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Study of the interaction of two hexagonal neodymium oxides with atmospheric CO_2 and H_2O

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The present work deals with the behaviour in air of two neodymia samples prepared by calcination of a hydroxynitrate phase at 1020 and 1310 K, respectively. Both oxides behave similarly so that after approximately 50 days of air exposure, at normal temperature and pressure, they are thoroughly transformed into hydroxide. When stabilization is reached the two aged samples are also carbonated in the bulk; evidence for this latter process, which is much less intense than the hydration reaction, cannot be obtained from X-ray diffraction studies. These findings indicate the existence of close analogies between the oxides investigated here and several hexagonal lanthana and monoclinic samaria samples studied earlier, which supports the classification of the rare earth oxides based on their behaviour with atmospheric CO_2 and H_2O, as recently proposed by us. The additional experiments of carbonation reported here suggest that the ageing in air of the hexagonal neodymium oxides leads to the formation of a hydroxycarbonate-like phase, which does not agree with the crystalline ancylite-type hydroxycarbonate, formed when these oxides are suspended in water.

1. Introduction

In the past few years we have been investigating the reactivity with atmospheric H_2O and CO_2, at normal temperature and pressure, of the lanthanide sesquioxides [1–7]. The results of this study have been analysed in a very recent review work [8], where three groups of rare earth sesquioxides have been distinguished. Differences between the three groups of oxides were found both in the intensity of the ageing process and in the nature of the resulting aged phases. Our study of the behaviour in air of the 4f sesquioxides has also shown that one of the clues to interpret the differences observed might well be the structural nature of the starting oxide phases. Thus, we have found [5–7] that oxides of the same element with different structure, i.e. monoclinic [5, 7] and cubic [5, 6] samaria, show differences of behaviour larger than those observed between oxides of different elements [8].

The present work is aimed at extending the experimental basis of the classification of the rare earth oxides proposed in earlier [8] by investigating the evolution in air, at normal temperature and pressure, of two hexagonal neodymia samples, prepared in our laboratory. Some preliminary results on a commercial neodymium oxide, also with a hexagonal structure [8] have been obtained.

The properties of neodymium oxide as a catalyst [9] and support of highly dispersed metals [10, 11], have been reported earlier. However, studies devoted to characterization of the phases resulting from its storage and manipulation in air are rather scarce [12–14]. Furthermore, these latter works have ignored an important aspect of the chemistry in air of neodymia, i.e. the occurrence of carbonation reactions affecting the oxide in bulk.

From our point of view, a study of the evolution undergone by the rare earth sesquioxides when exposed to atmospheric CO_2 and H_2O should be considered essential not only to improve our current knowledge of the general chemistry of this interesting group of oxides, but also to devise new synthetic routes to prepare mixed oxide phases containing 4f elements which, according to the very recent literature [15], constitute novel ceramic materials with very interesting electric properties.

2. Experimental details

The two neodymia samples investigated in the present work, Nd_2O_3-A1 and Nd_2O_3-A2 were prepared by decomposing, in flowing helium, at a heating rate of $9\,K\,min^{-1}$, a partly carbonated neodymium hydroxynitrate phase precipitated from an aqueous solution of the neodymium nitrate, Fluka 99.9% pure, with a large excess of concentrated ammonia p.a. from Merck. The precipitate was carefully washed with distilled water to eliminate excess ammonia. The differences between samples A1 and A2 consisted of the final calcination temperature, 1020 K for Nd_2O_3-A1, and 1310 K for Nd_2O_3-A2, as well as the time that the sample was held at that temperature, 4 h in the case of A1, and 3 h in the case of A2. As soon as the samples were cooled, again under a flow of helium, they were studied by X-ray diffraction, and their nitrogen adsorption isotherms at 77 K determined.

The two samples showed the hexagonal, A-type, structure of the rare earth sesquioxides, and their surface areas were found to be 6.4 m^2 g^{-1} for Nd$_2$O$_3$-A1, and 2.2 m^2 g^{-1} for Nd$_2$O$_3$-A2.

