

REVIEW**BEHAVIOUR OF RARE EARTH SESQUIOXIDES EXPOSED TO ATMOSPHERIC CARBON DIOXIDE AND WATER**

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ABSTRACT

The behaviour of the rare earth sesquioxides, when exposed to atmospheric water and carbon dioxide under ordinary conditions of temperature and pressure, is reviewed. Data corresponding to eleven samples from seven different oxides systematically investigated by X-ray diffraction (XRD), IR spectroscopy, thermogravimetry (TG) and temperature-programmed decomposition (TPD), are reported. The BET surface areas of all these samples are also given. In accordance with the results summarized, upon exposure to air, the lanthanide sesquioxides all become hydrated and carbonated in bulk. However, the rate and intensity of these processes, as well as the nature of the resulting phases, are not the same for the whole group of oxides. Furthermore, the characterization carried out on the oxides aged in air suggests that throughout the lanthanide series at least three types of behaviour can be distinguished. In some cases, the behaviour has been found to depend on the origin of the samples, which prevents the generalization of definite sequences of reactivity for the whole series of oxides. Also, the use of a single technique, particularly XRD, does not allow one to establish the nature of the aged phases, or even to determine whether or not alterations in the bulk of the starting oxides have occurred.

1. INTRODUCTION

The ternary systems $\text{Ln}_2\text{O}_3\text{-H}_2\text{O-CO}_2$, as well as the binary systems $\text{Ln}_2\text{O}_3\text{-H}_2\text{O}$ and $\text{Ln}_2\text{O}_3\text{-CO}_2$ have been extensively investigated. Many of these studies have been carried out under hydrothermal conditions [1–14]. In other cases the reactivity of rare earth sesquioxides with either water [15–26] or, to a lesser extent, carbon dioxide [27,28] has been studied at pressures below 1 atm and temperatures ranging from ambient to 623 K. Likewise, the evolution undergone by several phases belonging to $\text{Ln}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ systems, when dispersed in water, at room temperature, under different carbon dioxide pressures ranging from 1 to $1 \cdot 10^{-6}$ atm, has also been investigated [29–36]. Nevertheless, no systematic studies are at present available on the behaviour of lanthanide sesquioxides exposed to air at ordinary temperature and pressure.

Since the rare earth sesquioxides are considered to be basic oxides [37], their storage and manipulation under atmospheric water and carbon dioxide should be expected to induce in them notable chemical and structural modifications. In spite of the obvious interest in this particular aspect of the chemistry of 4*f* sesquioxides, the information regarding this topic is currently rather scarce, fragmentary and even contradictory.

In ref. 38 it is reported that when Nd_2O_3 , Pm_2O_3 and Sm_2O_3 are exposed to air they undergo considerable hydration but no carbonation. Several $\text{Ln}_2\text{O}_3\text{-H}_2\text{O}$ systems (Ln: La, Pr, Nd and Sm) have been investigated [39,40] under conditions which imply the exposure of the phases studied to air. Although IR spectra showing the existence of carbonate bands have been reported [39], it was assumed that only hydration of the oxides had occurred. More recently, the carbonation of La_2O_3 has been reported [23,37]. However, the authors suggest that this process takes place only at surface levels. These results are not in agreement with ours [41–46], according to which carbonation in the bulk of rare earth sesquioxides aged in air does occur.

A further issue open to discussion is whether or not the heaviest 4*f* sesquioxides, when aged in air at normal temperature and pressure, become hydrated and carbonated in the bulk. To our knowledge, no studies other than ours [42,46] and those by Trillo and co-workers [26,47,48] have dealt with this topic. Nevertheless, on the grounds of some previous studies on the rate and intensity of the hydration process on rare earth sesquioxides [20], it is generally considered [37] that this reaction does not affect the bulk of oxides beyond Dy_2O_3 , even when they are soaked in boiling water.

In contrast with the results above, we have recently reported that ytterbium sesquioxide, when aged in air for a long enough period of time, undergoes hydration and carbonation phenomena in the bulk [42,46]. Furthermore, Alvero et al. [26] have found that, when appropriate experimental conditions are chosen ($P_{\text{H}_2\text{O}} > 8$ Torr, $T < 350$ K), ytterbia takes up amounts of water higher than those corresponding to a simple surface process.

Similar findings have been reported by Alvero et al. [25] for lutetia.

Since the rare earth sesquioxides are usually stored and manipulated in air, it seems to us that the present work, the major objective of which is to gather and discuss the information at present available on this topic, can contribute to a better understanding and use of this interesting group of oxides. Here, data concerning the actual nature of the 4*f* sesquioxides aged in air, as well as the experimental conditions under which the regeneration of the oxide phases can be achieved, are reported. This information can be particularly useful to those involved in the study of the properties as catalysts [49–51], transition metal supports [52–56] or promoters [57] of rare earth sesquioxides, topics to which increasing attention is being paid.

2. AGING OF RARE EARTH SESQUIOXIDES IN AIR

In the present work, the behaviour of the lanthanide sesquioxides, when exposed to atmospheric, water and carbon dioxide, at ordinary temperature and pressure, is studied. Results pertaining to La_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Dy_2O_3 , Ho_2O_3 and Yb_2O_3 are reviewed. In two cases, lanthana and samaria, data are reported for three different samples.

