



Binary rare earth oxides

edited by G. Adachi, N. Imanaka,
and Z. C. Kang.

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To Professor LeRoy Eyring

PREFACE

A number of functional materials based on rare earth oxides have been developed in various fields. Up to 1990, many review articles describing rare earth oxides have been reported and several intensive articles deal the properties e.g. preparation, structure and transformation and have been published early nineteen nineties. In these ten years, much progress has been made in the characterization of rare earth oxides from high-resolution electron microscopy (HREM), as well as in a unique preparation of ultra-fine particles and in the theoretical calculation.

The purpose to publish this book arose out of the realization that, although excellent surveys and reviews of rare earths are available, some of them have been already several decades passed since their publication and in these years, there is no single source covering the field of rare earth oxides. This book means to provide guidance through a comprehensive review of all these characteristics of rare earth oxides for scientists and engineers from universities, research organizations, and industries.

We have chosen a multi-author format in order to benefit from scientists who are active in their fields and who can give the best account for their subjects. As is true for nearly all fields of modern science and technology, it is impossible to treat all subjects related to rare earth oxides in a single volume. In the present case, therefore, we have focused on the binary rare earth oxides and their physical and chemical properties are mainly discussed in detail, because these provide both basic knowledge and fundamental aspects which make it possible to control a variety of properties in many materials.

We cordially hope that this reference book will be appreciated by material scientists and solid-state chemists with an interest in rare earth oxides, as well as researchers and graduate students who require an approach to familiarize them with this field.

The editors are much obliged to all those who cooperated in bringing this project to a successful close. In the first place, we thank the authors of the individual chapters. We are also grateful to Publishing Manager, Dr. Liesbeth Mol and the staffs of Mrs. Vaska Krabbe and Mrs. Marianne van den Hurk, Kluwer Academic Publishers. Finally, it is our great honor to dedicate this book to Professor Dr. LeRoy Eyring, who is a professor emeritus at Arizona State University and has done an enormous contribution not only to rare earth oxides but also to all aspects of rare earths.

*Osaka, Japan
April 2004*

Gin-ya Adachi
Nobuhito Imanaka
Zhenchuan Kang

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1. INTRODUCTION

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1. Why are rare earth oxides so important?

From your personal items such as a portable compact disc player to a super computer or a huge atom-smashing accelerator, there are many rare earth materials having crucial roles in such systems. An automobile is a heap of rare earth materials. This is because rare earth ions exhibit some unique properties. Usefulness of rare earth materials for permanent magnets and luminescent materials for television and lighting systems goes without saying. Most of rare earth materials have been produced from rare earth oxides. Perovskite type rare earth mixed oxides are well known for high temperature super conductors, ferroelectric materials, or refining processes of rare earth metals needs their oxides as starting materials. Rare earth oxides are of importance for glass industry, for example, not only glass components but also surface polishing [1].

Most rare earth oxides are thermally stable, as well as chemically active. As is seen below, the C-type sesquioxides R₂O₃, are related to the fluorite structure CaF₂ or RO₂, from which the C-type sesquioxides are derived by removing one-quarter of the oxide anions. In other words, the C-type sesquioxides have a lot of defects which may act as effective diffusion paths for reactants at chemical reactions. Rare earth sesquioxides of other type structures too are in similar situation. Relatively, low reactivity of rare earth dioxide, CeO₂, are understandable from this point of view.

2. A variety of rare earth oxides

Oxidation states of rare earth ions in oxides can be understood in terms of reduction potentials. a) Generally the trivalent state is the most stable in aqueous solution and therefore, sesquioxides R₂O₃ exist for all rare earth ions [2]. However,

some conditions allow lower or higher oxides. As a matter of course, the composition of any rare earth oxide depends on the temperature, oxygen potential and whether or not it is in equilibrium although, the stability of the valence state of a given ion in aqueous solution is a good quick reference for the stability of the oxide.

The sesquioxides R_2O_3 crystallize in three forms, A-type(hexagonal), B-type(monoclinic) and C-type(cubic) structures, according to the ionic radius of the rare earth ion. Lighter rare earth ions, from La^{3+} to Nd^{3+} give A-form. These ions have happened to be seen to form the C-type structure, but this observation seems to be due to impurity stabilization or a metastable phase. An example of the B-type oxide is given by Sm_2O_3 . Other rare earth sesquioxides yield the C-type oxides [3-6].

Stability of divalent ions is in order of $Eu^{2+} \gg Yb^{2+} \gg Sm^{2+}$ and a NaCl type monoxide EuO is the most stable one among these three monoxides but the existence of SmO seems to be doubtful. A unique orthorhombic 34 oxide Eu_3O_4 where Eu^{2+} and Eu^{3+} coexist is also stable [7].

The higher oxides where the oxygen to metal ratio x in the oxides is in the range of 1.5 to 2.0 are observed for cerium, praseodymium and terbium. These oxides exhibit fluorite-typed dioxides, which do not necessary mean $x = 2.0$ but usually the x value is slightly smaller than 2.0. Again, the composition of these oxides depends on the temperature, oxygen potential and physical state, besides their history of preparation and treatment [8-11].

This compositional obscurity is named as non-stoichiometry. However, the phase may mean an equilibrium state between stoichiometric oxides having slightly different composition. Details of this phase shall be discussed separately.

3. Simplicity and complexity of rare earth oxides

It is shunless to have some kinds of defects in solids, especially in transition metal oxides and rare earth oxides, because molecules of oxygen, which is a counter component of the metal oxide, are highly volatile even at low temperatures and are able to escape easily from the solid. More basically, the entropy term of the state requires the existence of defects. Most of the transport phenomena in solids, for example, diffusion of ions, are controlled by defects [12, 13].

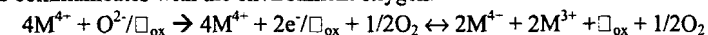
In last century the knowledge of defects in a solid, especially an oxide, has been explored comprehensively. The contribution of Schottky and Wagner successfully put the problem on a quantitative basis and promote the discovery of semiconductor transistor. The idea of non-stoichiometry was developed by Berthollet more than a hundred years ago and the controversy between berthollides, which do not obey the Dalton's law, and daltonides, which follow Dalton's law of constant and multiple proportions based originally upon the study of simple ionic and molecular species, encouraged the scientific debates on how existence of point defect in a compound is: is it random statistic distribution or the structure related? The experimental data are the best way to explore the truth. Indirect and direct observations of atom

arrangement of a solid are powerful experimental method. X-ray, neutron, and electron diffraction theory and techniques were developed for indirect observation of atom structure of a compound [14] and high-resolution electron microscopy was developed for direct observation of atom arrangement of a compound at atomic level.

