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THERMAL INVESTIGATION OF METAL FLUOBERYLLATE HYDRATES AND METAL FLUORIDE HYDRATES

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ABSTRACT

The thermal decompositions of $MBeF_4 \cdot x\ H_2O$ and $MF_2 \cdot x\ H_2O$, where M = Ni(II), Co(II) or Cu(II) and $x = 0$—6, have been carried out using a MOM derivatograph. Dehydration takes place in multiple steps. Anhydrous fluoberyllates dissociate first to MF_2 and BeF_2 and then decompose to MO and BeO in two steps. Metal fluorides give ultimately oxyfluoride in one step. None of the intermediate hydrates is thermally stable, except $CuF_2 \cdot 2\ H_2O$. The probable mechanisms of thermal decomposition have been reported. Pyrolysed products are characterised by elemental analysis and X-ray powder patterns. The value of enthalpy change is reported for each decomposition step.

INTRODUCTION

Numerous works on the thermal dehydration of metal salt hydrates have been carried out [1—8]. Similar work on the hydrates of double sulphate [9—13], double selenate [14], sulphate selenate [9], and sulphate fluoberyllate [15] has also been done. The thermal decomposition of anhydrous metal salt and double salt is receiving extensive attention, and recently some attention has been paid to the thermal decomposition of metal fluoborate [16]. Investigations on the simple beryllium salts are not adequate, whilst thermal studies of double fluorides containing beryllium are scanty [17—21]. The beryllium element itself is receiving tremendous attention from both the chemist and physicist for its application in nuclear technology as well as in industry concerned with glass, ceramics, alloys, etc. Naturally, one may think some potential observations may evolve from the thermal investigation of any beryllium compound. The thermal investigation of transition metal fluoberyllates has not yet been studied. This paper describes the thermal investigation of Co(II), Ni(II) and Cu(II) fluoride hydrates and fluoberyllate hydrates. The investigation includes the identification of pyrolysed products at different temperatures by elemental analysis and X-ray powder pattern, and also includes the probable mechanism of decomposition for each decomposition step, along with the values of enthalpy change.

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EXPERIMENTAL

All the chemicals used were of A.R. grade.

Preparation of $NiF_2 \cdot 4\ H_2O$, $CoF_2 \cdot 4\ H_2O$ *and* $CuF_2 \cdot 6\ H_2O$

Fluorides of Ni(II), Co(II) and Cu(II) were prepared by treatment of the corresponding carbonate (a little excess) with hydrofluoric acid. The mixture of acid and the metal carbonate was kept overnight. The neutral solution was filtered and the filtrate was evaporated in a desiccator containing H_2SO_4 and P_2O_5 at room temperature.

Preparation of $MBeF_4 \cdot 6\ H_2O$ *[where M = Ni(II) or Co(II) or Cu(II)]*

Fluoberyllates of Ni(II), Co(II) and Cu(II) were prepared by treatment of the corresponding carbonate with H_2BeF_4 which is generated by passing $(NH_4)_2BeF_4$ through a cation exchange resin [22,23]. The acid and metal carbonate mixture was kept overnight. The neutral solution was filtered and evaporated to dryness in a desiccator containing H_2SO_4 and P_2O_5 at room temperature.

Thermal measurements

Thermal analysis was carried out using a MOM derivatograph. The operation was done in dynamic air. Platinum crucibles were used. The particle size of the sample was within 150—200 mesh. Enthalpy changes (ΔH) were calculated from DTA peak areas using indium metal as calibrant.

Elemental analyses

Nickel and cobalt were analysed gravimetrically. Copper was estimated volumetrically. Fluorine was estimated following the method adopted by Ray and co-workers [23].

X-Ray powder diffraction

The X-ray powder diffraction patterns of the heated products were obtained on a Philips powder diagram camera, using CoK_α and CuK_α radiation.

