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FTIR AND HIGH-RESOLUTION PHOTOLUMINESCENCE STUDIES OF THE THERMAL DECOMPOSITION OF CRYSTALLINE EUROPIUM HYDROXIDE

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ABSTRACT

The thermal decomposition of crystalline europium hydroxide has been studied by dynamic (differential thermal analysis and thermogravimetry) and static (fourier transform infrared and high-resolution photoluminescence spectroscopies) methods. It was deduced that crystalline europium hydroxide was thermally stable up to 200 ° C, and at 250 ° C decomposed to europium hydroxide (existing in the monoclinic crystal form). The oxyhydroxide was thermally stable between 300 and 350 ° C, but between 400 and 450 ° C decomposed to europium sesquioxide. This phase of the oxide (denoted as the C-phase) was stable between 500 and 900 ° C, but above this temperature evidence was obtained from the luminescence data that conversion to the B-phase was possible.

INTRODUCTION

The production of lanthanide oxides suitable for catalytic use requires the generation of materials having high purity. The thermal decomposition of lanthanide hydroxides offers a particularly convenient route to the production of pure lanthanide oxides suitable for catalytic applications since these can be obtained free from contaminants [1]. The thermal degradation of these materials involves an initial decomposition to an oxyhydroxide species, and further calcination results in formation of the oxide [2]. Due to its particularly simple spectroscopy, the Eu(III) ion serves as an excellent optical probe of site structure, and consequently a detailed study of the thermal decomposition of europium hydroxide would be extremely useful in the study of the calcination pathways. Detailed probing of the thermal decomposition of hydrated europium sulfate [3] and fluoride [4] has been accomplished through studies of the Eu(III) photoluminescence, and analogous work on europium hydroxide forms the basis of the present report.

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EXPERIMENTAL DETAILS

(a) Compound synthesis

Basic hydrolysis of Eu(III) solutions results in the precipitation of europium hydroxide, although the material forms as an amorphous gel unsuitable for luminescence work. The production of crystalline hydroxide powders was effected through procedures similar to those reported previously [5,6]. About 1 mmol of europium nitrate was added to a 15 cm^3 crimp top serum vial together with 5 cm^3 of water. When the salt was dissolved, 7 cm^3 of 7 N ammonium hydroxide was added. A europium hydroxide gel formed immediately. The vial was capped with a Teflon-lined stopper, crimped and shaken to homogenize the gel. The vial and its contents were transferred to a 100 °C oven, and allowed to age for 3–5 days. After 24 hours the gel was observed to break with the formation of small particulates in the vial, and the aging process was ended when the gel was observed to be totally broken into particulate matter. The cap was then removed, and the contents transferred to a 50 cm^3 screw cap centifuge tube. The solid was alternatively centrifuged and suspended in distilled water until the pH of the supernatent was neutral. The precipitate was placed in a vacuum dessicator and dried over indicating calcium chloride at ambient temperature.

(b) Thermal decomposition studies

The thermal decomposition of crystalline europium hydroxide was studied both by dynamic (differential thermal analysis and thermogravimetry) and isothermal (photoluminescence and fourier transform infrared spectroscopies) methods. The DTA and TG analyses were obtained on a DuPont model 951 apparatus. For each determination approximately 20 mg of sample was loaded, and ramped at 10 °C min^{-1} between ambient and 1000 °C. FTIR data was obtained on an Analect model 6160 spectrometer, at a resolution of 4 wavenumbers. The data were obtained on the powdered samples using a diffuse reflectance attachment (the DRIFTS unit, from Spectra-Tech). A sample weighing 5–10 mg was mixed with 400 mg KBr in a laboratory mixer mill, and approximately 350 mg of this blend was used to fill the sample cup. Material which was to be isothermally pretreated was heated in the sample cup, and then returned to the spectrometer.

All luminescence data were obtained on a laboratory-constructed instrument. Samples were excited by the 350 nm output of a 5 W argon ion laser (Coherent Laser, model Innova 90-5), using between 100 and 250 mW of excitation power to observe the various Eu(III) transitions. The emission was collected at right angles to the excitation, and analyzed by a 1 m grating monochromator (Spex Industries, model 1704) at 2 A resolution. The luminescence was detected by an EMI-9558B photomultiplier tube, cooled to −20 °C to reduce dark current and noise. For 77 K work approximately 20–40 mg of sample was contained in 3 mm o.d. quartz tubing, and immersed in liquid nitrogen contained in a suprasil quartz dewar. Spectra were also obtained at 10 K using a gaseous helium refrigator system (Model LTS-21, Lake Shore Cryogenics), where the sample was coated onto a copper block attached to the cold stage.