Part of the results summarized here have been reported previously [41–46]. Others, specifically those for europia, dysprosia and holmia, are given for the first time.

To our knowledge, no information, similar to that discussed here, is currently available for the remaining 4*f* sesquioxides. In spite of this limitation, we believe that the present work allows one to obtain a general view on the behaviour of lanthanide sesquioxides exposed to air.

All the oxide samples were in contact with atmospheric water and carbon dioxide for long periods of time (one or more years). In every case it was checked whether stabilization of the samples had been achieved.

When stabilized in air, the oxides were studied by X-ray diffraction (XRD), IR spectroscopy, thermogravimetry (TG) and temperature-programmed decomposition (TPD). In the case of the latter technique, the gases evolved were analysed either by gas chromatography (GC) or mass spectrometry (MS). The TG and TPD experiments were carried out in a flow of inert gas, at a heating rate of 0.1 K s^{-1} . The TPD–MS experimental device has been described and characterized elsewhere [58–60].

2.1. X-ray diffraction

Eleven different samples, corresponding to the seven 4*f* sesquioxides studied here, have been investigated by XRD. Six samples, hereafter referred to as Ln_2O_3 (S), were prepared in our laboratory following the procedure reported in ref. 42. Three samples, La_2O_3 (F), Nd_2O_3 (F) and Sm_2O_3 (F),

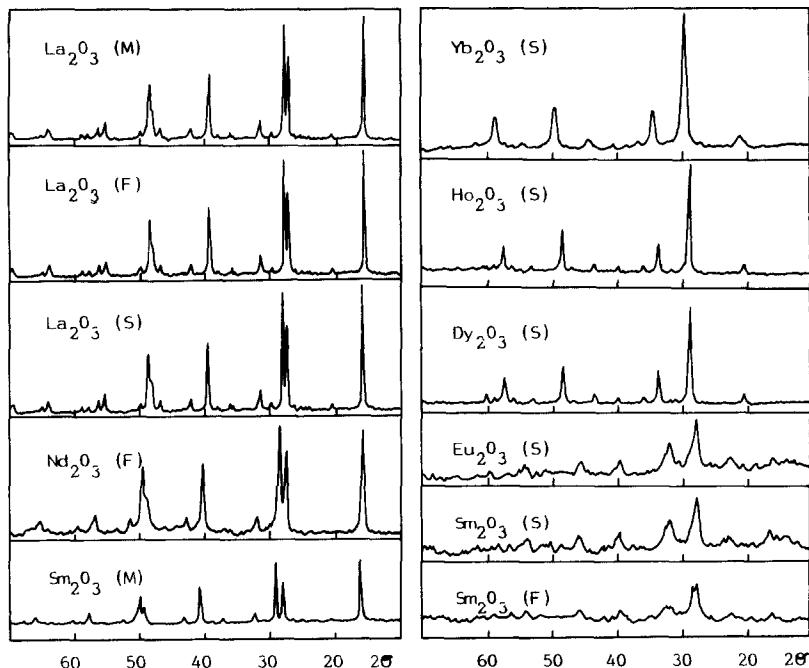


Fig. 1. X-ray diffraction patterns of rare earth sesquioxides stabilized in air.

were commercial oxides from Fluka, and the remaining two samples, La_2O_3 (M) and Sm_2O_3 (M), also commercial oxides, were from Merck.

The study of the starting oxides showed that the three lanthana samples, as well as the neodymium oxide investigated here, were hexagonal (A). The remaining samples, except Sm_2O_3 (M) for which the structure was not determined, were cubic (C).

Regarding the oxides aged in air, Fig. 1 depicts the corresponding XRD patterns. The hydroxide, $\text{Ln}(\text{OH})_3$, was the only crystalline phase identified in the case of the three lanthana samples [41,43], neodymia and Sm_2O_3 (M) [45]. For the remaining eight samples, the XRD patterns essentially corresponded to the cubic phase of the starting oxides. In some instances, Sm_2O_3 (F), the process of aging in air induces broadening, slight displacements and alterations of the relative intensities of some lines belonging to the oxide [61]. These effects, even stressed when the sample stabilized in air is heated at 383 K, are interpreted in ref. 61 as being due to the formation of an hydroxycarbonate phase. Broadening of the diffraction lines of the cubic oxides caused by the aging process has also been reported for Yb_2O_3 and Lu_2O_3 [26,62,63].

In the cases of lanthana and Sm_2O_3 (F), the XRD study was extended to the phases obtained upon heating the oxides stabilized in air at several increasing temperatures from 373 to 1200 K. These thermal treatments were carried out in a flow of inert gas.

When heated, the La_2O_3 (S) sample, oxyhydroxide, $\text{LaO}(\text{OH})$, di-oxy monocarbonate, $\text{La}_2\text{O}_2\text{CO}_3$, and finally, the hexagonal phase of the oxide, were successively identified, as the temperature was raised to 625, 725 and 1000 K, respectively [43]. For Sm_2O_3 (F) no crystalline phases, other than the cubic oxide and probably hydroxycarbonate, could be observed up to approximately 1200 K, at which temperature the cubic to monoclinic phase transition of the Sm_2O_3 was found to occur. This phase transition has been reported earlier [64].

