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LUMINESCENCE STUDIES OF THE THERMAL DEHYDRATION OF EUROPIUM TRIFLUORIDE

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ABSTRACT

The thermal dehydration of hydrated europium trifluoride has been followed by high-resolution luminescence spectroscopy and thermogravimetric analysis. For EuF_3 precipitated by aqueous HF, it was determined that the bound water of hydration actually existed in two forms, which were removable at low (100–250°C) and high (350–550°C) temperatures. Calcination of this material at still higher temperatures produced anhydrous EuF_3 contaminated by EuOF. Precipitation of EuF_3 by NH_4F resulted in the occlusion of variable amounts of ammonium fluoride, but in these materials only the low-temperature water was contained. Extensive ethanol washing of the NH_4F-precipitated EuF_3 led to removal of the ammonium fluoride, but this hydrated material was not found to contain the high-temperature water. Neither material prepared by NH_4F precipitation exhibited any tendency towards EuOF formation. It would thus appear that the EuOF compound is formed only during the loss of the high-temperature water, and if this water is not present in the sample then one may form anhydrous EuF_3 free from EuOF contamination.

INTRODUCTION

Lanthanide trifluorides are of extreme commercial importance in that these materials may be used to produce pure lanthanide metals subsequent to a metallothermic reaction [1]. Several different preparative routes to the anhydrous lanthanide trifluorides are known [2]. They can be obtained from the reaction of anhydrous HF with the sesquioxides at 700°C, or by direct fluorination of the oxides. An alternative method is to react the sesquioxide with ammonium fluoride at 200–300°C, followed by sublimination of the excess reagent at elevated temperatures.

It is far easier to prepare anhydrous lanthanide fluorides via an aqueous preparation, with the desired product being obtained after dehydration of these materials. In these dehydrations, the occluded water must be removed at low temperatures in an inert atmosphere or in vacuum to avoid produc-

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tion of the oxyfluoride [3]. The hydrated lanthanide fluorides may be prepared through precipitation with either aqueous HF or NH_4F [4–7], although the products obtained with each method vary. The use of aqueous HF results in the production of pure $LnF_3 \cdot 0.5H_2O$. This material is difficult to dehydrate to the pure anhydrous fluoride, since formation of LnOF materials is facile. Precipitation with aqueous NH_4F yields a mixed salt containing hydrated trifluoride and ammonium fluoride [4,7]. However, this material may be dehydrated in vacuum (followed by sublimination of the NH_4F) to yield an anhydrous fluoride in which LnOF contamination has been minimized.

In the present work, we have used the intrinsic luminescence associated with the Eu(III) ion as a means for the characterization of europium trifluorides obtained through both preparative routes. In addition, we have used a combination of conventional thermal techniques together with luminescence spectroscopy in order to study the dehydration pathways of the hydrated europium trifluorides.

EXPERIMENTAL

Anhydrous EuF_3 (99.5% pure) was obtained from Alfa/Ventron. Hydrated EuF_3 was prepared by precipitation from an aqueous nitrate solution using either aqueous HF (Baker reagent grade) or aqueous NH_4F (Fischer Scientific). The precipitates were boiled in CO_2-free water for 1 h, and recovered on sintered glass filters. Precipitates prepared in this manner were dried to constant weight in a vacuum dessicator. EuOF was prepared by pyrohydrolysis of hydrated EuF_3 in a tube furnace at 950°C. Calcinations were performed under isothermal conditions, with solid samples being sealed in evacuated glass capillary tubes for spectral analysis.

Thermogravimetric analyses were performed on a DuPont thermal analyzer (model 951). The analysis was performed in a stream of air at 50 cm^3 min^{-1}, and the temperature was ramped at 20°C min^{-1}. The typical starting temperature was 25°C, and the final temperature was instrumentally limited to 750°C.

All spectra were obtained on a high-resolution emission spectrometer constructed in our laboratory. Samples were excited by the UV output (typically, 25–100 mW at 350 nm was used) of an Ar-ion laser (Coherent model Innova 90-5). The emission was analyzed at 5 cm^{-1} resolution by a 1-m grating monochromator (Spex model 1704), and detected by a cooled photomultiplier tube (S-20 response). All data were obtained at room temperature, since cooling the samples to cryogenic temperatures (10 K) did not reveal the existence of any new spectral features, and only slightly improved the degree of resolution.

RESULTS

Thermal analysis

Preliminary information regarding the dehydration/decomposition pathways associated with the hydrated europium trifluorides was obtained by means of thermogravimetric analysis. Figure 1 contains the thermograms of hydrated EuF_3 as prepared by the various synthetic procedures.

