Journal of Thermal Analysis, Vol. 34 (1988) 189–194

THERMAL AND X-RAY ANALYSIS OF CERIUM OXY-CARBONATE

*N. Afify, A. S. Abdel-Halim** and *S. M. El-Hout**

PHYSICS DEPARTMENT, FACULTY OF SCIENCE, ASSIUT UNIVERSITY ASSIUT, EGYPT
*METALLURGY DEPARTMENT, NRC–INCHASS, ATOMIC ENERGY AUTHORITY,
CAIRO, EGYPT

(Received April 7, 1987)

This work describes the thermal decomposition behaviour of cerium oxy-carbonate. DTA, TG, DTG and X-ray examinations were performed.

The results indicate that the thermal decomposition of cerium oxy-carbonate in static air at a heating rate of 10 deg $\min^{-1}$ involves three steps: dehydration at 58 °C, removal of crystal water at 200 °C and CO_2 release at 235 °C.

The activation energies of removal of crystal water and carbon dioxide release were found to be 59.48 and 82.33 kJ mol^{-1}, respectively.

Ceria-based oxygen ion conductors have high ionic conductivity, which makes them interesting materials for application as solid electrolytes at moderate temperature ($<600°$), oxygen sensors and fuel cells [1]. The powder preparation is an important step in the fabrication of homogeneous materials. Chemical coprecipitation has been used. The properties of the final product (the sintered material or a mixed oxide powder) are largely dependent on the precipitation conditions. Precipitation as oxalate followed by calcination has been used to prepare doped oxide powders.

This work describes a study of the thermal analysis and X-ray diffraction of cerium oxy-carbonate, which was prepared by precipitation from cerium nitrate solution with ammonium carbonate in the presence of ammonium hydroxide [2].

Experimental

Material

The cerium oxy-carbonate powder was prepared by precipitation from cerium nitrate solution with ammonium carbonate in the presence of ammonium hydroxide. The precipitation was carried out at a C/Ce mole ratio of 2.0, at 60° and pH 8.75.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Examination techniques

Thermal analysis (DTA, TG and DT) of the cerium oxy-carbonate powder was carried out with a DuPont thermal analyser (Type 1090) in static air in the temperature range 25–900°. The heating rate varied from 2 to 40 deg min^{-1}.

An X-ray investigation of the cerium oxy-carbonate powder was performed with a Philips diffractometer (Type 1140). The patterns were run with Cu as target, Ni as filter ($\lambda = 1.54178$ Å), at 40 kV and 30 mA, with a scanning speed of 2 deg min^{-1}.

Results and discussion

Thermal behaviour of cerium oxy-carbonate

The precipitated cerium oxy-carbonate powder was pale-yellow. Figure 1 shows typical DTA, TG and DTG curves for the decomposition of the cerium oxy-carbonate powder to CeO_2 in static air at a heating rate of 10 deg min^{-1}.

The thermal analysis results reveal three stages of decomposition, each involving a loss in weight. The three DTA stages are listed in Table 1 together with the peak temperatures. The DTA curve indicates that all three stages are endothermic. The first stage is characteristic of the removal of adsorbed water, the second stage of the removal of crystal water and the third stage of carbon dioxide release. The peaks are maximized at 58, 200 and 235°, respectively.

The TG and DTG curves reveal a total weight loss of 21%. This value is close to the theoretical weight loss (20.7%) calculated from the equation for the

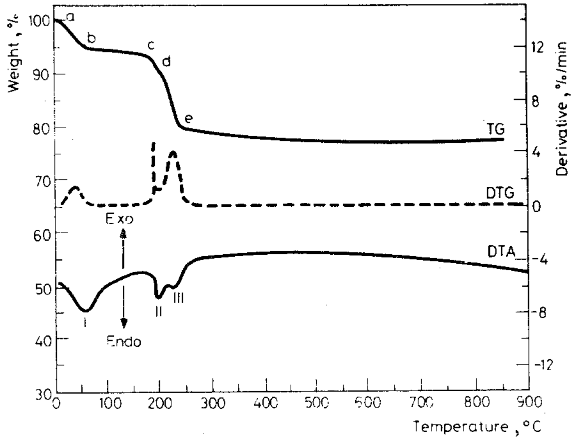

Fig. 1 Thermal analysis of cerium oxy-carbonate at a heating rate of 10 deg min^{-1}

Table 1 DTA of cerium oxy-carbonate powder at a heating rate of 10 deg min^{-1}

Stage	Peak temperature, °C	Type of deflection	Function
I	58	endothermic	removal of adsorbed H_2O
II	200	endothermic	removal of crystal water
III	235	endothermic	CO_2 release

Table 2 TG of cerium oxy-carbonate powder at a heating rate of 10 deg min^{-1}

Stage	Temperature range, °C	Weight loss, %	Function
a–b	25– 75	5	removal of adsorbed water
c–d	180–210	4	removal of crystal water
d–e	210–260	12	removal of CO_2 gas

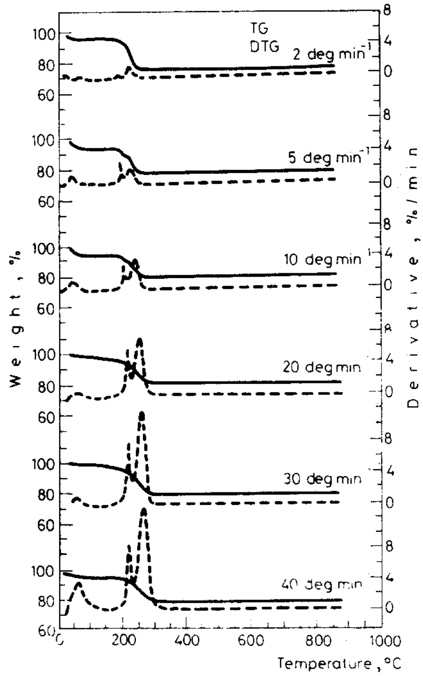

Fig. 2 ——— TG and — — — DTG curves of cerium oxy-carbonate at different heating rates

decomposition of cerium oxy-carbonate [$CeO_2(CO_3)_2 \cdot H_2O$]. Table 2 shows the various stages of weight loss within the different temperature ranges.

