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LUMINESCENCE STUDIES OF THORIUM HYDROLYSIS PRODUCTS

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ABSTRACT

Raising the pH of an aqueous solution of thorium nitrate results in the precipitation of a hydrated thorium oxide, rather than in the generation of a hydroxide species. At room temperature, this material does not exhibit any emissive properties, but upon cooling to 77 °K a strong green luminescence can be observed. The emission spectrum is fairly broad and is characterized by an emission lifetime of 125 usec. Emission from a thorium hydrolysis product has not hitherto been reported in the literature. Calcination of this material at 800 °C for three hours produces thorium dioxide after dehydration of the hydrolysis product, and this material does not exhibit any luminescence properties at any temperature.

The nature of the luminescence associated with the thorium hydrolysis product was further investigated by examining the emission of a series of mixed-hydrolysis products. It was found that the coating of hydrolyzed thorium onto silica resulted in the production of the emission, but that precipitation from a mixed Th/La solution yielded hydrolysis products which only exhibited luminescence at low La concentrations. Precipitation from mixed Th/Gd solutions yielded material which could emit over much wider ranges of Th concentration. Finally, production of the mixed Th/Eu product enabled the demonstration that excitation energy could be transferred to the Eu ion, resulting in enhanced emission from this species. These observations lead one to conclude that the green Th emission is due to luminescence associated with an inorganic eximer. Separation of the Th centers (by bulky La ions, or less bulky Gd ions) eliminates the luminescence in a manner not linear with concentration, and the emission lifetime associated with the green emission also does not vary in a linear manner.

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INTRODUCTION

Thorium dioxide, ThO_2 , is normally obtained by ignition of the hydrated oxide, which is in turn prepared by the addition of hydroxide ion to an aqueous Th(IV) solution. While the photoluminescence of a variety of ions may be sensitized upon substitution into ThO_2 , the actual host itself displays no intrinsic luminescence. Any emission which has been obtained has been shown to arise from the presence of trace impurities or in the defect structure associated with crystalline material [1].

Little work has focused on the possible luminescent properties of the hydrolysis products. In the present work, it has been determined that while hydrated ThO_2 exhibits no emission at room temperature, cooling to cryogenic temperatures resulted in the observation of relatively strong photoluminescence. This emission was not found to result from the presence of impurities, and is observed only from the hydrolysis product.

EXPERIMENTAL

Aqueous solutions of thorium and lanthanide nitrates were used to prepare a variety of pure and mixed hydrolysis products. These materials were generally of 99.99% purity, and only quartz-distilled water was used as a solvent. All hydrolyses were effected by the addition of NaOH. The hydrolysis products were merely air-dried and not calcined.

All spectra were obtained on a high-resolution emission spectrometer constructed in our laboratory. Samples were excited by the 325 nm output (10 mW) of a He-Cd laser, and the emission was analyzed at 4 Å resolution by a 1-meter

grating monochromator (Spex Model 1704). The emission was then detected by a cooled photomultiplier tube (S-20 response), and processed through the Spex digital photometer. In all work, the sample temperature was 77 °K, with the hydrolysis products being contained in a suprasil quartz tube immersed in liquid nitrogen.

Emission lifetimes were obtained by exciting the samples with a nitrogen laser having a 300 psec pulsewidth. The luminescence decay curves were obtained by photographing the decay curves as displayed on a storage oscilloscope, and these were analyzed by a least-squares method. In these experiments, the current output of the photomultiplier tube was converted to a voltage signal through the use of a 200 K load resistor. Given the 47 pf input capacitance of the oscilloscope, the system was calculated to exhibit an inherent 10 µsec RC time constant. However, all the measured lifetimes were at least 10 times longer than that of the system time constant, and thus no correction had to be made for system response.

RESULTS AND DISCUSSION

a. Pure Th(IV) Hydrolysis Products

Hydrolysis of an aqueous solution of Th(IV) yields an insoluble material which does not appear to consist of a simple hydroxide. Rather, the isolated substance can best be described as being a hydrated oxide [2]:



At room temperature, this material was not found to exhibit any luminescence, but after cooling to 77 °K UV excitation led to the observation of reasonably

strong green emission. An example of the luminescence spectrum may be found in Figure 1.