The thermogravimetric (TG) experiments were carried out with a microbalance, Mettler, model ME-21. The flow of helium was 1 cm^3 sec^{-1}, and the heating rate 0.1 K sec^{-1}.

The temperature-programmed decomposition (TPD) experiments were recorded under the following conditions: helium flow rate, 1 cm^3 sec^{-1}; heating rate, 0.1 K sec^{-1}. Analysis of the evolved gases was performed by mass spectrometry (MS) with an instrument Vacuum Generator, model spectralab SX 200, interfaced to a microcomputer Apple IIe.

The infrared spectra were recorded either with an FTIR instrument, Nicolet, model 5 DXE, or with a grating spectrometer, Perkin Elmer, model 710 B. The sample discs were prepared by pressing a mixture containing about 5% of the oxide and 95% KBr under 5×10^{8} Pa.

The X-ray diffraction (XRD) patterns were obtained using a Siemens instrument, model D-500. The radiation was either Mo$K\alpha$ or Cu$K\alpha$; the filters were zirconium in the former case, and nickel in the latter.

3. Results and discussion

The evolution in air of samples A1 and A2 of neodymia, was investigated by means of TG, TPD-MS, infrared spectroscopy and XRD. In addition, the total weight increase of a reference portion of the two oxides was routinely determined throughout the whole stabilization process with a conventional analytical balance. The results obtained from the latter of these studies are reported in Fig. 1.

According to Fig. 1, ageing in air of the two hexagonal neodymia samples exhibitions an induction period of several days in which no weight gain can be detected. This induction period is shorter in the case of Nd$_2$O$_3$-A1, and oxide prepared at lower temperature, 1020 K, and concomitantly with higher BET surface area, 6.4 m^2 g^{-1}. It can also be deduced from Fig. 1 that, in order to reach the apparent stabilization of the samples, approximately 50 days of exposure to air are needed. In the case of hexagonal lanthana [4] the stabilization is achieved in less than 24 h. This would indicate that the rate of ageing of 4f sesquioxides becomes slower as the atomic weight of the lanthanide ion increases. Quite similar findings have already been reported for the rate of hydration of rare earth sesquioxides [16]. It should be noted, however, that this conclusion, generally assumed in the literature [17], should not be considered in its strict sense, because, as Trillo *et al.* [18, 19] have shown for some heavier members of the series and our own results support, factors other than the nature of the 4f ion, specifically those related to the method followed in the preparation of the oxides, can have a strong influence on their reactivity.

Figs 2 to 5 show results for the study of the

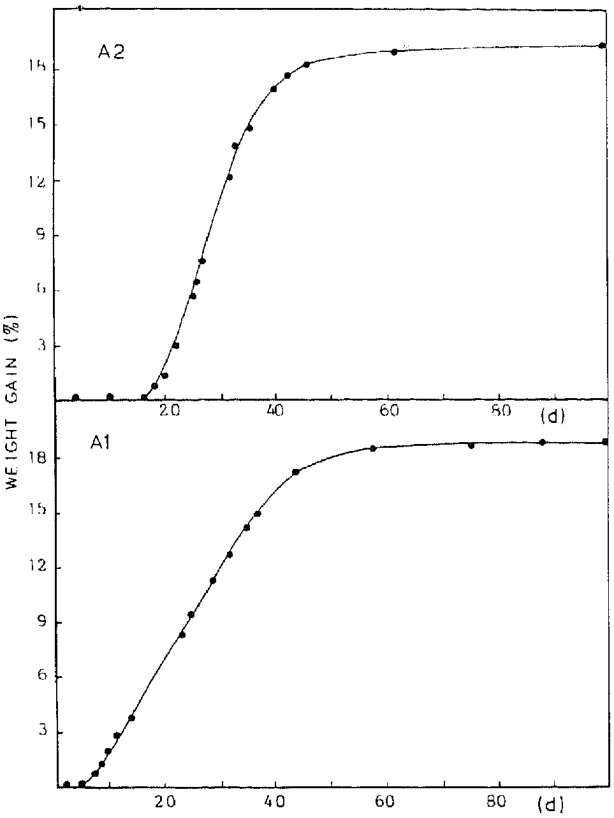

Figure 1 Total weight gain against time curves corresponding to Nd$_2$O$_3$-A1 and Nd$_2$O$_3$-A2 exposed to air, at normal temperature and pressure. The weight increase is given as a precentage of the initial weight. The time is expressed in days (d).