Now it seems to be clear that there are two categories of non-stoichiometry: (a) the non-stoichiometry of a compound is structurally accommodated, which means it does not caused by traditional "point defects", but by disordered arrays of blocks of ordered structure forming by corner- or edge-sharing of MO_6 octahedra and/or MO_4 tetrahedra. In other words, it contains the "chemical twinning", "crystallographic shear planes". Therefore, the result of a local rearrangement of coordination polyhedra eliminates the point defect. The compounds with a strong ligand field, for example transition metal oxides, always have this type of non-stoichiometry, and (b) the non-stoichiometry is due to assimilation of vacancies or interstitial atoms as structure elements of the crystal [15]. The non-stoichiometry of rare earth higher oxides is the best example. The composition domains in rare earth higher oxides have different content of oxygen vacancy, but the fluorite structure is still held with modulated displacement of metal and oxygen atom. Ordered oxygen vacancies of oxygen deficient fluorite-related rare earth higher oxides form the superstructures in parent fluorite lattice as homologous series phases, R_nO_{2n-2m} .

The so called "line phases" are compounds of ordered structure and definite composition. Thermodynamic sense means that in equilibrium a single phase has univariant: $\mu_i = \mu(T)$. However wide non-stoichiometry of rare earth higher oxides definitely has bivariant: $\mu_i = \mu(T, X)$ (X is oxygen content), even the homologous series phases also have bivariant because their oxygen content varies in narrow range as temperature changes. At constant oxygen partial pressure, the oxygen content of cerium, praseodymium, and terbium oxides varies as temperature increases or decreases and at constant temperature. The composition of cerium, praseodymium, and terbium oxides varies as oxygen partial pressure increased or decreased. The response time of composition change of the rare earth higher oxides for varying temperature or oxygen partial pressure is very short (for example at 300 °C it is about a second for PrO_x). It is worth to notice that the published phase diagrams of CeO_2-O_2 , PrO_2-O_2 , and TbO_2-O_2 only given the existed phases, but it does not mean that the composition of a phase existed at corresponding temperature shown on the diagram, because these diagrams were built at different oxygen partial pressures. Usually a phase diagram is built at a constant pressure, for example one atmospheric pressure.

In general, the point defect in a crystal is a function of temperature, especially at higher temperature, but not sensitive to the environment oxygen pressure or temperature. However, the oxygen vacancy in cerium, praseodymium, and terbium oxides communicates with the environment oxygen.



The reaction between gas oxygen and oxygen vacancy in the oxides is easy and fast even at above 300 °C as mentioned before. This is a unique feature of rare earth higher oxides.

For transition metal oxides, for example TiO_2 , the non-stoichiometry does not create the "point defect" and is induced by the "crystallographic shear planes" and intergrowth of "chemical twinning" block structures. The oxygen content variation is due to changing the corner-or edge-sharing of the MO_6 octahedra. This change may be related to the valence variation of the metal and form mixed valence compound. The electron transfer between different metal cation usually has to be helped by the ligand oxygen, i.e. M-O-M. However the electron hopping between the rare earth cation is facilitated by oxygen vacancy having positive charge. Therefore correlation between oxygen vacancy and mixed valency is a significant property for rare earth higher oxides.

Based on thermodynamics, the "point defects" in a solid lattice are natural tendency due to increasing the configuration entropy to minimizing the free energy of the system. However, the oxygen vacancy and non-stoichiometry of rare earth higher oxides are closely related to a peculiar electron configuration of cerium, praseodymium and terbium atom and inscrutable relationship between the valence instability and the electron transfer of 4f electron of the Ce, Pr, and Tb cations. Decipherment of these formidable relationships will make the rare earth higher oxides to be most important materials for catalyst, solid oxide fuel cell, sensor, and hydrogen production devices [16].

Surface, interface between two grains or phases, dislocation, and stacking faults are the imperfections of a solid. In rare earth sesquioxides, the twinning and twin boundary are common phenomenon. Especially in B-type of rare earth sesquioxide the twinning is basic feature due to its low symmetry of the structure. The phase transformation between A- and B-type or C- and B-type structure of rare earth sesquioxides can form the twinning and twin boundary. Mechanical stress may also cause the twinning [17]. In rare earth higher oxides the twinning is not dominate imperfection, but the composition domain boundary, which is coherent interface, dislocation and stacking fault usually have been observed. The surface of rare earth oxide has steps and the facet of the steps usually is closed packing plane, especially in the rare earth oxides with C-type and fluorite-related structure.

Professor L. Eyring spent 50 years to search and to decipher the formidable structural principle of the rare earth higher oxides and the clue unraveling the mysterious phenomena in non-stoichiometry of the rare earth higher oxides. There are several reasons to be resisted solution for these problems, one of which is that the synthesis of complete ordered crystal of these rare earth higher oxides is inhibited by the extraordinary ease of transfer of oxygen between the RO_x lattice and gaseous oxygen.

Since the mid 1970s, the principle and technique of transmission electron microscopy have made significant progress, in which the electron beam probe can

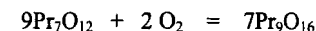
be minimized to less than 1 μm and imaging technique is able to demonstrate the atom arrangement of a small thin crystal on an image with atomic scale. Eyring immediately used these techniques to solve the formidable task. The micro-beam electron diffractions have revealed the unit cell dimensions, space groups, and transformation matrices defining the unit cells in terms of the fluorite subcell. In comparison of the electron diffraction data with thermodynamic data of the rare earth higher oxides there are some contradictions, especially the composition derived from the formulae of the homologous series, $\text{R}_n\text{O}_{2n-2}$, and the tensimetric thermodynamic data.

