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STUDY OF THE AGING IN AIR OF A CUBIC SAMPLE OF SAMARIA

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ABSTRACT

The aging in air of a cubic sample of samarium sesquioxide has been studied by TPD and X-ray Diffraction. Though the hydration and carbonation of the oxide occur in bulk, when the apparent stabilization of the sample is reached, the starting phase is only partially transformed. The thermal evolution of the aged in air sample, as deduced from IR Spectroscopy and X-ray Diffraction studies, suggests that an hydroxycarbonate phase as well as samarium hydroxide are formed when this samaria sample is exposed to the air.

MATERIALS INDEX: Samarium Oxide/Aging in Air/Hydroxycarbonate/Hydroxide

Introduction

The lanthanide sesquioxides are generally considered to be highly active phases against water and carbon dioxide (1). In spite of this, no detailed studies are at the present available on the evolution undergone by these oxides when exposed to the air at the ordinary temperature and pressure.

Since the 4f oxides are usually stored and manipulated in air, the information concerning the actual nature of the phases under study, when not specially protected lanthanide oxides are investigated, should be considered very valuable. This prompted us to initiate a research program aimed at investigating the behavior of lanthanide oxides exposed to the atmospheric water and carbon dioxide (2-7).

In the present work, data concerning a commercial sample of samaria are reported. To our knowledge, a few papers have dealt with the behavior of Sm_2O_3 exposed to the air (8). Here, the evolution undergone by this oxide throughout the process of aging in air has been studied, and the final phases resulting from this process characterized. The results are discussed by comparison to those previously obtained by us for other 4f oxide samples, as well as to those reported in the literature for some phases of the ternary system Ln_2O_3-H_2O-CO_2.

Methods

The samaria sample investigated here was Fluka, 99.9% pure oxide. No details regarding the preparation procedure could be obtained from Fluka. The BET surface area of this sample, as determined by nitrogen adsorption at 77 K, was found to be 8.2 $m^2.g^{-1}$.

The thermogravimetric (TG) experiments were carried out in a Mettler, model ME-21, microbalance. The flow of helium was : $10^{-6}m^3.s^{-1}$ and the heating rate : 0.1 $K.s^{-1}$.

The temperature progammed decomposition (TPD) experiments were recorded under the following conditions: flow of helium: $5.8.10^{-7}m^3.s^{-1}$; heating rate: 0.1 $K.s^{-1}$. The analysis of evolved gases was carried out by gas chromatography.

The IR spectra were recorded with a Pye-Unicam instrument, model SP-3-300. Self supported disks, obtained by pressing the powdered oxide under 5.10^8 Pa, were studied with the help of a quartz IR cell, which could be heated either in a vacuum or inert gas flow. The windows of the IR cell were of CaF_2.

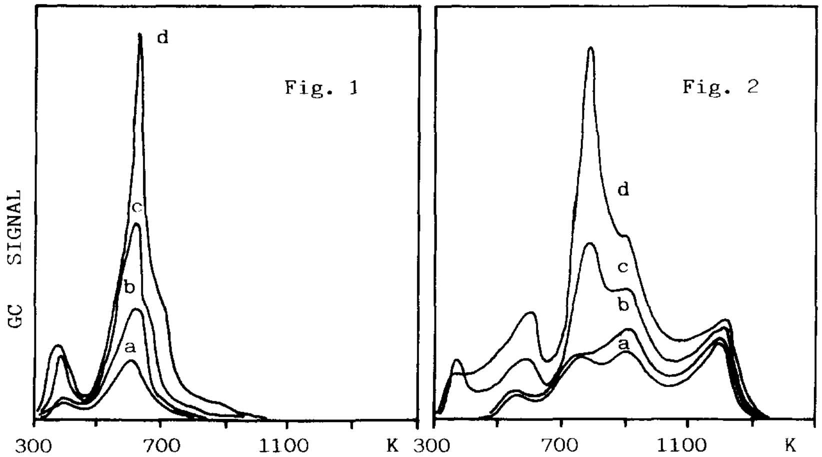
The X-ray diffraction studies were carried out with a Siemens, model D-500, instrument. The Debye-Scherrer camera was Philips, model PW 1024/30. The radiation was Mo-Kα . The samples were studied in sealed capillary tubes of Lindeman glass, 0.3 mm diameter.

Results

The evolution of the samaria samples exposed to the air, at ambient temperature, has been studied by TPD, Figures 1 and 2.