Regarding the influence of the origin of the samples on their behaviour, our XRD study shows that there are no significant differences among the three lanthana samples investigated. Moreover, analogous XRD patterns were obtained for the phases resulting from the exposure to air at room temperature, for an oxide sample prepared by heating at 1130 K in a flow of helium and the starting samples of lanthana aged in air [41]. In contrast, for samaria, two distinctly different behaviours are observed [45]. On the one hand, Sm_2O_3 (M) behaves like the lighter oxides, i.e., lanthana and Nd_2O_3 (F); on the other hand, Sm_2O_3 (F) and Sm_2O_3 (S) show greater similarity to the heavier sesquioxides.

2.2. IR spectroscopy

Fig. 2 depicts the IR spectra corresponding to the oxides aged in air. The samples were studied in a potassium bromide matrix (97.5% KBr, 2.5% of the aged oxide).

Since the three lanthana samples showed very similar IR spectra, that corresponding to La_2O_3 (F) is the only one included in Fig. 2. Spectra of the samples of Sand M, stabilized in air are reported elsewhere [41]. For samaria, the IR spectroscopic study, like that carried out by XRD, shows two different types of behaviour. Accordingly, spectra representative of these two behaviours, specifically those corresponding to Sm_2O_3 (F) and Sm_2O_3 (M), are reported in Fig. 2.

When analysed in a little more detail, Fig. 2 shows notable differences among the various sesquioxides. In particular, the spectra in the OH stretching range suggest that three groups of oxides can be distinguished. Group I would consist of the three lanthana samples, Nd_2O_3 (F) and Sm_2O_3 (M), Group II would include Sm_2O_3 (S), Sm_2O_3 (F) and Eu_2O_3 (S) and the heaviest oxides, Dy_2O_3 (S), Ho_2O_3 (S) and Yb_2O_3 (S) would belong to group III.

The oxides of Group I are characterized by a sharp and strong absorption at 3600 cm^{-1} , and a broader less intense band centred at $3420\text{--}3440\text{ cm}^{-1}$. The frequency of the first of these bands does not significantly vary when going from lanthana to samaria.

According to several authors [23,39,65], and our own results [33,35,37], the band at 3600 cm^{-1} can be assigned to the corresponding hydroxide

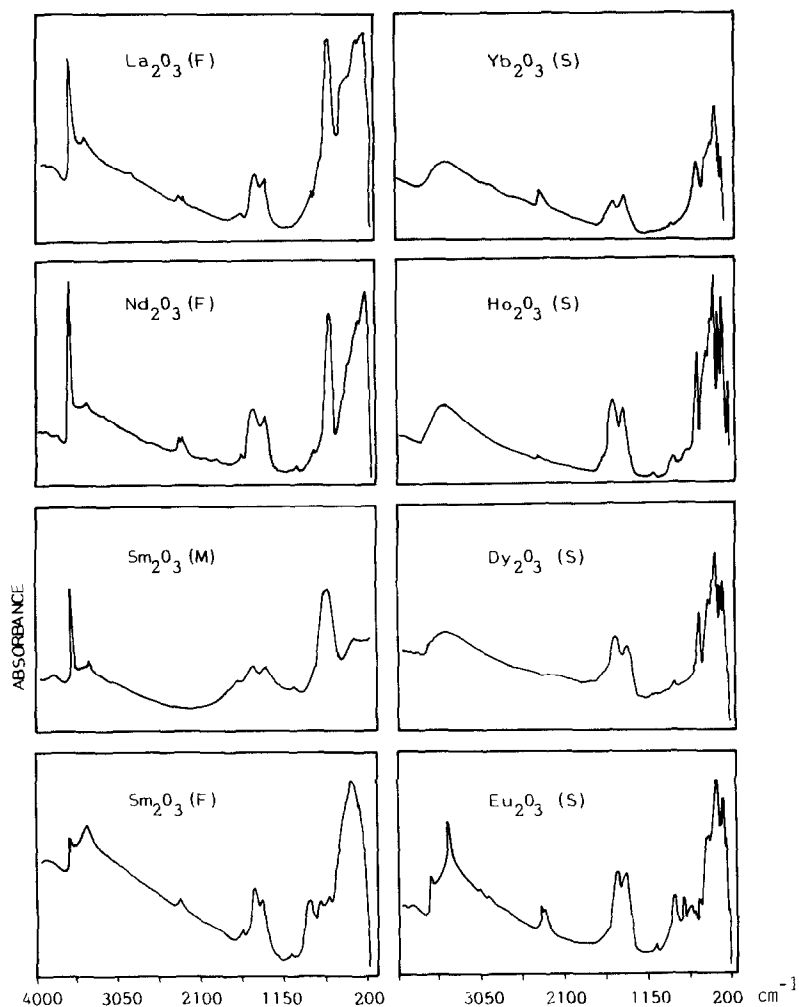


Fig. 2. IR spectra of lanthanide sesquioxides aged in air.

phases. In contrast to the oxides belonging to Groups II and III, the lighter 4f sesquioxides, when aged in air, show a very strong feature, appearing at 640 cm^{-1} for lanthana, 650 cm^{-1} for neodymia and 680 cm^{-1} for Sm_2O_3 (F) [45]. In refs. [41,43 and 45], on the basis of previous discussions [39,66], this low-frequency band is assigned to a deformation mode of Ln–O–H in the corresponding hydroxides. This interpretation is also consistent with the changes in the IR spectrum of a sample of La_2O_3 , exposed to air for increasing periods of time [41]. As can be seen in Fig. 3, the bands at 3600 cm^{-1} and 640 cm^{-1} grow in a quite parallel way.