Based on the understanding the structure of the R_7O_{12} phase, Eyring suggested that linear infinite RO_6 "strings", surrounded by a contiguous "sheaths" of RO_7 , were the structural entities that generated the series $\text{R}_n\text{O}_{2n-2}$ from the parent RO_2 [18]. If $1/n$ of the cations were located in the "strings", the compositions of the ordered phases become $\text{RO}_2 [1-1/n]$ or $\text{R}_n\text{O}_{2n-2}$. The "string" might then be regarded as the "extended defect" in the f transition metal oxides analogous to the Wadsley "shear defect" in the d transition metal oxides.

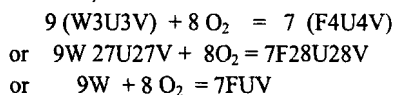
The formula, $\text{R}_n\text{O}_{2n-2}$, was used as the generic homologous series formula of the rare earth higher oxides for more than 30 years until Kang and Eyring established an all-inclusive formula, $\text{R}_n\text{O}_{2n-2m}$, based on the fluorite-type module theory.

Using high-resolution neutron diffraction data, Eyring published the refined structures of Tb_7O_{12} , Pr_9O_{16} , $\text{Pr}_{40}\text{O}_{72}$, $\text{Tb}_{11}\text{O}_{20}$, and $\text{Pr}_{24}\text{O}_{44}$. These refined structures have useful information for structural principle of rare earth higher oxides [19].

In 1996, Kang and Eyring published the fluorite-type module theory [20], which rationalizes all of the known experimental intermediate phases in the rare earth higher oxides into the single generic formula $\text{R}_n\text{O}_{2n-2m}$. The fluorite-type module theory is not only providing a method to modeling the structure, but also giving the basis for elucidating the hysteresis, transition between homologous series phases, and interaction between the oxide and gas oxygen. For example, the thermodynamic data show that when the temperature is decreased from 800 °C to 650 °C the Pr_7O_{12} is transformed to the Pr_9O_{16} at 150 Torr oxygen partial pressure according to the following reaction.



The Pr_7O_{12} phase is the most reduced phase in the homologous series of the praseodymium oxides. The seven fluorite-type modules that compose the structure of the Pr_7O_{12} phase contain one W and six U and V unit modules. The meaning of these symbols will be given in 3.2.4. As this is oxidized to the Pr_9O_{16} phase the module W disappears, and an F module has replaced it. Using the modular formula to write the above reaction, it will be:



These equations may be stated as follows: there are two W modules each of which absorbs one oxygen atom to become a U or V module. Each of remaining W modules takes two oxygen atoms to become F modules. The reaction process is the absorption of oxygen from the gaseous phase at the surface followed by oxygen migration into the bulk. The oxygen atoms migrating from the surface fill the oxygen vacancies in the W modules. This changes the W modules to F, U or V modules with the concomitant change of the coordination numbers of the cations producing the oxidized phase Pr_2O_3 .

It seems that as the module theory developed the knowledge of rare earth higher oxides may be matured and multi-component rare earth higher oxides may be developed. Rare earth higher oxides, for which Professor L. Eyring spent his lifetime to understand, will be the most important materials for catalyst, solid oxide fuel cell, hydrogen production, and sensors.

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2. CHEMICAL REACTIVITY OF BINARY RARE EARTH OXIDES

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2.1. INTRODUCTION

Despite the term traditionally applied to this group of elements, rare earths, their crustal abundance is not particularly low. Cerium ranks around 25th in the listing of all the naturally occurring elements, its abundance being similar to that of Ni or Cu [1]. Even the least abundant lanthanoid elements, Tb, Tm, and Lu, are more abundant than Ag [2]. Because of their geo-chemical characteristics, however, the rare earth-containing minerals consist of mixtures of the elements with relatively low concentration of them [3]. Accordingly, the number of their exploitable deposits, mainly consisting of phosphates and fluoro-carbonates, is rather small [1,3].

The development of appropriate separation technologies has therefore represented a classic, very challenging, chemical and technological problem [3]. Wet methods are presently used for this purpose [3,4]. Though laborious, these methods have allowed the preparation of high purity rare earths at, in some cases, reasonable costs. As a result, a continuous increase of the research effort on lanthanoid-containing materials, and particularly on their oxides, has occurred during the last twenty five years. Very recently, an alternative dry procedure, very much enhancing the separation efficiency of the in-use technology, has been developed [5]. As stressed in [3], the application of this new methodology would substantially reduce the number of separation steps, and therefore, the overall production costs. A scenario of accelerated increase of both fundamental and applied research on rare earth oxides may reasonably be devised for the years to come.

As deduced from a recent review work [6], a great deal of data on the structural, physical and chemical properties of the binary rare earth oxides are presently available. This wealth of information has substantially modified our view about them. Formerly considered as a rather exotic group of oxides, with mainly academic interest, it is presently acknowledged that they may find very relevant applications as catalysts [7-11], optical materials [1,2,4,12,13], or ionic conductors [14-17]. Some of these applications have reached the technological maturity, large scale industrial consumption of the rare earth oxides being associated with them [4]. Such is the case of the three-way catalysts [9,10,18,19], or the lighting applications of lanthanoid-containing photo-luminescent materials [1,4,13].

This chapter is aimed at reviewing the chemical reactivity of rare earth oxides. Special attention will be paid to those aspects closely related to the thermal

and chemical environments associated with their current applications either as pure phases, as components of multi-phasic systems, or as reactants in the preparation of several other lanthanoid-containing materials.

From the chemical point of view, the lanthanoid elements are characterized by a regular variation of their 4f electron configuration throughout the series, Table 2-1. Due to the nature of the orbital group, (n-2)f, involved in the variation of their electron configuration, these elements are often referred to as the first inner transition series. Inherent to this peculiar electron configuration, the lanthanoid elements show a number of atomic properties that are considered to determine the chemical and structural properties of their compounds, and, particularly, those of their oxides.