The hydrated EuF_3 obtained after HF precipitation appears to contain two forms of water of hydration. The first of these is lost between ambient temperature and about 250°C, and the second is lost between 350 and 550°C. The total weight loss associated with these dehydrations corresponds to 0.42 H_2O of hydration per EuF_3 unit. This is slightly lower than the 0.5 H_2O of hydration normally reported [1]. However, since these materials are thought to consist of a mixture of anhydrous and hydrated trifluorides, a non-stoichiometric result is not disturbing. The thermograms indicate the presence of a small plateau of limited stability corresponding to the anhydrous trifluoride, which is immediately followed by decomposition to EuOF.

When hydrated EuF_3 is prepared by precipitation with NH_4F, a double salt is obtained which may be considered as a mixture of hydrated europium trifluoride and ammonium fluoride [4,7]. The dehydration of this material proceeds most smoothly at low temperatures and under high vacuum. The remaining NH_4F is sublimable at a higher temperature. This low-temperature dehydration results in the least amount of EuOF contamination, and the thermograms obtained for EuF_3 prepared by NH_4F precipitation reflect this

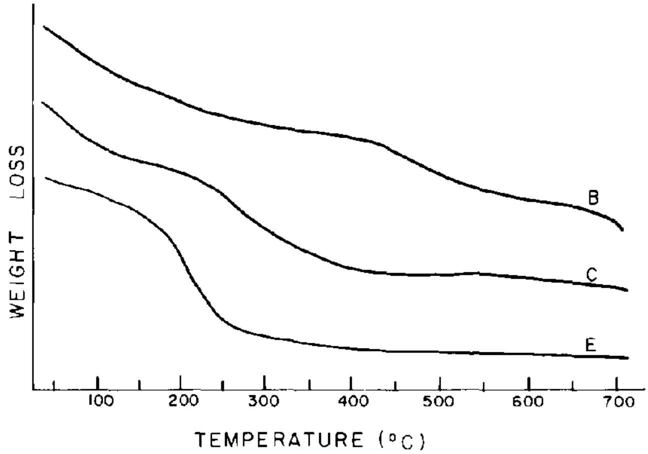

Fig. 1. Thermograms corresponding to the thermal decomposition of hydrated europium fluoride prepared by precipitation with aqueous HF (B), aqueous NH_4F (C), and aqueous NH_4F followed by extensive ethanol washing (E).

behavior. The initial weight loss results in the observation of a well-defined plateau, which is attributable to anhydrous EuF_3. The loss of NH_4F during these initial steps was confirmed by placing the material on a heated probe, and analyzing the effluent gases by mass spectrometry. Using exact mass analysis, fragments consistent with the presence of NH_4F were observed. The formation of EuOF was only apparent at temperatures exceeding 600°C. The results indicate that occlusion of ammonium fluoride takes place at the expense of the high-temperature form lattice water, and that this salt probably plays a similar structural role. Thus, the anhydrous trifluoride is obtainable at lower temperatures, and the anhydrous EuF_3 compound is able to exist over a much larger thermal range.

Since both water and ammonium fluoride are soluble in alcohols, the possible dehydration of the EuF_3 precipitates through ethanol washing was investigated. The remaining trace in Fig. 1 illustrates the thermogram obtained after thorough ethanol washing of a hydrated EuF_3 material obtained after NH_4F precipitation. The first large weight loss is complete by 275°C, and appears to consist of the loss of ethanol and water. There is a weight loss of 0.9% between 275 and 450°C, which is probably due to the removal of any residual NH_4F. The significant result of these studies is that anhydrous EuF_3 could again be obtained at quite low temperatures, and that further decomposition to EuOF was avoidable.

Luminescence studies

The luminescence associated with the Eu(III) ion is well characterized. Since little covalency exists in lanthanide complexes, the origin of each spectral transition can be identified from a comparison of the reported free

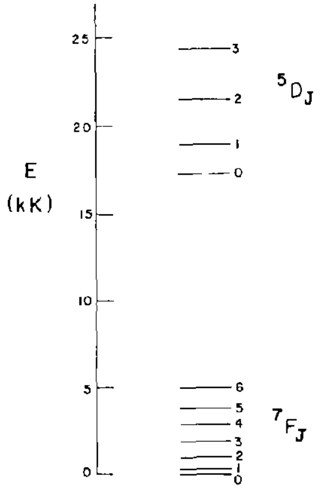

Fig. 2. Energy level diagram for the free Eu(III) ion.

ion values [8]. The luminescent transitions all originate from the $^5D_0$ excited state, and terminate in the ^7F_J levels of the ground-state manifold. In the present work, we have studied the bands characterized by $J = 0, 1, 2, 3$, and 4. Since only the J quantum numbers define the properties of each state, we shall henceforth label the transitions solely by the quantum numbers which characterize the spectroscopic change. An energy-level diagram for the free Eu(III) ion is provided in Fig. 2.