RESULTS

Upon heating, $NiBeF_4$ becomes anhydrous via an intermediate hydrate $NiBeF_4 \cdot 5.5\ H_2O$, as shown from its TG curve (Fig. 1), but its DTA curve shows two peaks for the second step of dehydration, indicating that dehydration takes place via another intermediate hydrate. Anhydrous $NiBeF_4$ decomposes to the mixed oxide in a single step, as is evident from its TG curve, but its DTA curve shows clearly that the decomposition takes place in two overlapping steps. On the other hand, the dehydration phenomenon of

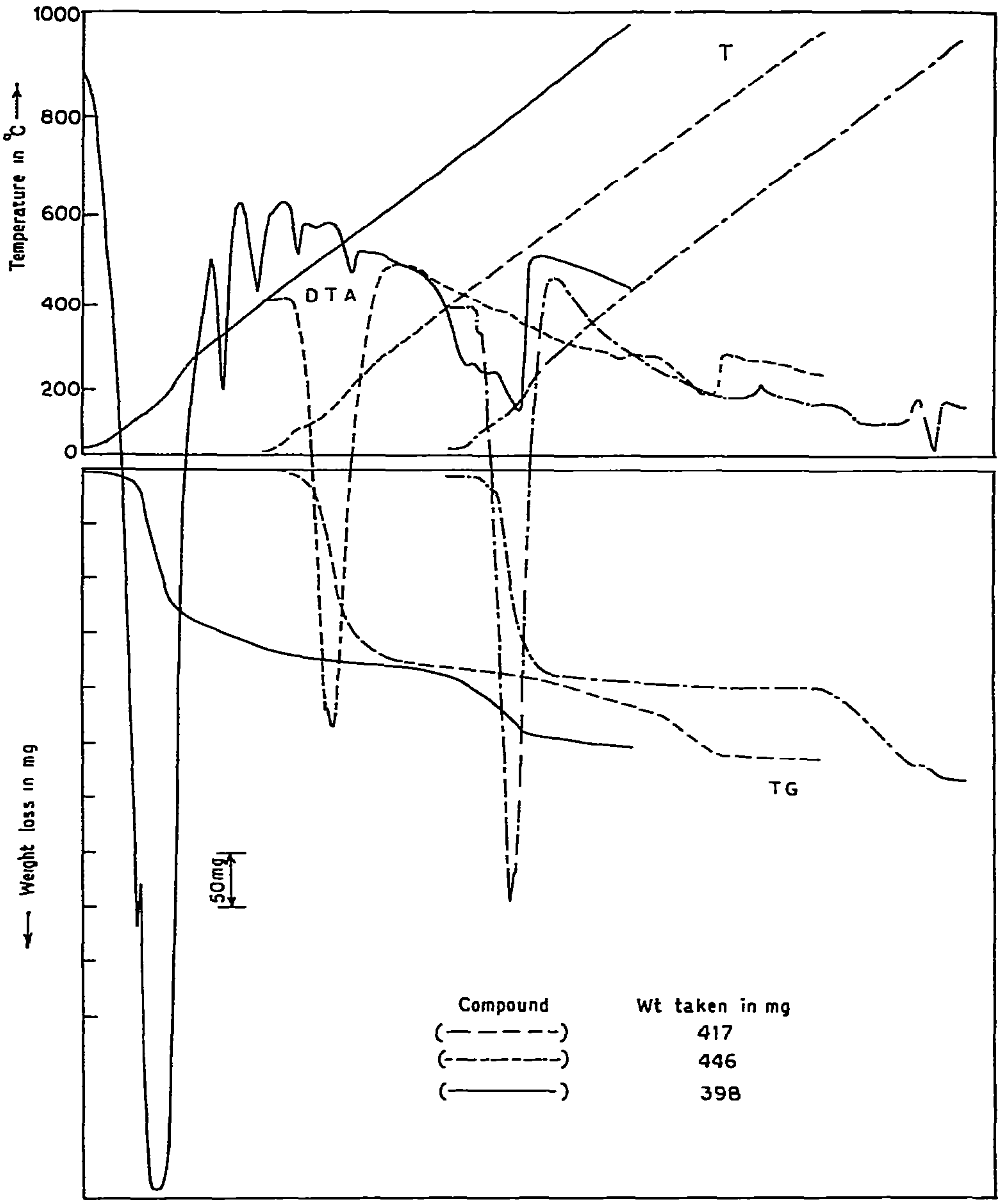

Fig. 1. Thermal curves for the decomposition of $NiBeF_4 \cdot 6\ H_2O$ (------), $CoBeF_4 \cdot 6\ H_2O$ (· — · — ·), and $CuBeF_4 \cdot 6\ H_2O$ (————).

