In the insoluble fraction, the amount of silver was determined using the Volhard method and the amount of cobalt by the complexometric method [7]. In the soluble fraction, the amount of alkali metal was determined [7,8]. It was also examined for silver or cobalt content. The results of the analysis of nitritocobaltates(III) of the silver group obtained at 300°C are presented in Table 1.

X-Ray analysis

X-Ray analysis of the sinters was carried out on a DRON-2 diffractome-

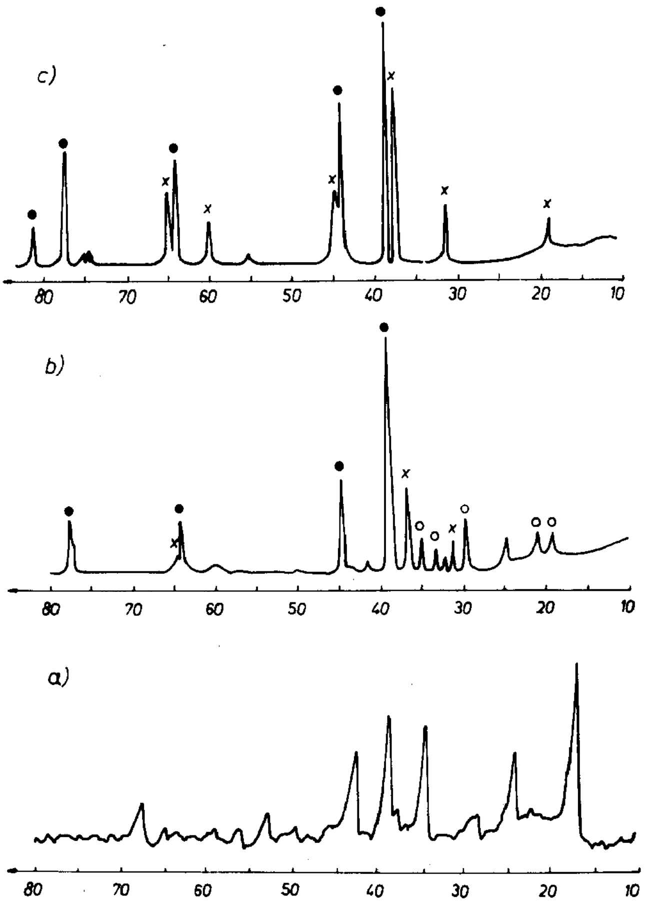

Fig. 4. X-Ray diffraction of ammonium–silver nitritocobaltate(III): (a), before sintering; (b), after sintering to 300°C; and (c), after sintering to 950°C. ○, $AgNO_3$; ●, AG; and ×, Co_3O_4.

TABLE 2

X-Ray identification of the potassium–silver nitritocobaltate(III) sinter prepared at 300°C

Data from X-ray pattern of the sinter		Literature data	
2θ	d/n (Å)	d/n (Å)	Compound
19.0	4.67	4.66	KNO_3
23.6	3.77	3.77	KNO_3
29.5	3.028	3.03	KNO_3
33.8	2.652	2.66	KNO_3
37.0	2.43	2.43	Co_3O_4
38.1	2.362	2.36	Ag
41.3	2.186	2.19	KNO_3
44.4	2.04	2.04	Ag
46.6	1.949	1.96	KNO_3
59.4	1.556	1.56	Co_3O_4
64.5	1.445	1.445	Ag
65.0	1.435	1.432	Co_3O_4
77.5	1.232	1.23	Ag
81.8	1.177	1.179	Ag

ter using CuK_α radiation with a nickel filter. The diffraction curves were recorded over the range 2θ angles from 10 to 90°.

Figure 3 presents an X-ray diffraction pattern for caesium–silver nitritocobaltate(III). In the sinter, at 300°C, the presence of Ag, Co_3O_4 and $CsNO_3$ was noticed, whereas at 950°C Cs_2O, Ag and Co_3O_4 were identified. The X-ray diffraction pattern for a sinter of ammonium–silver nitriticobal-

TABLE 3

X-Ray identification of the rubidium–silver nitritocobaltate(III) sinter prepared at 300°C

Data from X-ray pattern of the sinter		Literature data	
2θ	d/n (Å)	d/n (Å)	Compound
20.8	4.27	4.28	$RbNO_3$
29.7	3.01	3.02	$RbNO_3$
36.5	2.46	2.46	$RbNO_3$
37.0	2.43	2.43	Co_3O_4
38.1	2.362	2.36	Ag
42.4	2.132	2.13	$RbNO_3$
44.4	2.04	2.04	Ag
47.5	1.914	1.925	$RbNO_3$
52.4	1.746	1.74	$RbNO_3$
64.5	1.445	1.445	Ag
65.3	1.429	1.432	Co_3O_4
77.5	1.232	1.23	Ag

tate(III) is presented in Fig. 4. In the sinter obtained at 300°C Ag, $AgNO_3$ and Co_3O_4 were found, whereas at 950°C Ag and Co_3O_4 were identified. Tables 2 and 3 present reflexes occurring in the diffractogram of the sinter at 300°C for $K_2Ag[Co(NO_2)_6]$ and $Rb_2Ag[Co(NO_2)_6]$.