The emission at cryogenic temperatures was definitely structured. Well-defined peaks were found at 5129 Å ($19,497 \text{ cm}^{-1}$) and 5303 Å ($18,857 \text{ cm}^{-1}$), and a shoulder was noted at 549 nm ($18,215 \text{ cm}^{-1}$). The placement of these bands was found to be invariant with the conditions associated with production of the hydrolysis product and with the source of the Th(IV) used for the preparation. Reagent grade $\text{Th}(\text{NO}_3)_4$ from a variety of sources yielded hydrolysis products whose luminescence spectra were identical to those prepared from sources of higher purity.

Interestingly, the spacing between the three luminescence peaks just mentioned was found to be a constant quantity (640 cm^{-1}). The emission lifetimes obtained at emission wavelengths corresponding to peak maxima were all found to be identical to within experimental error (120 μsec). These observations suggest that the three peaks are due to emission from the same thorium species and represent a vibronic progression corresponding to a ground state vibration.

b. Mixed Th(IV)/La(III) and Th(IV)/Gd(III) Hydrolysis Products

Since the Th(IV) ion does not contain any spectroscopic states capable of leading to intrinsic photoluminescence, some sort of cooperative phenomena between Th(IV) centers probably led to the observed green emission. To test this hypothesis, a series of hydrolysis products was prepared in which Th(IV) was hydrolyzed in the presence of either La(III) or Gd(III). Neither lanthanide ion possesses any low-lying excited states, and thus could not act as

traps for the excitation energy. But if the lanthanide ions could effect a greater separation of the thorium centers, then the observed luminescence ought to have decreased with increasing lanthanide ion concentration.

Such a decrease in the luminescence associated with the thorium hydrolysis products was actually observed, as is illustrated in Figure 2. Interestingly, the decrease in emission intensity was not found to be linear with concentration. Such behavior clearly indicated the existence of cooperative behavior and provided confirming evidence that the origin of the luminescence of the thorium hydrolysis products originated in a pair interaction.

It was observed that coprecipitation of La(III) or Gd(III) hydroxides with the thorium hydrolysis product did not lead to equivalent quenching rates. Relatively small amounts of La(III) led to total loss of thorium luminescence, but appreciably larger quantities of Gd(III) could be tolerated. This effect may be related to the different ionic sizes of the various ions: assuming a coordination number of 8 for each ion, one finds that $\text{Th(IV)} = 1.19 \text{ \AA}$, $\text{La(III)} = 1.30 \text{ \AA}$ and $\text{Gd(III)} = 1.19 \text{ \AA}$ [3]. It is significant to observe that it was the largest ion which perturbed the luminescence to the greatest extent. Thus, one could conclude that in the formation of the mixed hydrolysis products, the Th(IV) centers became separated by the lanthanide complexes and were prevented from interacting.

While the emission intensities associated with the thorium emission were found to decrease with increasing amounts of lanthanide ion, the emission lifetimes remained essentially unchanged from the 120 μsec value. This behavior

was noted with both La(III) and Gd(III), and was good evidence that the luminescence quenching was purely static in nature. Standard Stern-Volmer kinetics described by the equation

$$\frac{I_0 - I}{I} = K_{sv} [Q] \quad (2)$$

could not be applied to the quenching data, since molar concentrations of the La(III) and Gd(III) species could not be determined. In Equation (2), I_0 is the emission intensity of the pure thorium hydrolysis product, I is the resulting intensity at a quencher concentration $[Q]$, and K_{sv} is the Stern-Volmer quenching constant. One can, however, evaluate $(I_0 - I)/I$ as a function of the percentage of La(III) and Gd(III) present, and this has been done in Table 1. These values clearly do not follow any simple linear relationship. Taken with the trends of the preceding work, the quenching results provide further evidence for the presence of cooperative phenomena in the thorium hydrolysis products.

c. Th(IV)/silica Hydrolysis Products

Another experiment was carried out to learn more about the nature of the thorium hydrolysis products. Hydrolysis of a Th(IV) solution was conducted in a solution in which silica gel had been suspended. Through this procedure, the thorium hydrolysis product could be coated onto the silica particles (as opposed to the intimate mixture obtained with the lanthanide systems). As before, no emission could be observed at room temperature, but after cooling to 77 °K, luminescence identical in bandshape to that presented in Figure 1 was obtained. The luminescence maxima essentially coincided with those

mentioned earlier, and they were found to be separated by an equivalent vibronic spacing. The only difference which could be observed was that the luminescence lifetime of hydrated thorium oxide coated onto silica was found to be 185 μ sec.

d. Th(IV)/Eu(III) Hydrolysis Products

The photoluminescence of Eu(III) doped into a ThO₂ host has been actively studied in the past [4-6], and chemiluminescence produced during the course of catalytic reactions has proved useful in the study of reaction mechanisms [7]. However, in all of these studies the materials were calcined at elevated temperatures before the examination of the luminescence. In this work, a series of mixed hydrolysis products containing Th(IV) and Eu(III) has been prepared, and the luminescence of these samples was obtained at 77 °K.