As can be seen on Fig. 1, the decomposition of the hydrated phase takes place through two major steps. The first one, peaking at 373 K, should be associated to weakly retained water, whereas the second one should correspond to the broad peak centered at 625 K. As deduced from Fig. 1d, for the second of the steps mentioned above, a single narrow peak at 625 K, as well as two shoulders at both sides of the major peak can be distinguished. Accordingly, as confirmed by our IR spectroscopic study reported below, the second step corresponds to a rather complex process.

The thermal evolution of CO_2, Fig. 2, is characterized by five peaks at 350 K, 600 K, 800 K, 920 K and 1225 K. According to Fig. 2, the highest temperature peak is only slightly modified throughout the whole process of aging of the oxide, which suggests that this peak corresponds to residual carbonate species, not thoroughly decomposed during the preparation of the oxide. In this sense, it would be mentioned that the X-ray diffraction



Figs. 1 and 2.- TPD traces corresponding to the thermal evolution of H_2O (fig.1) and CO_2 (fig.2) from the samaria sample aged in air: a) 0 days; b)21 days; c) 90 days; d) 270 days

TABLE 1

Amounts of H_2O and CO_2 Taken up by the Samaria Sample after Exposure to the Air for Increasing Periods of Time

Exposure Time	H_2O		CO_2		Total Weight Loss
(days)	mg/g(Sm_2O_3)	molec/nm^2	mg/g(Sm_2O_3)	molec/nm^2	mg/g(Sm_2O_3)
0	10.6	43	4.4	7	15.0
21	19.1	78	6.2	10	25.3
180	33.3	136	11.4	19	44.7
270	48.9	199	17.9	30	66.8
270(*)	--	-	--	--	68.0

(*) determined by Thermogravimetric Analysis.

data shown below indicate that the sample investigated here ought to be prepared by calcination at relatively low temperatures.

Upon integration of the traces reported on Figs. 1 and 2, the amounts of water and carbon dioxide evolved from the sample could be determined. Table 1 accounts for the corresponding data. This table also includes the total weight loss of the aged in air sample as determined by TG.

On the grounds of the surface model for the cubic phase of Ln_2O_3, discussed in ref.(7), it can be deduced that the amounts of water and carbon dioxide evolved from our sample are much higher than those corresponding to simple surface processes.

The evolution of the sample throughout the aging process has also been studied by X-ray diffraction. On Figs. 3a and 3b the diffraction patterns corresponding, respectively, to the oxide as received from Fluka and to the sample stabilized in air are shown. The diagram on Fig. 3a fits well to that reported for the cubic phase of samaria. For the aged oxide, Fig. 3b, the diffraction lines become broader, their relative intensities are modified, and even, some of them are slightly moved. As the TPD results reported above, the X-ray diffraction data suggest that the hydration and carbonation of samaria are bulk processes, inducing alterations on the structure of the oxide.

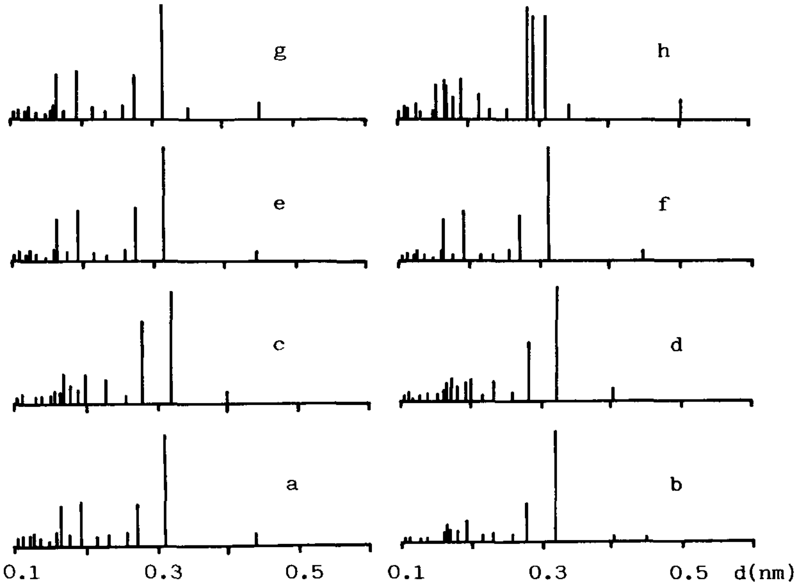


Fig. 3.- X-ray Diffraction Patterns Corresponding to Samaria Exposed to the Air for 0 Days (a) and 270 Days (b);and to the aged in air sample and further heated at 393 K (c), 553 K (d), 743 K (e), 923 K (f) and 1198 K (g).