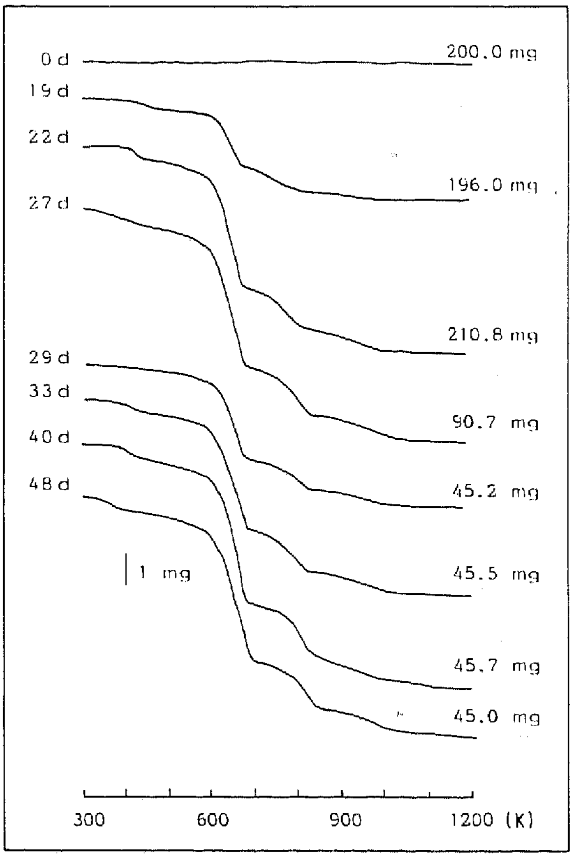

Figure 2 Study by TG of the process of ageing in air of Nd$_2$O$_3$-A2. The exposure time in days (d) is indicated on the left-hand side. The initial weight of sample is given on the right-hand side.

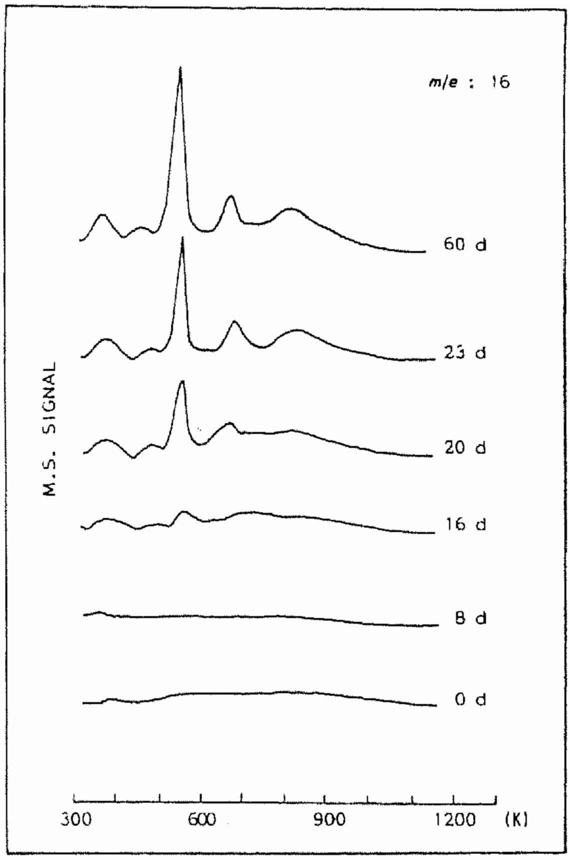

Figure 3 Study by TPD-MS of the evolution in air of Nd_2O_3-A2. The exposure time in days (d) is given on the right-hand side.