Analysis of the gaseous products

Analysis of the gaseous products released during thermal decomposition of nitritocobaltates(III) at 300°C was also carried out.

A precipitate of potassium–silver nitritocobaltate(III) was placed in a silica vessel and heated to 300°C. Nitrogen oxides evolved were absorbed in three bubblers filled with: (a) 20 ml 0.2 M NaOH; (b) 20 ml 0.02 M $KMnO_4$; and 1 ml 0.5 M NaOH. After the decomposition had been completed, the composition of the absorbed nitrogen oxides was determined by (1) acidimetry and (2) oxidimetric titration.

DISCUSSION

The temperature curves for nitritocobaltates(III) of alkali metals from the silver group indicate that during the heating of $K_2Ag[Co(NO_2)_6]$ $Rb_2Ag[Co(NO_2)_6]$ and $Cs_2Ag[Co(NO_2)_6]$, three thermal processes connected with a loss in mass take place.

Stage I

In the first stage of thermal decomposition (300°C) alkali metal nitrate, metallic silver and cobaltous–cobaltic oxide are formed. The presence of these products was confirmed by chemical and X-ray analysis of the sinters at 300°C. Based on the results of investigations on the gaseous products it was assumed that during thermal decomposition of nitritocobaltates(III) at 300°C, an equimolar mixture of nitrogen oxide and dioxide is formed. The mixture results from the reaction of evolved nitrogen oxides and oxygen from the air. The following decomposition reaction was suggested

$$3\ M_2Ag[Co(NO_2)_6] + 2\ O_2 = 6\ MNO_3 + Co_3O_4 + 3\ Ag + 6\ NO + 6\ NO_2 \quad (1)$$

where $M = K^+$, Rb^+ or Cs^+.

Stage II

The second stage of thermal decomposition starts at about 400°C and is accompanied by a loss in mass. The loss in mass determined from the derivation pattern of $K_2Ag[Co(NO_2)_6]$ for this stage is 8.74%, for $Rb_2Ag[Co(NO_2)_6]$, 7.41%, and for $Cs_2Ag[Co(NO_2)_6]$, 7.62%.

If only the loss in mass of the heated compounds is taken into account, it seems that alkali metal nitrate is decomposed to a nitrite. The calculated loss in mass for such a conversion for potassium–silver nitritocobaltate(III) would be 8.2%. However, investigations on the sinter $K_2Ag[Co(NO_2)_6]$ prepared at 500°C (diffractometric analysis, i.r. spectrophotometric methods and manganometric determination) did not confirm the presence of nitrites.

Diffractometric analysis of the investigated sinter allowed identification of KNO_3, Ag and Co_3O_4. The following course of the decomposition reaction at 500°C was suggested *

$$6\ KNO_3 + 3\ Ag + Co_3O_4 = 4\ KNO_3 + K_2O + 3\ Ag + Co_3O_4 + N_2O_5 \qquad (2)$$

The loss in mass calculated according to this equation is 9.22%. The presence of K_2O was confirmed indirectly by determination of the amount of nitrogen in the sinter at 500°C. The percentage of nitrogen determined by means of elementary analysis in a sinter of potassium–silver nitritocobaltates(III) is 5.52%, whereas that calculated according to reaction (2) is 5.27%. If the investigated sinter contained 6 KNO_2, 3 Ag and Co_3O_4, the amount of nitrogen would be 7.82%.

Stage III

The third stage of decomposition of nitritocobaltates(III) starts at ~ 700°C and brings about further decomposition of alkali metal nitrates to oxides according to the reaction *

$$4\ MNO_3 + M_2O + 3\ Ag + Co_3O_4 = 3\ M_2O + 3\ Ag + Co_3O_4 + N_4O_{10} \qquad (3)$$

where $M = K^+$, Rb^+ or Cs^+.

The presence of metallic silver, cobaltous–cobaltic oxide and alkali metal oxide was confirmed by diffractometric investigations in a sinter of compounds obtained at 950°C.

The results of these investigations indicate a slightly different course for the decomposition reaction of ammonium–silver nitritocobaltates(III). It occurs in two stages.

Stage I

In the first stage (180°C), the mass losses estimated from the TG curve are 44.4%. Among the products of this decomposition, $AgNO_3$ and Co_3O_4 were identified. The course of the decomposition is described by the reaction *

$$3(NH_4)_2Ag[Co(NO_2)_6] = 3\ AgNO_3 + Co_3O_4 + 3\ N_2 + 12\ H_2O + N_{15}O_{11} \qquad (4)$$

The mass losses calculated according to this equation are 47.75%.