In Figure 3, the luminescence spectrum of the 88%:12% Th/Eu hydrolysis product is shown and one may easily note the characteristic Eu(III) sharp-line spectrum (beginning at 580 nm) superimposed on the spectrum of the emitting species. The luminescence spectrum of a pure Eu(III) hydrolysis product at 77 °K does not resemble that shown in Figure 3; no fine structure can be observed in the emission of pure Eu(OH)₃. Calcining the mixed hydrolysis product for 3 hours at 800 °C resulted in the production of a material which exhibited no thorium luminescence. In the calcined samples only, the Eu(III) luminescence could be observed, and the emission patterns strongly resembled those reported by Linares [4].

The spectrum of Eu(III) in the hydrolysis products is quite different from that obtained in the calcined samples. The presence of one band in the $5D_0 \rightarrow 7F_0$ band region (580 nm) and three bands in the $5D_0 \rightarrow 7F_1$ band system (595 nm) indicated that the symmetry of the Eu(III) ion in the hydrolysis product was probably quite low. The featureless nature of the emission obtained from the pure Eu(III) hydrolysis product prevented a determination of the metal ion site symmetry in this compound. One may then conclude that in the mixed Th(IV)/Eu(III) hydrolysis products, the Eu(III) ion had been forced to occupy a site dictated by the nature of the hydrated ThO_2 . This observation provided additional evidence for the previous contention that substitution of La(III) and Gd(III) into the Th(IV) hydrolysis product effected a separation of the thorium centers.

The dependence of thorium emission intensity and lifetime on europium concentration provides information on the nature of the Th-Eu interaction. Values for both quantities (as a function of Eu(III) concentration) have been plotted in Figure 4. Both Eu(III) and Gd(III) are essentially the same size, and one notes that at low Eu(III) concentrations, the thorium emission decreased at exactly the same rate as when Gd(III) was coprecipitated with the Th(IV). At the same time, the luminescence lifetime of the Th(IV) emission did not decrease from 120 μsec . However, above 12% Eu(III), the similarity ended. The intensity quenching rate with Eu(III) decreased quite rapidly, and the emission lifetime decreased in magnitude. The lifetime result was especially striking, as in the La(III) and Gd(III) mixed hydrolysis products; the thorium lifetime was constant as long as the emission could be observed.

These differences provide strong evidence that at moderate Eu(III) concentrations, a second quenching mode comes into play. This new mode would involve energy transfer from the luminescent thorium centers to the Eu(III) quencher species. Below the critical Eu(III) concentration (found to be approximately 12%), the Eu(III) ion merely acts as a spacer ion in the same manner as do La(III) and Gd(III). It is interesting to note that the emission lifetime of the Eu(III) species was approximately constant at 250 μ sec, regardless of the process by which the thorium centers were quenched.

CONCLUSIONS

In the course of the present work, it has been determined that luminescence intrinsic to paired Th(IV) centers may be observed at cryogenic temperatures in hydrated ThO₂. Dehydration of this material (through calcination) causes total loss of this luminescence. Through studies on mixed hydrolysis products, it was demonstrated that spatial separation of the thorium centers would result in quenching and eventual loss of the emission. Thin films of the hydrated ThO₂ product onto silica particles were also found to exhibit the photoluminescence. Finally, Eu(III) luminescence may be sensitized via energy transfer from the thorium centers, but this process requires significant quantities of Eu(III) in the hydrolysis product.

One final note concerns the nature of the clustered thorium species responsible for the emission observed at cryogenic temperatures. A fairly extensive series of mononuclear and polynuclear species have been proposed [8-12], although the [Th₂(OH)₂]⁶⁺ and [Th₆(OH)₁₅]⁹⁺ species seem to have been postulated to the highest degree. In a very recent study of the hydrolysis of

Th(IV) in potassium nitrate, analysis of the titration data (using the MINIQUAD program) has indicated that the only acceptable model involves $[\text{Th}(\text{OH})]^{3+}$, $[\text{Th}_4(\text{OH})_{12}]^{4+}$, and $[\text{Th}_6(\text{OH})_{15}]^{9+}$ [13]. That a dependence should exist in the nature of the hydrolysis products with the identity of the counterion appears to be a given fact. The luminescence results cannot determine the chemical composition of the precipitated solid, but the results definitely illustrate the polymeric nature of the material.

