Synthesis and thermoanalytical characterization of samarium peroxocarbonate

Carlos A. da S. Queiroz [a,*], Mari E. de Vasconcellos [a], Soraya M.R. da Rocha [a],
José A. Seneda [a], Walter R. Pedreira [b], Jivaldo do R. Matos [c], Alcídio Abrão [a]

[a] *Instituto de Pesquisas Energéticas e Nucleares (IPEN), Cx postal 11049, CEP 05422-970 Pinheiros, São Paulo, Brazil*
[b] *Instituto de geologia, Universidade de Brasília, Brasília, Brazil*
[c] *Instituto de química, Universidade de São Paulo, São Paulo, Brazil*

Abstract

This paper presents the samarium peroxocarbonate synthesis and the data collected by thermogravimetry (TG)–differential thermogravimetry (DTG), active oxygen determination via iodine generation and total oxide content by gravimetry and elemental analysis of CHN by microanalyses. By thermal analysis (DTG), a mass loss corresponding to volatile components and water, equivalent to 29.22% of the total mass was observed. This value is in accordance with the mass loss of the compound when it was fired at $900\,°C$ toward the Sm_2O_3 oxide. With the DTG program a process of thermodecomposition in multisteps, was observed, corresponding to the loss of water (up to $200\,°C$), evolution of oxygen gas from the peroxide compound and a partial decomposition to CO_2 ($200–550\,°C$) and a second evolution of CO_2 (from 500 to $900\,°C$). This final evolution of CO_2 probably came from the intermediary compound $Sm_2O_2CO_3$. By microanalyses the carbon and hydrogen contents were 4.7 and 1.0%, respectively. In summary, the analytical data collected allowed one to conclude that the stoichiometric formula for the studied compound is $Sm_2O_2(CO_3)_2 \cdot 2H_2O$.
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1. Introduction

The role of rare earth carbonate system is of uppermost importance not only from the analytical point of view but from the industrial side as well. Taketatsu [1] reported the results of this system and studied the minimum concentration of ammonium carbonate and potassium carbonate for the complete dissolution of the basic rare earth carbonate precipitates formed when the rare earth solutions are treated with the alkaline carbonates. He concluded that the amounts of rare earth elements dissolved increase with the increase in the concentration of carbonate, and also with the increase in atomic number, except for cerium, yttrium, and scandium. The precipitates of praseodymium, neodymium, samarium, gadolinium, erbium, yttrium, and scandium carbonates are dissolved completely in potassium carbonate solution of higher concentration than about 0.55, 0.45, 0.35, 0.30, 0.25,

0.15, and $0.10\,M$, respectively. The lanthanum carbonate precipitate could not be dissolved completely even in $1\,M$ potassium carbonate. As cerium is oxidized by air to the tetrapositive state in a potassium or ammonium carbonate solution, its behavior differs from that of the other rare earth elements. Taketatsu [2] also studied the behavior and dissolution of the rare earth in potassium bicarbonate ($KHCO_3$) when an excess of potassium bicarbonate is added to a solution of rare earth chloride or nitrate. The corresponding bicarbonates of rare earths are precipitated and then the precipitates are partially or completely dissolved by shaking. As for the potassium carbonate, the amount of rare earth dissolved increased with the increase of the bicarbonate solution and also with the increase in atomic number, except for cerium and yttrium. So, these results are similar to the potassium carbonate treatment.

Sinha [3] reported the solubility of Eu(III) in potassium carbonate solution specially for the spectrofluorimetric determination of small amounts of europium.

A series of experiments worked out by the authors [4] lead to the conclusion that the addition of hydrogen peroxide to

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* Corresponding author.
E-mail address: cqueiroz@baitaca.ipen.br (C.A.d.S. Queiroz).

the soluble rare earths carbonates resulted in the formation of a typical precipitate. The new compound was identified as being a rare earth peroxocarbonate. Starting from this finding, a systematic study of the precipitation of rare earth carbonates with hydrogen peroxide was undertaken. Ammonium carbonate and ammonium carbonate plus ammonium hydroxide were used for the solubilization and complexation of the rare earths.

The solubilization of rare earths by ammonium carbonate and mixture of ammonium carbonate with ammonium hydroxide was reported elsewhere [5].

