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Luminescence Studies of Lanthanide Oxides

I. Thermal and Hydration Effects on the Metal Ion Site Symmetry in Europium Oxide Catalysts

HARRY G. BRITTAIN*,[1] AND DALE L. PERRY†

*Chemistry Department, Seton Hall University, South Orange, New Jersey 07079, and †Earth Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

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High-resolution luminescence spectroscopy has been used to study the site symmetry of Eu(III) ions in Eu_2O_3 prepared under conditions suitable for catalytic use. It was found that the Eu(III) site symmetry was a sensitive function of the pretreatment procedure, and it proved possible to determine the number of spectroscopically nonequivalent Eu(III) ions in the oxide material from an analysis of the fine structure within the emission bands. The site symmetry is altered primarily by thermal effects, and hydration of the oxide is not found to induce large changes in site symmetry.

INTRODUCTION

The binary oxides of lanthanide ions are basic in their nature, and are capable of catalyzing a wide variety of chemical reactions (*1*). The lanthanide oxides greatly resemble the alkaline earth oxides in their properties, but they are able to offer possible systematic studies resulting from their smoothly varying periodic behavior. Since the ionic radius of the trivalent ions decreases as one passes through the series, a resulting decrease in basicity of the sesquioxides (Ln_2O_3) is found to result (*1*). The lanthanide ions differ from each other only in the number of f-electrons possessed by each ion, although these tend to be highly shielded. A few correlations of catalytic selectivity have been reported (*2–4*), and the activation energy of tetralin dehydrogenation has been found to depend on the orbital angular momentum of the lanthanide ion catalyst (*5*).

While it is well known that a large number of Tb(III) and Eu(III) complexes are found to exhibit strong luminescence when excited with ultraviolet light, such studies on catalytic lanthanide materials have been relatively rare in spite of the sensitivity inherent in the emission technique (*6*). One of the main advantages of the luminescence method is that it may be used to study lanthanide catalysts *in situ* during a particular reaction. The lanthanide ions generally do not experience strong crystal fields, and the spectra in host systems tend to strongly resemble the spectra obtained for the free ion. However, under high-resolution conditions (1–5 Å bandpass), fine structure is usually visible in lanthanide ion luminescence, and these details *do* contain information regarding the environment of the metal ions.

In the present report, these authors will summarize the results of high-resolution luminescence studies on Eu_2O_3, and they will attempt to correlate the spectroscopic observations with known physical properties of the lanthanide oxides (*7*). As will be shown in a following section, the spectroscopy of the Eu(III) ion is particularly simple and exceptionally well-suited for studies of catalytic oxide surfaces. While Eu_2O_3 is not as basic as the better characterized La_2O_3 or Nd_2O_3, it should be possible to use the spectroscopic results to provide details regarding known catalytic reactions. Previous luminescence studies of Eu_2O_3 had been carried out at the low-resolution characteristic of commercial spectrometers (*6*). In

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[1] Teacher-Scholar of the Camille and Henry Dreyfus Foundation, 1980–85, and author for correspondence.

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this work, the authors have found that fine structure can be observed in the emission spectra. This structure can be obtained even at room temperature, and an analysis can provide very interesting conclusions.

EXPERIMENTAL METHODS

Eu_2O_3 was obtained as the 99.9% pure oxide from Kerr McGee, or from Research Chemicals. Rosynek (*8*) has noted that the commercial materials contain very little surface area as a result of the high temperatures used in the purification and refining schemes, and he has outlined a method whereby catalytically active oxide is prepared by hydration and subsequent calcination of the pure oxide. Eu_2O_3 was processed in this manner by heating in glass-distilled water at 80°C for 15 hr, drying at 115°C for 24 hr, and then igniting at temperatures ranging from 300 to 700°C. In addition, Eu_2O_3 was also hydrated by soaking the oxide in water for 3 days, drying at 115°C for 72 hr, and then igniting for 3 hr at 800°C. It was found that the same spectral changes (hence site symmetries) could be obtained with either method. In addition, a series of studies were run where the commercial oxide was not hydrated before calcination but was merely heated between 300 and 700°C before spectroscopic analysis.

X-Ray powder diffraction data were obtained using a Debye–Scherrer 114.6-mm powder camera and Cu*Kα* radiation.