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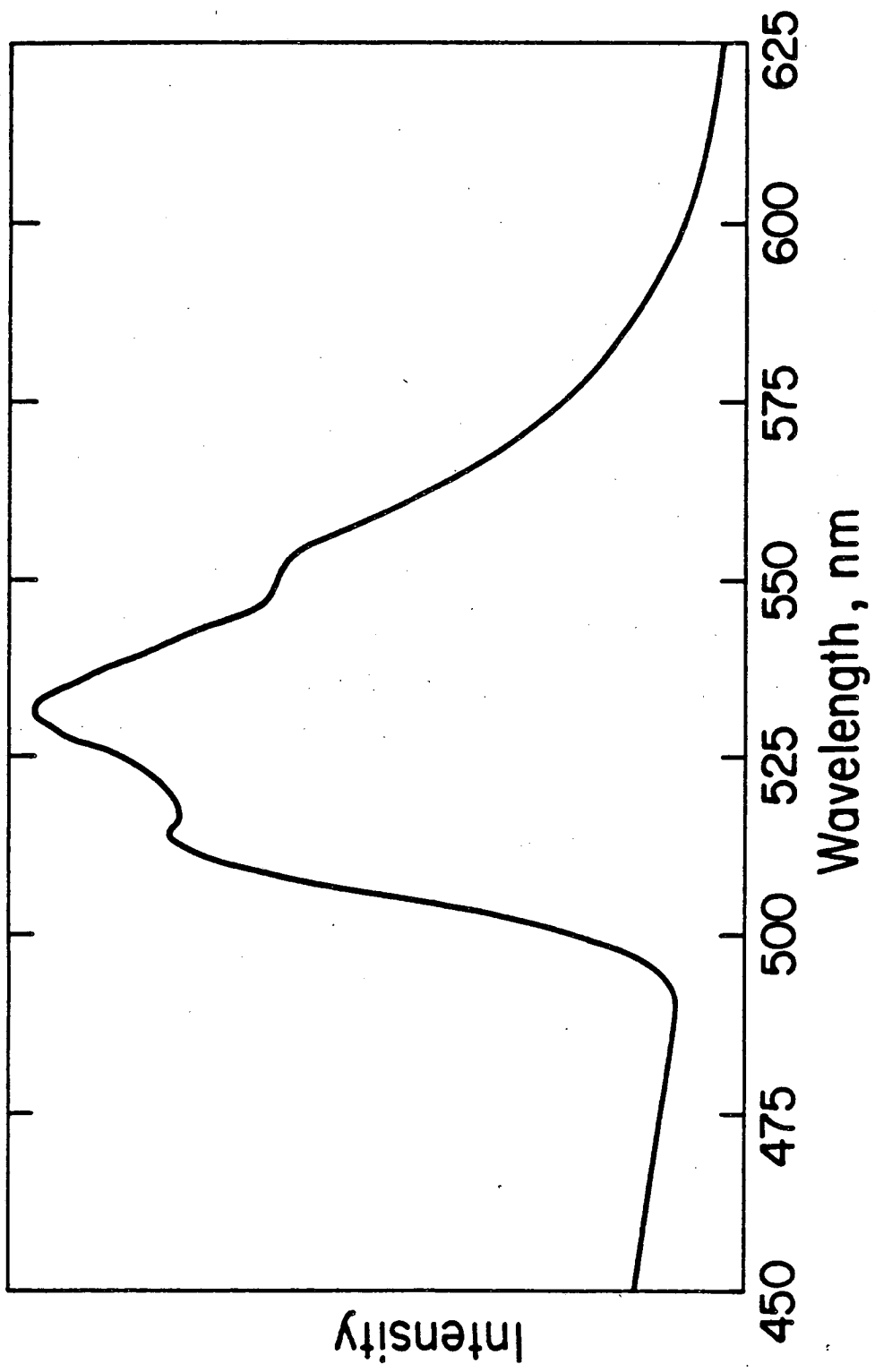
Table 1. Stern-Volmer Quenching Kinetic Data Obtained in the Mixed Hydrolysis Products.

