Thermochimica Acta, 46 (1981) 77--82
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

STUDIES ON DOUBLE SELENATES. II. THERMAL DECOMPOSITION OF CERIUM(III) AND ALKALI METAL DOUBLE SELENATES

I. GIOLITO *

Instituto de Química, Universidade de São Paulo, São Paulo CP 20.780 (Brazil)

M. IONASHIRO

Instituto de Química de Araraquara, Universidade Estadual Paulista, Araraquara, São Paulo (Brazil)

(Received 21 November 1980)

The first communication on the double selenates of cerium(III) and alkali metals [1] described the compounds $Ce_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 5\ H_2O$ and $Ce_2(SeO_4)_3 \cdot 5\ K_2SeO_4$. More recently, these compounds were prepared by drying a mixture of the solutions of cerium(III) carbonate and the corresponding alkali metal carbonates in selenic acid [2]. No reference was found to the application of TG and DTA in the study of these double salts.

EXPERIMENTAL

Alkali metal selenates [3], selenic acid and cerium(III) selenate [4] and cerium(III) and alkali metal double selenates [5] were prepared as described previously. In the case of cerium(III) and lithium double selenate the isolated crystals proved to be only cerium(III) selenate.

Cerium(III) ions were determined by the usual oxalate—oxide method and the alkali metal ions by atomic absorption in a Perkin-Elmer 403 atomic absorption spectrophotometer. Water of crystallization and selenium content were determined from TG curves. The TG and DTA curves were obtained as described previously [5].

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared having the formula $Ce_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O$ (Me = Na, K, Rb, Cs).

The thermal decomposition of the cerium(III) and alkali metal selenates was quite similar in the part corresponding to the thermal decomposition of

---

* To whom correspondence should be addressed.

TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Analytical results							
	Cerium (%)		Alkali metal (%)		Selenium (%)		Water (%)	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$Ce_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	29.72	29.52	4.88	4.34	33.49	30.41	7.64	7.41
$Ce_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 8\ H_2O$	26.09	26.59	7.28	7.67	29.40	29.01	13.40	13.17
$Ce_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\ H_2O$	24.01	23.42	14.65	14.74	27.06	26.71	12.34	12.65
$Ce_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot H_2O$	24.67	24.02	23.40	22.55	27.81	27.05	1.58	1.82

cerium(III) selenate and it does not seem to be influenced by the alkali metal selenate present, as occurred in the case of lanthanum and alkali metal double selenates [5].

All the reactions taking placing during the thermal decomposition of the cerium(III) and alkali metal (except lithium) double selenates can be summarized by the following equations

$$Ce_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O \rightarrow Ce_2(SeO_4)_3 \cdot Me_2SeO_4 + n\ H_2O \qquad (1)$$

$$Ce_2(SeO_4)_3 \cdot Me_2SeO_4 \rightarrow Ce(SeO_3)_3 \cdot Me_2SeO_4 + 1.5\ O_2 \qquad (2)$$

$$Ce_2(SeO_3)_3 \cdot Me_2SeO_4 + 0.5\ O_2 \rightarrow 2\ CeO_2 \cdot Me_2SeO_4 + 3\ SeO_2 \qquad (3)$$

$$2\ CeO_2 \cdot Me_2SeO_4 \rightarrow 2\ CeO_2 \cdot Me_2O + SeO_2 + 0.5\ O_2 \qquad (4)$$

$$2\ CeO_2 \cdot Me_2SeO_4 \rightarrow 2\ CeO_2 + |Me_2SeO_4| \qquad (5)$$

Table 2 attributes to each compound the probable set of the above reactions and their temperature ranges corresponding to the various mass losses observed in the TG curves.

Table 3 gives the temperature of DTA peaks (all endothermic) corresponding to the reactions or fusion occurring for each compound.

The first mass losses in the TG curves (Fig. 1) up to 200°C are due to dehydration. The mass losses between 317 and 496°C are due to decomposition of cerium(III) selenate to cerium(IV) oxide and they occur at lower temperatures as compared with the lanthanum and alkali metal double selenates [5], probably due to the rapid and quantitative oxidation of Ce(III) to Ce(IV). Although the TG curves do not show any evidence of the formation of intermediate compounds, selenate ion undergoes reduction to selenite ion simultaneously with the oxidation of Ce(III) to Ce(IV), resulting in CeO_2.

Samples of cerium(III) and sodium double selenate heated up to 350°C in platinum crucibles suspended inside a furnace near a thermocouple of Pt/Pt—Rh 13% connected to a pyrometer, showed the yellowish colour of Ce(IV) ion; the content of selenite ion in these samples, determined iodometrically [4], was 32.0%, which corresponds to a 96% conversion of selenate to

TABLE 2

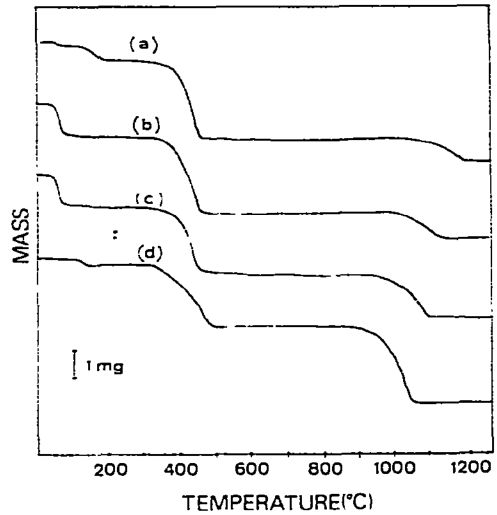
Reactions and corresponding temperature ranges observed in the TG curves of the compounds $Ce_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O$