All luminescence spectra were obtained on a spectrometer constructed recently in this laboratory. Samples were excited by the 325 nm output of a helium–cadmium laser (Liconix), a power level of 10 mW being used. The emission from the Eu_2O_3 samples was collected at 90° to the excitation beam, passed through a 1 *M* solution of $KCrO_4$ to remove any scattered excitation energy, analyzed by a 1-m grating monochromator (Spex Industries, model 1704), and finally analyzed by an EMI-9558B photomultiplier tube (S-20 response). The monochromator contained a holographic grating to reduce stray light, and it had a dispersion of 4 Å/mm slit. The photomultiplier tube was cooled to −20°C to reduce noise and dark current.

Emission spectra were routinely recorded at 2 Å resolution, although even better resolution was obtained in a few cases. Spectra were obtained at room temperature by suspending a quartz tube containing the Eu_2O_3 in front of the monochromator slit, and data were taken at 77°K by immersing the same tube into liquid nitrogen (held in an EPR dewar made of suprasil quartz, Wilhmad Associates). Spectra were also taken at 10°K using a gaseous helium refrigerator system (Model LTS-21, Lake Shore Cryogenics) by coating the Eu_2O_3 onto a copper block inside the cold head. While better separation of luminescence peaks was obtained at the lower temperatures, perfectly acceptable data could be obtained at room temperature.

SPECTROSCOPY OF THE Eu(III) ION

The luminescence of Eu(III) is eminently suited for a study of the structural environment of this ion via high-resolution luminescence spectroscopy. As is shown in Fig. 1, all room temperature emission originates from the $^5D_0$ excited state, which lies approximately 17,310 cm^{-1} above the ground state. Excitation into higher levels results in prompt and efficient population of the luminescent $^5D_0$ level. The lanthanide ions are characterized by extremely strong spin-orbit coupling, and as a result only the J quantum number is required to describe the properties of a particular state. The splitting between J levels of a particular term can be very large; for instance, the $^5D_1$ excited state is found 1725 cm^{-1} higher in energy than the $^5D_0$. The position of these energy levels is only slightly affected by the environment of the metal ion, and as a result the emission bands corresponding to various transitions tend to be found at characteristic wavelengths.

The ground states of the Eu(III) ion are

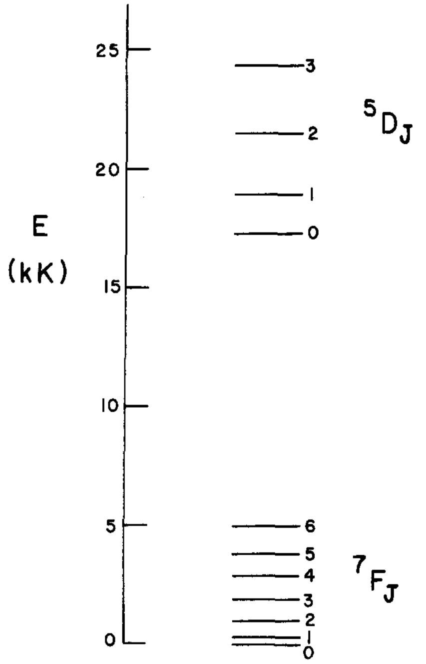

FIG. 1. Energy level diagram for the Eu(III) ion.

derived from the ^7F_J term, with transitions to the $J = 0$, 1, and 2 levels being most easily observed in the emission spectrum. The various transitions can be identified solely by the J quantum numbers of the states, and the $0 \rightarrow 0$ band is found at 580 nm, the $0 \rightarrow 1$ at 595 nm, and the $0 \rightarrow 2$ at 615 nm. The bands are quite sharp, and they exhibit fine structure corresponding to the crystal-field perturbations only at the highest degree of resolution.

If one now considers the J degeneracy of the energy levels (defined as $2J + 1$), all $J = 0$ levels are seen to be nondegenerate, while the $J = 1$ and $J = 2$ levels are three- and fivefold degenerate, respectively. This implies that in the lowest possible crystal field symmetry, the $0 \rightarrow 0$ transition would consist of a maximum of one peak, the $0 \rightarrow 1$ could show three peaks, and the $0 \rightarrow 2$ band could display a maximum of five peaks. Of course, if the symmetry were higher, then fewer peaks would be seen. However, the presence of more than one peak in the $0 \rightarrow 0$ spectral region can be taken as conclusive proof that more than one spectroscopically nonequivalent Eu(III) site exists on the catalyst surface. In fact, the number of $0 \rightarrow 0$ peaks can be used to count the number of different Eu(III) ions in the oxide host material, since no crystal field is capable of splitting the $0 \rightarrow 0$ peak.

