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Study of the reduction/reoxidation cycle in a La/Ce/Tb mixed oxide

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Abstract

The redox behavior of a La/Ce/Tb mixed oxide used as a precursor for preparing green emitting phosphors has been investigated by means of temperature programmed reduction mass spectrometry (TPR-MS), oxygen pulse/temperature programmed oxidation (TPO), X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). The experimental conditions ensuring the complete reduction of the starting oxide to a Ce^{III} and Tb^{III} containing phase have been established. In accordance with the XRD study, the reduced phase consists of a hexagonal, A-type, mixed sesquioxide. The quantitative O_2 pulses/TPO data for the reoxidation of this sesquioxide phase are consistent with the formation of a fully oxidized: $La_2O_3/CeO_2/TbO_2$ mixed oxide. Neither the XRD study nor the HRTEM images suggest the occurrence of phase segregation phenomena.

1. Introduction

The rare earth elements are currently used in many luminescent materials of the last generation [1,2]. In particular, the replacement of the classic lamp phosphor $Ca_5(PO_3)_3(F,Cl):Sb^{3+}$, Mn^{2+} by a mixture of three phosphors, all of them activated with lanthanide elements [3] has represented a real breakthrough [1,4,5]. A typical composition of the so-called three-color lamps contains a red-emitting $Y_2O_3:Eu^{3+}$ phosphor, a blue-emitting $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor, and a green-emitting one consisting of a Tb^{III} activated phosphor [1].

For the past few years, the use of mixed rare earth oxides as starting materials has proved to be a better method of controlling the quality of the final phosphors; a number of Y/Eu, La/Ce/Tb and Gd/Ce/Tb oxide samples are used for preparing the three lamp phosphors above [1,6]. Because of the specificity of their applications, these tailored mixed rare earth oxides have a sharply defined chemical composition. However, their general chemical and structural properties have not yet been extensively investigated.

Several authors have been working on mixed rare earth oxides [7–15]. However, most of these studies have dealt with structural aspects [7–9,11,15], electric conductivity properties [12–14], and to a much lesser extent with their chemical behavior [10]. Here, we report on the structural and chemical characterization studies carried out on a La/Ce/Tb mixed oxide used as a precursor for the preparation of $(La/Ce/Tb)PO_4$ green phosphors. Since this mixed oxide contains Ce^{IV} and Tb^{IV} ions, and the luminescent materials are made up of fully reduced cerium and terbium ions, our study has paid special attention to the redox behavior.

2. Experimental details

The La/Ce/Tb mixed oxides investigated here were two high purity samples from Rhône-Poulenc. The oxides, referred to as MO-1 and MO-2, have the same chemical composition: La_2O_3 42.4%, CeO_2 43.4% and Tb_4O_7 14.2%. Their surface areas, as determined from N_2 adsorption at 77 K, were 13.8 m^2 g^{-1} and 10.5 m^2 g^{-1}, respectively. The preparation procedure was similar to that reported in [6]. In addition, we studied two single cerium and terbium oxides, which were used as reference systems. The terbium sample, hereafter referred as TbO_x, consisted of a non-stoichiometric oxide, $TbO_{1.81}$.

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The experimental device used in the temperature programmed reduction studies with mass spectrometry as analytical technique (TPR-MS) was similar to that described in [16]. The mass spectrometer was a VG Spectralab SX-200 instrument, interfaced to a microcomputer. The experiments were run in a flow of H_2 under the following conditions: flow rate through the reactor, $60\,cm^3\,min^{-1}$, heating rate, $10\,K\,min^{-1}$.

The oxygen pulses and temperature programmed oxidation (TPO) studies were carried out in an experimental setup similar to that described in [17]. This device was equipped with a thermal conductivity detector. The gaseous mixture used for both pulses and TPO experiments was $O_2(5\%)/He$. The flow rate of either pure He or the $O_2(5\%)/He$ mixture was always $60\,cm^3\,min^{-1}$. The heating rate in the TPO experiments was $10\,K\,min^{-1}$. Before use, the gases, N-50 type (99.9990 %), from SEO, were further purified by passing them through either a series of deoxo and zeolite traps or a zeolite trap only (O_2/He mixture).