$CoBeF_4 \cdot 6\ H_2O$ is similar to the observation made from the TG curve of $NiBeF_4 \cdot 6\ H_2O$. However, the DTA curve does not show the existence of any intermediate hydrate between $CoBeF_4 \cdot 5.5\ H_2O$ and anhydrous $CoBeF_4$ which shows an exotherm in the temperature range 605—730° C, but the corresponding TG curve shows no mass loss within that temperature range. After this exotherm, cobalt fluoberyllate starts decomposition at 750° C and is completely transformed to the mixed oxide at 930° C, as is clear from its TG curve (Fig. 1). Further, the corresponding DTA curve shows two peaks which indicate that the decomposition takes place in two steps. In the case of $CuBeF_4 \cdot 6\ H_2O$, it is evident from both the TG and DTA curves that six

TABLE 1

Thermal parameters of decomposition of metal(II) fluoberyllate hydrates and metal (II) fluoride hydrates

Decomposition reaction		Temp. range (°C)	DTA peak temp. (°C)	Enthalpy change (ΔH) (kJ mole^{-1})
I	(a) $NiBeF_4 \cdot 6\ H_2O \rightarrow NiBeF_4 \cdot 5.5\ H_2O$	60—125	120	70.5 *
	(b) $NiBeF_4 \cdot 5.5\ H_2O \rightarrow NiBeF_4$	125—380	135, 145	
	(c) $NiBeF_4 \rightarrow NiO \cdot BeO$	418—840	680, 820	
II	(a) $CoBeF_4 \cdot 6\ H_2O \rightarrow CoBeF_4 \cdot 5.5\ H_2O$	80—120	100	68.3 *
	(b) $CoBeF_4 \cdot 5.5\ H_2O \rightarrow CoBeF_4$	120—305	140	
	(c) $CoBeF_4 \rightarrow CoBeF_4$	605—730	662	3.8
	(d) $CoBeF_4 \rightarrow CoO \cdot BeO$		820, 910	**
III	(a) $CuBeF_4 \cdot 6\ H_2O \rightarrow CuBeF_4 \cdot 5.66\ H_2O$	30—120	100	
	(b) $CuBeF_4 \cdot 5.66\ H_2O \rightarrow CuBeF_4 \cdot 1.10\ H_2O$	120—305	160	77.3 *
	(c) $CuBeF_4 \cdot 1.10\ H_2O \rightarrow CuBeF_4 \cdot 0.84\ H_2O$	305—360	330	
	(d) $CuBeF_4 \cdot 0.84\ H_2O \rightarrow CuBeF_4 \cdot 0.51\ H_2O$	330—440	400 **	
	(e) $CuBeF_4 \cdot 0.51\ H_2O \rightarrow CuBeF_4 \cdot 0.34\ H_2O$	440—485	470	
	(f) $CuBeF_4 \cdot 0.34\ H_2O \rightarrow CuBeF_4 \cdot 0.17\ H_2O$	485—520	500	
	(g) $CuBeF_4 \cdot 0.17\ H_2O \rightarrow CuBeF_4$	520—590	560	
	(h) $CuBeF_4 \rightarrow CuO \cdot BeO$	590—865	720, 760 810	55.7
IV	(a) $NiF_2 \cdot 4\ H_2O \rightarrow NiF_2 \cdot 3.5\ H_2O$	110—130	125	62.7 *
	(b) $NiF_2 \cdot 3.5\ H_2O \rightarrow NiF_2 \cdot 0.3\ H_2O$	130—140	140	
	(c) $NiF_2 \cdot 0.3\ H_2O \rightarrow NiF_2$	140—340	160	
	(d) $NiF_2 \rightarrow NiO_{0.9}F_{0.2}$	420—720	660	29.7
V	(a) $CoF_2 \cdot 4\ H_2O \rightarrow CoF_2$	58—258	178	60.6
	(b) $CoF_2 \rightarrow CoO_{0.8}F_{0.4}$	380—760	722	**
VI	(a) $CuF_2 \cdot 6\ H_2O \rightarrow CuF_2 \cdot 5.63\ H_2O$	60—105	100	
	(b) $CuF_2 \cdot 5.63\ H_2O \rightarrow CuF_2 \cdot 4.63\ H_2O$	105—165	150	
	(c) $CuF_2 \cdot 4.63\ H_2O \rightarrow CuF_2 \cdot 4.0\ H_2O$	165—210	180	38.6 *
	(d) $CuF_2 \cdot 4.0\ H_2O \rightarrow CuF_2 \cdot 3.43\ H_2O$	210—280	230	
	(e) $CuF_2 \cdot 3.43\ H_2O \rightarrow CuF_2 \cdot 2.75\ H_2O$	280—360	320	
	(f) $CuF_2 \cdot 2.75\ H_2O \rightarrow CuF_2 \cdot 2.35\ H_2O$	360—450	407	
	(g) $CuF_2 \cdot 2.35\ H_2O \rightarrow CuF_2 \cdot 2\ H_2O$	450—510	495	
	(h) $CuF_2 \cdot 2\ H_2O \rightarrow CuO_{0.75}F_{0.5}$	720—880	750, 865	42.0

* The overall enthalpy change derived from overlapping DTA curves.