Since the spectra in Fig. 2 show a band at 1620 cm^{-1} assignable to the bending mode of molecular water, the feature observed at $3420\text{--}3440\text{ cm}^{-1}$, mentioned above, might well be due, at least in part, to the stretching mode

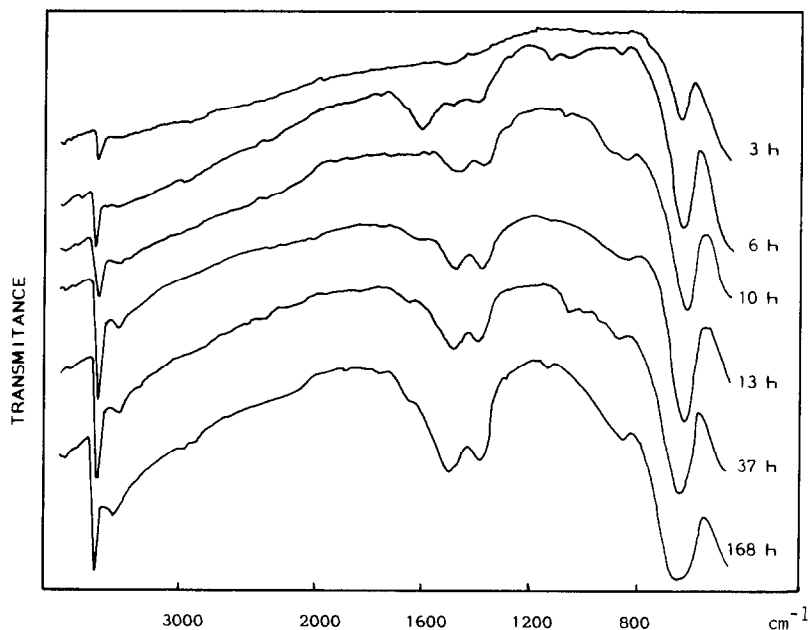


Fig. 3. Study by IR spectroscopy of the process of stabilization of a sample of lanthana in air.

of water. Nevertheless, as discussed for lanthana [41,43] and for samaria [45], the oxides of Group I, when aged in air, are partially transformed into hydroxycarbonate-like phases, $\text{Ln}_2(\text{OH})_{2(3-x)}(\text{CO}_3)_x$ where x is ca. 1. This is consistent with the strong features observed in the range of $1300\text{--}1500\text{ cm}^{-1}$ for the aged oxides. The existence of the hydroxycarbonate phases has been reported earlier [31,35,36]. The polymorphs, ancylite type (A type) and bastnaesite type (B type), of the rare earth hydroxycarbonates have been identified [65]. The hydroxycarbonates of type B are more easily prepared under hydrothermal conditions [4,6,7], whereas type A can be obtained, among other procedures, by hydrolysis of lanthanide carbonates or exposure of the hydroxides to air [31].

According to Dexpert et al. [65], the ancylite-like hydroxycarbonates are characterized in the range $3000\text{--}4000\text{ cm}^{-1}$ by a doublet, hardly resolved for the elements belonging to the first half of the lanthanide series. The average frequency of this doublet ranges from 3425 cm^{-1} to 3515 cm^{-1} as the atomic weight of the rare earth element increases. Therefore, the hydroxycarbonate phases can also contribute to the band at $3420\text{--}3440\text{ cm}^{-1}$ observed in the spectra of oxides belonging to Group I.

The O–H stretching range for the spectra of the oxides belonging to Group II, Sm_2O_3 (S), Sm_2O_3 (F) and Eu_2O_3 (S), is characterized by bands at around 3600 cm^{-1} and 3420 cm^{-1} . Though the frequencies at which these bands are observed are similar to those reported for the oxides of Group I, their relative intensities are quite different, the most intense being now that

at 3420 cm^{-1} . As discussed in ref. 61, the ν O–H spectra of oxides of Group II suggest that the stabilization of these oxides in air primarily implies the formation of hydroxycarbonate-like phases, similar to those reported by Caro and co-workers [31,35,65]. In accordance with this interpretation, the weak band at 3600 cm^{-1} would indicate the existence of hydroxide as a residual phase. In fact, no lines of $\text{Ln}(\text{OH})_3$ could be observed in the XRD patterns reported in Fig. 1 for the oxides of Group II.

Regarding the IR spectra of oxides belonging to Group III, the O–H stretching range is characterized by a broad featureless absorption, centered at 3425 cm^{-1} . These spectra are very similar to those reported in ref. 32 for $\text{Er}_2(\text{CO}_3)_3 \cdot 2.25\text{H}_2\text{O}$, and in ref. 67 for $\text{Gd}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ (where $n = 2, 3$).

As far as the low-frequency range of the spectra is concerned, all the oxides belonging to Group III show a sharp, well resolved band at about 560 cm^{-1} . In accordance with ref. 68, this band should be assigned to the cubic phase of the corresponding $4f$ sesquioxides. This suggests, like the XRD study reported in Fig. 1, that when the oxides of Group III attain apparent stabilization in air, the aged phases coexist with the original cubic phase of the corresponding oxides.