The X-ray powder diffraction diagrams were recorded on a Philips diffractometer, model PW1820.

The high resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL JEM-2000-EX instrument, equipped with a top entry specimen holder and an ion pump. The structural resolution was 2.1 Å. The samples to be investigated were prepared as reported elsewhere [18].

3. Results and discussion

3.1. Characterization of the starting La/Ce/Tb mixed oxides

Some earlier studies from our laboratory [19] have shown that, upon exposure to atmospheric moisture for several months at 295 K, praseodymia can undergo a disproportion reaction, inherent to which a phase segregation leading to $Pr(OH)_3$ and PrO_2 occurs. A rather similar effect has been observed by Eyring *et al.* in aqueous solution [20,21]. Moreover, the high sensitivity of lanthana to atmospheric H_2O and CO_2 is well known [22]. For these reasons, it seemed interesting to check the likely occurrence of significant aging-in-air phenomena on the mixed oxide exposed to air at room temperature for 6 months. Figure 1 shows the X-ray diffraction pattern for the MO-1 mixed oxide sample. The cerium XRD diagram is also included for comparison. The analogy of both diagrams suggests that the MO-1 sample consists of a solid solution with a fluorite like crystalline structure. This observation is in good agreement with the results reported in the literature for cerium containing binary mixed rare earth oxides [14,15]. No evidence for the existence of other crystalline phases could be obtained from the XRD study. Similarly, the high resolution electron micrographs, as well as the selected area electron diffraction (SAED) patterns obtained for the mixed oxide (Fig. 2(a)), do not provide any evidence for the occurrence of additional phases. Furthermore, the HRTEM images show that no amorphous phases like those observed upon aging in air lanthana (Fig. 2(b)), are present in our La/Ce/Tb oxide samples. Finally, the Fourier transform infrared (FTIR) spectra for the mixed oxides show the absence of the characteristic $Ln(OH)_3$ bands [22], clearly observed on aged-in-air praseodymium [19]. To summarize, the characterization studies carried out on the starting La/Ce/Tb mixed oxides show that they have good stability, thus favoring their processability through the different steps of the phosphor preparation.

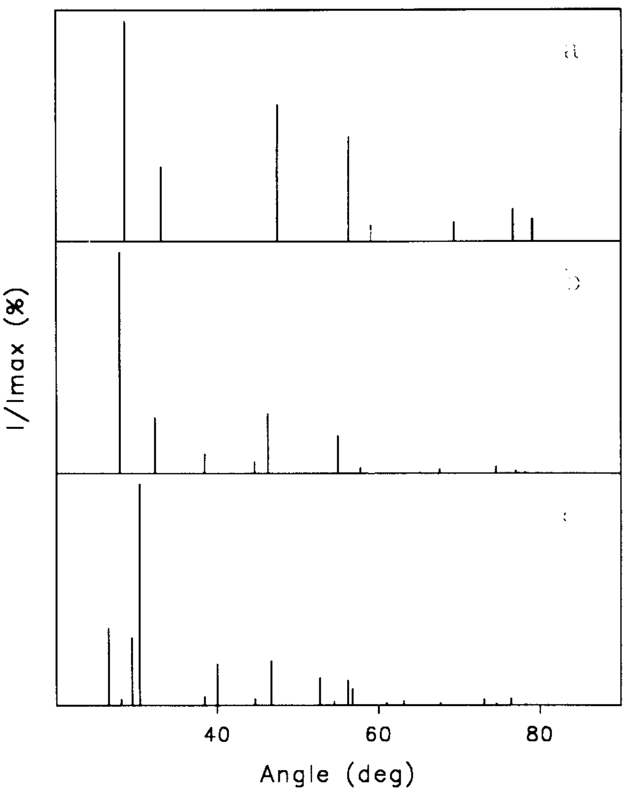

Fig. 1. XRD powder diffraction diagrams corresponding to: (a) CeO_2; (b) MO-1 La/Ce/Tb mixed oxide sample; (c) sample (b) reduced at 1223 K.

