Thermochimica Acta, 190 (1991) 335–343
Elsevier Science Publishers B V , Amsterdam

Preparation, thermal stability and luminescence properties of selected rare earth oxycarbonates

Jorma Hölsä [1] and Tarja Turkki

Helsinki University of Technology, Department of Chemical Engineering, SF-02150 Espoo (Finland)

(Received 20 March 1991)

Abstract

A comparative TG and DTG study of the preparation and thermal stability of selected rare earth oxycarbonates, $(REO)_2CO_3$ (RE = La and Gd), shows that the ease of formation as well as the stability of these compounds decreases strongly with increasing atomic number of the host cation According to X-ray powder diffraction analyses, the RE oxycarbonates obtained as decomposition products of acetate and carbonate hydrates belong to the tetragonal IA-type UV- and dye laser-excited luminescence studies of Eu^{3+}-doped $(LaO)_2CO_3$ and $(GdO)_2CO_3$ reveal the presence of two different sites for the host cation One of the sites resembles closely that prevailing in the tetragonal RE oxysalts, i e oxyhalides, oxysulphates, oxymolybdates and oxynitrates. A crystal field analysis carried out on the $^7F_1$ and $^7F_2$ level schemes according to a C_{2v} site symmetry confirms this hypothesis

INTRODUCTION

The preparation and properties of rare earth (RE) oxycarbonate phases (corresponding to a general formula $(REO)_2CO_3$) have received relatively sparse attention despite the fact that they are the most stable RE carbonates known to exist. The preparation of RE oxycarbonates usually involves the thermal decomposition of RE materials containing both carbon and oxygen. Accordingly, it has been shown that RE oxalates [1–3], acetates [4,5], formates [3,6,7] and (hydroxy) carbonates [1,8–10] decompose to the corresponding oxides through an oxycarbonate phase. Several organic RE compounds also yield oxycarbonates [11–14]. Other methods used to prepare RE oxycarbonates include the reaction of RE oxide with CO_2 [2,15–17] and anion exchange between RE trichlorides and alkaline carbonates [18]. Oxycarbonates have also been obtained through the hydrothermal reaction between neodymium trihydroxide and aqueous CO_2 [19].

---

[1] Author to whom correspondence should be addressed

0040-6031/91/$03.50

The existence of three different types of RE oxycarbonate structures I-, IA- and II-$(REO)_2CO_3$, have been noted [1,2]. All these structures possess a layered arrangement of individual $(REO)_n^{n+}$ and CO_3^{2-} ions [20,21]. However, there are two types of $(REO)_n^{n+}$ complex cations; the tetragonal and trigonal ones found in the I and II types of oxycarbonates, respectively. The former type bears very close resemblance to the rather extensively studied rare earth oxysalt series [22] while the latter is similar to the conventional RE sesquioxides. The IA form has been concluded to have a structure rather similar to the I-form; the small differences might arise from the different packing of the carbonate groups [15].

In addition to the investigations concerning the preparation and crystal structure of RE oxycarbonates, the optical absorption of the Nd^{3+} ion in $(NdO)_2CO_3$ [23] and the luminescence of Eu^{3+} ion in $(LaO)_2CO_3$ [15,24] have been studied to a limited extent.

In this paper we describe the results of our investigation on the preparation, thermal stability and luminescence properties of Eu^{3+}-doped lanthanum and gadolinium oxycarbonates. This study is a continuation of our studies concerning the properties of the rare earth oxysalt systems [25–29].

EXPERIMENTAL

Preparation of $(REO)_2CO_3$

The preparation of rare earth oxycarbonates, $(REO)_2CO_3$ (RE = La and Gd) was studied by using the two most promising starting materials, the rare earth carbonate and acetate hydrates. The initial materials were obtained in the case of the carbonates, by direct precipitation of the RE^{3+} ions from an aqueous nitrate solution by sodium carbonate, followed by filtration of the solid residue. The filtrate was washed thoroughly with water. The product dried at 80 °C was found to correspond to a phase of composition $RE_2(CO_3)_3 \cdot xH_2O$ ($x = 3$ for lanthanum and 4.5 for gadolinium).