** Enthalpy change could not be evaluated due to very poor resolution of the curves.

intermediate hydrates (Table 1) are generated during dehydration. It appears from the TG curve that anhydrous $CuBeF_4$ decomposes to the mixed oxide in one step, but the corresponding DTA curve clearly shows three overlapping endotherms which indicate that decomposition takes place in three steps.

$NiF_2 \cdot 4\ H_2O$ becomes anhydrous, generating two intermediate hydrates (Table 1), as is clear from its TG and DTA curves (Fig. 2). Anhydrous NiF_2 starts decomposition at 420°C and at 720°C transforms to a compound with

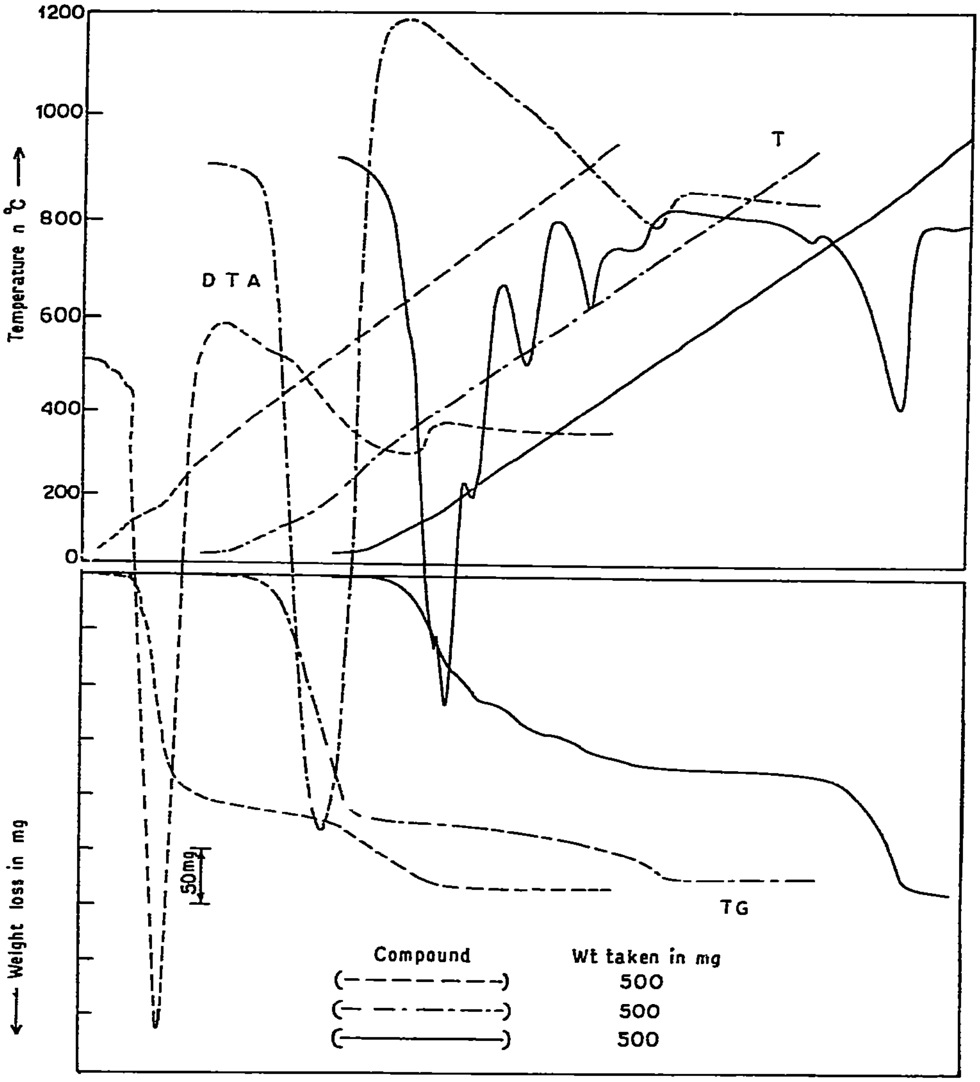

Fig. 2. Thermal curves for the decomposition of $NiF_2 \cdot 4\ H_2O$ (------), $CoF_2 \cdot 4\ H_2O$ (· — · — ·), and $CuF_2 \cdot 6\ H_2O$ (———).