The most appropriate Eu(III) transitions for structural probing are those of lowest *J* degeneracy. Consequently, all luminescence examined as part of the present work concentrated only on the $^5D_0 \rightarrow {}^7F_0$ (denoted as the 0–0 band and located at 580 nm), the $^5D_0 \rightarrow {}^7F_1$ (denoted as the 0–1 band and located around 595 nm) and the $^5D_0 \rightarrow {}^7F_2$ (denoted as the the 0–2 band and located around 615 nm). The maximum number of luminescence bands which could exist in the lowest symmetry would be one for the 0–0 band, three for the 0–1 band system, and five for the 0–2 band system. In higher symmetries (anticipated for the Eu(III) compounds formed as part of the thermal decomposition of europium hydroxide), fewer bands than the maximum should be observed. Knowledge of the splitting patterns and group theoretical principles enables the deduction of Eu(III) site symmetries.

RESULTS AND DISCUSSION

The thermal decomposition of europium hydroxide is known to proceed through two discrete steps [2]. The first of these involves formation of europium oxyhydroxide:

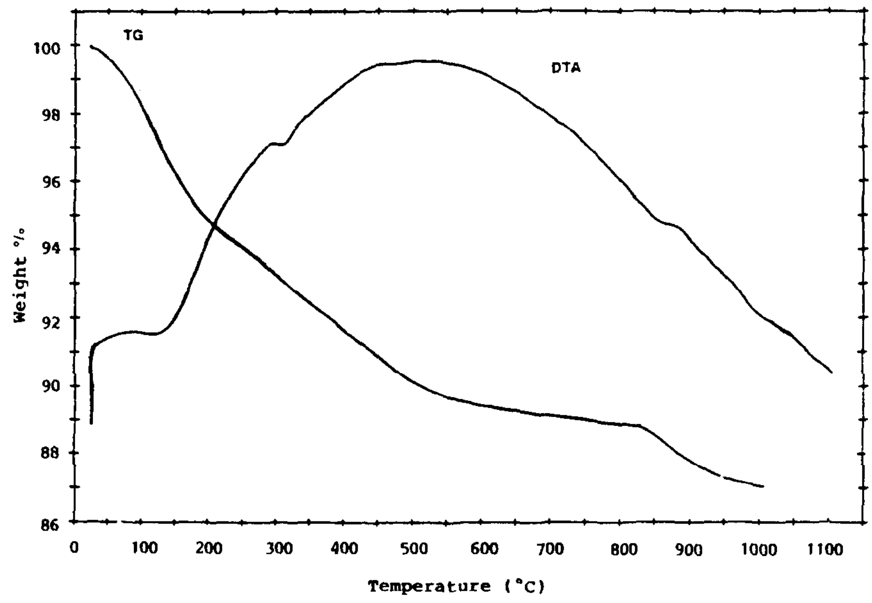
$$\mathrm{Eu(OH)_3 \rightarrow EuOOH + H_2O} \qquad (1)$$

and the second step involved final decomposition to the sesquioxide:

$$\mathrm{2\ EuOOH \rightarrow Eu_2O_3 + H_2O} \qquad (2)$$

The quality of the thermal data is particularly dependent on the degree of crystallinity of the europium hydroxide used. In Fig. 1, TG and DTA thermograms are shown for the decomposition of dried gel and for precipitate which had been hydrothermally aged. It is clear that the amorphous gel does not yield any detail in the thermograms, while the crystalline material exhibits well defined thermal events corresponding to eqns. (1) and (2). The formation of the oxyhydroxide would be accompanied by a weight reduction to 91.1%, while the formation of the sesquioxide would require a final weight reduction to 86.7%. These are exactly the weight loss quantities evident at the TG plateaus.

It is concluded from the DTA and TG data that decomposition of the trihydroxide to the oxyhydroxide begins at 275 °C, and is essentially complete by 350 °C. Decomposition of the oxyhydroxide begins at 425 °C, and is complete by 475 °C.