RESULTS AND DISCUSSION

Luminescence of Commercial Eu_2O_3

Europium oxide can be obtained commercially in a highly pure form, and this material displays reasonably strong luminescence when excited with uv light. The emission associated with each band is highly structured, and the pattern of bands does not depend on the source of the material (samples from Kerr McGee and Research Chemicals gave identical spectra). While cooling of the oxide from room temperature to 10°K results in a strong increase in the emission quantum yield, only slight changes in relative band intensities are noted and only a small increase in peak resolution are obtained. Room temperature and 10°K spectra of the $0 \rightarrow 0$ and $0 \rightarrow 1$ transitions are in Fig. 2, and corresponding spectra for the $0 \rightarrow 2$ transition in Fig. 3.

An examination of the figures reveals that more than the maximum allowable number of components are associated with each transition, and this observation can be

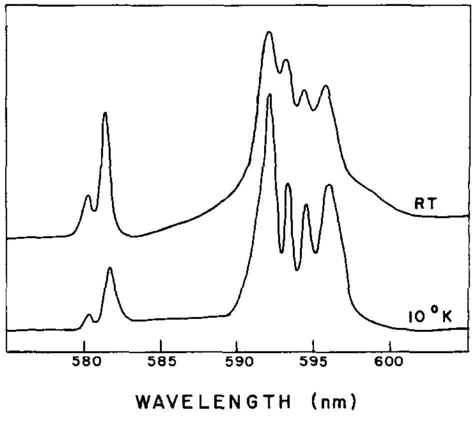

FIG. 2. Room temperature and 10°K luminescence spectra obtained for the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ bands of commercial Eu_2O_3.

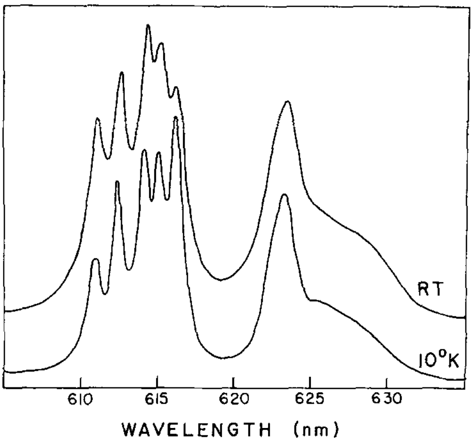

FIG. 3. Room temperature and 10°K luminescence spectra obtained for the $^5D_0 \rightarrow {}^7F_2$ bands of commercial Eu_2O_3.

TABLE 1

Wavelength, Maxima, Energies, and Relative Intensities for the Emission bands of Eu_2O_3 as Obtained Commercially[a]

Wavelength[a] (energy, in cm^{-1})	Site	298°K	77°K	10°K
a. $^5D_0 \rightarrow {}^7F_0$ band				
5803 (17,232)	I	28	14	14
5814 (17,200)	II	85	84	83
b. $^5D_0 \rightarrow {}^7F_1$ band				
5921 (16,889)	I	134	192	187
5932 (16,858)	II	118	118[b]	118[b]
5943 (16,827)	II	98	102	96
5958 (16,784)	II	110	121	116
c. $^5D_0 \rightarrow {}^7F_2$ band				
6112 (16,361)	I	350	272	240
6126 (16,324)	II	432	417	408
6144 (16,277)	II	515	502	472
6152 (16,255)	II	483	494	470
6162 (16,228)	I	408	566	552
6235 (16,040)	II	387	387[c]	387[c]
~6255 (~16,000)	II	200	187	195

[a] All spectra are recorded in arbitrary units, and have been normalized to a single peak height to account for quantum yield increases which take place upon cooling to the lower temperatures.

[b] The 0–0 and 0–1 data were normalized using this peak.