In some cases, the IR spectroscopic study has been extended to the thermal evolution of the oxides aged in air. Results corresponding to studies on different samples of lanthana and Sm_2O_3 (F) are reported in refs. 41 and 43, and in ref. 61 respectively. Fig. 4 shows the IR spectra of La_2O_3 (S) stabilized in air, spectrum A, as well as of the phases obtained upon heating

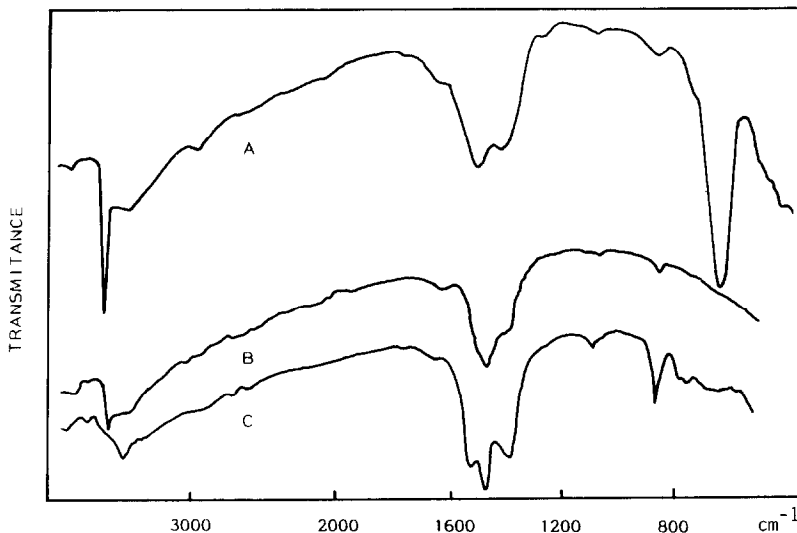


Fig. 4. Study by IR spectroscopy of the thermal evolution of a lanthana sample aged in air. (A) Sample stabilized in air. (B) Sample A heated at 625 K. (C) Sample A heated at 725 K.

this sample at 625 K, spectrum B, and at 725 K, spectrum C. These thermal treatments were carried out in a flow of helium.

From the comparison of spectra A and B, it can be noted that on heating the sample at 625 K the band at 640 cm^{-1} completely vanishes, and the intensity of that at about 3600 cm^{-1} strongly decreases. In addition, a notable morphological change in the carbonate bands can be observed. As discussed in ref. 43, these alterations of the IR spectrum of lanthana can be interpreted as due to the simultaneous decomposition of $\text{La}(\text{OH})_3$ and the hydroxycarbonate, $\text{La}_2(\text{OH})_{2(3-x)}(\text{CO}_3)_x$ where x is ca. 1, the actual phases constituting lanthana aged in air. The lanthanum hydroxide would decompose to the oxyhydroxide, $\text{LaO}(\text{OH})$, an intermediate phase in the dehydration of $\text{La}(\text{OH})_3$ to oxide [17,23,40], whereas the hydroxycarbonate would decompose to dioxymonocarbonate, $\text{La}_2\text{O}_2\text{CO}_3$. The rare earth dioxymonocarbonates are well characterized phases in the $\text{Ln}_2\text{O}_3\text{-CO}_2$ system. In particular, their IR spectra have been discussed by Turcotte et al. [69]. The lanthanide dioxymonocarbonates have been identified as intermediate phases in the decomposition of several lanthanide carboxylates [70,71], carbonates [32,72], as well as hydroxycarbonates [32,73].

Upon heating the sample at 725 K, spectrum C in Fig. 4, the band at 3600 cm^{-1} disappears, which can be interpreted as a result of the dehydration of $\text{LaO}(\text{OH})$ to La_2O_3 . The bands in the range $1300\text{--}1500\text{ cm}^{-1}$, though better resolved, remain essentially unmodified with respect to those observed after the thermal treatment at 625 K. Temperatures as high as 1000 K are necessary to decompose the carbonated phase thoroughly.

2.3. TG and TPD

Figs. 5 and 6 show the TG and TPD diagrams for the series of oxides aged in air.

In accordance with Fig. 5, the TG traces for La_2O_3 , Nd_2O_3 and Sm_2O_3 (M) are very similar to each other, showing three well defined steps. For the remaining oxides, the TG curves also indicate the occurrence of multiple steps which, however, cannot easily be resolved.

The total weight losses, as determined by TG, were found to range from approximately 17% for the lanthana samples to 6% for holmia (data referred to pure oxide).

Although three samples of lanthana, La_2O_3 (S), La_2O_3 (M) and La_2O_3 (F), were investigated by both TG and TPD, no significant differences have been observed among them [41]. Therefore, Figs. 5 and 6 show only the traces corresponding to La_2O_3 (S). As in the IR spectroscopic study, the TG and TPD curves for Sm_2O_3 (S) and Sm_2O_3 (F) are similar to each other [45]. Accordingly, those for Sm_2O_3 (F) are not shown. On the contrary, the behaviour of the two samaria samples above and that of Sm_2O_3 (M) were found to be quite different. Therefore, TG and TPD diagrams representative