Compound	Temp. range of mass loss reactions in the TG curves (°C)			
	(1)	(2) (3)	(4)	(5)
$Ce_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	63— 89, 117—200	317—470	1030—1185	
$Ce_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 8\ H_2O$	63—130	333—484	977—1135	
$Ce_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\ H_2O$	57—117	333—480	952—1114	952—1114
$Ce_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot H_2O$	120—153	327—496		900—1060

TABLE 3

Temperature of DTA peaks (all endothermic) corresponding to reactions and fusion of the compound $Ce_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O$

Compound	Peak temp. in DTA curves (°C)					
	(1)	(2)	(3)	(4)	(5)	Fusion
$Ce_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	144–214–239	505	540	1060–1240		760
$Ce_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 8\ H_2O$	115	517	550		1086–1200	
$Ce_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\ H_2O$	110		557		1174	
$Ce_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot H_2O$	205		538		1200	



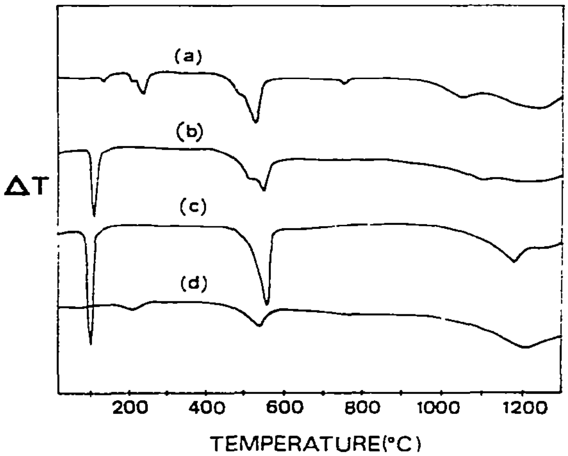


Fig. 1. TG curves of the double selenates of cerium(III) and alkali metal. Heating rate: 5.2°C min^{-1}. (a) $Ce_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$ (7.42 mg); (b) $Ce_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 8\ H_2O$ (8.35 mg); (c) $Ce_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\ H_2O$ (8.30 mg); and (d) $Ce_2(SeO_4)_3 \cdot Cs_2\ SeO_4 \cdot H_2O$ (8.25 mg).

Fig. 2. DTA curves of the double selenates of cerium and alkali metal, diluted to 20% in α-alumina. Heating rate; 9.0°C min^{-1}. (a) $Ce_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$; (b) $Ce_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 8\ H_2O$; (c) $Ce_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 8\ H_2O$; and (d) $Ce_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot H_2O$.

selenite. The content of selenite ion in samples of the same compound heated up to 400°C decreased to 8.2%.

The last step of the TG curves of the cerium(III) and alkali metal double selenates depends upon the nature of the alkali metal considered [3]. Above 1030°C the sodium selenate decomposes to sodium oxide, probably with intermediate formation of sodium selenite [3], but without evaporation; at 1185°C the residue is probably a mixture of CeO_2 and Na_2O. Potassium selenate starts decomposition to potassium oxide above 977°C, without formation of selenite [6] or evaporation; at 1135°C the residue is possibly a mixture of CeO_2 and K_2O. Above 950°C rubidium selenate partly decomposes to rubidium oxide and the remainder evaporates, so that the residue at 1114°C contains CeO_2 and about 54.5% of the theoretical amount of Rb_2O. In the case of cerium(III) and caesium double selenate the final mass loss starting at 900°C corresponds to total evaporation of caesium selenate, so that the final residue at 1060°C contains only CeO_2.

The DTA curves of Fig. 2 show the peaks corresponding to all mass losses in the TG curves and only one peak associated with fusion. The temperature of each DTA peak and its probable interpretation are summarized in Table 3.

The peaks in the DTA curves of cerium(III) and sodium and cerium(III) and potassium at 505 and 517°C respectively, are probably indicative of the intermediate reduction of Se(VI) to Se(IV).

CONCLUDING REMARKS

The thermal behaviour of the cerium(III) and alkali metal (except lithium) double selenates revealed many variations as compared with the thermal behaviour of the corresponding simple selenates, so that each double selenate presents typical TG and DTA patterns.

REFERENCES

1 S. Jolin, Jaresb., (1874) 255.
2 L.A. Gomez Madrazo, J.G. Ribas Bernat and F.J. Arnaiz Garcia, Ion (Madrid), 33 (1973) 242.
3 I. Giolito and M. Ionashiro, Thermochim. Acta, 38 (1980) 341.
4 I. Giolito and E. Giesbrecht, Ann. Acad. Bras. Cienc., 41 (1971) 2921.
5 M. Ionashiro and I. Giolito, Thermochim. Acta, 38 (1980) 285.
6 A. Chrétien and O. Hoffer, Bull. Soc. Chim., 6 (1939), 1587.