The evaporation of the RE acetate solutions at 80 °C yielded a solid product of composition $RE(CH_3COO)_3 \cdot yH_2O$ ($y = 1.5$ for lanthanum and 2/3 for gadolinium).

For the luminescence measurements, the host cations were, in all cases, partially replaced by a small amount of Eu^{3+} ion, nominally 2 mol.%. The uniform, random distribution of the Eu^{3+} ion in the host cation sites was assumed, as there are only slight mutual differences in solubilities between the different RE^{3+}n the 2 ions.

Thermoanalytical measurements

A Perkin–Elmer TGA7 TG/DTG analyser of the Perkin–Elmer 7 Series thermal analysis system was employed to recorder the thermal decomposition of the lanthanum and gadolinium carbonate and acetate hydrates in a dynamic air atmosphere, between 50 and 1100 °C. In a typical dynamic TG/DTG run, a heating rate of 2.5 °C $\min^{-1}$ was used.

The isothermic runs of the materials in a dynamic air atmosphere were carried out at a constant temperature obtained after rapid heating. The heating time at constant temperature was 20 h.

X-ray powder diffraction

The powder diffraction patterns of lanthanum and gadolinium oxycarbonates were measured at room temperature with a Philips PW 1800 series powder diffractometer system (with Cu $K\alpha$ radiation) in the 2θ range between 5 and 60 °.

Optical measurements

The luminescence of the $(REO)_2CO_3:Eu^{3+}$ powder samples was measured under UV, argon ion and dye laser excitation at ambient and liquid nitrogen temperatures (300 and 77 K, respectively). UV radiation from a 200 W mercury lamp restricted with wide band filters around 300 nm, was used to excite the strongly absorbing charge-transfer band of the Eu^{3+} ion. An alternative global excitation source is offered by the argon ion laser line at 476.5 nm which excites the $^5D_{0-2}$ levels of the Eu^{3+} ion.

In order to resolve the superimposed luminescence spectra originating from Eu^{3+} ions in different crystallographic sites, the lowest excited ^5D level, $^5D_0$, near 580 nm, was excited selectively by a Spectra Physics 375 continuous wave rhodamine 6G dye laser (line width 0.7 cm^{-1}) pumped by a Spectra Physics 2016 argon ion laser. The luminescence was detected by a Hamamatsu R374 photomultiplier through a 1 m Jarrell–Ash Cerny–Turner-type monochromator. The resolution of the equipment was better than 1.0 cm^{-1}. The emission originating from the $^5D_0 \rightarrow {}^7F_{0-2}$ transitions between 575 and 645 nm were considered in detail.

Crystal structures

The $(NdO)_2CO_3$ prepared from a mixture of $Nd(OH)_3(aq)$ and $CO_2(aq)$ solutions by hydrothermal methods, has been shown to crystallise in a hexagonal crystal system with $P6_3/mmc$-D_{6h}^4 (No. 194) as the space group [19]. The unit cell contains 2 molecular units in an arrangement where the Nd atom occupies a single crystallographic site of C_{3v} point symmetry resulting from a rhombohedral coordination to eight oxygens. The $(NdO)_2CO_3$ seems to belong to the II-$(REO)_2CO_3$ type with a trigonal $(REO)_n^{n+}$ complex cation [20].