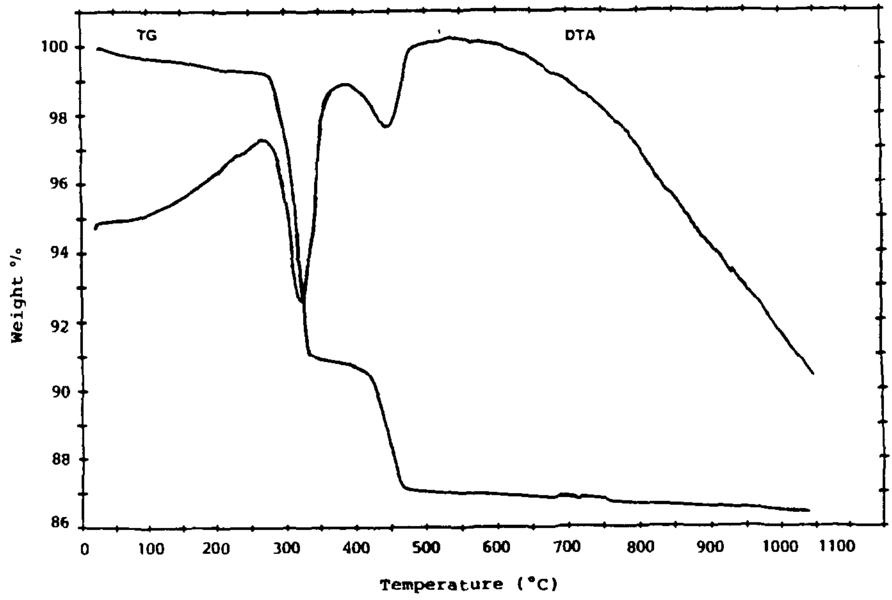


Fig. 1. DTA and TG traces for amorphous europium hydroxide gel (upper thermograms) and for crystalline europium hydroxide (lower thermograms). The crystalline material was obtained through hydrothermal aging at pH = 9.5.

The infrared spectrum of europium trihydroxide is shown in Fig. 2. The amorphous gel yielded very broad featureless spectra, which mainly indicated water/hydroxide absorption around 3500 cm^{-1}. The FTIR spectrum

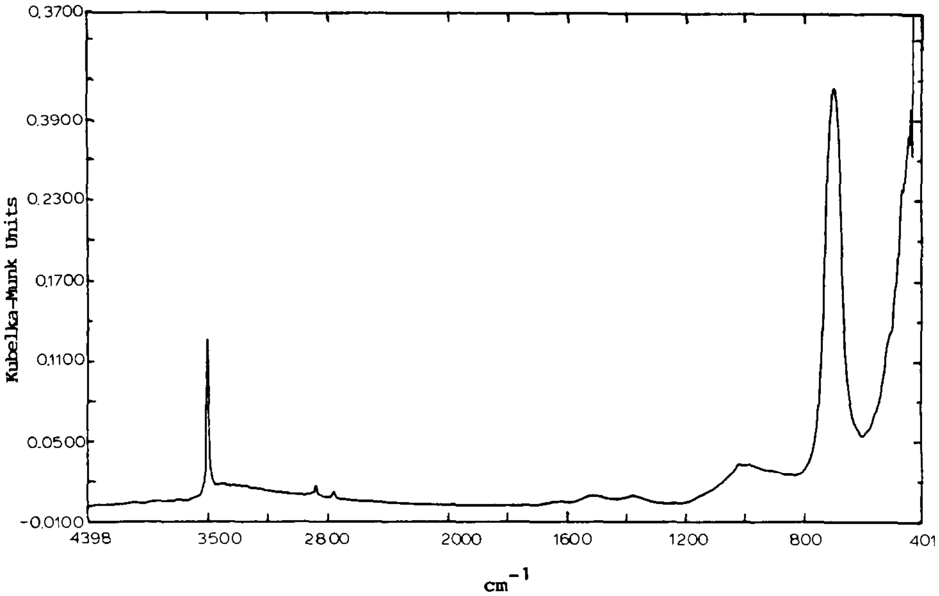


Fig. 2. Diffuse reflectance FTIR spectrum of crystalline europium hydroxide.

of crystalline europium hydroxide (contained in Fig. 2) consists of two sharp bands. The low energy band at 695 wavenumbers) corresponds to the –OH bending mode, while the 3595 wavenumber band corresponds to the –OH stretching mode. These observations are consistent with dispersive IR and raman studies on the lanthanide hydroxides [7].