This paper outlines the synthesis and the characterization by chemical and thermoanalysis of the samarium peroxocarbonate.

2. Experimental

2.1. Reagents and materials

Samarium chloride stock solution: $70 \, g \, l^{-1} \, Sm_2O_3$.

Samarium oxide (99.9% purity) were prepared at the IPEN/S. Paulo using the monazite rare earth chlorides as raw material.

Ammonium carbonate, ammonium hydroxide, and hydrogen peroxide (analytical-reagent grade, 30%) (130 volumes) were of analytical-grade.

For the starch solution, use $2.5 \, g \, l^{-1}$ aqueous solution recently prepared. Dissolve the starch into hot water, cool down, and make up to the volume.

For 0.1 M sodium thiosulfate, dissolve 25 g of analytical-grade $Na_2S_2O_3 \cdot 5H_2O$ in hot water. Add 0.1 g of Na_2CO_3, cool down, and make up to 1 l. Keep the sodium thiosulfate stock solution in a amber flask. Sodium thiosulfate (0.01 M) solutions were prepared by dilution. Standardize this solution using 0.1 g of KI dissolved into $20 \, g \, l^{-1} \, H_2SO_4$. Dissolve 2 g of potassium iodate in water. Mix the iodide and iodate solutions, homogenize, and make up to 250 ml with $20 \, g \, l^{-1} \, H_2SO_4$ using a volumetric flask.

Pipette a 25 ml aliquot and adjust to pH 2, add 1 ml starch solution and titrate with thiosulfate until the fading of the blue color.

For the potassium iodide stock solution. Prepare $1 \, g \, l^{-1}$ dissolving the salt with demineralized water. Keep the solution in an amber colored flask.

2.2. Samarium peroxocarbonate synthesis

A $400 \, g \, l^{-1}$ ammonium carbonate solution was prepared adding 20 ml of ammonium hydroxide to 20 g of ammonium carbonate and made up to 50 ml with water. To this ammonium carbonate solution, 28 ml of a samarium chloride solution of $70 \, g \, l^{-1} \, Sm_2O_3$ was added dropwise with constant agitation. In a previous determination, we found that the solubility of the neodymium carbonate is $25.1 \, g \, l^{-1}$ at room temperature (about 25 °C).

To the respective recently prepared soluble carbonates hydrogen peroxide 30% is added dropwise, under agitation at room temperature. The precipitate is separated out by centrifugation, washed with demineralized water and oven dried at 80 °C.

2.3. Analytical instrumentation

(a) For C, H, and N analysis an Elemental Analyzer 2400 CHN Perkin-Elmer was used.
(b) A Thermobalance TGA-50 from Shimadzu was used.
(c) A Spectrophotometer 1750 from Perkin-Elmer was used.

2.4. New compounds characterization: peroxide reconnaissance

For the qualitative reconnaissance of the rare earth peroxide, a simple test is made dissolving a small aliquot of the dried sample with hydrochloric acid in the presence of potassium iodide. The generous and instant generation of free iodine is observed. This test can be made using a test tube or even over a filter paper strip.

For the new compounds characterization, the following analytical techniques were applied: total oxide gravimetric determination [5,6], rare earths complexometric determination [7,8], hydrogen, carbon and nitrogen microanalysis, and active oxygen determination by iodometry [6,8].

A very small precipitate aliquot dissolved with hydrochloric acid in the presence of a few drops of KI generates free iodine due to the presence of –O–O– radical. The peroxy ligand and the C–O band were identified by infrared spectroscopy. The total carbon content was determined by microanalysis. With data collected by thermogravimetry (TG)–differential thermogravimetry (DTG), the thermal stability and stoichiometry was established. Finally, the corresponding stoichiometry and thermal decomposition mechanism for the above mentioned compounds were proposed [9,10].

For the gravimetric determination of total oxide, a weighed aliquot of the dried precipitate was fired into a platinum crucible to 900 °C during 1 h.

Total rare earth in the dried precipitate was assayed by EDTA complexometric titration.

2.5. Active oxygen

Active oxygen is defined as the excess of oxygen related to the rare earth sesquioxides, specially in the case of cerium, praseodymium, and terbium.