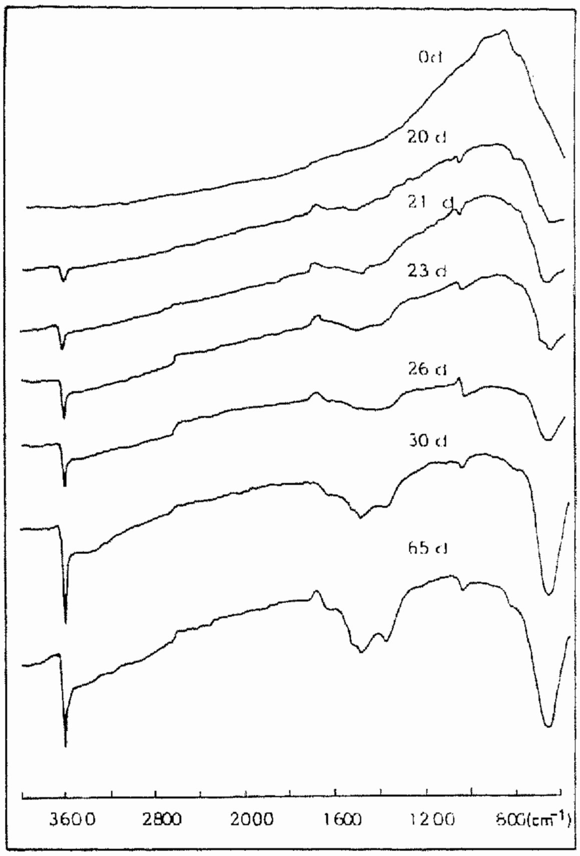

Figure 4 Infrared spectra corresponding to Nd_2O_3-A2 exposed to air for the time, in days (d), indicated in the Figure.

stabilization process carried out by means of TG, TPD-MS, infrared spectroscopy and XRD, respectively. Because the behaviour of samples A1 and A2 was found to be essentially the same, Figs 2 to 5 correspond all to Nd_2O_3-A2.

Fig. 2 shows the TG diagrams of the neodymia sample exposed to atmospheric CO_2 and H_2O for increasing periods of time. For exposure times longer than 48 days, the TG diagram does not undergo further modifications. Accordingly, the last diagram in Fig. 2 agrees with that of the sample stabilized in air. The shape of the diagrams depicted in Fig. 2, which, on the other hand, does not seem to suffer significant alterations throughout the whole stabilization process, is characterized by three well-defined steps, being similar to those reported earlier for hexagonal lanthana aged in air [4, 20] as well as for monoclinic samaria [5, 7]. These analogies of behaviour are also supported by the results of our studies by TPD-MS, infrared spectroscopy and XRD reported below.

Fig. 3 shows results for the TPD-MS experiments carried out at different stages of stabilization in air of Nd_2O_3-A2. Among the signals routinely analysed in the mass spectrometer are those for *m/e*: 18 (H_2O), 44 (CO_2) and 16 (H_2O and CO_2). In Fig. 3 we have plotted the latter of these signals because it summarizes the evolution of both water and carbon dioxide. The choice of $m/e = 16$ is particularly suitable in the present case because, on the one hand, no gaseous products other than H_2O and CO_2 have been detected, and on the other, the evolution of H_2O and CO_2 occurs through well-resolved steps. In effect,