The luminescence spectrum of Eu(III) normally consists of relatively few sharp lines, as long as this ion is located at well defined crystalline sites of a single structural type [8]. The luminescence spectra obtained from heterogeneous Eu(III) compounds invariably consist of broad bands, from which structural information is unavailable. The effect of sample aging on the crystallinity of europium hydroxides is shown in Fig. 3. The spectra of the dried gel are broad, and consist of many more peaks than would be allowed in even the lowest symmetry crystal fields. Aging the precipitate around neutral pH sharpens up the spectra considerably, therefore indicating the presence of greater crystallinity. The most crystalline material was obtained by aging the precipitates at pH 9.5. No 0–0 Eu(III) peak could be noted at its anticipated position of 580 nm, but two 0–1 peaks were observed at 592 and 595 nm, and a single 0–2 peak was observed at 618 nm.

The crystal structure of europium hydroxide has been determined, and it is known that it belongs to the hexagonal P63/m space group [9]. In this structure the metal ion is nine-coordinate, occupying a site which has approximately D_{3h} symmetry. Forsberg [10] has shown that D_{3h} symmetry, the splitting pattern observed in Fig. 3 is exactly that which should be observed for the 0–1 and 0–2 transitions.

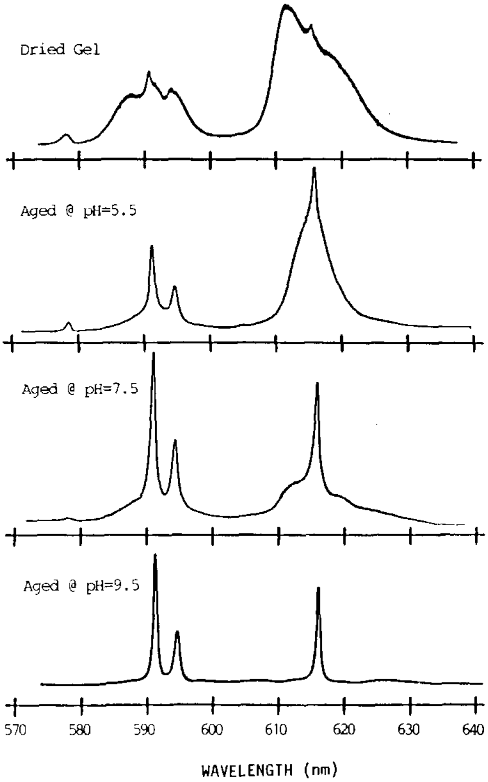


Fig. 3. Luminescence spectra of europium hydroxide precipitates aged under various pH conditions: (a) dried amorphous gel, (b) gel aged at pH = 5.5, (c) gel aged at pH = 7.5, and (d) gel aged at pH = 9.5. Data are illustrated for the 0–0, 0–1 and 0–2 Eu(III) emissive transitions.

More detailed probing of the thermal decomposition of europium hydroxide was obtained by obtaining spectral characterization of material heated under isothermal conditions. Since Eu(III) luminescence spectra are most suited for structural characterization (especially when the crystallinity of the sample is low), these results will be described first. The 0–0 and 0–1 Eu(III) spectra are shown in Fig. 4, while the 0–2 spectra are shown in Fig. 5. Heating of the initial crystalline hydroxide to 200 °C does not produce any Eu(III) site symmetry changes, thus indicating that no alteration in the metal ion inner coordination spheres has taken place. This of course implies that no thermal decomposition of the material has taken place. At 250 °C new spectral peaks appear, and a new pattern is established at 300 °C. This spectral pattern persists up to 350 °C, and comparison with the literature data on EuOOH [11,12] indicates that the europium oxyhydroxide formed at this temperature region is formed in the monoclinic phase.

Continued heating at 400 and 450 °C yielded complicated spectra indicative of new decompositions. These become established at 500 °C, where a