In order to get some further insight into the nature of the phases resulting from the stabilization in air of samaria, we have also studied by X-ray diffraction and IR spectroscopy the thermal evolution of the aged sample.

Figures 3c through 3h account for the diffraction patterns obtained after heating the sample, in flow of He, for 4 h, at 393 K, 553 K, 623 K, 743 K, 923 K and 1148 K.

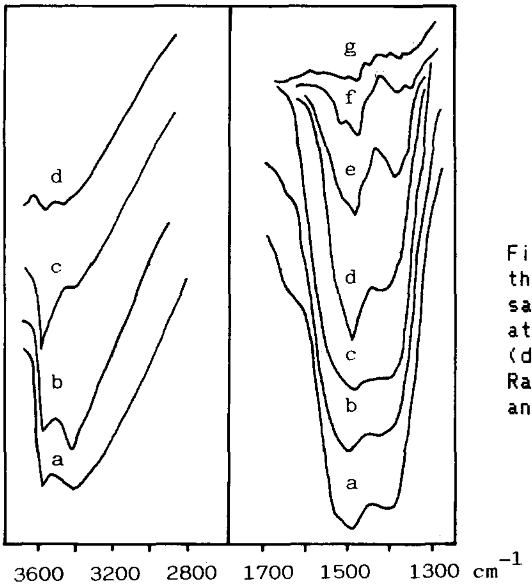
When the sample is heated at 393 K, Fig. 3c, the differences found between the diagrams depicted on Figs. 3a and 3b become more obvious. Lines appearing at 0.314 nm and 0.273 nm on fig. 3a are now observed at 0.323 nm and 0.282 nm, respectively. On the other hand, lines which are not found on Figs. 3a and 3b, can be observed on Fig. 3c. Such is the case of peaks at 0.200 nm and 0.170 nm. Some low intensity lines belonging to the cubic oxide (i.e. 0.447 nm) vanish, and others not adscribible to samaria (i.e. 0.403 nm) increase their intensity.These results suggest that, when heated at 393 K, the phase resulting from the stabilization in air of samaria improves its crystallinity and, as a consequence, the departure of the X-ray diffraction pattern from that corresponding to the unaltered oxide are greater.

For the sample heated at 623 K, Fig. 3e, the difraction pattern resambles that of Sm_2O_3-C. No crystalline phases other than the cubic oxide could be observed after this thermal treatment.

After heating the sample at either 743 K (Fig. 3f) or 923 K (Fig. 3g) the corresponding diagrams do not show significant changes with respect to that reported on Fig. 3e. On the contrary, when the sample is heated at 1148 K, the phase transition cubic (C) $\longrightarrow$ monoclinic (B) of samaria can be observed. Accordingly, the oxide studied here was probably prepared at temperatures well below 1100 K, which would explain the existence on the original sample of residual carbonate species.

The study by IR spectroscopy is summarized on Figures 4 and 5. Fig. 4 accounts for the O-H stretching range of IR spectrum. Fig. 5, on the other hand, shows spectra corresponding to the range 1700-1250 cm^{-1} . The spectra were recorded succesively after heating the sample, in flow of He, 4 h, at 403 K, 553 K, 723 K, 923 K and 1173 K. Spectra corresponding to the thermally untreated sample are also included in both Figs. 4 and 5.

The aged in air samaria sample, Fig. 4a, shows a broad absorption in the range 3000-3700 cm^{-1} , featuring at 3415 cm^{-1} and 3600 cm^{-1} . After heating at 403 K, Fig. 4b, the broad tail below 3400 cm^{-1} , due to weakly retained water, desappears and the two bands at 3415 and 3600 cm^{-1} become better resolved.When the sample is heated at 553 K,the band at 3415 cm^{-1} vanishes, whereas that centered at 3600 cm^{-1}, though less intense remains. As the TPD results on Fig. 1, the evolution of the IR spectra indicates that the second step of the dehydration reaction does not take place through a simple process. Caro et al (9) have recently discussed the IR spectra corresponding to A-type, ancylite-like, lanthanide hydroxycarbonates, characterized in the O-H region by a doublet hardly resolved for the elements belonging to the first half of the lanthanide series. The mean position of this doublet ranges from 3425 to 3515 cm^{-1}, as the atomic weight of the 4f ion increases. In ref. (9) it is emphasized the differences existing between the IR spectra of the hydroxycarbonate and hydroxide phases, the latter of them being characterized in the O-H range by a sharp band at about 3600 cm^{-1} .