the empirical formula $NiO_{0.9}F_{0.2}$. This remains stable even on further heating to 980°C. On the other hand, $CoF_2 \cdot 4\ H_2O$ becomes anhydrous in a single step at 258°C (Fig. 2). At 760°C the anhydrous CoF_2 transforms to a compound with the empirical formula $CoO_{0.8}F_{0.4}$. The DTA curve shows two peaks for the decomposition of CoF_2 to $CoO_{0.8}F_{0.4}$ which indicates that the decomposition takes place in two steps. In the case of $CuF_2 \cdot 6\ H_2O$ the dihydrate is formed at 450°C via six intermediate hydrates (Table 1). None of the intermediate hydrates is stable enough to be isolated. The hydrate appears from the TG curve to decompose to $CuO_{0.75}F_{0.5}$, as obtained from analytical data, but the corresponding DTA curve shows two overlapping endothermic peaks (Fig. 2), indicating that the decomposition takes place in

TABLE 2

Analytical data (calculated values in parentheses) of metal(II) fluoberyllate hydrates, and metal(II) fluoride hydrates and their pyrolysed compounds

Compounds	Metal (Ni/Co/Cu) (%)	Beryllium (%)	Fluorine (%)
$NiBeF_4 \cdot 6\,H_2O$	23.34 (23.32)	3.57 (3.58)	30.16 (30.19)
$CoBeF_4 \cdot 6\,H_2O$	23.36 (23.39)	3.55 (3.57)	30.14 (30.16)
$CuBeF_4 \cdot 6\,H_2O$	24.74 (24.76)	3.50 (3.51)	29.61 (29.62)
$NiF_2 \cdot 4\,H_2O$	34.81 (34.79)		22.50 (22.52)
$CoF_2 \cdot 4\,H_2O$	34.85 (34.88)		22.48 (22.49)
$CuF_2 \cdot 6\,H_2O$	30.31 (30.32)		18.11 (18.13)
$CuF_2 \cdot 2\,H_2O$	46.21 (46.19)		27.59 (27.62)
$NiO \cdot BeO$	58.84 (58.88)	9.05 (9.02)	
$CoO \cdot BeO$	58.94 (58.97)	9.02 (9.00)	
$CuO \cdot BeO$	60.76 (60.78)	8.60 (8.61)	
$NiO_{0.9}F_{0.2}$	76.36 (76.33)		4.93 (4.94)
$CoO_{0.8}F_{0.4}$	74.24 (74.28)		9.56 (9.57)
$CuO_{0.75}F_{0.5}$	74.69 (74.71)		11.15 (11.17)

TABLE 3

X-Ray powder data for end products obtained in the thermoanalytical experiments of metal(II) fluoberyllates and metal(II) fluorides at 980° C

d (obsd.)					
$NiBeF_4$	$CoBeF_4$	$CuBeF_4$	NiF_2	CoF_2	CuF_2
3.98 (s)	4.64 (vw)	4.84 (w)	3.16 (vs)	2.82 (w)	2.77 (vw)
3.42 (vw)	4.62 (vw)	3.93 (w)	2.93 (w)	2.40 (s)	2.50 (vs)
2.73 (vw)	3.16 (m)	3.73 (w)	2.64 (m)	1.99 (w)	2.30 (vs)
2.42 (vs)	2.82 (w)	3.098 (vw)	2.55 (s)	1.55 (m)	2.07 (vw)
2.35 (m)	2.60 (vw)	2.91 (w)	2.39 (vs)	1.42 (m)	1.87 (m)
2.20 (m)	2.42 (vs)	2.69 (s)	2.29 (s)	1.04 (vw)	1.71 (w)
2.15 (m)	2.22 (vw)	2.62 (w)	2.08 (vs)	0.84 (w)	1.58 (m)
2.11 (vs)	1.99 (vw)	2.52 (m)	1.62 (m)		1.50 (m)
2.08 (s)	1.93 (vw)	2.31 (m)	1.47 (vs)		1.42 (s)
1.88 (w)	1.70 (m)	2.29 (vs)	1.39 (w)		1.38 (s)
1.76 (w)	1.55 (s)	2.19 (vw)			1.31 (w)
1.62 (w)	1.40 (s)	2.12 (s)			1.26 (m)
1.50 (s)		2.09 (vs)			
1.47 (vw)		2.00 (m)			
1.46 (vw)		1.91 (m)			
1.34 (vw)		1.88 (vw)			
1.30 (w)		1.81 (w)			
1.25 (m)		1.80 (m)			
1.24 (w)		1.71 (vw)			
1.23 (vw)		1.68 (w)			
1.20 (w)		1.66 (m)			
1.18 (vw)		1.59 (m)			
1.15 (vw)		1.58 (s)			
1.11 (vw)		1.57 (vw)			
		1.51 (m)			
		1.47 (vw)			
		1.43 (m)			
		1.40 (s)			

vw = Very weak, w = weak, m = medium, s = strong, vs = very strong.