RESULTS AND DISCUSSION

Thermoanalytical studies

The thermal decomposition of the RE acetate hydrates first involves complete dehydration between 50 and 125 ° C for $La(CH_3COO)_3 \cdot 1.5H_2O$, and between 50 and 145 ° C for $Gd(CH_3COO)_3 \cdot 0.67H_2O$ (Fig. 1). After the initiation of the decomposition of the anhydrous acetate, one can observe in the lanthanum case, the presence of a metastable intermediate close to 330 ° C, probably corresponding to an oxydicarbonate phase. The formation of the $(REO)_2CO_3$ phase occurs at 380 and 365 ° C for lanthanum and gadolinium, respectively. The stability range of the gadolinium compound is considerably less than that of the lanthanum compound, i.e. 165 against 240 degrees. The general decomposition scheme as a whole is presented in eqns. (1)–(4):

$$RE(CH_3COO)_3 \cdot xH_2O \rightarrow RE(CH_3COO)_3 + xH_2O \qquad (1)$$

$$2RE(CH_3COO)_3 + 12O_2 \rightarrow RE_2O(CO_3)_2 + 9H_2O + 10CO_2 \qquad (2)$$

$$RE_2O(CO_3)_2 \rightarrow (REO)_2CO_3 + CO_2 \qquad (3)$$

$$(REO)_2CO_3 \rightarrow RE_2O_3 + CO_2 \qquad (4)$$

In order to test the stability of the oxycarbonate phase, isothermal runs at constant temperature (360 and 340 ° C for $(LaO)_2CO_3$ and $(GdO)_2CO_3$, respectively) were carried out with otherwise similar experimental conditions

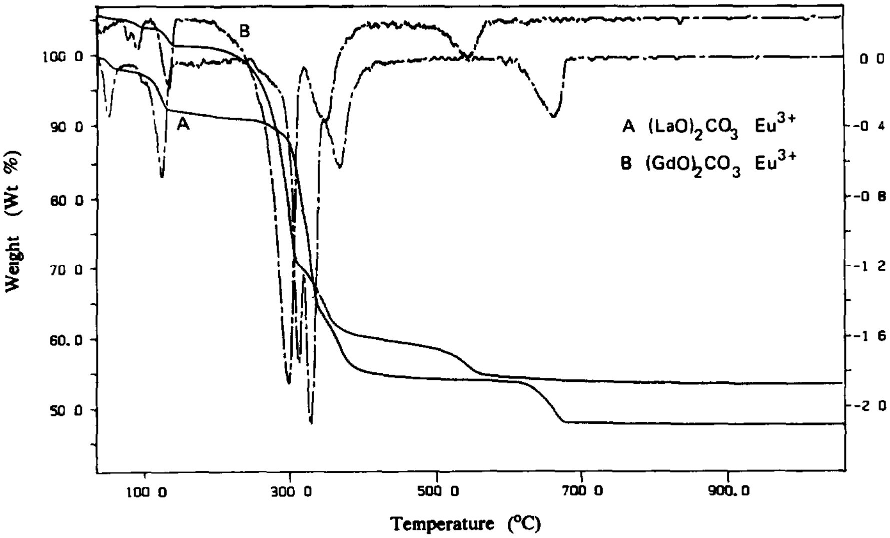

Fig 1 The formation and thermal decomposition of $(LaO)_2CO_3$ (A) and $(GdO)_2CO_3$ (B) in dynamic air atmosphere at a heating rate of 2 5 ° C min^{-1}

as in the previous runs. The weight of the both samples remained practically constant: only a decrease of 0.5% could be observed. It should be noted that this value is closer to the calculated one than that obtained in the dynamic run.

In contrast to the acetate case, the thermal decomposition of the lanthanum carbonate trihydrate only yielded a stable oxycarbonate phase after the dehydration step. Even though the DTG curve for $Gd_2(CO_3)_3 \cdot 4.5H_2O$ shows a well defined peak, no stable oxycarbonate phase could be detected. Furthermore, the stability range of the $(LaO)_2CO_3$ phase is clearly less than in the acetate case: 210 against 240 degrees. However, the stability of the oxycarbonate phase to prolonged heating proved to be excellent: no decrease in weight was detected after heating at 390 °C for 20 hours.

From the thermoanalytical studies, it must be concluded that despite the apparent similarity in stoichiometry between the carbonate and oxycarbonate phases, the thermal decomposition of the RE acetate seems to involve less drastic rearrangements in bonding resulting in the extended stability of the La oxycarbonate phase.