TABLE 2-1. Some relevant properties of the lanthanoid elements

Element	Electron Conf.	$\Delta H_{\text{atom}}^{\circ}$ (KJ.mol ⁻¹)	ΣIP (1-3) (KJ.mol ⁻¹)	4th. IP (KJ.mol ⁻¹)	$r_{\text{ion}}(\text{M}^{3+})$ (pm)*
La	5d ¹ 6s ²	431.0	3455	4819	117
Ce	4f ¹ 5d ¹ 6s ²	420.1	3523	3547	115
Pr	4f ² 6s ²	356.9	3627	3761	113
Nd	4f ⁴ 6s ²	326.9	3697	3899	112
Pm	4f ⁶ 6s ²	-----	3740	3966	111
Sm	4f ⁶ 6s ²	206.9	3869	3994	110
Eu	4f ⁷ 6s ²	177.4	4036	4110	109
Gd	4f ⁷ 5d ¹ 6s ²	397.5	3749	4245	108
Tb	4f ⁹ 6s ²	388.7	3791	3839	106
Dy	4f ¹⁰ 6s ²	290.4	3911	4001	105
Ho	4f ¹¹ 6s ²	300.6	3924	4101	104
Er	4f ¹² 6s ²	316.4	3934	4115	103
Tm	4f ¹³ 6s ²	232.4	4045	4119	102
Yb	4f ¹⁴ 6s ²	155.6	4194	4220	101
Lu	4f ¹⁴ 5d ¹ 6s ²	427.6	3887	4360	100

Ionic Radius for Y³⁺ (C.N. = 6): 104 pm

(*) Shannon ionic radii (C.N. = 6) taken from ADVANCED INORGANIC CHEMISTRY (6th. Ed.), F.A. Cotton, G. Wilkinson, C.A. Murillo, and M. Bochman; John Wiley & Sons (1999)

As deduced from Table 2-1, the lanthanoid elements show relatively low standard atomization enthalpies and ionization potentials. These properties make them highly active reducing metals, with Allred-Rochow electronegativities ranging from 1.01 (Eu) to 1.14 (Lu), similar to that reported for Ca (1.04) [20].

In accordance with the variation observed in their successive ionization potentials, Table 2-1, the (3+) oxidation state is a common characteristic chemical feature of the lanthanoid series. With a few exceptions, typically associated with elements having a relatively low fourth ionization potential (Ce, Pr, Tb), Table 2-1, the (3+) oxidation state exhibits a high stability. In the case of the three elements mentioned above, the (4+) oxidation state is very relevant as well. In particular, higher oxides, i.e. dioxides and mixed-valent (+3/+4) compounds are well known for

them. In the latter case, an extensive and complex homologous series, whose generic formula is Ln_nO_{2n-2m}, has been prepared and characterized [6,21]. As will be shown throughout this chapter, these oxides, particularly ceria and ceria-based mixed oxides, are finding very interesting applications [9,11]. Thermochemical data corresponding to both sesquioxides and dioxides of the lanthanoid elements are reported in refs. [22,23].

Lower rare earth oxides, those corresponding to the occurrence of the (2+) oxidation state, are also known. The information currently available about them has been recently reviewed [6]. In accordance with the standard redox potentials reported in [24], for Ln³⁺/Ln²⁺ pairs (Ln: Sm, Eu, Tm and Yb), in solution, the Ln (2+) ions typically behave as reducing species, Eu²⁺ being by far the less reductant of them ($E^{\circ} \text{Eu}^{3+}/\text{Eu}^{2+}$: -0.35 V; to be compared with those for Sm³⁺/Sm²⁺: -1.5 V; Tm³⁺/Tm²⁺: -2.3 V; Yb³⁺/Yb²⁺: -1.1 V). This observation may qualitatively be extended to the oxides, LnO, that of Eu showing the highest stability [6].

In general, strong reducing conditions are required for the preparation of LnO phases [6]. Thus, EuO can be obtained by heating a mixture of the metal and the corresponding sesquioxide at 2053-2098 K [25]. Though some other monoxides have been proposed to occur, all of them with NaCl-type structure [6], EuO and YbO are probably the best characterized ones [6,26]. In the case of Eu, a mixed-valent Eu²⁺/Eu³⁺ oxide, Eu₃O₄, has also been prepared by reducing the sesquioxide in a flow of hydrogen, at 1573 K [27].

In accordance with the special thermal/chemical conditions required for the preparation of LnO oxides, and their inherent strong reducing behavior, the rare earth mono-oxides cannot be easily stabilized and manipulated. This probably explains why they have not been extensively investigated nor found relevant applications as yet.

The Ln³⁺ ions exhibit large ionic radii ranging from 117 pm for La³⁺ to 100 pm for Lu³⁺, Table 2-1. Also well known, the Ln³⁺ radii steadily decrease throughout the series as a result of the so-called lanthanoid contraction effect. These are very characteristic chemical features of the lanthanoid elements.

Because of the inner nature of the 4f orbitals, the differences of electron configuration between the lanthanoid elements are associated to electrons relatively well screened from the chemical surroundings by the outer (5s²p⁶) shell. This implies weak crystal fields splitting effects [28], and a relatively small covalent contribution to the bonding, particularly in the sesquioxides. Accordingly, the ionic model plays an important role in determining their chemistry [21]. Also related to these chemical characteristics, the lanthanoid compounds exhibit a rich variety of structures, often reflected in the occurrence of polymorphism phenomena.

In accordance with the well known phase diagram for the rare earth sesquioxides [6], as much as five different structural varieties have been identified for them. They are referred to as: A, B, C, H, and X types. A theoretical analysis of the equilibrium crystal lattice dimensions for A, B, and C structures in Ln₂O₃ has also been recently reported [29]. Three of the polymorphs above, the hexagonal, A-type, monoclinic, B-type, and cubic, C-type, are known to occur at room temperature, and atmospheric pressure, whereas H and X forms have only been observed at temperatures above 2273 K [6]. For the lighter members of the series, La through Nd, though not exclusively [6,30], the hexagonal, A-type, form is the most usually found, Fig. 2-1. By contrast, the heaviest lanthanoid sesquioxides, from

Gd₂O₃ onwards, normally occur as cubic, C-type, phase. For Sm and Eu, though the stable form under the usual temperature and pressure conditions is the cubic one, the rate of B → C phase transition is slow enough as to allow the observation of the monoclinic phase at room temperature and atmospheric pressure.