two steps. The temperature range, DTA peak temperature and enthalpy change for each step of decomposition are tabulated in Table 1. The end product of the metal fluoberyllates as well as of the metal fluorides at 980°C is one thermally stable intermediate hydrate, i.e. $CuF_2 \cdot 2\ H_2O$. All the metal fluoberyllate hydrates as well as the metal fluoride hydrates were analysed, the results of which are shown in Table 2. The IR spectrum of $CuF_2 \cdot 2\ H_2O$ and X-ray powder diffraction patterns of all the residues after pyrolysis of the metal fluoberyllates and fluorides were taken and the corresponding X-ray powder data are given in Table 3.

DISCUSSION

Earlier workers [22,23] reported the preparation of metal fluoberyllates. Co and Ni-fluoberyllates having hexa- and hepta-hydrates are known [22, 24]. Ghosh et al. [23] show Cu-fluoberyllate as a pentahydrate, but in our case we isolated Ni-, Co- and Cu-fluoberyllate as the hexa-hydrate only. We expected that the dehydration phenomena of these fluoberyllates would be similar to those of sulphates [9—13] as well as of selenates [14] owing to the same size and symmetry of the anions. However, the dehydration curves show no similarity. It appears from Table 1 that none of the intermediate fluoberyllate hydrates is found to be thermally stable. It is observed that dehydration takes place via several intermediate salt hydrates having a fractional molecule of water. Earlier, we studied [15] a large number of salt hydrates having a fractional molecule of water where the number of intermediate hydrates was observed during dehydration. We also studied a series of metal halide oxo-adducts [25,26] which showed the formation of various oxo-adducts having a fractional oxo-adduct moiety. Besides these, there are examples [27—33] of metal salt hydrates having a fractional molecule of water. $CuBeF_4 \cdot 6\ H_2O$ exhibits a very complicated dehydration phenomenon. A similar type of dehydration was also observed in our earlier work [15]. Both $NiBeF_4 \cdot 6\ H_2O$ and $CoBeF_4 \cdot 6\ H_2O$ show the existence of an intermediate hydrate having 5.5 H_2O, but these intermediates, i.e. $MBeF_4$ 5.5 H_2O, where M = Ni(II) or Co(II), are characterised only on the basis of weight loss. We failed to isolate these intermediates even using a slow heating rate. One exotherm observed in the case of anhydrous cobalt fluoberyllate in the temperature range 605—730°C was not observed in the case of nickel(II) or copper(II). The exotherm is reversible in nature. It is expected that the cobalt fluoberyllate is dissociated to the mixed fluoride of cobalt(II) and beryllium(II) before decomposition to the mixed oxide. The ΔH value of this exotherm is very low. It is presumed that this type of dissociation is also taking place in the case of nickel(II) and copper(II). This dissociation is not detected by the DTA curve probably due to simultaneous decomposition of the metal fluoride generated from fluoberyllate which nullifies the exothermic character responsible for the dissociation. Decomposition of fluoberyllate of cobalt(II) and nickel(II) takes place in two overlapping steps. These two compounds may decompose in either of the two ways.

$$MF_2...BeF_2 \xrightarrow{\Delta} MF_2 \cdot BeO \cdot BeF_2 + HF\uparrow$$

$$MF_2 \cdot BeO \cdot BeF_2 \xrightarrow{\Delta} MF_2 \cdot MO \cdot BeF_2 \cdot BeO + HF\uparrow \quad (1)$$

$$MF_2 \cdot MO \cdot BeF_2 \cdot BeO \xrightarrow{\Delta} MO \cdot BeO + HF\uparrow$$

$$MF_2...BeF_2 \xrightarrow{\Delta} MF_2 \cdot MO \cdot BeF_2 + HF\uparrow$$

$$MF_2 \cdot MO \cdot BeF_2 \xrightarrow{\Delta} MF_2 \cdot MO \cdot BeF_2 \cdot BeO + HF\uparrow \quad (2)$$

$$MF_2 \cdot MO \cdot BeF_2 \cdot BeO \xrightarrow{\Delta} MO \cdot BeO + HF\uparrow$$

where M = Ni(II) or Co(II).