X-ray powder diffraction studies

The X-ray powder diffraction patterns of the RE oxycarbonates are almost identical and correspond well to the data for the IA-type of $(LaO)_2CO_3$ available in the literature [30]. In general, the X-ray diffraction reflections are rather broad indicating low crystallinity, due to crystal imperfections and/or small crystal size. However, this is the case with most samples prepared by thermal decomposition.

The quality of the X-ray pattern of the $(GdO)_2CO_3$ sample is inferior to those obtained for lanthanum compounds; this follows from the lower stability of the gadolinium oxycarbonate phase. As this pattern has not been published before it is presented in Table 1. From a comparison with the literature data for $(PrO)_2CO_3$, it can be concluded that $(GdO)_2CO_3$ is also isomorphic with the IA-type.

Finally, no reflections originating from the starting materials or the final decomposition products could be observed in either case.

Luminescence studies

The luminescence of the Eu^{3+} ion is due to electronic transitions from the $^5D_J (J = 0\text{–}4)$ levels to the ground multiplet $^7F_J (J = 0\text{–}6)$ [26]. In most cases, when high-frequency lattice phonons are available, transitions from the ^5D_J $(J = 1\text{–}4)$ levels are relaxed by multiphonon de-excitation to the lowest excited ^5D state, $^5D_0$. The $^5D_0 \rightarrow {}^7F_J$ transitions result in very sharp emission lines in the visible spectral range from 575 to 850 nm. The $^5D_0 \rightarrow {}^7F_0$ transition cannot be split by any interaction and thus the number

TABLE 1

X-ray powder diffraction patterns of $(LaO)_2CO_3$ and $(GdO)_2CO_3$

$(LaO)_2CO_3$		$(GdO)_2CO_3$	
d (Å)	I/I_{100} (%)	d (Å)	I/I_{100} (%)
6.745	90	6.554	50
3.907	40	6.394	50
3.370	20	3.815	50
3.174	10	2.929	80
3.039	100	2.844	70
2.910	40	2.818	100
2.858	30	2.146	20
2.246	40	1.990	40
2.189	20	1.981	20
2.042	30	1.766	10
1.957	10	1.716	10
1.680	10	1.645	20

of $^5D_0 \rightarrow {}^7F_0$ transitions gives directly the different species of Eu^{3+} ions present in the sample. Furthermore, the crystal field (c.f.) fine structure of the other $^5D_0 \rightarrow {}^7F_J$ transitions yields information on the nature of the environment of the Eu^{3+} ion, i.e. of the site symmetry and of interactions with neighboring atoms. In the latter case the c.f. analysis can provide us with invaluable data on the bonding characteristics between ligands and the Eu^{3+} ion.

The UV-excited luminescence spectrum of $(LaO)_2CO_3:Eu^{3+}$ (Fig. 2) shows immediately that in this matrix the Eu^{3+} ion occupies two different sites (one can observe a double $^5D_0 \rightarrow {}^7F_0$ transition). This conclusion is supported by the X-ray powder diffraction analyses which revealed no trace of impurity phases. The high intensity of these transitions as well as the c.f. fine structure of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, imply that the symmetries of the Eu^{3+} sites are low, i.e. C_s, C_n or C_{nv} [31]. The only crystallographic structure data available for the RE oxycarbonate system gives only one possible site for the RE^{3+} ion in the II-$(REO)_2CO_3$ phase. It has been previously shown [15] that the Eu^{3+} luminescence spectrum of this phase differs considerably from the present one. Accordingly, it should be concluded that luminescence spectroscopy supports strongly the concept of the basic structural differences between the I- (and IA-) and II-types of RE oxycarbonates inferred previously in an indirect way [20].