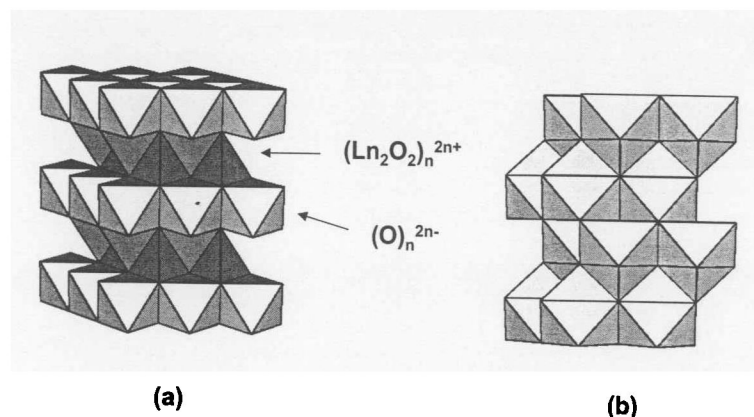


Figure 2-1. A-Ln₂O₃ structure. It consists of a hcp Ln³⁺ sublattice with one half of both octahedral and tetrahedral holes occupied by O²⁻ (a). The (Ln₂O₂)_n²ⁿ⁺ layers have C₃ symmetry. An alternative description consists of linked sevenfold LnO₇ polyhedra (b).

The considerations above suggest that the rare earth oxides, particularly the sesquioxides, might well be described as an ensemble of mainly ionic, basic oxides made up by cations with a rather large size smoothly decreasing throughout the series. This regular variation, as a result of which the basic behavior of the sesquioxides would be expected to steadily decrease throughout the series, makes them an appealing family of oxides for checking the likely existence of correlations between chemical properties, particularly acid-base behavior, and their catalytic activity and selectivity [7]. A number of attempts pointing at this direction have been reported in the literature [31].

These general principles have allowed Johnson [32] to propose the existence of two major categories of chemical processes involving the lanthanoid elements. The first one, that implying changes in their oxidation state, would be essentially controlled by the differences in their successive ionization potential. For this group of processes, irregular variations of behavior throughout the lanthanoid series should be expected to occur. The second category would consist of reactions implying no changes in the oxidation state of the rare earth elements. In accordance with [32], in this second case, the chemical behavior would show a rather smooth regular variation throughout the series. When applied to the oxides, the first category of reactions would obviously be related to their redox chemistry. In the second category, the acid-base processes might well be included. Some relevant examples of these two types of chemical processes involving the rare earth oxides will be discussed in the following sections. Accordingly, this chapter has been organized in two major sections. The first one, will be devoted to the rare earth sesquioxides, the reactivity of which is mainly determined by their acid-base properties. The second

one will deal with the reactivity of the higher oxides, being therefore focused on their redox chemistry.

2.2. CHEMICAL REACTIVITY OF THE RARE EARTH SESQUIOXIDES

2.2.1. Preliminary Considerations about the Ln₂O₃-H₂O-CO₂ System

Because of their acknowledged basic character [7], the rare earth sesquioxides are expected to be highly active against H₂O and CO₂. In fact a good deal of information is at present available about the ternary system Ln₂O₃-CO₂-H₂O. In the next pages we shall review this information. The attention will be focused on two major aspects: the processes occurring when the oxides are exposed to atmospheric CO₂ and H₂O under the usual storage and handling conditions, and those inherent to their soaking in water, at room temperature, under variable CO₂ pressure. These latter conditions are, for instance, those occurring during the preparation of rare earth oxide-supported metal catalysts [33-36].

To rationalize these behaviors, we shall review first the information available on the phases belonging to the binary systems: Ln₂O₃-H₂O and Ln₂O₃-CO₂, then we shall analyze the structural nature of the ternary phases: Ln₂O₃-H₂O-CO₂. Finally, we shall discuss the chemical aspects of these interactions.

This section is aimed at establishing how the textural, structural and chemical properties of the rare earth oxides are modified by their interaction with the atmospheric H₂O and CO₂. Both, thermodynamic and kinetic information about the aging-in-air phenomena is relevant. Likewise, the nature of the phases resulting from these processes, and the way of recovering the oxides from them will be analyzed. This information can be critically important to fully understand their behavior, and to properly use them when applied as pure oxides, as one of the phases constituting a multi-component system, or as starting reactant in the preparation of a variety of materials.

2.2.1.1. Phases Belonging to the Ln₂O₃-H₂O System

Though a number of phases resulting from the hydration of the rare earth sesquioxides have been suggested to occur, only two are well characterized: the hydroxide, Ln(OH)₃, Fig. 2-2, and the corresponding oxy-hydroxide: LnO(OH), Fig. 3-3. The first one is known for all the lanthanoid elements. Except the hydroxide of lutetium for which a cubic structure (Space group: Im $\bar{3}$) has been reported [37], all the rare earth hydroxides show a hexagonal UCl₃-type structure (Space Group: P6₃/m) [38]. According to [39], the reaction of the lanthanoid sesquioxides with water leads to the corresponding hydroxides phases, the process becoming slower and less intense throughout the series. Though this point will be discussed below in some detail, it has been stated that from Dy₂O₃ onwards bulk hydration is impossible, even by soaking the oxides in boiling water [39].

If lanthana is previously treated with CO₂, however, the hydration reaction becomes slower [40]. Also worth of noting, with a few exceptions, like the one reported in ref. [41], where the hydration of the monoclinic B-Nd₂O₃ is proposed to occur through an intermediate NdO(OH) phase, there is a general agreement in the sense that the hydration of the rare earth oxides leads directly to the formation of the corresponding hydroxide [39].

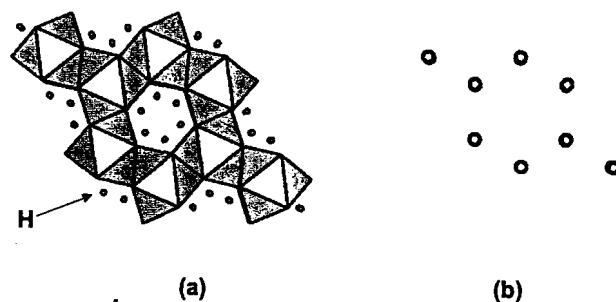


Figure 2-2. The structure of $\text{Ln}(\text{OH})_3$ contains a ninefold coordinated polyhedra showing empty columns (a). The projected cation sublattice along the c-axis shows a close relationship with the hcp substructure present in $\text{A-La}_2\text{O}_3$ (b) but expanded.