The determination of the active oxygen [11] in the new compounds was made by the titration of the free liberated iodine after treatment of the dried sample with hydrochloric acid in the presence of KI. The free iodine was titrated by the conventional sodium thiosulfate/starch procedure. The easy oxidation of the iodide indicates the presence of a superior

oxide, until now specially described only by the cerium(IV), praseodymium, and terbium higher oxides.

For the determination of the active oxygen, weigh about 100 mg of the rare earth dried precipitate and transfer to an Erlenmeyer flask with the aid of 100 ml of 1 g l^{-1} KI solution. Add slowly a 1:1 HCl solution under constant agitation, at room temperature. Add 5 ml of the starch indicator solution and titrate with 0.01 M thiosulfate.

2.6. Analytical thermal analysis

The thermal gravimetric analysis covered the range 25–900 °C under dynamic nitrogen and/or compressed air (50 ml min^{-1} flow), the sample in a platinum crucible, and a heating rate of 10 °C min^{-1}. The samples had mass ranging from 2 to 7 mg. The correspondent differential thermogravimetry curve was recorded via the first derivative TG curve.

3. Results

3.1. The samarium compound

This compound was synthesized adding hydrogen peroxide to the soluble samarium complexes in an ammonium carbonate/ammonium hydroxide mixture. Table 1 shows the results of the elemental and water assay for the samarium compounds compared with the respective theoretical values.

Table 2 exhibits the results collected by the correspondent TG–DTG thermograms by which the formula $Sm_2O_2(CO_3)_2 \cdot 2H_2O$ is derived.

Based upon the values presented in Table 2 it is allowed one to conclude to the hydrate samarium peroxocarbonate, $Sm_2O_2(CO_3)_2 \cdot 2H_2O$. The TG curve from Fig. 1 ex-

Table 1
Elemental and water assay for the samarium compound

Sm (%)	Calculated: 61.5; experimental: 6.1
O (%)	Calculated: 6.5; experimental: 6.4
C (%)	Calculated: 4.9; experimental: 4.7
H (%)	Calculated: 0.8; experimental: 1.0
H_2O (%)	Calculated: 7.4; experimental: 7.7
Probable formula weight	$Sm_2O_2(CO_3)_2 \cdot 2H_2O$

Table 2
Collected data from the TG–DTG curves (Fig. 1) for the Sm compounds

TG–DTG (°C)	Loss of mass		Assigned
	mg	%	
0–200	0.20	7.71	H_2O
200–550	0.46	17.18	$CO_2 + O_2$
550–900	0.11	4.33	CO_2
Probable formula weight	$Sm_2O_2(CO_3)_2 \cdot 2H_2O$		

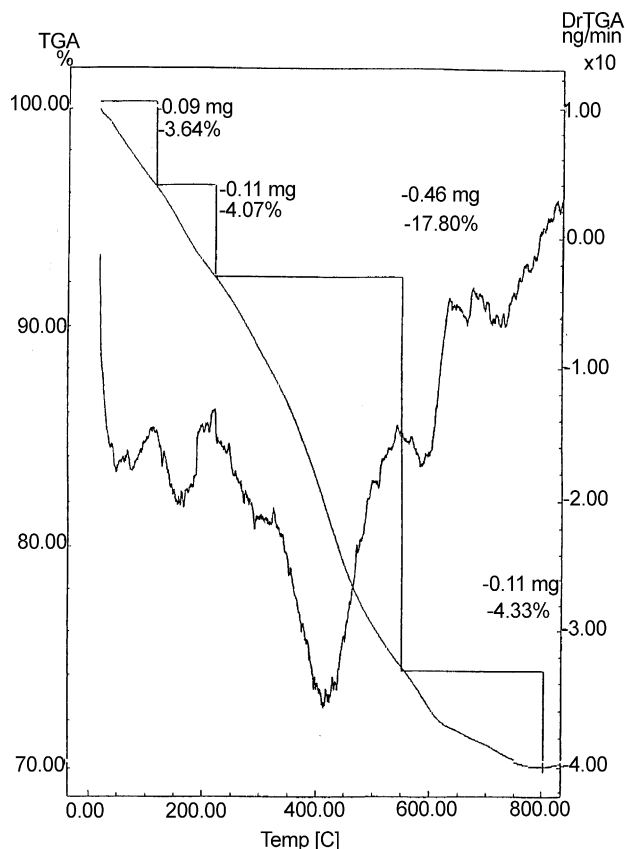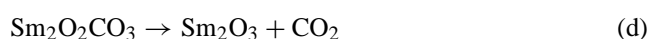Sm sample initial mass: 2.603 mg; atmosphere: nitrogen; proposed min. formula weight: $Sm_2O_2(CO_3)_2 \cdot 2H_2O$.
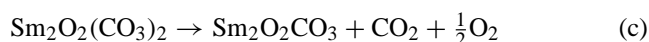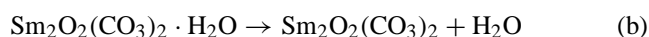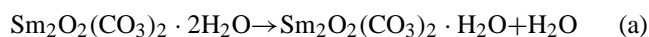