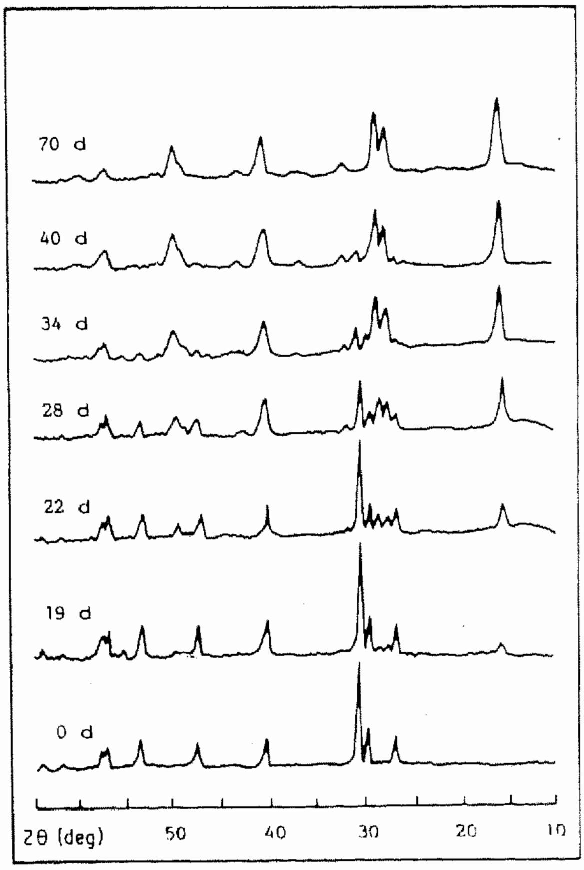

Figure 5 XRD pattern of Nd_2O_3-A2 exposed to air for the time, in days (d), indicated on the left-hand side. The radiation used was $CuK\alpha$.

TABLE I Study of the ageing in air of two hexagonal, A-type, neodymia samples

Samples	Starting oxides		Aged samples					
	C.S.*	S_{BET}†	Weight gain				C.S.*	S_{BET}†
			H_2O (%)	CO_2 (%)	H_2O (mol nm^{-2})	CO_2 (mol nm^{-2})		
A1	890	6.4	15.0	2.5	289	20	320	14.8
A2	1180	2.2	15.3	2.2	389	23	240	11.2

*C.S., crystallite size (nm).
† S_{BET}, surface area (m^2 g^{-1}).

according to the TPD traces for $m/e = 18$ and $m/e = 44$, the peaks at around 560 and 680 K correspond to H_2O, whereas that centred at 800 K can be assigned to CO_2. From these results, it is obvious that the TG diagrams in Fig. 2 would allow an easy determination of both the total weight gain and the amounts of H_2O and CO_2 taken up by the neodymia samples. These data are reported in Table I, in which the latter amounts have also been expressed in the form of molecules per square nanometre of BET surface area of the samples aged in air.

Taking into account that for purely surface reactions the amounts of either H_2O or CO_2 should not exceed 8 mol nm^{-2} [21], it is obvious that both the hydration and carbonation undergone by samples A1 and A2 of neodymia occur in the bulk. As we observed in the case of lanthana [8], it can also be deduced from Table I that the hydration is much heavier than the carbonation reaction. Furthermore, if we consider the series of rare earth sesquioxides that behave similarly, which includes, in addition to Nd_2O_3-A1 and Nd_2O_3-A2, the three lanthana samples investigated by us [4], the so-called Sm_2O_3-M [5], as well as the commercial sample of hexagonal neodymia studied earlier [8], it can be noted that the amount of CO_2 per unit of BET surface area remains approximately constant: 20 to 30 mol nm^{-2}, whereas that corresponding to H_2O varies within a much wider range. This suggests that, in contrast to the hydration reaction, the extent of which does not seem to be related to the surface area of the oxides, the intensity of the carbonation process, though affecting the bulk of the oxides, is in some way related to the surface of the samples.

If it is taken into account that the theoretical weight increase for the transformation of Nd_2O_3 into $Nd(OH)_3$ is around 16%, the results in Table I suggest that, when stabilization in air is reached, the neodymium oxides have completely disappeared. A quite similar effect has also been observed by us on the samples that behave like the hexagonal neodymias [4, 5].

In order to gain some structural information concerning the nature of the phases formed through the ageing process of Nd_2O_3-A1 and Nd_2O_3-A2 we have also investigated their evolution in air by infrared spectroscopy and XRD. Figs 4 and 5 account for the results obtained from the studies carried out on Nd_2O_3-A2.