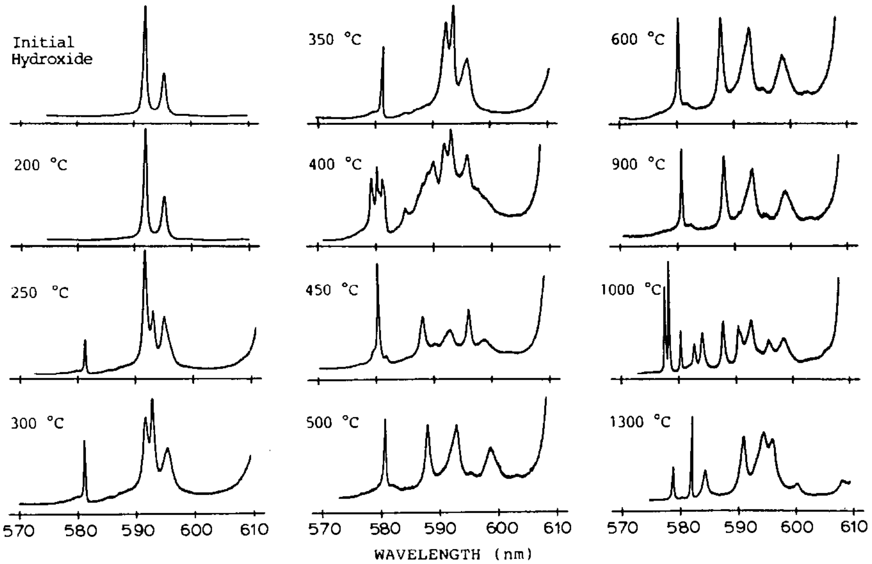


Fig. 4. Luminescence spectra obtained for crystalline europium hydroxide, heated isothermally at the indicated temperature values. Data are illustrated for the 0–0 and 0–1 Eu(III) emissive transitions.

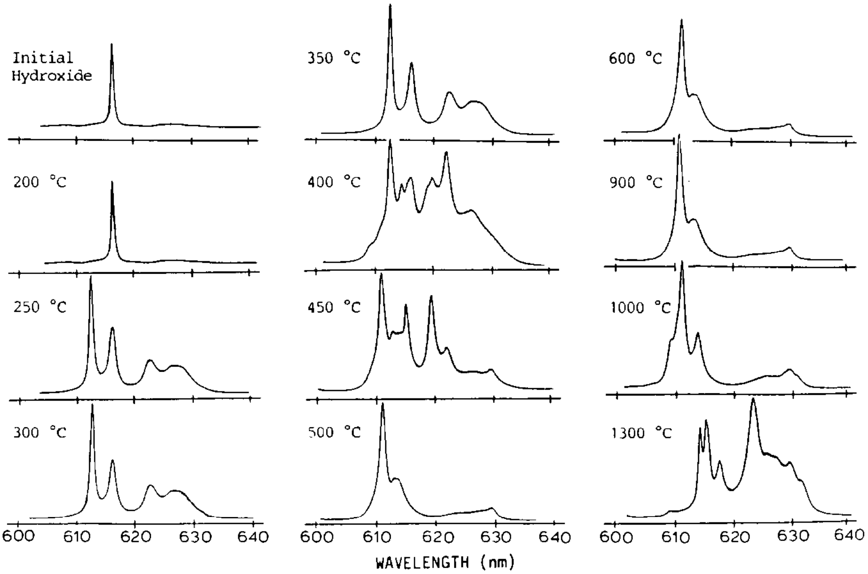


Fig. 5. Luminescence spectra obtained for crystalline europium hydroxide, heated isothermally at the indicated temperature values. Data are illustrated for the 0–2 Eu(III) emissive transition.

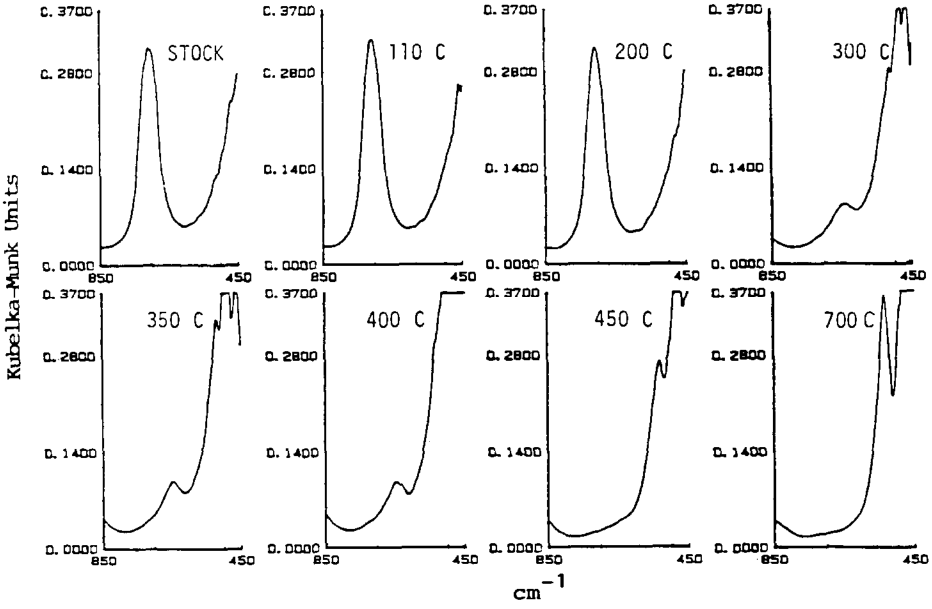


Fig. 6. Diffuse reflectance FTIR spectra measured for crystalline europium hydroxide, heated isothermally at the indicated temperature values. Data are illustrated for the –OH bending mode.