[c] The 0–2 data were normalized using this peak.

taken as direct proof of the existence of nonequivalent Eu(III) ions in the oxide material. The presence of two distinct peaks in the 0 → 0 region implies that at least two Eu(III) sites must be present.

A detailed examination of the temperature dependence of band intensities is able to provide information relating peaks with sites. In Table 1, the wavelength maxima and energies of each transition are shown, accompanied by the relative intensity of each band at 298, 77, and 10°K. The 0 → 0 and 0 → 1 spectra are of comparable intensity, and the measured intensity of the 0 → 1 peak at 5932 Å has been used to normalize the intensities. Different scales were required for the 0 → 2 band system, and the 6235 Å component was used to normalize these bands. Using this procedure, one can directly compare the intensities obtained at the various temperatures.

One may easily see that for a few bands, the relative intensity changes drastically on passing from room temperature (298°K) to 77°K. Little change in intensity is noted in further lowering the temperature from 77 to 10°K.

Alternately for the majority of bands, no change in relative intensity takes place on lowering the temperature. In neither case does the resolution improve greatly, indicating that the Eu(III) sites are probably not in a crystalline environment. While the theory regarding intensities of f–f transitions is still in a state of early development, the different patterns of behavior are strongly suggestive of different crystal fields for the two types of Eu(III) ions present in the oxide material. It is known that differing Eu(III) site symmetries will display different temperature dependence in luminescent transitions (*9*).

Two classes of ratios are observed: one where the room/low temperature is essentially unity, and one where the ratio is radically different from one. The authors believe this behavior indicates which peaks correspond to which site. This enables one to assign the 5803 Å peak from the 0 → 0 band region, the 5921 Å peak from the 0 → 1 system, and the 6112/6162 Å peaks from the 0 → 2 region as belonging to one site, which can be termed Site I. The other peaks (5814 Å in the 0 → 0, 5932/5943/5958 Å from the 0 → 1, and 6126/6144/6152/6235/6255 Å from the 0 → 2 region) then orginate from Eu(III) ions in the other site, which is designated Site II.

The observation of one 0 → 0 peak, one 0 → 1 peak, and two 0 → 2 peaks is consistent only with the Eu(III) existing in a site of either tetrahedral or octahedral symmetry (*9*). An octahedral site could certainly exist for Site I, since the sesquioxide phase existing at room temperature and atmospheric pressure is cubic in nature (*10*); this phase has been termed Type C in the earlier work. Another phase (Type B) has been found for Eu_2O_3 at temperatures higher than 1100°C, and this phase is monoclinic in nature (*10*). The experimental observation of one 0 → 0 peak, three 0 → 1 peaks, and five 0 → 2 peaks for Site II represents the maximum splitting possible, thus indicating that this site must be of very low symmetry. It is entirely possible that the commercial oxide retains some sites resulting from the very high temperatures of the material preparation. We cannot as yet determine with any degree of certainty exactly what the symmetry of the Eu(III) ion in Site II must be, but an examination of the group theory of the situation (*9*) indicates that the site must be of C_2 or lower symmetry.

It is interesting to note that the number of sites can vary with the host material of the Eu(III) ion. In a previous study, Rice and DeShazer (*11*) found that three spectroscopically nonequivalent Eu(III) ions could be detected in $Eu^{3+}:Gd_2O_3$, although the evidence for the existence of one of the three is somewhat dubious. The energies of the transitions are within 50 cm^{-1} of those reported here, which indicates that the energy levels are not highly perturbed by a change in environment.

Eu_2O_3 Prepared by a Hydration/Dehydration Procedure

Roseynek has shown that lanthanide oxides from commercial sources contain very little surface area, and he has described a hydration/dehydration procedure by which highly active catalyst materials can be obtained (*8*). Scanning electron micrographs of the untreated and treated oxides show the dramatic increase in surface area which accompanies the pretreatment procedure (*8*), and Roseynek has also shown how different pretreatments can affect catalytic activities in a profound way (*12*). However, one cannot determine from these studies whether the geometry of the lanthanide sites is affected by the pretreatment procedure which has been used.