% Lanthanide ion	$\frac{I_0 - I}{I}$ (a)	$\frac{I_0 - I}{I}$ (b)
0	0.00	0.00
2	0.48	0.10
4	1.93	0.21
6	4.51	0.34
8	10.3	0.48
10	20.3	0.62
12	33.0	0.77
14	55.7	0.95
16	84.0	1.13
18	169.0	1.30
20	(c)	1.46

Notes: (a) Data obtained on the Th(IV)/La(III) hydrolysis products.

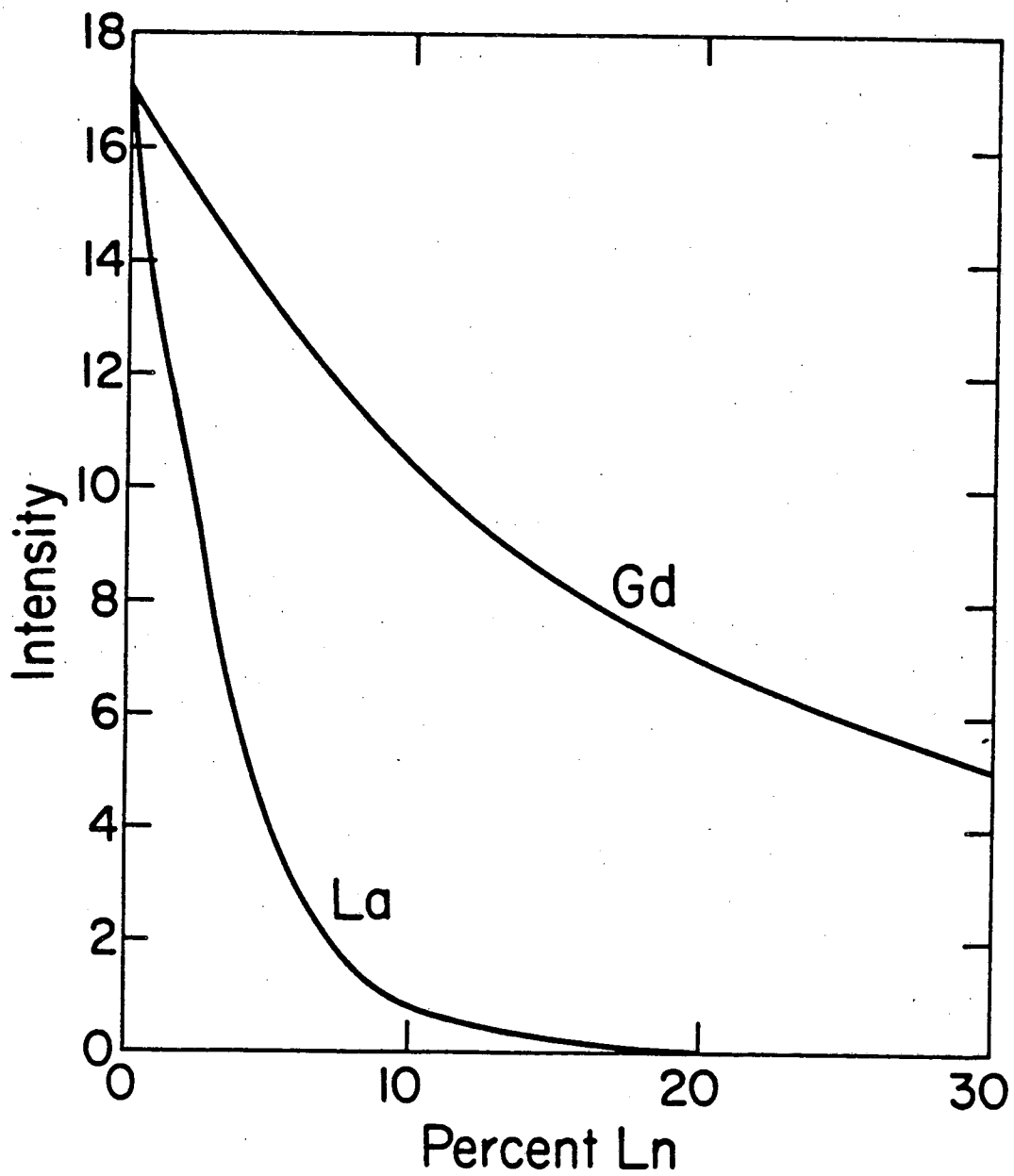
(b) Data obtained on the Th(IV)/Gd(III) hydrolysis products.