Figs. 4 and 5.- IR spectra of the stabilized in air samaria sample (a), and further heated at 403 K (b), 553 K (c), 723 K (d), 923 K (e) and 1173 K (f). Ranges: 3000-3700 cm^{-1} (Fig. 4) and 1700-1250 cm^{-1} (Fig. 5).

On Fig. 5a, in addition to the bands due to carbonate species, it can be observed a shoulder at 1620 cm^{-1}. This feature, corresponding to the bending mode of H_2O, vanishes when the sample is heated at 403 K, Fig. 5b.

After heating the sample at 553 K, Fig. 5c, simultaneously to the desappearance of the band at 3415 cm^{-1}, a very broad featurless absorption can be observed in the carbonate region. This morphological change of the spectrum is not accompanied by a significant modification of the intensity. In reference (10), the formation of a dioxymonocarbonate phase, $Sm_2O_2CO_3$, resulting from the dehydration of the corresponding hydroxycarbonate has been suggested.

Upon heating the sample at 723 K, Fig. 5d, the shape of the bands assignable to carbonate species undergoes a notable alteration with no parallel modification of their intensities. This phenomenon, also observed in ref. (2), can be interpreted as being due to the ordering of the initially disordered carbonate species belonging to the dioxymonocarbonate formed by dehydration of the hydroxycarbonate phase.

When the sample is heated at 923 K, Fig. 5e, the intensity of the carbonate bands notably decreases, which would indicate that the decomposition of the dioxymonocarbonate phase has occurred. However, residual bands due to carbonate species are found even after heating the sample at 1173 K, Fig. 5f. This observation is consistent with the TPD results reported on Fig. 2.

Discussion

In accordance with the results reported above, the cubic phase of samaria investigated here, when exposed to the atmospheric H_2O and CO_2, at ambient temperature, becomes hydrated and carbonated in bulk. The weight loss by calcination in flow of He (6.7%) is, however, lower than that corresponding to the thorough transformation of the initial oxide. Therefore, when the apparent stabilization of the sample is reached, after nine months of air exposure, the oxide coexists with the hydrated and carbonated phases. This is confirmed by the X-ray diffraction data, Fig. 3, which suggest that the cubic phase of the oxide is always present. The displacement and broadening of the lines at 0.314 nm and 0.273 nm, observed on the diffraction pattern corresponding to the aged in air sample, and even stressed when this sample is heated at 393 K, should be related to the appearance of unresolved lines due to an hydroxycarbonate-like phase at interplanar distances slightly larger than those corresponding to the lines of Sm_2O_3-C mentioned above.

The partial hydration and carbonation of Sm_2O_3 contrasts with the behavior of hexagonal (A) lanthana and neodymia, for which a complete transformation of the initial oxide into partially carbonated hydroxide has been found (2,3). Furthermore, in refs. (7,10), for a samaria sample from an origin different to that of the investigated here, the same behavior reported for La_2O_3-A and Nd_2O_3-A has been observed. As discussed in ref. (7), the differences found between the two samaria samples mentioned above should probably be related to structural differences in the starting oxide samples.

Regarding the nature of the hydrated and carbonated phases generated throughout the process of aging in air of the samaria sample, it is worthnoting that in ref. (11), when cubic Nd_2O_3 is dispersed in not degassed H_2O, an ancylite type hydroxycarbonate is obtained. In ref. (12) phases described as $Nd_2(CO_3)_x(OH)_{2(3-x)}\cdot H_2O$ (x ranging from 1 to 2.3) have been found. Within the range above, no significant differences are observed in the corresponding X-ray diffraction patterns and optical absorption spectra. Accordingly, the authors (12) suggest the existence of non-stoichiometric hydroxycarbonate phases, the structure of which would be closely related to that of the ancylite.

As several authors have suggested (14,3), the thermal evolution of the ancylite-like hydroxycarbonates can be summarized as follows:

$$Ln_2(CO_3)_x(OH)_{2(3-x)} \longrightarrow Ln_2O_2CO_3 \longrightarrow Ln_2O_3$$

When x > 1, the first step of the process above would imply not only a dehydration reaction, but also the evolution of CO_2, the amount of which would depend on the x value.