3.2. Study of the reduction/reoxidation cycle

Figure 3 accounts for the TPR-MS study of the mixed oxides. Specifically, it reports on the signal corresponding to the mass to charge ratio (*m/c*), 18 (H_2O). The diagrams for the single reducible oxides, CeO_2 and TbO_x (Figs. 3(a) and (b), are also included as references. According to Fig. 3(c), the reduction of sample MO-1 shows a well defined peak at 650 K, a second one

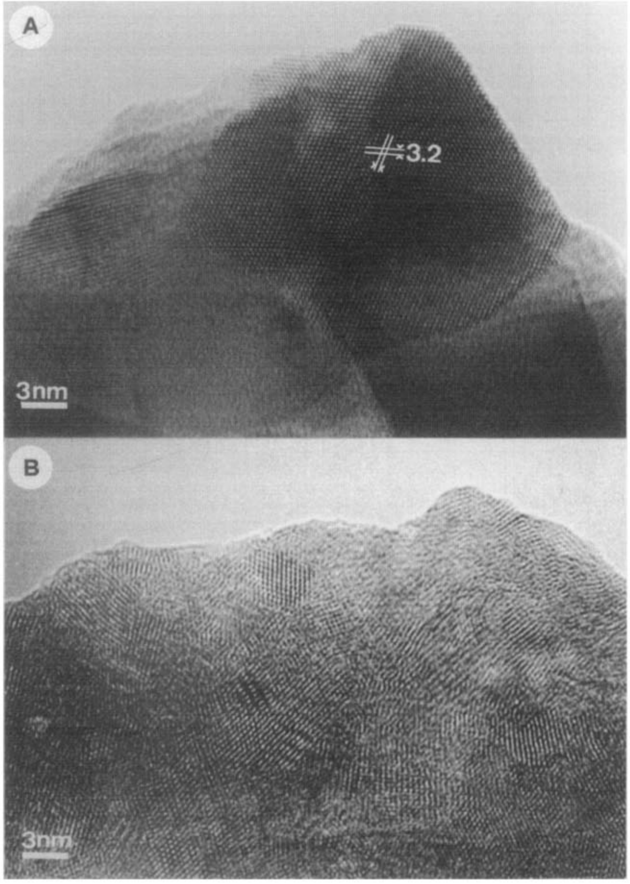

Fig. 2. HRTEM images corresponding to: (a) MO-2 La/Ce/Tb mixed oxide sample; (b) aged-in-air La_2O_3.

at 773 K, and a third singular feature at 1223 K. This latter effect accounts for the water evolution occurring at constant temperature (1223 K for 1 h). As confirmed by parallel TPR-MS and FTIR experiments, the shoulder observed on the low temperature (373 K) side of Fig. 3(c) would be assigned to the elimination of H_2O weakly adsorbed on the starting oxide. Similarly, the reduction of chemisorbed CO_2 would also contribute to the trace for H_2O in Fig, 3. Compared to the oxide reduction, these two latter contributions to the TPR-MS spectrum can be considered rather minor.