According to Fig. 4, from 20 days of exposure, the time at which the first indications of ageing are observed, onwards, the structure of the infrared spectra remains essentially unmodified, no matter what stage of the stabilization is considered. The only differences between one spectrum and the next consists of the steady increase of intensity of the bands, all of which can actually be observed in the early steps of the ageing process. One of the most characteristic features of the spectra depicted in Fig. 4, otherwise very similar to those recorded by us for several lanthana samples as well as for the so-called Sm_2O_3-M [8], previously stabilized in air, is the sharp and strong band at 3600 cm^{-1}. According to various authors [20, 22, 23] this band should be ascribed to a stretching OH mode in rare earth hydroxides. As can be deduced from the work of Swanson *et al.* [24], the frequency at which this band is observed does not significantly change with the lanthanide ion. The presence of $Nd(OH)_3$ in the two neodymia samples aged in air is also suggested by the strong band appearing at 660 cm^{-1}. As is discussed previously [8], on the grounds of the study of the vibrational modes of $Ln(OH)_3$ carried out by Swanson *et al.* [24], this band can be assigned to a deformation mode of Ln–OH, the frequency of which increases on going from $La(OH)_3$ to $Yb(OH)_3$. A quite similar band has been observed by us at 640 cm^{-1} in the case $La(OH)_3$, and 680 cm^{-1} for $Sm(OH)_3$ [8].

Fig. 4 also confirms the occurrence of carbonation phenomena, which is supported by the presence of two strong characteristic features in the region 1300 to 1600 cm^{-1} of the infrared spectra.

Fig. 5 accounts for the evolution undergone by the XRD diagrams of Nd_2O_3-A2 exposed to air for increasing periods of time. As in the case of the studies reported above, the first alterations to the starting oxide are observed after approximately 20 days. For this exposure time, in effect, the intense diffraction line, appearing at 0.557 nm (15.9° in Fig. 5) characteristic of $Nd(OH)_3$, can already be observed. For increasing periods of time, the XRD diagrams show the coexistence of lines of the hexagonal, A-phase, of Nd_2O_3 with those due to hydroxide. After 40 days exposure to air, the oxide appears as a residual phase, and finally, after 70 days, the only diffraction lines present in the diagram are those corresponding to $Nd(OH)_3$.

Two aspects of the results reported in Fig. 5 deserve further comment. Firstly, the XRD study, like those by TG, TPD-MS and infrared spectroscopy, indicate that the phases formed in the first stages of the ageing process are the same as found later on in the sample stabilized in air. Secondly, it is worth noting that, in spite of the occurrence of bulk carbonation phenomena on the two hexagonal neodymia samples, the

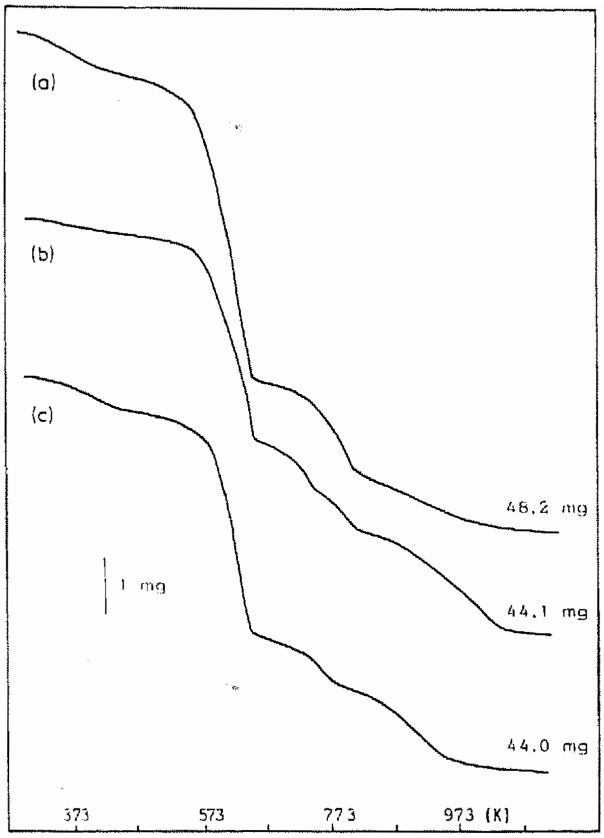

Figure 6 TG study of (a) Nd_2O_3-A2 aged in air; (b) sample (a) further suspended in water for 10 days; (c) sample (a) treated with flowing CO_2, at normal temperature and pressure, for 10 days. The initial weight of the samples is indicated on the right-hand side.