The dye laser-excited luminescence spectra corresponding to the two different Eu^{3+} sites yield rather similar spectra (Fig. 2). A slight difference can be found in the total splitting of the $^5D_0 \rightarrow {}^7F_1$ transition while that of the $^5D_0 \rightarrow {}^7F_2$ is markedly similar in the two spectra. As the splitting of the $^7F_1$ and $^7F_2$ levels is governed by the short-range effects involving only the

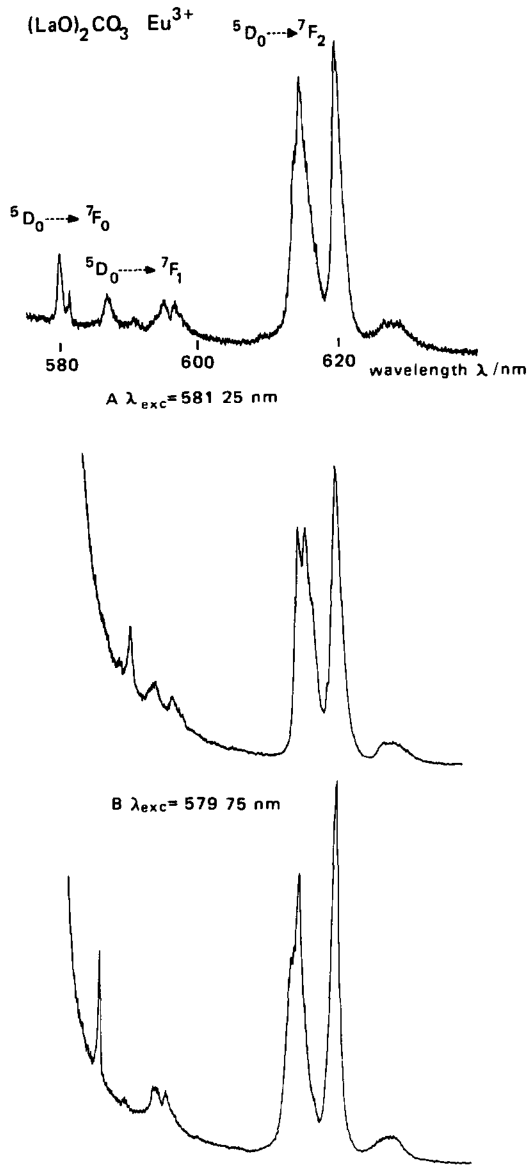

Fig 2 The luminescence spectrum of Eu^{3+} ion in (LaO)$_2$CO$_3$ matrix The global spectrum was obtained with Ar ion laser excitation at 77 K, while the others were obtained with dye laser excitation

closest neighbours of the Eu^{3+} ion [25], one can conclude that the reason for the spectral differences lies probably in the long-range effects of the packing of the carbonate groups.

A comparison of the luminescence spectra obtained in this study with those of other RE oxysalts [25–29] reveals a close relationship, especially in the case of spectrum B. Due to this interesting fact, a c.f. analysis was

TABLE 2

Comparison of the second and fourth rank crystal field B_q^k parameter values for $(LaO)_2CO_3$ Eu^{3+}, $(LaO)NO_3:Eu^{3+}$, $(LaO)_2MoO_4:Eu^{3+}$, $(LaO)_2SO_4$ Eu^{3+} and LaOX Eu^{3+} (X = Cl, Br, and I)

B_q^k	$(LaO)_2CO_3$	$(LaO)NO_3$	$(LaO)_2MoO_4$	$(LaO)_2SO_4$	LaOCl	LaOBr	LaOI
B_0^2	−1133	−1129	−914	−981	−1281	−1499	−1492
B_2^2	91	−224	166	117	–	–	–
B_0^4	−1049	−1199	−1389	−651	−467	−519	−620
B_2^4	−71	143	258	258	–	–	–
B_4^4	−871	−737	−556	−720	−1036	−1071	−1038