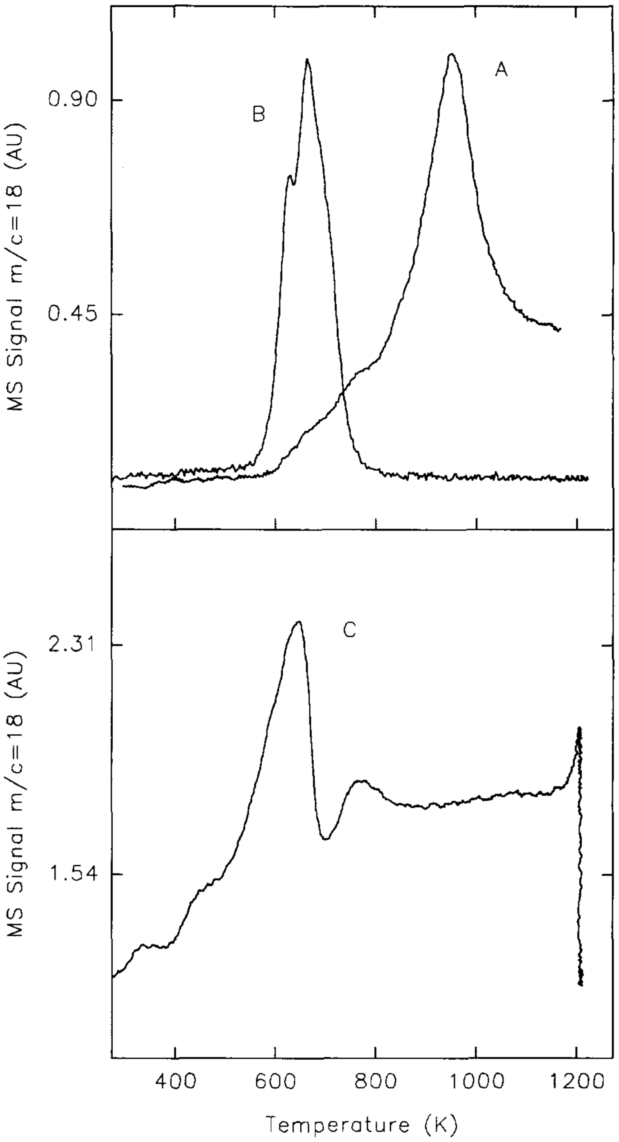

Fig. 3. Trace for H_2O (*m/c*: 18) corresponding to the TPR-MS study of: (a) CeO_2; (b) TbO_x; and (c) MO-1 La/Ce/Tb mixed oxide sample.

The reoxidation of the reduced La/Ce/Tb mixed oxides has also been studied. The experimental procedure was as follows: the samples were first reduced in a flow of H_2 (60 cm^3 min^{-1}) at 1223 K, for 1 h (heating rate 10 K min^{-1}), then, they were treated with flowing He at 1223 K for 1 h, and cooled to room temperature, always in a flow of He. This latter treatment was aimed at preventing any hydrogen chemisorption on the reduced oxides. It is known that the rare earth oxides [23], and particularly cerium [24,25] can strongly chemisorb large amounts of hydrogen. Obviously, the presence of hydrogen would disturb the interpretation of the oxygen uptake data obtained from the reoxidation experiments. To determine the oxygen consumption, two consecutive experiments were carried out. First, the samples were treated at 295 K with 0.25 cm^3 pulses of O_2(5%)/He (P_{O2} 40 Torr) until the signal recorded for several successive pulses was constant, thus indicating that no further oxygen uptake occurred. Then, the gas flowing through the reactor was switched from pure He to O_2(5%)/He, and the TPO experiment was run. Parallel oxygen pulses/TPO experiments were also carried out on the single reduced oxides, CeO_2 and TbO_x. Figure 4 summarizes representative TPO diagrams recorded from these experiments.