The oxyhydroxide phase, $\text{LnO}(\text{OH})$, has been identified in experimental studies aimed at establishing the phase diagram for the binary $\text{Ln}_2\text{O}_3\text{-H}_2\text{O}$ system under hydrothermal conditions [42,43]. It has also been observed as intermediate phase in the decomposition of the hydroxides [7,30,43-49]. Though not proved, it has been suggested that the two step decomposition of $\text{Ln}(\text{OH})_3$ to Ln_2O_3 throughout $\text{LnO}(\text{OH})$ requires the presence of traces of carbonate species [50].

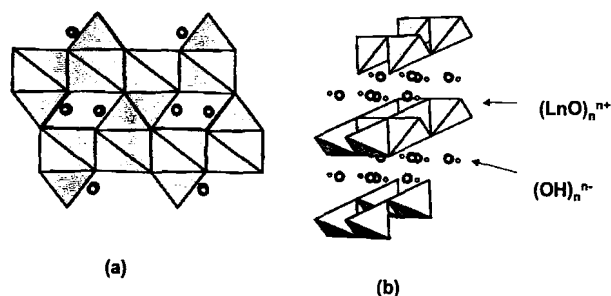


Figure 2-3. LnOOH structure. The cations (a) are sevenfold coordinated and the oxygen anions fourfold coordinated (b). The $(\text{LnO})_n^{n+}$ layers have a symmetry (C_4) different from the one observed in Ln_2O_3 .

The lanthanoid oxyhydroxides, $\text{LnO}(\text{OH})$, show a monoclinic structure which can be described in terms of $(\text{LnO})_n^{n+}$ layers consisting of sharing edges tetrahedral OLn_4 units, the interlayer space being occupied by the OH groups. As will be commented on further below, the structure of a number of phases belonging to the $\text{Ln}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ system can be described with the help of layer models like the one mentioned above [51].

The lanthanoid hydroxide and oxyhydroxide phases have also been characterized by means of infrared spectroscopy [30,37,45,46,52-58]. The

hexagonal $\text{Ln}(\text{OH})_3$ phases exhibit two characteristic features: a strong narrow band at 3600 cm^{-1} , the position of which not being very much sensitive to the nature of the lanthanoid cation [54], that has been assigned to the stretching mode of the hydroxide ions [53,54]; and an intense and broader band, the wavenumber of which shifting from 640 cm^{-1} for $\text{La}(\text{OH})_3$ [57], to 650 cm^{-1} for $\text{Nd}(\text{OH})_3$ [56], and to 680 cm^{-1} for $\text{Sm}(\text{OH})_3$ [58]. In accordance with the structural analysis of the vibration modes of the hexagonal $\text{Ln}(\text{OH})_3$ phase reported in [54], this latter band has been assigned to a deformation mode Ln-O-H [55]. In the case of a $\text{La}(\text{OH})_3$ sample prepared by "in situ" hydration of the oxide, two O-H stretching bands at 3590 and 3610 cm^{-1} are observed. They are interpreted as due to the two structurally distinct hydroxyl species present in the hydroxide [52]. In [52], the dehydration of the hydroxide phase was also investigated by heating the sample disk in an infrared cell, under vacuum, at increasing temperatures. The authors observe two decomposition steps. During the first one, at 473 K , the high frequency OH species would be preferentially eliminated, thus leading to the corresponding oxyhydroxide phase, LaOOH , which would be further dehydrated to sesquioxide at 573 K , under vacuum. In accordance with this interpretation, the OH stretching region of the $\text{LaO}(\text{OH})$ infrared spectrum would be characterized by a major band at 3590 cm^{-1} . Also characteristic, this latter band shows a broad tail towards the low frequency region interpreted as due to extensive hydrogen bonding. This interpretation was further confirmed by parallel hydration/dehydration experiments with D_2O [52].

The structural evolution undergone by a $\text{La}(\text{OH})_3$ gel throughout its decomposition to sesquioxide has also been investigated by EXAFS [59] and ^{17}O -NMR spectroscopy [44]. Though EXAFS data suggest the formation of highly disordered phases which do not allow their unambiguous characterization [59], the changes occurred in the ^{17}O -NMR spectra support that, as already noted, the decomposition process takes place throughout a $\text{LaO}(\text{OH})$ intermediate phase.

2.2.1.2. Phases Belonging to the $\text{Ln}_2\text{O}_3\text{-CO}_2$ System

The most interesting $\text{Ln}_2\text{O}_3\text{-CO}_2$ binary phases are the three well characterized structural varieties of lanthanoid dioxymonocarbonate: $\text{Ln}_2\text{O}_2\text{CO}_3$. Amorphous or very poorly crystallized anhydrous phases, $\text{Ln}_2(\text{CO}_3)_3$, resulting from the dehydration of the corresponding hydrated carbonates are also known.

The dioxymonocarbonate phases are known for the whole series of lanthanoid elements [60]. They are stable intermediate phases in the thermal decomposition to oxides of a number of salts including: formates [61,62], acetates [63-67], benzoates [66], oxalates [67,68], carbonates [69-71], and hydroxycarbonates [69,72-76]. In [60], the structural nature of the three lanthanoid dioxymonocarbonate phases is discussed. They are referred to as I (Tetragonal; Fig. 2-4a), IA (Monoclinic) and II (Hexagonal; Fig. 2-4b). All of them can be described as layered structures built up of slabs of $(\text{Ln}_2\text{O}_2^{2-})_n$, the carbonate ions occupying the interlaminar space. Type I, isostructural of the $\text{Bi}_2\text{O}_2\text{CO}_3$, would consist of layers like the ones exhibited by the lanthanoid oxyhydroxides or oxychlorides, LnOCl . As deduced from the results reported in [60], type I polymorph is known for all the lanthanoid elements. Type IA, which has been prepared for lanthanum and praseodymium, can be described as a monoclinic distortion of the tetragonal unit cell of type I [60]. Finally, type II would consist of hexagonal $(\text{Ln}_2\text{O}_2^{2-})_n$ layers like

those found in A-Ln₂O₃ sesquioxides. Type II polymorph has been identified for the lighter lanthanoid elements: La, Pr, Nd, Sm, and possibly Gd [60].