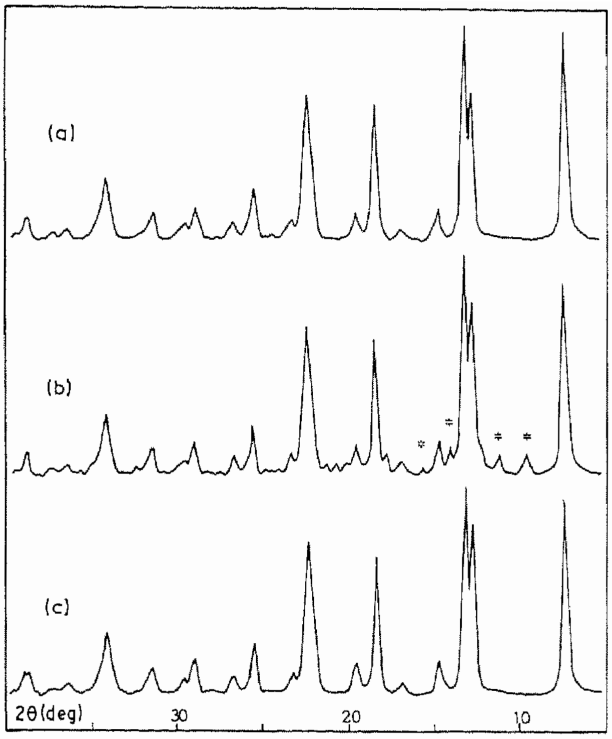

Figure 7 Study by XRD of (a) Nd_2O_3-A2 aged in air; (b) sample (a) further suspended in water for 10 days; (c) sample (a) further treated with flowing CO_2, at normal temperature and pressure, for 10 days. The radiation used was Mo$K\alpha$.

study by XRD of either the phases corresponding to intermediate stages of the ageing process or to the final samples stabilized in air does not support the existence of any sort of carbonated phase. This seems to be a characteristic feature of the whole series of rare earth sesquioxides which behave like Nd_2O_3-A1 and Nd_2O_3-A2.

The results above pose the question of the actual nature of the carbonated phase formed upon ageing in air the series of oxides above. In the case of lanthana [4], it has been suggested the formation of an hydroxycarbonate-like phase, $Ln(OH)_{2(3-x)}(CO_3)_x$, $x = 1$, similar to those reported by Caro and Lemaitre-Blaise [25] in their study of the ternary system $Ln_2O_3-H_2O-CO_2$, under conditions that can be considered not too far from those operating in air; i.e. suspension in water, in contact with air, at room temperature, of lanthanide oxides, hydroxides, carbonates and oxycarbonates. The tentative suggestion made by us [4] was based on stoichiometric calculations carried out on the corresponding TG diagrams, as well as on some additional evidence obtained from the study by infrared spectroscopy and XRD of the phases formed throughout the whole process of the thermal decomposition of the aged lanthana samples.

As in [25] the hydroxycarbonate phase could be identified by XRD, and we fail in the observation of any line belonging to such a phase, we devised two types of additional experiments aimed at obtaining some further information about the carbonated phase formed when the hexagonal neodymia samples were exposed to air. On the one hand, we treated a sample of Nd_2O_3-A2 aged in air as Caro and Lemaitre-Blaise [25] did, i.e. we suspended a portion of the oxide above distilled water, not specially pretreated, for approximately 10 days, at room temperature. In the second experiment, we treated the Nd_2O_3-A2 aged in air with flowing CO_2, at normal pressure and ambient temperature, in an attempt to increase the carbonation level reached spontaneously by the oxide in air.

The results of the study by TG and XRD of the phases resulting from the two treatments above are reported in Figs 6 and 7, respectively. For comparative purposes these figures also include diagrams corresponding to Nd_2O_3-A2 simply aged in air.