Figure 5 gives some further details about the TPO experiments. It includes not only the heating of the sample in a flow of O_2(5%)/He, but also its cooling under the same gaseous mixture. In particular, the

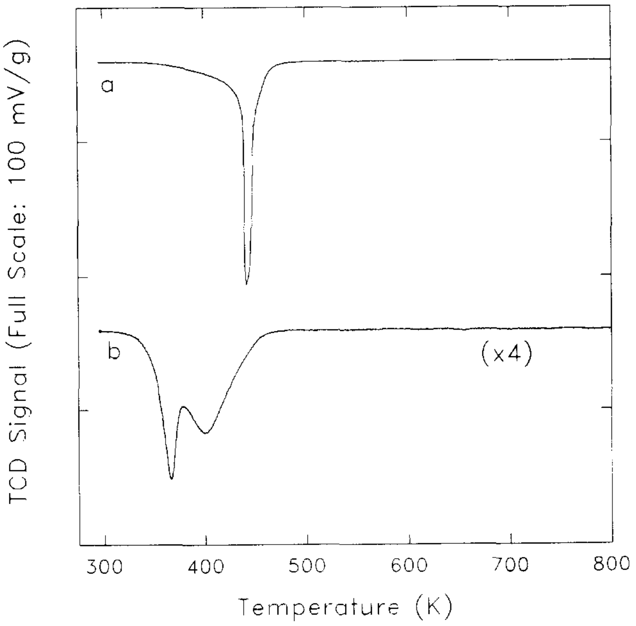

Fig. 4. TPO diagrams recorded for the following reduced oxide samples: (a) MO-1 La/Ce/Tb mixed oxide; and (b) cerium. Details of the experimental procedure are given in the text. (Trace (b): TPO signal × 4).

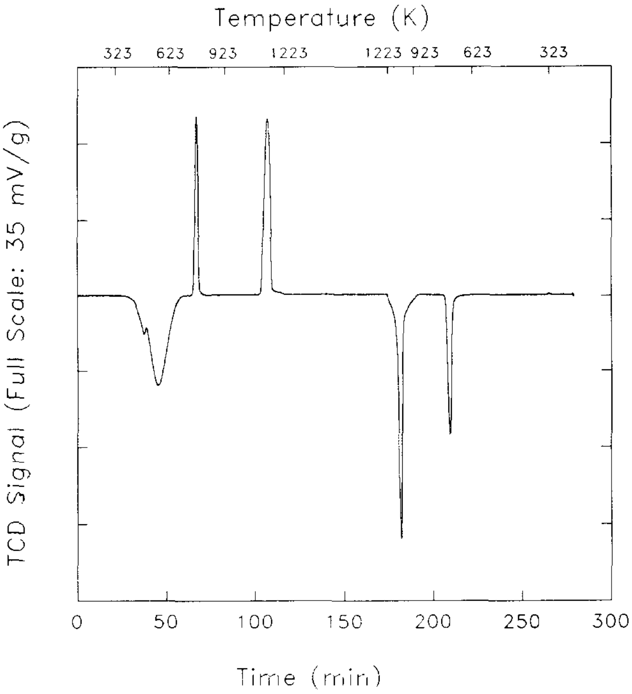

Fig. 5. TPO trace for reduced terbium. The complete experimental cycle (heating from 295 K to 1223 K followed by cooling to 295 K) is reported.

trace for TbO_x is reported in Fig. 5. Three different regions can be distinguished. The first (298–623 K) consists of two unresolved negative peaks indicating oxygen consumption. Region 2 (623–1223 K) shows two narrow well resolved positive peaks. This indicates that even under oxygen pressure, the terbium oxide becomes reduced. Finally, upon cooling the sample from 1223 K to 295 K, under O_2(5%)/He, region 3, a reoxidation process, again through two well defined steps, takes place.

Quantitative data from the reoxidation studies described above are reported in Table 1. Partial oxygen consumption data associated with both pulse at 295 K and TPO experiments are included in Table 1. The latter data were determined by integrating the trace for region 1 in the whole series of TPO diagrams. The total oxygen uptake values are also given in Table 1. They were determined by adding the two partial consumptions above. Finally, Table 1 gives the theoretical amount of oxygen required to thoroughly reoxidize the fully reduced sesquioxides ($La_2O_3/Ce_2O_3/Tb_2O_3$) to dioxides ($La_2O_3/CeO_2/TbO_2$).