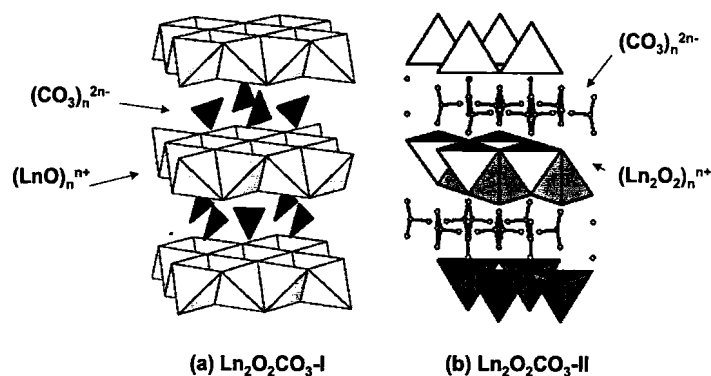


Figure 2-4. Ln₂O₂CO₃ structures I (a) and II (b). (LnO)_n²⁺ layers in type I are similar to those observed in LnOOH. (Ln₂O₂)_n²⁺ structure in type II resembles that found in A-La₂O₃. The carbonate groups in type II are statistically distributed in 3 positions.

As a function of the specific nature of the precursor salt and the experimental reaction conditions, different polymorphs often coexist. This is particularly true for the lighter elements of the series. Though a considerable scatter may be found in the available thermodynamic data for the decomposition of lanthanoid dioxymonocarbonate phases [77], it is generally assumed that, as expected, their thermal stability progressively decreases throughout the series. Thus, decomposition temperatures, as determined by thermogravimetric analysis, ranging from 1188 K for La₂O₂CO₃ (II) to 873 K for the heavier, type I, dioxymonocarbonates have been reported in [60].

The IR spectra of the different dioxymonocarbonate polymorphs have also been discussed in detail [60]. For type II, Turcotte et al propose a C_{2v} site symmetry for the carbonate ions with a weak splitting of modes ν₃ (E' Asymmetric stretching modes in D_{3h} free ion), and a nondetectable splitting in modes ν₄ (E' Bending modes in D_{3h} free ion). For types I and IA the spectra are more complex, being interpreted as due to the presence of two and three non-equivalent carbonate positions, respectively. The number of bands, two for type I and three for type IA, associated to the non-degenerate ν₂ mode (A''₂ out of plane bending mode in D_{3h} free ion) is particularly relevant in this respect. Multiple splitting of ν₃ is also observed. In [60], C_{2v} symmetry is proposed for the two nonequivalent carbonates in phase I, whereas for carbonate species in phase IA, C_{2v} symmetry is suggested for one of them, the symmetry of the remaining two crystallographic positions being C_s. Table 2-2 summarizes the wavenumbers associated to some characteristic carbonate bands in dioxymonocarbonate phases. They were estimated from the spectra reported in [60] for the different La₂O₂CO₃ polymorphs.

TABLE 2-2. Infrared spectra corresponding to phases I, IA and II of La₂O₂CO₃. Wavenumbers (cm⁻¹) estimated from the spectra reported in [60].

Polymorph	ν ₃	ν ₁	ν ₂	ν ₄
Type I	1375	1070	870	730
	1500		850	680
Type IA	1500	1080	880	730
	1470	1060	870	680
	1380	1050	860	660
Type II	1510	1090	860	750
	1480			

2.2.1.3. Phases Belonging to the Ln₂O₃-CO₂-H₂O System

Among the phases belonging to the Ln₂O₃-CO₂-H₂O two major groups can be distinguished: the hydrated carbonates and the hydroxycarbonates.

For the first of these groups, two crystalline phases: Ln₂(CO₃)₃.nH₂O (n = 3; n = 8), both orthorhombic, have been reported [68,74,78]. Some other hydrated carbonates reported in the literature are: La₂O(CO₃)₂.1.4H₂O, which has been prepared by ultrasound activation of an aqueous solution containing urea and La(NO₃)₃ [71], and a neodymium peroxycarbonate, Nd₂O₂(CO₃)₂.2H₂O [79].

Regarding the hydroxycarbonate phases, there are two well characterized structural varieties which are known for most of the lanthanoid elements [80]: the ancylite-like, orthorhombic, A-Ln(OH)CO₃, Fig. 2-5, the structure of which is described in detail in [81,82]; and the hexagonal one, B-Ln(OH)CO₃, Fig. 2-6, isostructural of the bastnaesite mineral (LnFCO₃), the characterization of which is reported in [83,84].

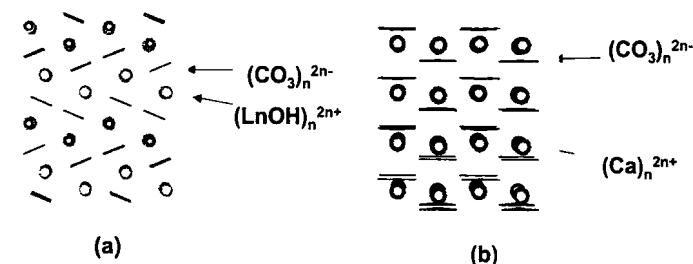


Figure 2-5. Structure of the A-variety of Ln(OH)CO₃ (a). View stressing its relationship with the structures of the ancylite and aragonite-form of CaCO₃ (b).

Bastnaesite-like hydroxycarbonates are more easily prepared under hydrothermal conditions [84,86,87], while the ancylite-type phases can be obtained at ordinary pressure and temperature conditions by hydrolysis of carbonates [88] and trichloroacetates [74], or homogenous precipitation of the corresponding lanthanoid cations from hot aqueous solutions of urea [89-91].

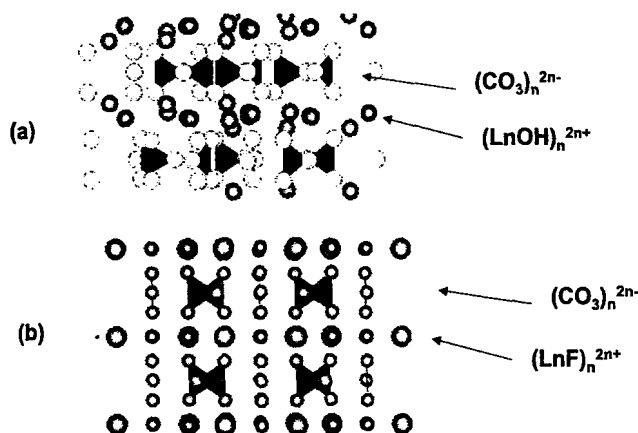


Figure 2-6. Structure of the B-variety of LnOHCO_3 (a). View stressing its close relationship with the one of the bastnaesite mineral, CeFCO_3 (b).