Roseynek has shown that $La(OH)_3$ may be prepared in high purity free from contamination by hydrolyzing commercial La_2O_3 in water (*8*). Hydration of Eu_2O_3 is more difficult due to its lower basicity, but is still possible. Only the oxides of Dy(III) through Lu(III) appear to resist hydrolysis by this procedure (*13*). The authors have successfully hydrated Eu_2O_3 following the procedure of Rosynek (which involves heating the oxide in water) and also by suspending the oxide in water (without heating) for a number of days. The hydrated material was isolated and dried, and it was found that the infrared spectrum of the Eu(III) product matched the published spectrum of $Eu(OH)_3$ (*14*). This spectrum is substantially different from that obtained for Eu_2O_3.

The commercially obtained Eu_2O_3 gave powder diffraction *d*-spacings which were in excellent agreement with those reported previously (*1*) for the body-centered cubic crystalline form of the compound. After drying the hydrated oxide, the powder pattern of the resulting compound differed markedly from the original powder pattern. This new pattern exhibited several weaker lines not found in the pattern of untreated Eu_2O_3, but a few lines were found which could be identified as being present in the orginal compound (with changes in intensity, however). Upon calcining this hydrated compound, a powder pattern strongly resembling that of the original material was obtained. However, a number of additional weak lines appeared in this dif-

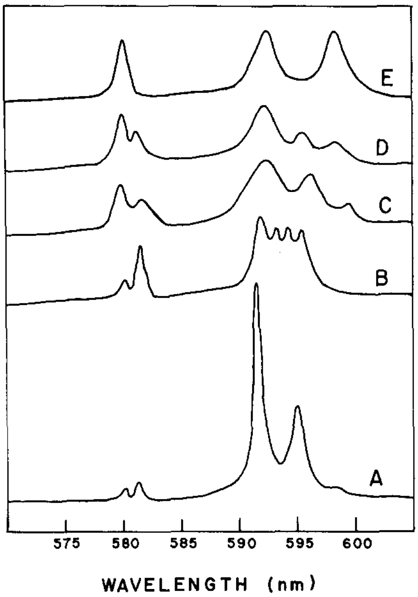

FIG. 4. Effect of calcination temperatures on the luminescence of hydrated Eu_2O_3. Data are shown for the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ bands corresponding to pretreatment temperatures of 115°C (A), 325°C (B), 400°C (C), 450°C (D), and 700°C (E).

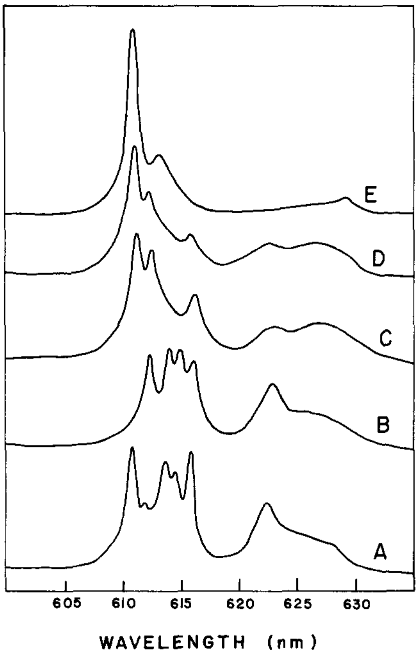

FIG. 5. Effect of calcination temperature on the luminescence of hydrated Eu_2O_3. Data are shown for the $^5D_0 \rightarrow {}^7F_2$ band corresponding to pretreatment temperatures of 115°C (A), 325°C (B), 400°C (C), 450°C (D), and 700°C (E).

fraction pattern, and these features indicate that while Eu_2O_3 is re-formed by the calcination process, the final product is somewhat different from the original material.

These structural changes were found to yield remarkable differences in the luminescence spectra. In Fig. 4, the luminescence spectra within the 0 → 0 and 0 → 1 Eu(III) bands for the hydrated Eu_2O_3 (which we now know is actually $Eu(OH)_3$) are shown, and in Fig. 5, the analogous spectra for the 0 → 2 transition are shown. The lowest trace in each figure represents the spectra obtained on unfired material. A comparison with corresponding spectra in Figs. 2 and 3 shows that the site symmetry of the Eu(III) ion has changed with the hydration process. One still observes the presence of two peaks in the 0–0 spectral region, which indicates that two nonequivalent Eu(III) sites remain in the material. However, the symmetry of these sites has changed, as evidenced by the new appearance of the 0 → 1 and 0 → 2 band systems. It would appear that the Eu(III) site of very low symmetry (present in the commercial oxide and identified as site II) has been changed into a site of higher symmetry, akin to Site I of the commercial Eu_2O_3 sample.