---

* The reactions contain a summary formula of the gaseous products due to the loss in mass.

Stage II

Almost immediately after the stage described by reaction (4), a decomposition of silver nitrate to metallic silver takes place at about 200°C according to the reaction *

$$3\ AgNO_3 + Co_3O_4 = 3\ Ag + Co_3O_4 + N_3O_9 \qquad (5)$$

The process ceases at about 400°C and further heating does not result in changes in the sample's mass.

Since the sinter of $(NH_4)_2Ag[Co(NO_2)_6]$ was prepared at 300°C, an intermediate state between stages I and II was observed. Based on the loss in mass estimated from the TG curve and during preparation of the sinter, and on the chemical analysis of the sinter at 300°C, the following decomposition reaction was suggested *

$$3(NH_4)_2Ag[Co(NO_2)_6] = 2\ Ag + AgNO_3 + Co_3O_4 + 3\ N_2 + 12\ H_2O + N_{17}O_{17} \qquad (6)$$

The above composition of the decomposition products was confirmed by diffractometric analysis. Ag, $AgNO_3$ and Co_3O_4 were identified in the X-ray pattern of the ammonium–silver nitritocobaltate sinter at 300°C.

In the second stage, the decomposition of $AgNO_3$ occurs, during which metallic silver is formed *

$$2\ Ag + AgNO_3 + Co_3O_4 = 3\ Ag + Co_3O_4 + NO_3 \qquad (7)$$

Diffractometric investigations of the sinter at 950°C confirmed the presence of Ag and Co_3O_4.

Of the investigated compounds, $K_2Ag[Co(NO_2)_6]$, $(NH_4)_2Ag[Co(NO_2)_6]$, $Rb_2Ag[Co(NO_2)_6]$ and $Cs_2Ag[Co(NO_2)_6]$, ammonium–silver nitritocobaltates(III) proved to be the least thermally stable. This follows from the properties of the ammonium group. Similarly, a much lower stability is shown by thiocyanatobismuthates(III) containing ammonium as compared with alkali metal thiocyanatobismuthates in which the radius of the alkali metal cation is close to that of the ammonium ion [9,10]. Of the remaining compounds, the most thermally stable proved to be rubidium–silver nitritocobaltate(III) and the least stable, caesium–silver salt. The dependence of the thermal decomposition temperature on the size of the radius of the outer sphere cation is presented in Fig. 5.

Double nitritocobaltates(III) of the silver group are isostructural. They form a regular crystal lattice and belong to the type of structure found in $K_2Ca[Ni(NO_2)_6]$ [11]. The highest stability of rubidium–silver nitritocobaltates(III) can be accounted for by the close-packed structure in the ionic crystal lattice. For the rubidium salt, the spaces are occupied by rubidium

---

* The reactions contain a summary formula of the gaseous products due to the loss in mass.

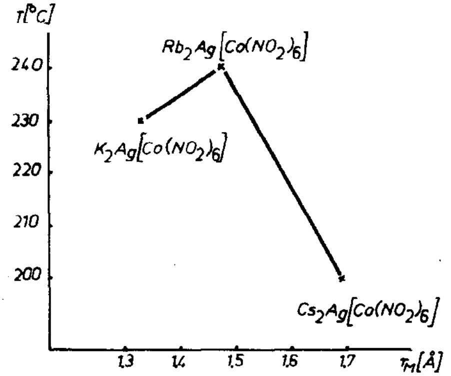

Fig. 5. Dependence of the starting temperature of thermal decomposition of the silver group of alkali metal nitritocobaltates(III) on the radius of the outer-sphere cation.

ions, resulting in the densest structure. A decrease in the radius of the cation (e.g., K^+), and particularly an increase in the radius of cation (e.g., Cs^+) results in destabilization of the structure because the close-packed nature of the crystal lattice is disrupted.

REFERENCES

1 I.M. Kolthoff and P.J. Elving, Treatise on Analytical Chemistry, Part II, Vol. 1, Interscience Publishers, New York, London (1961).
2 L.L. Burgess and O. Kamm, J. Am. Chem. Soc., (1912) 652.
3 G. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1953.
4 C. Duval, Inorganic Thermogravimetric Analysis, 2nd edn., Elsevier, New York, 1963.
5 W.W. Wendlandt and T. Suthern, J. Therm. Anal., 2 (1970) 87.
6 R. Fresenius and G. Jander, Handbuch der analytischen chemie, Part b, Band. Ia, Springer-Verlag, Berlin, 1944.
7 A. Cygański, Chem. Anal. (Warsaw), 9 (1964) 103.
8 L.K. Wilcox, Ind. Eng. Chem., Anal. Ed., 9 (1937) 136.
9 A. Cygański, Rocz. Chem., 50 (1976) 391.
10 A. Cygański, Rocz. Chem., 51 (1977) 2061.
11 W.G. Ralph Wyckoff, Crystal Structures, Vol. III, Interscience, New York, 1953.