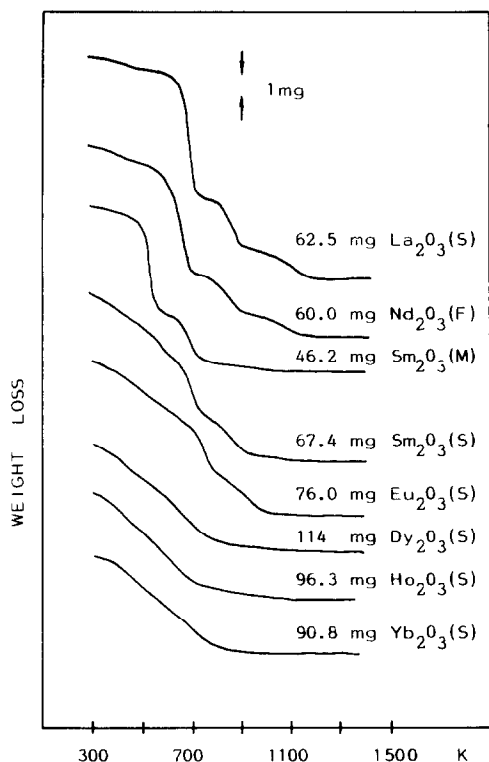


Fig. 5. TG traces depicting the thermal evolution, in a flow of helium, of 4f sesquioxides aged in air.

of the two behaviours observed for the samaria samples have been included in Figs. 5 and 6.

Upon integration of the TPD traces for water and carbon dioxide, the total amounts of these substances evolved from each of the oxide samples aged in air have been determined (Table 1). The calculated total weight losses reported on Table 1 agree well with those determined by TG.

In Table 1, the amounts of water and carbon dioxide taken up by the eleven samples of the 4f sesquioxides stabilized in air are expressed in three different ways: mg/g of Ln₂O₃, mol/mol of Ln₂O₃ and molecules/nm². Data expressed in the last way were estimated from the BET surface area of the oxides stabilized in air, also included in Table 1.

The structure of both the starting oxides and the final phases resulting from the exposure to air, as deduced from the XRD study reported above, are also given in Table 1.

From the surface model for the cubic phase of rare earth sesquioxides described in ref. 46, and the estimate made by Rosynek and Magnuson [28] for the lighter oxides of the series, the amounts of either water or carbon dioxide taken up by the rare earth sesquioxides by virtue of a simple surface

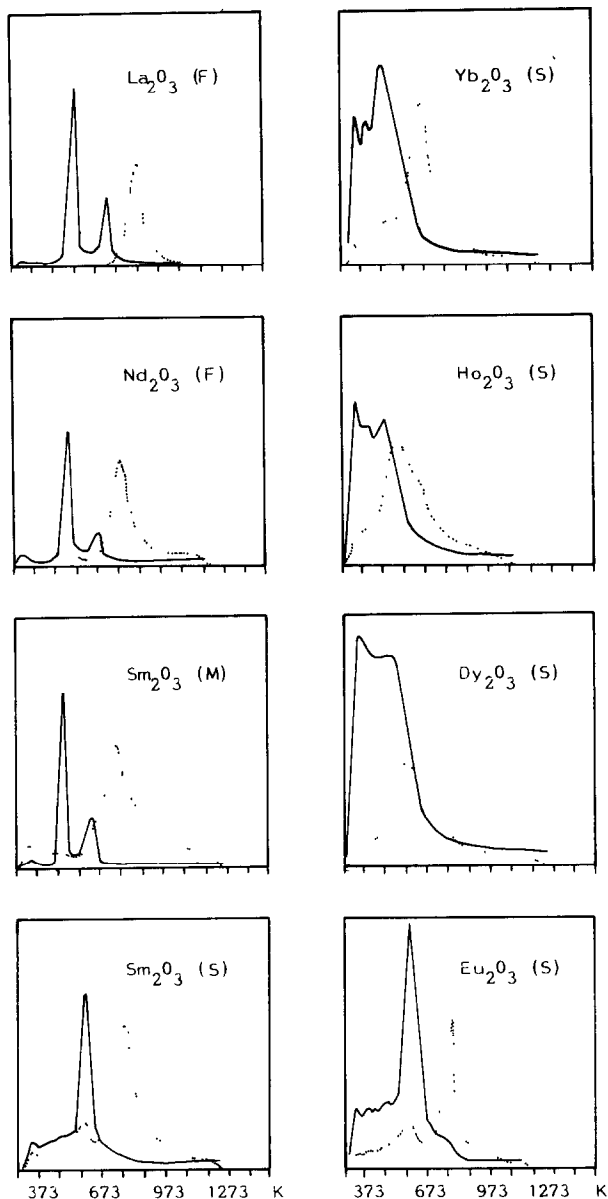


Fig. 6. TPD traces corresponding to the thermal evolution of water (—) and carbon dioxide (· · · · ·) from rare earth sesquioxides aged in air. The amounts of sample and the scales for the GC signals are not the same for the different oxides.

process should not exceed 8 molecules/nm². Accordingly, a first interesting conclusion can be drawn from Table 1: upon exposure to air, all the lanthanide sesquioxides become hydrated and carbonated in bulk. In particular, in the case of the lighter oxides, the H₂O to Ln₂O₃ mol ratios