Calcination of the hydrated oxide results in the development of a completely new spectral pattern, and this material is completely developed (as evidenced by the spectral changes) by a temperature of 600°C. The conversion of the hydrated oxide to this new form of Eu_2O_3 is also detailed in Figs. 4 and 5 as a function of calcination temperature. Examination of the trends reveals interesting features, and these are most evident in the 0 → 2 spectra. In the unfired material, the peak at highest energy (6108 Å) is found to be the most intense, but heating the oxide to 325°C for several hours causes this peak to disappear completely. However, if a sample of hydrated oxide is heated at 400°C for several hours, this peak reappears (at 6112 Å) and is again the most intense peak in the spectrum. At the same time, the other 0 → 2 peaks shift by measurable amounts at calcination temperatures of 325°C. Most of these vanish if the oxide is calcined at 400°C.

These observations can be interpreted knowing details of the thermal decomposition of $Eu(OH)_3$. Rosynek has studied the decomposition of $La(OH)_3$ in detail (*8*) and has reported that between 250 and 350°C, decomposition of the hydroxide yields a well-defined, hexagonal LaOOH intermediate. Subsequent dehydration of the oxyhydroxide ultimately yields Eu_2O_3 between temperatures of 350 and 420°C. Finally, between 450 and 800°C, a surface layer of carbonate (formed by absorption of CO_2 by the hydroxide species) is lost and one obtains pure oxide material. The authors believe that the spectra obtained at 325°C (and shown in Figs. 4 and 5) are those of the EuOOH species; the further spectral changes outline the site symmetry changes taking place as the dehydration processes take place. Absorption of carbon dioxide onto Eu(III) hydroxides is not expected to be as great a problem as it is for La(III) compounds due to the lower basicity of the $Eu(OH)_3$. Indeed, the authors were unable to find any trace of carbonate absorption bands in the infrared spectra of the hydrated Eu_2O_3.

As mentioned previously, the hydrated oxide material was also prepared by simply soaking Eu_2O_3 in water for a few days. The infrared spectrum of this material demonstrated that $Eu(OH)_3$ had been prepared, but the luminescence spectra revealed that some differences did exist. The spectra of the $0 \rightarrow 0$ and $0 \rightarrow 1$ bands are shown in Fig. 6 for the unfired material and oxide fired at 800°C. Analogous data are shown in Fig. 7 for the $0 \rightarrow 2$ band system. The spectra of the unfired material are essentially superimposable with those of the untreated commercial oxide, while the spectra of calcined oxide are superimposable with those just obtained in the previous section.

The results of these two studies lead to a very important conclusion: hydration of the Eu_2O_3 and subsequent dehydration drastically changes the site symmetry of the Eu(III) ions, as well as increasing the surface area. The Eu(III) ions in the fired oxide are found to be entirely of one type, and the extreme simplicity of the luminescence spectra indicated that the site is of very high symmetry (perhaps even cubic). A comparison of the calcined oxide spectra with those of the unfired commercial oxide show that the high-symmetry site in the original material (present in a rather small

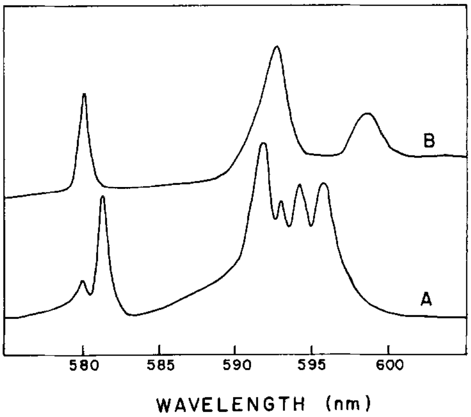

FIG. 6. Luminescence spectra within the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ bands of Eu_2O_3 which has been hydrated merely through soaking in water. Spectra are shown for material dried at 115°C (A) and material calcined at 800°C (B).