Fig. 1. TG–DTG curves for samarium peroxocarbonate. Atmosphere: nitrogen; heating rate: 10 °C min^{-1}.

hibits a continuous mass loss. In the correspondent DTG curve can be observed two peaks in the temperature range of 50–250 °C, which are characteristics of the dehydration process. Table 1 shows the theoretical and experimental values for water, which are reasonably in accordance with each other.

From the DTG curve (Fig. 1) can be observed a peak in the 250–600 °C range, with a mass loss of 16.71%, which was attributed to the summation of the mass loss of oxygen and carbon dioxide, both resulting from the thermal decomposition of the peroxocarbonate compound. As a consequence the intermediary compound $Sm_2O_2CO_3$ is formed. Next, in the temperature range 600–800 °C, the thermal decomposition is attributed to the liberation of CO_2, resulting the stable oxide Sm_2O_3.

The following reactions were suggested:

$$Sm_2O_2(CO_3)_2 \cdot 2H_2O \rightarrow Sm_2O_2(CO_3)_2 \cdot H_2O + H_2O \quad (a)$$

$$Sm_2O_2(CO_3)_2 \cdot H_2O \rightarrow Sm_2O_2(CO_3)_2 + H_2O \quad (b)$$

$$Sm_2O_2(CO_3)_2 \rightarrow Sm_2O_2CO_3 + CO_2 + \tfrac{1}{2}O_2 \quad (c)$$

$$Sm_2O_2CO_3 \rightarrow Sm_2O_3 + CO_2 \quad (d)$$

The IR spectrum of the samarium peroxocarbonate depicted in Fig. 2 displays a wide and strong band in the 3500 cm^{-1} region, which is characteristic of the stretching
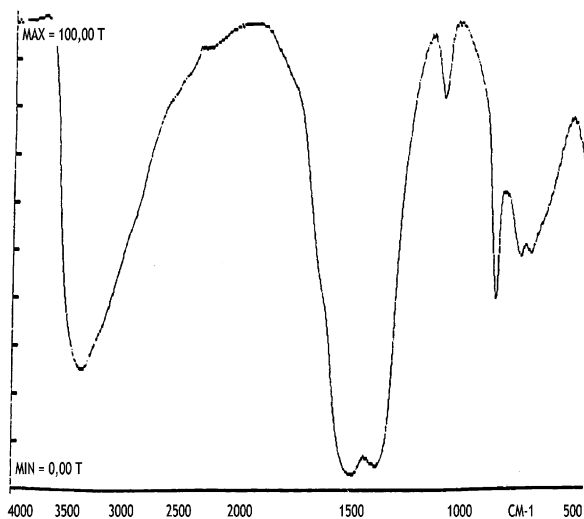
Fig. 2. Infrared spectroscopy of samarium peroxocarbonate.

of OH from water molecule. The presence of the carbonate ions in this compound is proved by the observation of two very strong bands in the $1500\,\mathrm{cm}^{-1}$ region. This band can be assigned to the vibrational mode ($\delta C = 0 + \delta CO$), with a probable monodentate coordination of the carbonate to the Ln(III).

4. Conclusion

Concluding, the existence of a new series of rare earths compounds is proposed, that is, the peroxocarbonates. The results reported here lead to new interesting rare earth compounds whose study is under progress at the IPEN laboratories.

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