If such a reaction scheme is applied to our results, a value for x slightly larger than 1 can be proposed. In effect, according to Figs. 1 and 2, simultaneously to the appearance of the major peak of H_2O (625 K), a peak of CO_2 is observed. These two peaks might be assigned to the decomposition of an hydroxycarbonate phase resulting from the aging in air of Sm_2O_3-C. The dioxymonocarbonate thus obtained would decompose at much higher temperature, the corresponding reaction being responsible for the peaks found on the TPD traces of CO_2 at 800 K and 920 K. In ref. (15) it has been found that, upon heating, the transformation of type I to type II of $Sm_2O_2CO_3$ occurs, the two phases showing different thermal stability. These results could account for the existence of the two CO_2 peaks mentioned above, however, it would not be excluded that the second of these peaks (920 K) corresponds to the decomposition of surface carbonate species.

Since for a phase $Sm_2(CO_3)(OH)_4$ (x = 1) the molar ratio H_2O/CO_2 = 2, and that found here is around 6, it is likely that, in addition to the hydroxycarbonate, the formation of $Sm(OH)_3$ had occurred. Although no diffraction lines of $Sm(OH)_3$ were observed here, the proposal above is consistent with the IR spectra on fig. 4, and the TPD traces included in fig. 1. Regarding fig. 4, the band at 3600 cm^{-1} might well be assigned to $Sm(OH)_3$ (9). On the other hand, it is known (16) that the decomposition of $Ln(OH)_3$ to Ln_2O_3 takes place through two steps:

$$Ln(OH)_3 \longrightarrow LnO(OH) \longrightarrow Ln_2O_3$$

Accordingly, the two shoulders appearing at both sides of the TPD peak for H_2O at 625 K might correspond to the two steps of the decomposition of $Sm(OH)_3$. This interpretation is also consistent with the IR spectra on Fig. 4, where the band at 3415 cm^{-1} vanishes at lower temperature than that at 3600 cm^{-1}.

In summary, when a cubic sample of samaria is exposed to the atmospheric H_2O and CO_2 , under the usual storage and manipulation conditions, it partially transforms into hydroxycarbonate and hydroxyde. Contrary to that observed on lighter 4f sesquioxides, and even on a different sample of samaria, in the present case the hydration reaction leading to hydroxide does not progress as to allow the detection of this phase by X-ray diffraction.

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References

1. M.P. Rosynek; Catal. Rev. 16, 111 (1977)
2. S. Bernal, F.J. Botana, R. Garcia and J.M. Rodriguez-Izquierdo Thermochim. Acta 66, 139 (1983)
3. S. Bernal, J.A. Diaz, R. Garcia and J.M. Rodriguez-Izquierdo J. Mater. Sci. 20, 537 (1985)
4. R. Alvero, J.A. Odriozola, J.M. Trillo and S. Bernal J. Chem. Soc. Dalton Trans., 87 (1984)
5. R. Alvero, I. Carrizosa, J.A. Odriozola, J.M. Trillo and S. Bernal J. Less Comm. Met. 94, 139 (1983)
6. S. Bernal, R. Garcia, J.M. Lopez and J.M. Rodriguez-Izquierdo Collect. Czech. Chem. Comm. 48, 2205 (1983)
7. S. Bernal, F.J. Botana, J. Pintado, R. Garcia and J.M. Rodriguez-Izquierdo; J. Less Comm. Met. 110, 433 (1985)
8. H.T. Fullam and F.P. Roberts BNWL-1421, Battelle-Northwest, Richland, Washington (1970)
9. H. Dexpert, E. Antic-Fidancer, J.P. Coutures and P. Caro J. Crystllogr. Spectrosc. Res. 12, 129 (1982)
10. R. Alvero, I. Carrizosa, J.A. Odriozola and J.M. Trillo J. Less Comm. Met. 109, 197 (1985)
11. H. Dexpert and P. Caro; Mat. Res. Bull. 9, 1577 (1974)
12. P. Caro and M. Lemaitre-Blaise; C.R. Acad. Sci. Paris 269,687 (1969)
13. J. Sawyer, P. Caro and L. Eyring; Rev. Chim. Min. 10, 93 (1973)
14. P. Caro, J.C. Achard and O. Pous Colloq. Int. CNRS on R.E. Elements 1, 285 (1970)
15. R.P. Turcotte, J.O. Sawyer and L. Eyring; Inorg. Chem. 8, 238 (1969)
16. M.P. Rosynek and D.T. Magnuson; J. Catal. 46, 402 (1977)