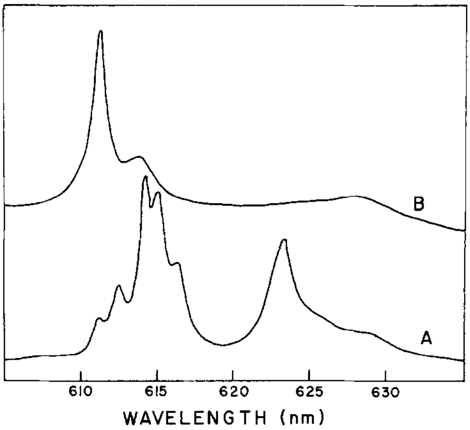

FIG. 7. Luminescence spectra within the $^5D_0 \rightarrow {}^7F_2$ bands of Eu_2O_3 soaked in water. Spectra are shown for material dried at 115°C (A) and material calcined at 800°C (B).

amount, as indicated by the intensity ratios of the 0 → 0 bands) appears to be the same as what was ultimately obtained in the calcination process. These authors thus conclude the pretreatment procedure increases catalytic activity not only by increasing surface area of the catalyst but also by producing more of a particular site symmetry which is better suited for the catalytic reactions. It was noted previously that cooling of commercial Eu_2O_3 from 300 to 10°K did not drastically alter the luminescence spectrum (Figs. 2 and 3). Quite different behavior is found when the calcined oxide is cooled to 10°K and its spectra obtained; these are shown in Figs. 8 and 9. It is clear that at low temperatures, the luminescence bands reminiscent of the low symmetry Eu(III) sites of the commercial oxide have appeared. These bands disappear upon warming of the sample to room temperature, and the process can be cycled as many times as desired without sample decomposition. It is quite clear that a crystal phase change takes place between 300 and 10°K, and this phase change is totally reversible. This result indicates that the use of cryogenic temperatures for site characterization of these Eu_2O_3 materials must be viewed with great caution when new bands appear upon cooling of the sample.

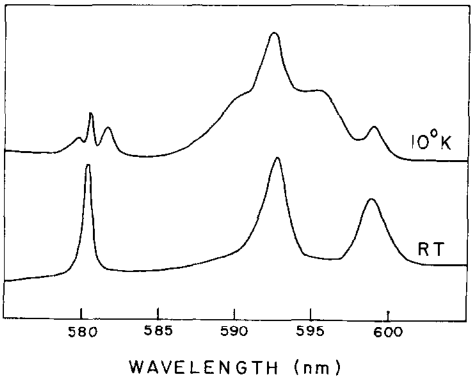

FIG. 8. Luminescence spectra of the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ bands of Eu_2O_3 prepared by calcination of hydrated oxide at 700°C. Data are shown at sample temperatures of room temperature (lower trace) and 10°K (upper trace).

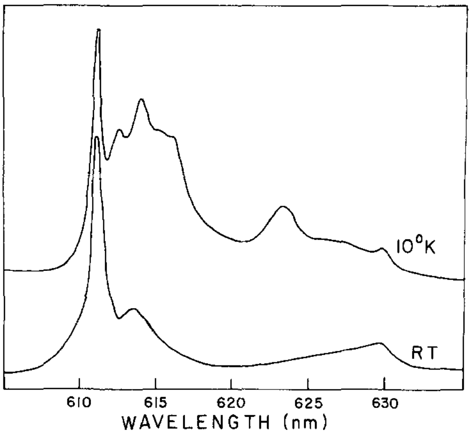

FIG. 9. Luminescence spectra of the $^5D_0 \rightarrow {}^7F_2$ bands of Eu_2O_3 prepared by calcination of hydrated oxide. Data are shown for sample temperatures of room temperature (lower trace) and 10°K (upper trace).

Heating Profile of Commercial Eu_2O_3

During the course of the above studies, the possibility was addressed that the site symmetry changes might have nothing to do with the hydration/dehydration procedure and might merely be a consequence of the calcination process itself. If this were true, then simple heating of the commercial oxide should result in the same spectral changes which were described in the preceding sections. It has been determined that simple heating of the commercial oxide has essentially no effect on the surface area of the lanthanide oxides (*15*) or on the catalytic activity of lanthanum oxide. The authors can therefore assign any spectral changes that are observed as being due solely to site symmetry alterations.