Mechanism

Beryllium fluoride is more covalent than either nickel(II) or cobalt(II) fluoride. Naturally, it is expected that in the presence of dynamic air BeF_2 will be hydrolysed, first eliminating HF from the system. BeF_2 and NiF_2 were heated separately in dynamic air and it was observed that BeF_2 was hydrolysed at a lower temperature in comparison to NiF_2. From this observation we expect the decomposition taking place to follow path (1). In the case of Cu(II) the existence of three overlapping DTA peaks is probably due to the following. BeF_2 is first hydrolysed to BeO and HF, while CuF_2 remains unchanged. After partial hydrolysation of BeF_2 the process ceases, and then hydrolysation of CuF_2 starts but ceases after partial hydrolysation and, finally, the hydrolysation of both the remaining BeF_2 and CuF_2 continues simultaneously. All these three processes (Fig. 1) account for the three DTA peaks overlapping one another.

It has been shown [34,35] that CoF_2 exists as the tetra-, tri- and dihydrate, NiF_2 as the tetrahydrate, and CuF_2 as the mono-, di- and pentahydrate along with 5 HF. Co(II) and Ni(II) fluoride were isolated as the tetrahydrates and Cu(II) fluoride as the hexahydrate. The thermal curve of $CoF_2 \cdot 4\ H_2O$ does not show the existence of tri- and dihydrates in the intermediate stage as expected from the literature [34,35]. On the contrary, dehydration of $CoF_2 \cdot 4\ H_2O$ appears very simple. The thermal curve of $CuF_2 \cdot 6\ H_2O$ does not show any existence of $CuF_2 \cdot H_2O$ but shows the presence of $CuF_2 \cdot 2\ H_2O$ which is isolated and characterised. Besides this intermediate ($CuF_2 \cdot 2\ H_2O$), copper(II) fluoride hexahydrate shows several intermediate hydrates having a fractional molecule of water while transforming to the dihydrate. On the other hand, $NiF_2 \cdot 4\ H_2O$ shows some unusual hydrates. In the case of $CuF_2 \cdot 6\ H_2O$, the very complicated nature of dehydration [15,29,33] is observed as for the dehydration of $CuBeF_4 \cdot 6\ H_2O$. A plateau in the temperature range 510—720°C was observed in the TG curve of $CuF_2 \cdot 6\ H_2O$. Initially, we thought this plateau must be due to anhydrous CuF_2, but after analysing the isolated product collected within the temperature range, it was found that the empirical formula coincides with $CuF_2 \cdot 2\ H_2O$. The presence of water is confirmed by the IR spectrum. The decomposition of CoF_2 and

NiF_2 takes place in a single step and in the case of $CuF_2 \cdot 2\ H_2O$, dehydration and decomposition occur simultaneously, although the dehydration process plays a vital role in the intial stage in comparison to the decomposition of CuF_2, as is evident from the DTA profile (Fig. 2).

It was observed that the fluorides are thermally very sensitive to decomposition in dynamic air. The very high thermal stability of metal fluorides shown in the literature [29] must be in a moisture-free medium. One peculiar observation is that pyrolysis of the simple fluoride produces the oxy-fluoride, whereas pyrolysis of the fluoberyllates results in the mixed metal oxide. The composition of the oxy-fluoride is not similar in all the metal ions, but it is evident from the *d*-lines of X-ray powder patterns that the residue after pyrolysis of the metal fluoride at 980°C in dynamic air exhibits the existence of the metal oxide as well as the metal fluoride. Therefore, the empirical formula $M_xO_yF_z$ obtained from analytical data corresponds well to the oxy-fluoride $lMO \cdot mMF_2$, where $x = 1, y < 1, z < 1$, l and m are integers and $l > m$. The mixed metal oxides resulting from pyrolysis of the metal fluoberyllates at 980°C are also supported by the X-ray powder data. The question may arise as to why fluoberyllate is not generating oxy-fluoride like metal fluoride. This is probably due to the fact that the metal fluoride generated from dissociation of the fluoberyllate is not as closely packed as the simple metal fluoride. Beryllium fluoride probably initiates the hydrolysis of the transition metal fluoride to the metal oxide due to the high affinity of BeF_2 towards water.