Taking into account that CO_2 is the only gaseous product evolved during the highest temperature step of the TG diagrams, it could be concluded from Fig. 6 that the two treatments described above considerably increase the carbonation level with respect to that reached by the sample of Nd_2O_3-A2 simply stabilized in air. When the results of the XRD study are considered (Fig. 7) it can be noted that in spite of the increase of the carbonation level occurring when the aged Nd_2O_3-A2 is treated with CO_2, no alteration of the XRD pattern can be observed at all. By contrast, the sample submitted to the wet treatment shows a diagram in which, in addition to the diffraction pattern characteristic of $Nd(OH)_3$, some weak lines, marked with asterisks in Fig. 7, which can be assigned to ancylite-like hydroxycarbonate, $Nd(OH)CO_3$-A [27] can be observed. This type of hydroxycarbonate phase is the same as that found by Caro and Lemaitre-Blaise [25] when several lanthanide phases, including carbonates and hydroxides, were suspended in water, in contact with air, at ambient temperature.

The results summarized in Figs 6 and 7 essentially agree with those recently reported by us [27] for a hexagonal phase of lanthana aged in air, treated as Nd_2O_3-A2. Furthermore, we also found [27] that once the nucleation of the ancylite-like hydroxycarbonate had occurred, this phase could grow by simple exposure to air, at normal temperature and pressure, of the wet pretreated sample. As neither on oxides exposed to air, even for years, nor on the samples treated with flowing CO_2, could the formation of $Ln(OH)CO_3$-A be detected [27], it could be concluded that the phase formed as a consequence of the wet treatment of the hexagonal samples of both lanthana and neodymia are not the same as those observed by us upon ageing these samples in air. In other words, the results reported by Caro and Lemaitre-Blaise [25] cannot be used as a general guide to interpret the behaviour in air of the rare earth sesquioxides. This means that in order to improve our current knowledge on the latter of the topics above, specific experiments should be devised.

We have also investigated the effect of the ageing process on the BET surface area as well as on the crystallite size of the two hexagonal neodymia samples. Table I gives the results of this study. The estimate of the mean crystallite size was carried out from studies of widening of the XRD lines. For this purpose, Scherrer's equation [28] was applied to the line at 0.221 nm in the diffraction pattern of both the hexagonal oxide and the hydroxide.

As can be deduced from Table I, the ageing process induces, on the one hand, a decrease of the mean crystallite size and, on the other hand, a notable increase of the BET surface area of the oxide sample. These results essentially agree with those reported by Rosynek for hexagonal lanthana [19, 20], who on the grounds of his studies of nitrogen adsorption at 77 K and scanning electron microscopy (SEM) suggested a procedure to increase the surface area of lanthana samples consisting of submitting the oxide sample to a series of hydration dehydration cycles. This procedure has been further applied to several other rare earth oxides, not always with hexagonal structure. It would be noted, however, that on cubic rare earth oxides the hydration process does not seem to induce alteration of their surface area [29].

To summarize, the present work, which should be included in a general research programme aimed at investigating the behaviour of the rare earth sesquioxides with atmospheric H_2O and CO_2, at normal temperature and pressure, reports the evolution in air of two hexagonal neodymia samples, prepared in our laboratory. According to our study, the TG, TPD-MS, infrared spectroscopy and XRD data support that from the first stages of the ageing process the only phases observed are those found later, on the samples finally stabilized in air. When the apparent stabilization of the samples is reached the starting oxides have thoroughly transformed into neodymium hydroxide The samples have also undergone carbonation phenomena, which, though much less intense than the hydration reaction, affect the samples in bulk. The behaviour of the two neodymia samples was found to be similar, the only difference worthy of note being the rate of the ageing process: somewhat slower in the case of Nd_2O_3-A2, the oxide calcined at higher temperature, with lower BET surface area, and larger crystallite size. This behaviour, on the other hand, agrees closely with that reported earlier by us for several lanthana samples, with hexagonal structure [4] as well as for monoclinic samaria samples [5, 7, 8]. The rate of the process was much faster in the case of the lanthana samples so that the stabilization was reached in less than 24 h, whereas in the case of the monoclinic samaria sample it was much slower [7]. By contrast, the behaviour of the hexagonal neodymium oxides was clearly different from that reported previously [5, 6, 8] for several cubic rare earth oxides. These results give further support to the classification into three well-differentiated groups of the lanthanide sesquioxides on the basis of their behaviour with atmospheric H_2O and CO_2.

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