The 0 → 0 and 0 → 1 spectra resulting from a series of calcination temperatures are shown in Fig. 10, while analogous spectra associated with the 0 → 2 transition may be found in Fig. 11. It is clear from these spectra that the same spectral changes obtained during dehydration of hydrated Eu_2O_3 are found to occur, with the difference that features attributable to a EuOOH species do not appear in the present se-

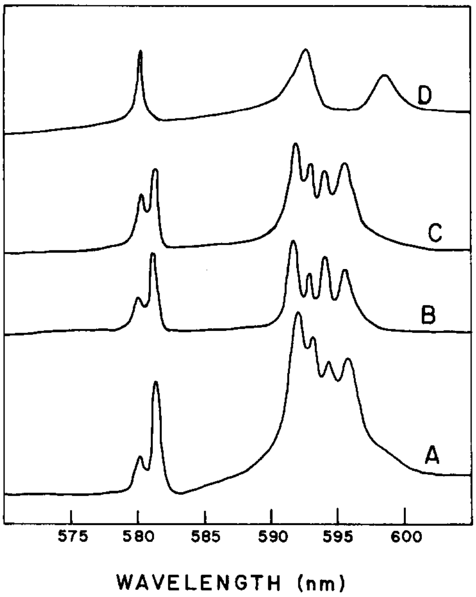

FIG. 10. Luminescence spectra obtained by simple heating of commercial Eu_2O_3. Data are shown for the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ bands, where the sample is unfired (A) and calcined at 375°C (B), 475°C (C), and 600°C (D).

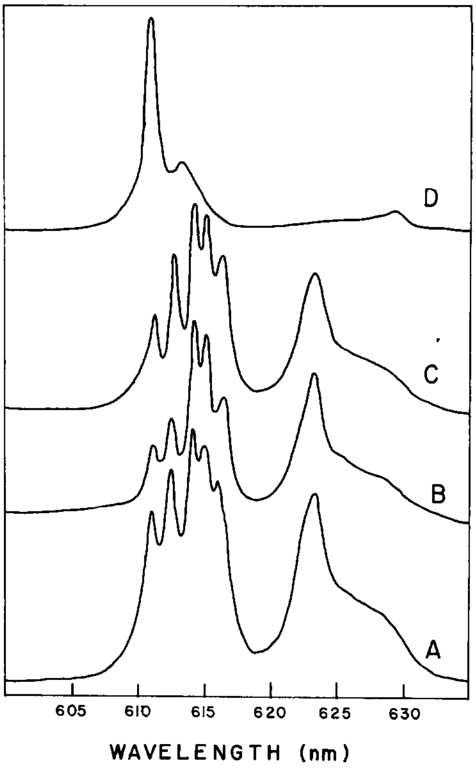

FIG. 11. Luminescence spectra obtained by simple heating of commercial Eu_2O_3. Data are shown for the $^5D_0 \rightarrow {}^7F_2$ bands for unfired material (A), and material calcined at 375°C (B), 475°C (C), and 600°C (D).

quence. These results indicate that it is the heating process which leads to the site symmetry changes and not a change in the morphology of the particles.

CONCLUSIONS

These authors have shown that high-resolution luminescence spectroscopy is a powerful method for the study of site symmetry of europium oxide catalyst materials. While the spectra do not display spectral shifts corresponding to covalent bonding interactions, the effect of the crystal field experienced by the Eu(III) ion is found to be a sensitive parameter detailing the structure of the luminescent metal ion. At the present time, one cannot determine whether one obtains spectra characteristic of the bulk material or the top layers of the oxide. By using low power in the irradiation beam (10 mW), however, it should be possible to restrict the excitation process somewhat. However, in the absence of evidence to the contrary it probably is true that the luminescence technique is reporting data on the bulk structure of the oxide. Given the low concentration of surface sites and the low quantum yield of Eu(III) emission in oxide systems, it is possible that surface Eu(III) sites make only a minor contribution to the observed spectra. Nevertheless, the site symmetry of the Eu(III) is found to be quite dependent on the pretreatment history, and the luminescence method is a potential procedure by which one can outline the properties of various type of metal sites. For reactions which exhibit variable rates and mechanisms dependent on site properties, the luminescence technique can be a very powerful tool for characterization studies.

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