carried out in order to confirm quantitatively the similarities. The following RE oxysalts were included in this verification: lanthanum oxyhalides (LaOX; X = Cl, Br and I) which can be considered as the "parent" compounds for the whole group [25,26]; lanthanum oxysulphate ($(LaO)_2SO_4$) [27]; lanthanum oxymolybdate ($(LaO)_2MoO_4$) [28] and lanthanum oxynitrate ($LaONO_3$) [29]. As only the $^7F_1$ and $^7F_2$ level schemes are available for the c.f. analysis, the simulation was restricted to the determination of the second (B_q^2, $q = 0$ and 2) and fourth (B_q^4, $q = 0$, 2 and 4) rank parameters only, while the sixth rank parameters were fixed to the values obtained for $LaONO_3:Eu^{3+}$. The results presented in Table 2 show a remarkable resemblance between all these rather different lanthanum oxysalts. The spectroscopic properties seem to confirm the inclusion of the IA-type RE oxycarbonates in the tetragonal type of RE oxysalts.

REFERENCES

1 J O Sawyer, P. Caro and L. Eyring, Monatsh. Chem., 103 (1971) 333.
2 R.P Turcotte, J O. Sawyer and L. Eyring, Inorg Chem., 8 (1969) 238
3 M Shyamala, S R. Dharwadkar and M S Chandrasekharaiah, Thermochim Acta, 56 (1982) 135.
4 K C. Patil, G V Chandrashekar, M.V. George and C.N Rao, Can J Chem., 46 (1968) 257.
5 M. Ogawa, K Saito and K. Manmbe, Tokyo Kogyo Daigaku Kogyo Kiyo, 7 (1985) 41
6 S.R. Dharwadkar, M S Kumbhar, M.S. Chandrasekharaiah and M.D Karkhanavala, J Inorg. Nucl. Chem , 42 (1980) 1621.
7 M. Dąbkowska, Ann Univ Mariae Curie-Sklodowska, AA31–32 (1980) 111
8 J.D Savin, N.P Mikhailova and Z.V Eremenko, Zh Neorg. Khim , 32 (1987) 2662.
9 J P Attfield and G Ferey, J Solid State Chem , 82 (1989) 132.
10 A.N Christensen, Acta Chem Scand., 27 (1973) 1835
11 W. Brzyska and W Ozga, J. Therm. Anal., 32 (1987) 2001
12 G N. Makushova and S B. Pirkes, Zh. Neorg. Khim., 32 (1987) 876
13 G.N Makushova and S.B. Pirkes, Zh. Neorg. Khim., 29 (1984) 921
14 W. Brzyska, A Krol and M M. Milanova, Thermochim Acta, 161 (1990) 95.
15 O.-K Moune-Minn and P Caro, J. Crystallogr. Spectrosc Res , 12 (1982) 157
16 J A K Tareen, T.R.N Kutty and I. Mohamed, Indian Mineral., 21 (1980) 43

17 T R N Kutty, I. Mohamed and J.A K. Tareen, Mater Chem. Phys., 10 (1984) 425
18 D A Habboush, D H Kerridge and S A. Tariq, Thermochim Acta, 84 (1985) 13
19 A.N Christensen, Acta Chem. Scand , 24 (1970) 2440.
20 P. Caro, J Less-Common Met , 16 (1968) 367
21 P. Caro, C.R. Acad. Sci (Paris) Ser. C, 262 (1966) 992.
22 P. Porcher and P. Caro, J. Less-Common Met., 93 (1983) 151
23 H Dexpert, PhD Thesis, University of Paris VI, 1976
24 D Svoronos, O -K Moune, O Beaury and P. Caro, C R Seances Acad Sci., 294 (1982) 653
25 J Hölsa and P. Porcher, J Chem Phys., 75 (1981) 2108.
26 J Hölsä and P. Porcher, J. Chem. Phys , 76 (1982) 2790
27 P Porcher, D R. Svoronos, M Leskelä and J. Hölsä, J. Solid State Chem., 46 (1983) 101
28 J. Huang, J. Loriers and P Porcher, J Solid State Chem., 43 (1982) 87.
29 J. Hölsä and M. Karppinen, Eur J. Solid State Inorg. Chem , 28 (1991) 135
30 JCPDS – Int Center Diffr Data, Powder Diffr. Files, Swathmore PA, 1987
31 B R. Judd, Phys Rev , 141 (1966) 4