Some additional hydroxycarbonate phases are known. Thus, a monoclinic phase, $\text{Ln}_2(\text{OH})_4\text{CO}_3$, has been reported for holmium [80]. Likewise, in a review work on the ternary $\text{Ln}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ hydrothermal systems [85], a number of phases: $\text{Ln}_6(\text{OH})_4(\text{CO}_3)_7$, $\text{Ln}_2\text{O}(\text{OH})_2(\text{CO}_3)$, $\text{Ln}_{12}\text{O}_7(\text{OH})_{10}(\text{CO}_3)_6$, $\text{Ln}_6\text{O}_2(\text{OH})_8(\text{CO}_3)_3$, and $\text{Ln}_4(\text{OH})_6(\text{CO}_3)_3$, have been identified for the heavier lanthanoid elements: Tm, Yb, and Lu. X-ray powder diffraction data for the five phases mentioned above are reported in [85].

Infrared spectroscopic data for both hydrated carbonates [69,92] and the hydroxycarbonate phases [53,84,92,93] are available from the literature. According to [53], the IR spectra of the ancylite-like hydroxycarbonates in the range $3000\text{-}4000\text{ cm}^{-1}$ are characterized by a doublet, hardly resolved for the elements belonging to the first half of the lanthanoid series. The average wavenumber of this doublet ranges from 3425 cm^{-1} to 3515 cm^{-1} as the atomic weight of the rare earth element increases. In the case of the bastnaesite-type phases, two well resolved OH stretching bands can easily be observed even in the case of $\text{La}(\text{OH})\text{CO}_3$ [84,93], for which they are found at 3630 cm^{-1} and 3490 cm^{-1} [93].

2.2.2. The Chemistry of the $\text{Ln}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{O}$ Systems

Upon reviewing the available literature on $\text{Ln}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{O}$, $\text{Ln}_2\text{O}_3\text{-H}_2\text{O}$, and $\text{Ln}_2\text{O}_3\text{-CO}_2$ chemical systems, we may note three different types of studies. The first one deals with experiments carried out under hydrothermal conditions [42,81,83,85,87,93-99]. In the second one, the interest was focused on the evolution undergone by different starting phases belonging to the $\text{Ln}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{O}$ system when dispersed in water, at room temperature, under different CO_2 pressures ranging from 1 atm to 1×10^{-6} atm. A major part of this work has been carried out by Caro et al [50,69,88,92,100-103]. The third type of studies was aimed at investigating the processes occurring upon exposure of the rare earth sesquioxides to the atmospheric

air, at room temperature [30,46,48,55-58,104-106]. As already noted, in this chapter special attention will be paid to the latter two groups of studies.

Table 2-3 summarizes some thermodynamic data reported in [107,108] for the hydration of the rare earth sesquioxides to hydroxides. ΔH°_f data were estimated from the corresponding ΔH°_f for $\text{Ln}(\text{OH})_3$, Ln_2O_3 , and $\text{H}_2\text{O}(\text{g})$. $\Delta H^\circ_f(\text{Ln}_2\text{O}_3)$ data were taken from the literature, whereas those for $\Delta H^\circ_f(\text{Ln}(\text{OH})_3)$ were estimated by means of a Born-Haber cycle as described in [107]. More recently, the standard thermodynamic data for the rare earth hydroxides have been critically reviewed, a new set of revised values being proposed [109]. For the calculation of ΔG°_f (298 K), an average value $T\Delta S^\circ_f = 158 \pm 15\text{ kJ/mol Ln}_2\text{O}_3$ was used for all the oxides [107].

Table 2-3 suggests that, as expected, the hydration of the sesquioxides is progressively less favored throughout the lanthanoid series. The anomalous behavior of lutetia has been interpreted [107] as due to the different structure exhibited by $\text{Lu}(\text{OH})_3$, cubic instead of the hexagonal one shown by the remaining lanthanoid hydroxides [37].

TABLE 2-3. Some thermodynamic data about the reaction: $\text{Ln}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{Ln}(\text{OH})_3(\text{s})$

Element	Electronic Configuration (Ln^{3+})	$\Delta H^\circ_f^*$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta G^\circ_f^*$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$P_{\text{H}_2\text{O}}^*$ (Torr)
La	$4f^0$	-360	-202	1.1×10^9
Nd	$4f^3$	-335	-177	3.3×10^8
Sm	$4f^6$	-303	-145	2.5×10^6
Eu	$4f^6$	-278	-120	7.2×10^5
Gd	$4f^7$	-268	-110	2.8×10^4
Tb	$4f^8$	-240	-82	1.2×10^2
Dy	$4f^9$	-224	-66	1.0×10^1
Ho	$4f^{10}$	-218	-60	2.3×10^{-1}
Er	$4f^{11}$	-199	-41	3.0×10^0
Tm	$4f^{12}$	-169	-11	1.7×10^2
Yb	$4f^{13}$	-178	-20	5.1×10^1
Lu	$4f^{14}$	-251	-93	2.7×10^{-3}

(*) ΔH°_f and ΔG°_f in $\text{kJ/mol Ln}_2\text{O}_3$, data taken from refs. [107,108]

(*) Equilibrium $P_{\text{H}_2\text{O}}$ in Torr at 298 K

$T\Delta S^\circ_f \approx 158\text{ kJ/mol Ln}_2\text{O}_3$ for all the Ln elements [107]

As deduced from the equilibrium data ($P_{\text{H}_2\text{O}}$) reported in Table 2-3, the hydration process would be favorable, at room temperature, for most of the rare earth oxides. Moreover, experimental hydration studies carried out on sesquioxides belonging to the second half of the lanthanoid series: Sm_2O_3 [107,110,111], Ho_2O_3 [111], Yb_2O_3 [107,111,112], and Lu_2O_3 [107,113,114] have confirmed that the process is actually favorable for the whole series of oxides. Thus, in the case of ytterbia, at 298 K, bulk hydration does occur for water pressures higher than 8 Torr [112], a limit value well below the equilibrium vapor pressure for water, at 298 K. These observations contrast with earlier studies suggesting that hydration in bulk of dysprosia and heavier sesquioxides is impossible [39]. Nevertheless, it would be