(c) No value could be calculated as the Th emission was undetectable.



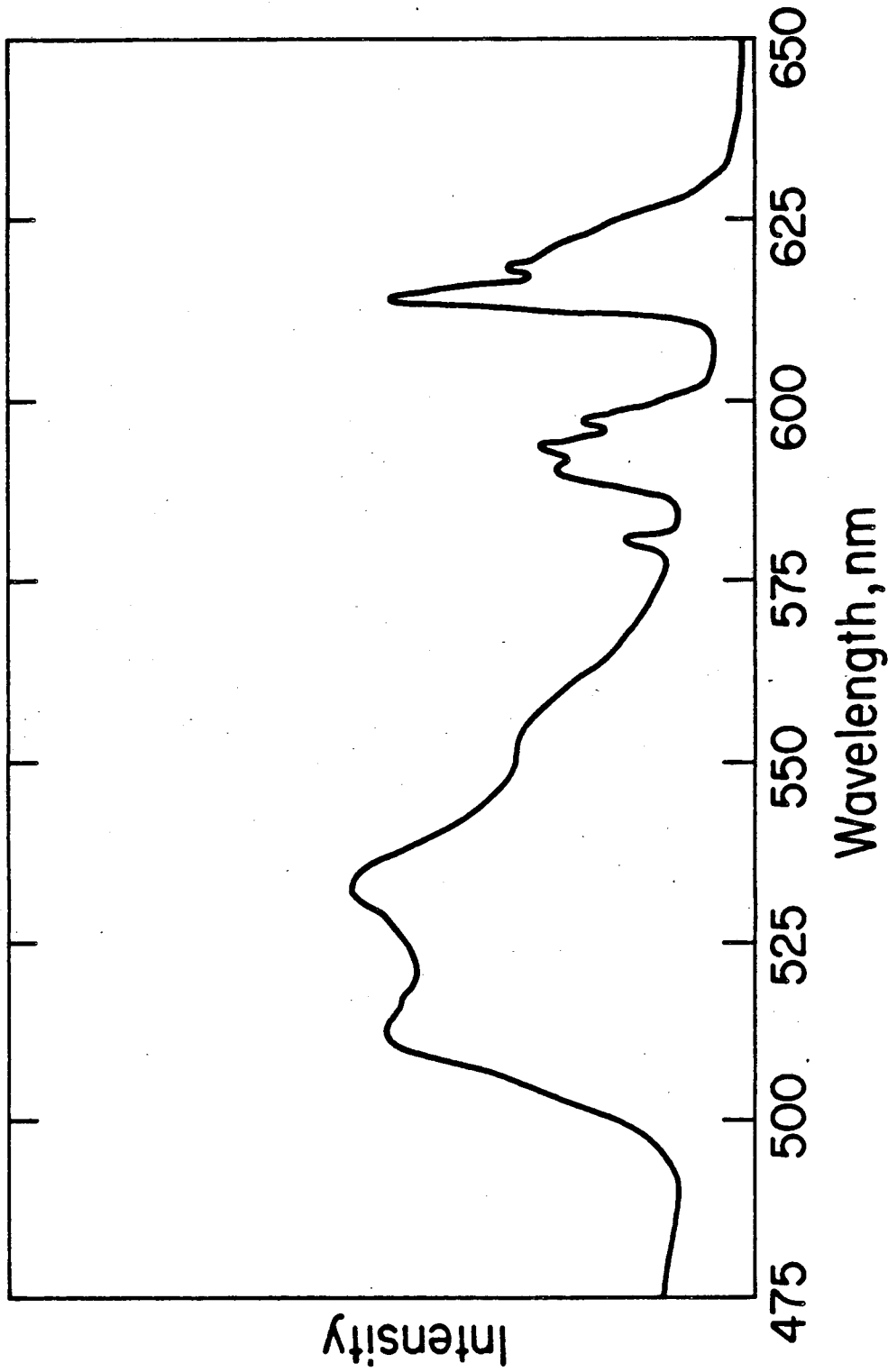
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Figure 1. Photoluminescence spectrum of the material obtained through hydrolysis of aqueous solutions of Th(IV). The spectrum was obtained at 77 °K, and the intensity scale is purely arbitrary.