spectral pattern identical with that of the sesquioxide [13] appears. This pattern persists unchanged up to 1000 °C, where a large number of new spectral bands appear. This shift corresponds to formation of the high-temperature europium oxide phase, which is also well known [14]. These changes are consistent with those observed during the dynamic experiments, indicating that data obtained from the isothermal experiments may be correlated with the conventional DTA and TG results.

FTIR spectra obtained within the same temperature regions may be interpreted in the same fashion. The temperature dependence associated with the –OH bending mode of crystalline europium trihydroxide is shown in Fig. 6, while analogous studies of the –OH stretching mode are shown in Fig. 7. Both modes are prominant in the starting material, but decrease greatly in intensity upon formation of the oxyhydroxide. Continued heating of the material to produce the oxide results in the complete loss of bands assignable to either –OH bending or stretching modes. The temperatures at which these bands are lost correlates with the luminescence data.

CONCLUSIONS

The isothermal calcination of europium hydroxide represents the situation most closely approximating equilibrium conditions for thermal decomposi-

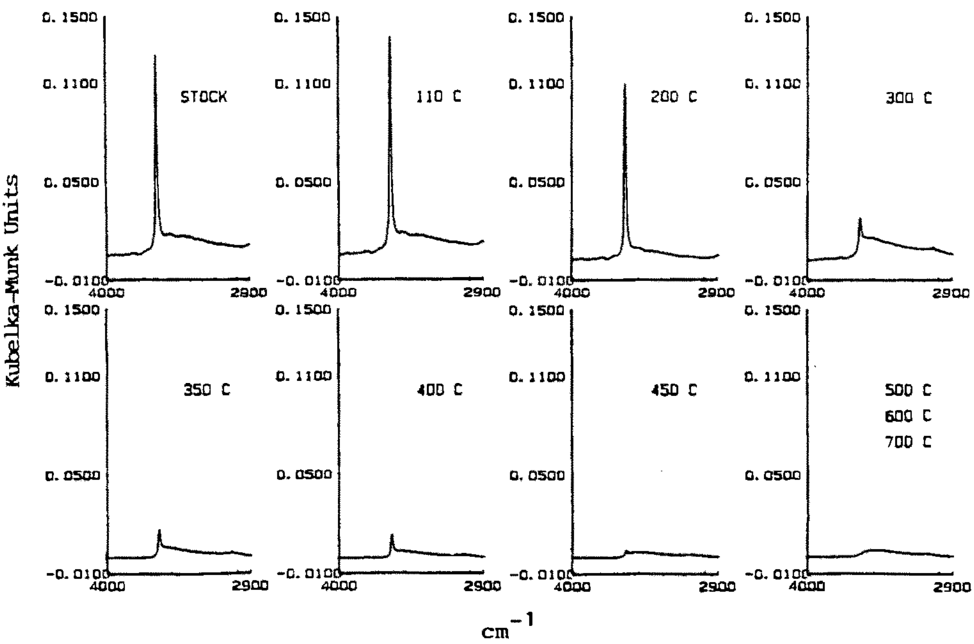


Fig. 7. Diffuse reflectance FTIR spectra measured for crystalline europium hydroxide, heated isothermally at the indicated temperature values. Data are illustrated for the –OH stretching mode.

tion. The dynamic experiments would yield identical temperature data only if they were obtained at sufficiently slow ramping rates so as to be considered at complete equilibrium. The isothermal spectral studies may therefore be assumed to yield information which contains less dependence on the kinetics of the decompositions. The FTIR and luminescence data are consistent with the following series of thermal decomposition pathways:

25–200 °C	stability region for $Eu(OH)_3$
250 °C	decomposition of $Eu(OH)_3$ to EuOOH
300–350 °C	stability region for EuOOH
400–450 °C	decomposition of EuOOH to Eu_2O_3
500–900 °C	stability region for the B-phase of Eu_2O_3
1000 °C	transition to the C-phase of Eu_2O_3

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