TABLE 1
 Characterization data for the series of rare earth sesquioxides

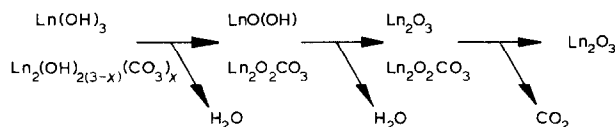
Sample	Crystal structure *		S_{BET} (m^2/g)	Weight loss		molecules/ nm^2			Molar ratio			
	Starting sample	Aged sample		Percentage		H_2O	CO_2	H_2O	CO_2	H_2O to Ln_2O_3	CO_2 to Ln_2O_3	H_2O to CO_2
				H_2O	CO_2							
La_2O_3 (S)	A	H	16.3	14.2	2.8	250	20	2.57	0.21	12.5		
La_2O_3 (F)	A	H	3.4	16.4	1.1	1372	38	2.97	0.08	36.1		
La_2O_3 (M)	A	H	5.2	15.7	1.5	859	34	2.84	0.11	25.3		
Nd_2O_3 (F)	A	H	5.9	13.3	2.3	717	51	2.49	0.18	13.8		
Sm_2O_3 (S)	C	C+U	14.9	6.3	3.1	130	27	1.23	0.25	4.9		
Sm_2O_3 (F)	C	C+U	8.2	4.9	1.7	187	28	0.95	0.14	6.8		
Sm_2O_3 (M)	-	H	6.4	15.6	1.6	696	29	3.02	0.13	23.2		
Eu_2O_3 (S)	C	C+U	25.6	10.6	2.0	111	8.5	2.08	0.16	13.0		
Dy_2O_3 (S)	C	C	22.3	5.4	2.5	74	14	1.12	0.21	5.3		
Ho_2O_3 (S)	C	C	32.5	3.2	2.6	30	10	0.67	0.22	3.0		
Yb_2O_3 (S)	C	C	40.0	6.4	4.6	48	14	1.40	0.40	4.0		

* C = Cubic oxide phase; A = hexagonal oxide phase; H = hydroxide phase; U = unidentified hydroxycarbonate phase.

suggest, in agreement with the XRD and IR spectroscopy studies, that considerable hydration of the starting samples, leading to hydroxides, occurs. In contrast, the CO_2 to Ln_2O_3 mol ratios indicate that the apparent stabilization of all the oxides is attained when the carbonation levels are relatively low.

The TPD diagrams depicted in Fig. 6 confirm the notable differences observed in the behaviour of the lanthanide sesquioxides. Moreover, the analysis of Fig. 6 suggests that the three groups of oxides deduced from the IR spectroscopic study can also be distinguished by TPD.

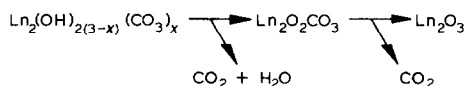
Regarding the oxides in Group I, the TPD diagrams demonstrate that the first two steps in the corresponding TG traces are due to the dehydration of the samples, whereas the third should be associated with decomposition of a carbonated phase. If the XRD and IR spectroscopy data, discussed above, are taken into account, the thermal evolution of the oxides belonging to Group I aged in air might well be described as follows [41,43,45]:



The temperatures at which the three steps of this reaction scheme occur (625, 730 and 900 K, respectively, in the case of lanthana) steadily decrease from La_2O_3 to Sm_2O_3 (M).

In accordance with the IR spectroscopic and XRD data reported above, the TPD diagrams of oxides of Group II can be interpreted assuming that the major phase which results from the aging in air of Sm_2O_3 (F), Sm_2O_3 (M) and Eu_2O_3 consists of a hydroxycarbonate, $\text{Ln}_2(\text{OH})_{2(3-x)}(\text{CO}_3)_x$, with x slightly greater than one.

In effect, for $x > 1$, the decomposition of the hydroxycarbonate phases can be described as follows:



The amount of carbon dioxide evolved from the first step depending on the specific value of x . This type of mechanism has been previously proposed for the thermal decomposition of ancylite-like hydroxycarbonates [32,73].

If such a reaction scheme is applied to the TPD diagrams for the oxides of group II, the simultaneous evolution of water and carbon dioxide occurring at around 600 K would correspond to the decomposition of the hydroxycarbonate phases. In accordance with this reaction scheme the process responsible for the major peak of carbon dioxide, on the other hand, would be the decomposition to oxide of the corresponding dioxymono-

carbonate phases. This second step would take place at much higher temperatures.

The TPD diagrams for the oxides belonging to Group III show notable differences regarding the thermal evolution of carbon dioxide with respect to the oxides of Groups I and II. In addition to a low-temperature feature, two poorly resolved peaks, centred at about 600 and 700 K, can be observed for Dy_2O_3 (S) and Ho_2O_3 (S). In the case of the Yb_2O_3 (S) aged in air only a single peak at approximately 700 K can be observed. As far as the evolution of water is concerned, all the oxides of Group III show at least two features, peaking at about 370 and 500 K.

Since the IR spectra in Fig. 2 indicate that the oxides of Group III upon aging in air are partially transformed into phases consisting of hydrated carbonates, the TPD traces reported in Fig. 6 for these oxides might be interpreted by assuming that the above phases evolve to sesquioxides through a dehydration step, followed by decomposition of the carbonated phase. The same reaction scheme has been proposed [32] for the thermal evolution of several $\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ phases. In ref. 32, on the other hand, it is suggested that the decomposition of the carbonates takes place through oxycarbonate-like intermediates.