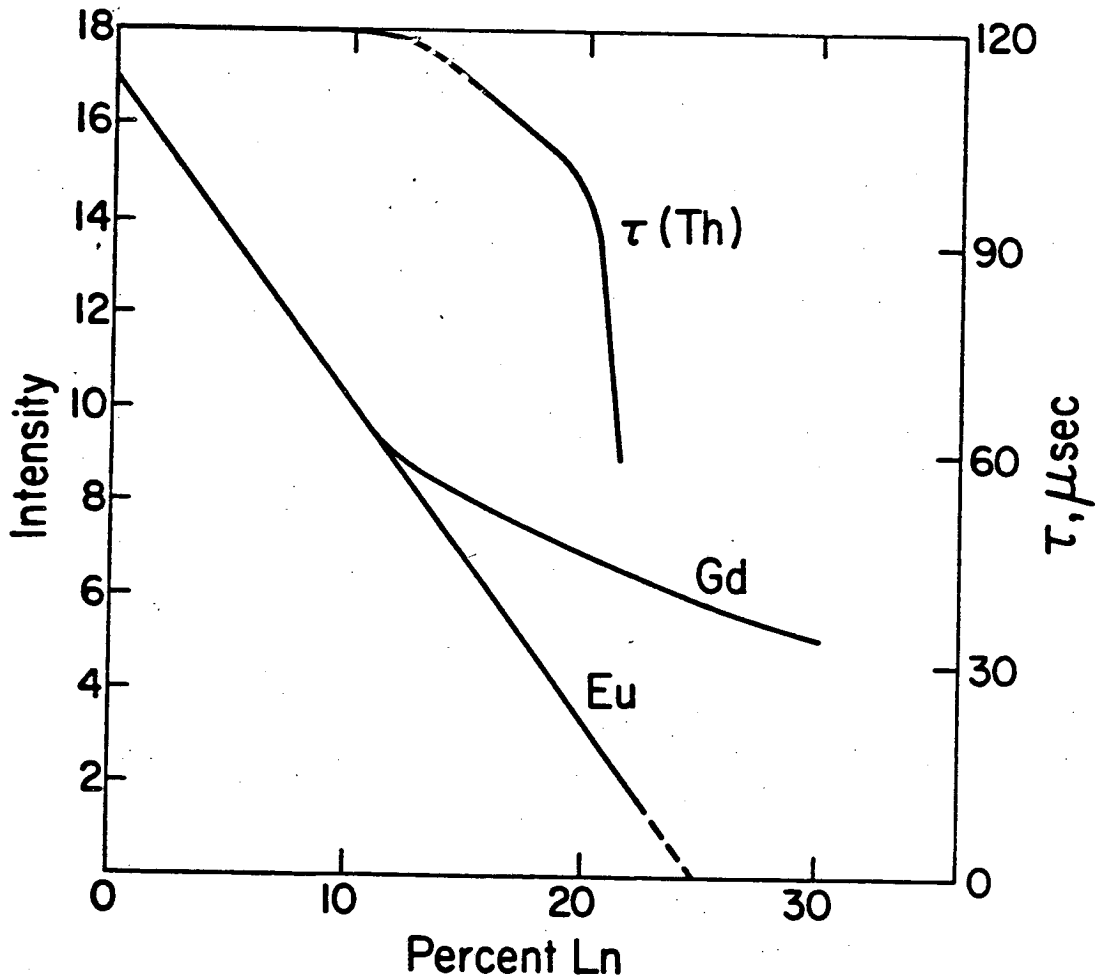
XBL 832-1708

Figure 2. Decrease in luminescence intensity of the thorium hydrolysis product caused by coprecipitation of $\text{La}(\text{OH})_3$ and $\text{Gd}(\text{OH})_3$.



XBL 832-1709

Figure 3. Photoluminescence spectrum of a mixed thorium/europium hydrolysis product, obtained at 77 °K. The material used to produce this spectrum contained 88% Th(IV) and 12% Eu(III).



XBL 832-1710

Figure 4. Perturbations in the emissive properties of the thorium hydrolysis product caused by coprecipitation of $\text{Eu}(\text{OH})_3$. The decrease in thorium emission (solid line) as a function of $\text{Eu}(\text{III})$ concentration correlates with the left-hand scale, and the data obtained in similar experiments with $\text{Gd}(\text{OH})_3$ are shown for convenience. The dependence of the thorium emission lifetime (dashed line) correlates with the scale on the right-hand side of the figure.

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