Kinetics of thermal decomposition of cerium oxy-carbonate

Thermogravimetric curves (Fig. 2) obtained at different heating rates (from 2 to 40 deg $\min^{-1}$) were utilized to calculate the activation energy for the removal of crystal water and for the release of carbon dioxide, by using the technique recommended by Carroll and Manche [3].

In this method,

$$-\frac{dW}{dt} = Kf(W) \tag{1}$$

where W is the weight of reacting sample and K is the rate constant related to temperature by the Arrhenius equation:

$$K = Z\exp(-E/RT) \tag{2}$$

If the heating rate is

$$\varphi = \frac{dT}{dt} \tag{3}$$

then

$$-\frac{dW}{dT} = \frac{Z}{\varphi}\exp(-E/RT)f(W) \tag{4}$$

$$\ln\varphi\left(-\frac{dW}{dT}\right) = \ln Zf(W) - \frac{E}{RT} \tag{5}$$

A plot of $\ln\varphi\left(-\frac{dW}{dT}\right)$ vs. $\frac{1}{T}$, for a given value of W, obtained at different heating rates, will lead to a value of E.

The calculated values of the activation energy (E) were found to be 59.48 and 82.33 kJ mol^{-1} for the removal of crystal water and carbon dioxide release, respectively.

X-ray diffraction analysis

The X-ray diffraction of cerium oxy-carbonate was studied by Henry et al. [4] and Bentzen et al. [5].

Table 3 gives the lattice parameters and relative intensities of our powder and those reported by Bentzen et al. for a powder prepared by hydrolysis. The comparison of our results with Bentzens data confirms that our powder is cerium oxy carbonate.

Table 3 X-ray diffraction data of cerium oxy-carbonate compared with those of Bentzen et al. [5]

d, Å		I/I_0	
This work	Bentzen et al.	This work	Bentzen et al.
—	6.417	—	6.8
5.556	5.574	32.0	30.3
4.320	4.311	100.0	100.0
3.717	3.723	65.0	60.0
3.359	3.363	46.0	43.6
2.954	2.959	75.0	77.0
2.658	2.659	34.0	36.2
2.507	2.508	33.0	39.0
2.432	2.429	23.0	26.1
2.347	2.347	80.0	79.5

Conclusion

The addition of ammonium carbonate to cerium nitrate solution in the presence of ammonium hydroxide produced a precipitate which was identified as cerium oxy-carbonate.

The thermal decomposition of cerium oxy-carbonate in static air involves three endothermic steps: removal of adsorbed water at 58°, removal of crystal water at 200° and carbon dioxide release at 235°.

The activation energies of removal of crystal water and carbon dioxide release were found to be 59.48 and 82.33 kJ mol^{-1}, respectively.

References

1 T. Kudo and H. Obayashi, J. Electrochem. Soc., 122 (1975) 142.

2 G. A. Hassanien, "Investigations on the prep aration of ceric oxide pellets.", MSc. Thesis, Cairo University, 1986.

3 B. Carroll and E. P. Manche, Thermochim. Acta, 3 (1972) 449.

4 N. F. M. Henry, H. Lipson and W. A. Wooster, "The Interpretation of X-ray Diffraction Photographs", 2nd, edn, McMillan & Co. Ltd., London, 1966, pp. 215–217.

5 J. J. Bentzen, P. L. Husum and O. Toft Sørensen, 6th CIMTEC Meeting, Milan, 1986 (In press).

Zusammenfassung — Das Verhalten von Ceroxycarbonat bei der thermischen Zersetzung wird beschrieben. DTA, TG, DTG und Röntgendiffraktometrie wurden zur Untersuchung herangezogen. Die thermische Zersetzung erfolgt in statischer Luftatmosphäre bei einer Aufheizgeschwindigkeit von 10° min^{-1} in drei Schritten. Der erste Schritt bei 58 °C ist der Dehydratisierung, der zweite bei 200 °C dem Austritt von Kristallwasser und der letzte bei 235 °C der Abspaltung von CO_2 zuzuschreiben. Für die Kristallwasserabgabe wurde eine Aktivierungsenergie von 59.48 kJ · mol^{-1} und für die CO_2-Abspaltung von 82.33 kJ · mol^{-1} berechnet.

Резюме — Методами ДТА, ТГ, ДТГ и рентгеноструктурного анализа изучено термическое разложение оксикарбоната церия. Результаты показали, что термическое разложение оксикарбоната церия в статической атмосфере воздуха при скорости нагрева 10°/мин протекает в три стадии. Первой стадией при 58° является дегидратация, второй при 200 °С-удаление кристаллизационной воды, а третьей стадией при 235 °С-выделение двуокиси углерода. Энергии активации второй и третьей стадий равнялись, соответственно, 59,48 и 82,33 кдж · моль$^{-1}$