3. FINAL REMARKS

According to the results reported above, the rare earth sesquioxides, when exposed to atmospheric carbon dioxide and water at ordinary temperature and pressure, become hydrated and carbonated in bulk. This has been observed to occur even in the case of the heaviest members of the series. Regarding the nature of the phases resulting from the aging process, notable differences have been found. This has allowed us to distinguish three types of behaviour throughout the series of oxides.

Oxides belonging to the so-called Group I, those corresponding to the lighter members of the series, are transformed into partially carbonated hydroxides. In contrast to the hydration process, which is practically complete, the carbonation reaction, as deduced from the CO_2 to Ln_2O_3 mol ratios, seems to be rather limited, leading to hydroxycarbonate phases. This suggests that the carbonation process is restricted to the outer layers of the samples. Accordingly, though quantitatively less significant, the carbonation process can play an important role in determining the surface chemistry of the resulting phases.

Regarding the sesquioxides of Group II, the XRD data suggest that the cubic phase of the starting oxides is always present, and therefore, as confirmed by TG, the transformation of these samples is only partial. On the other hand, the TPD and IR spectroscopic studies indicate that the transformed phases consist essentially of hydroxycarbonates. Likewise, the

TPD and IR spectroscopic results support the presence of a residual phase of hydroxides. Nevertheless, no confirmation of the existence of this phase could be obtained from XRD.

For the heaviest sesquioxides of the lanthanide series, Group III, the results summarized here indicate that, when the apparent stabilization of the samples is attained, the transformation of the oxides is only partial. Likewise, the results, particularly those obtained by TPD and IR spectroscopy, are consistent with the formation of hydrated carbonate phases.

As can be deduced from the differences in behaviour reported above, the results obtained for some 4*f* sesquioxides, especially the oxides more extensively investigated, i.e., lanthana, should not be extrapolated to the whole series.

In agreement with previous results [20,38] for the hydration reaction, it has been found that the rate and intensity of the aging process vary dramatically throughout the lanthanide series. In our case, for lanthana, the complete disappearance of the oxide occurs in less than 24 h of air exposure. On the other hand, the three lanthana samples investigated showed essentially the same behaviours. For Nd₂O₃ (F), apparent stabilization was attained after 45 days of air exposure. For the remaining oxides the process was much slowed. Thus, for Sm₂O₃ (F) nine months were necessary in order to achieve a complete stabilization.

In contrast to that observed for lanthana, in the case of the heaviest oxides of the series, there is evidence in support of both the rate and intensity of the aging process being influenced by the origin of the oxide samples. Thus we have reported [42] that, upon calcination of two ytterbia samples aged in air, the corresponding total weight losses differed by a factor of six. Slightly lower differences ($\times 4$) were also found between two samples of Gd₂O₃ [42]. Likewise, Alvero et al. [26], who investigated the influence of the preparation method on the reactivity towards water of three different samples of ytterbia, reported that both the rate of hydration and the amount of water taken up by the samples strongly depend on their origins. In a parallel study, Alvero et al. [25] observed a similar influence of the preparation method on the reactivity of lutetia to water.

Earlier papers [15,16,38] have reported the influence of factors such as the calcination temperature or the structural nature of the rare earth sesquioxides on their reactivity with either liquid water or water vapour. Accordingly, no precise sequences should be established for the rate or intensity of the aging processes throughout the whole series of 4*f* sesquioxides, because, as suggested by the results above, factors other than the chemical nature of the oxides can notably modify such correlations.

Our results also indicate that, when XRD is used as the only technique to characterize the lanthanide sesquioxides aged in air, wrong conclusions can be drawn. Thus, for the oxides of Group I, no evidence of their carbonation in bulk can be obtained by XRD. This, perhaps, explains why several

workers do not recognize the carbonation in bulk of oxides like lanthana or neodymia [23,37–40]. For the remaining oxides, the XRD patterns essentially agree with those of the corresponding cubic phase. In brief, the use of XRD techniques does not unequivocally establish whether or not the lanthanide sesquioxides aged in air undergo alterations of their bulk structure.

To our knowledge, no systematic studies like that reported here have appeared. However, it should be noted that several workers [29–36] have extensively investigated the ternary system $\text{Ln}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ under conditions, in some cases, resembling ours. Nevertheless, the results here do not agree with those previously published. Thus, in ref. 31 it was found that when several *4f* hydroxides, dispersed in water, are exposed to air, they slowly take up carbon dioxide, and, from lanthanum to europium, are transformed into hydroxycarbonates with a molar ratio CO_2 to Ln_2O_3 of 2. If this molar ratio is compared with that obtained here, see Table 1, it can be deduced that the carbonation levels reached in our case are much lower. It is apparent from our results that, even for the lighter oxides of the series, the carbonation process stops when the molar ratio CO_2 to $\text{Ln}_2\text{O}_3 \ll 2$. This suggests that, by relatively slight modifications of the experimental conditions, notably different phases may result. In other words, in order to improve our current knowledge on the behaviour of *4f* sesquioxides in air, specific experiments aimed at investigating this behaviour should be undertaken. From this point of view, the present review constitutes a first contribution to this particular aspect of the chemistry of *4f* sesquioxides. Since the rare earth sesquioxides are increasingly being investigated and applied, the interest of this topic cannot be overemphasized.

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