REFERENCES

1 G.G.T. Guarini and R. Spinicci, J. Therm. Anal., 4 (1972) 433.
2 V.G. Vasilev and Z.V. Ershova, Zh. Fiz. Khim., 46 (1972) 2098.
3 L. Paavo and V. Olli, Suom. Kemistil. B, 42 (1969) 306.
4 C. Murgulescu and E.I. Segal, An. Univ. Bucuresti. Ser. Stiint. Nat., 22 (1959) 75.
5 C.W.F.T. Pistorius, Z. Phys. Chem., 60 (1968) 114.
6 M.G. Habashy, J. Chem. U.A.R., 11 (1968) 167.
7 J. Cabicar and F. Einhorn, Acta Fac. Rerum. Nat. Univ. Comenianae, Chim., 12 (1968) 103.
8 W.W. Wendlandt, Thermochim. Acta, 1 (1970) 419.
9 N. Ray Chaudhuri, G.K. Pathak and S. Mitra, Proc. 4th ICTA, 1 (1974) 615.
10 N. Ray Chaudhuri and G.K. Pathak, Thermochim. Acta, 12 (1975) 71.
11 N. Ray Chaudhuri and G.K. Pathak, Thermochim. Acta, 12 (1975) 287.
12 N. Ray Chaudhuri and G.K. Pathak, Thermochim. Acta, 12 (1975) 397.
13 N. Ray Chaudhuri and G.K. Pathak, Thermochim. Acta, 12 (1975) 71.
14 N. Ray Chaudhuri, M.K. Dasgupta, S. Mitra and G.K. Pathak, Indian J. Chem., 17A (1979) 109.
15 N. Ray Chaudhuri and G.K. Pathak, Thermochim. Acta, 13 (1975) 207.
16 R.T. Marano and J.L. McAtee, Jr., Proc. 3rd ICTA, 2 (1971) 335.
17 K. Furukawa and H. Ohno, Nippon Kinzoku Gakkaishi, 41 (1977) 450.
18 E.I. Ardashnikova, L.R. Batsanova, M.P. Borzenkova, A.V. Novoselova and V.F. Chuvaev, Izv. Akad. Nauk S.S.S.R., Neorg. Mater., 13 (1977) 1034.
19 E.I. Ardashnikova, L.R. Batsanova, M.P. Borzenkova and A.V. Novoselova, Izv. Akad. Nauk S.S.S.R., Neorg Mater., 13 (1977) 1039.
20 C.E. Vallet and J. Braunstein, J. Am. Ceram. Soc., 60 (1977) 315.
21 J.L. Holm, Chem. Zvesti., 30 (1976) 759.

22 P.B. Sarkar and N.N. Ray, J. Indian Chem. Soc., 6 (1929) 987.
23 T.K. Ghosh, T.N. Chakraborty and N.N. Ray, J. Indian Chem. Soc., 42 (1965) 847.
24 A.F. Trotman-Dickenson (executive Ed.), Comprehensive Inorganic Chemistry, Vol. 1, Pergamon Press, Oxford, 1973, p. 550.
26 N. Ray Chaudhuri and S. Mitra, Bull. Chem. Soc. Jpn., 49 (1976) 1035.
27 D. Nathalie and F. Basile, C.R. Acad. Sci., 208 (1939) 1123.
28 D. Nathalie and F. Basile, C.R. Acad. Sci., 208 (1939) 1581.
29 A.I. Maier, K.K. Samplarskaya and N.M. Selivanova, Zh. Prikl. Khim., 36 (1963) 1659.
30 A.G. Brekhunets, I.F. Kokot, V.V. Mank and M.V. Mokhosoev, Zh. Neorg. Khim., 14 (1969) 1460.
31 L.N. Shchegrov, V.V. Pechkovskii and E.D. Dzyuba, Dokl. Akad. Nauk B. S.S.R., 13 (1969) 601.
32 S.M. Arkhipov, T.V. Revzina and N.I. Kashina, Zh. Neorg. Khim., 14 (1969) 2941.
33 M. Tudo and J. Tudo, C.R. Acad. Sci., Ser. C, 271 (1970) 507.
34 N.V. Sidgwick, The Chemical Elements and Their Components, Vol. II, Clarendon Press, Oxford, 1950, pp. 1378, 1432.
35 N.V. Sidgwick, The Chemical Elements and Their Compounds, Vol. I, Clarendon Press, Oxford, 1950, pp. 120, 150.