There are a number of aspects worth noting in Table 1. In the case of the mixed oxides, there is good agreement between the theoretical (Column 2) and experimental (Column 3) total oxygen consumption data. It can therefore be concluded that the standard hydrogen treatment applied here induces the complete reduction of the mixed oxides to the corresponding sesquioxides. This interpretation receives some further support from the XRD study reported in Fig. 1, in accordance with which the diffraction pattern for the reduced La/Ce/Tb oxide sample is similar to that reported for the hexagonal, A type, variety of the rare earth sesquioxides.

The behavior of the mixed oxide samples contrasts with that of pure cerium, for which the experimental value of the total oxygen consumption is around two-thirds of the theoretical value. Cerium ions are less easily reduced in pure cerium than in the mixed oxide. In the case of pure terbium, on the other hand, the TPR-MS diagram in Fig. 3, as well as the TPO experiment in Fig. 5, show that its reduction to Tb_2O_3 takes place rather easily. Accordingly, the disagreement between the theoretical and experimental total oxygen consumption values reported in Table 1 ought to be interpreted as due to an incomplete reoxidation of the sesquioxide.

The pulse experiments at room temperature also indicate the existence of some significant differences between cerium, on the one hand, and the mixed oxides and terbium, on the other hand. In effect, at 295 K, the latter oxides do not take up significant amounts of oxygen, whereas the former becomes reoxidized to a very large extent. This means that compared to reduced cerium, the Ce^{III} ions become relatively stabilized in the lattice of the mixed oxide. The structural changes involved in the reoxidation of the hexagonal sesquioxide to a fluorite like mixed oxide might be one of the reasons explaining the differences observed.

TABLE 1. Oxygen pulses and TPO study of the reoxidation of several single and mixed rare earth oxides (data in mmol of O_2/g of the starting oxide)

Sample	Theor. amount[a]	Total uptake	295 K uptake	TPO uptake Region 1	TPO desorp. Region 2	Cooling uptake Region 3
La/Ce/Tb	0.82	0.81	0.05	0.76	0.09	0.11
La/Ce/Tb	0.82	0.82	0.06	0.76	0.04	0.03
TbOX	1.34	0.89	5×10^{-3}	0.89	0.78	0.75
CeO_2[b]	1.45	0.96	0.54	0.42	0.0	–

[a]Reaction used to estimate the O_2 uptake: $Ln_2O_3+\frac{1}{2}O_2\rightarrow 2LnO_2$.
[b]Reduced at 1223 K for 2 h.

To summarize, we have carried out a chemical and structural characterization of some La/Ce/Tb mixed oxides used as starting materials for preparing green emitting phosphors. The XRD and HRTEM studies suggest that no phase segregation phenomena occur, the samples consisting of a solid solution with a cubic fluorite like structure. It has also been shown that the combination of oxygen pulses at 295 K and TPO can fruitfully be used to determine the actual redox state of the reduced oxides. From this work, we have been able to establish a specific treatment ensuring the complete reduction of the mixed oxides investigated here. Compared to cerium and terbium, the redox properties of the mixed oxides show some significant differences. In contrast with that found for cerium, hydrogen treatment at 1223 K of the mixed oxide leads to a deeply reduced, hexagonal La/Ce/Tb sesquioxide. At room temperature, the reoxidation rate of this reduced phase is much slower than that of cerium. Finally, the oxygen consumption associated with the reoxidation of the La/Ce/Tb sesquioxide is in very good agreement with that needed to fully oxidize the sample to $La_2O_3/CeO_2/TbO_2$. The interest in these mixed rare earth oxides as starting materials for preparing green emitting phosphors comes clear because of the improved reducibility of Tb^{IV} and particularly Ce^{IV} ions. This is a property to be added to the reactivity and processability advantages already known for these mixed oxides.

Acknowledgments

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