The transition characterized by $J = 0$ to $J = 0$ (around 580 nm) is particularly significant, as no crystal field can split this pair of nondegenerate levels. Consequently, one may equate the number of observed 0–0 peaks with the number of spectroscopically non-equivalent Eu(III) ions present in a given material. While the general location of the other 0–J transitions does not vary greatly, the fine structure within each band system contains all the details of the crystal field as are experienced by the Eu(III) ion. Should full resolution of all components be possible, then comparison of the observed number of lines observed for the 0–J transitions with published selection rules [9] permits a determination of the site symmetry of the Eu(III) ion.

Starting materials

The effect of incorporating hydration water into the EuF_3 compound was

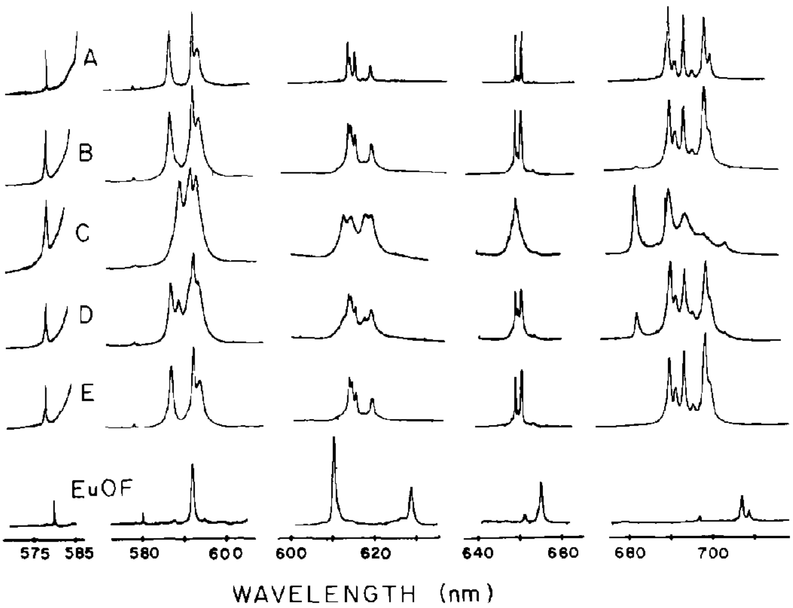

Fig. 3. Luminescence spectra of the europium fluoride starting materials. (A) anhydrous EuF_3, (B) obtained from hydrated EuF_3 as precipitated by aqueous HF; (C) and (D) two different preparations of hydrated EuF_3 precipitated by NH_4F; (E) NH_4F-precipitated EuF_3 which had been extensively washed with ethanol. The spectra of EuOF are included for comparision. The luminescence transitions illustrated are the 0–0 (575–585 nm), 0–1 (580–610 nm), 0–2 (610–630 nm), 0–3 (640–660 nm), and 0–4 (680–710 nm).

investigated through a study of the starting materials themselves. In Fig. 3, the spectra obtained within the 0–J band systems are illustrated for the various preparations of europium trifluoride. The spectrum corresponding to anhydrous EuF_3 is included for comparison, and this spectrum was found to agree excellently with the results published earlier [10].

Several trends are immediately apparent from the spectra shown in Fig. 3. All band shapes observed for anhydrous EuF_3 and hydrated EuF_3 obtained from an aqueous HF precipiation are essentially the same. The sole difference noted is a slight broadening of the bands obtained in the hydrated material. This result provides very strong evidence that the water of hydration is not coordinated to the Eu(III) ion, and that it must be bound loosely outside of the Eu(III) inner coordination sphere. Were the hydration water bound at the inner sphere, then changes in the Eu(III) crystal field would have accompanied its expulsion.

The results obtained with NH_4F precipitaion of hydrated EuF_3 stand in sharp constrast to those described above. As may be seen in Fig. 3, the spectra obtained with the NH_4F preparative route are considerably different and more complex than those of the anhydrous EuF_3. The non-stoichiometric nature of the precipitated compound is evident in the variability of spectra which were obtained. The broadening of the 0–0 peak in sequences C and D indicates the presence of more than one emitting Eu(III) compound. The remainder of the 0–J band systems also contain more peaks than permitted for a single species, and thus signify the existence of a complex material. Of particular interest is one emission peak within the 0–4 band system. The feature located at 6814 A appears only when working with NH_4F-precipitated materials, and its presence may be taken as an indicator of the presence of this lattice impurity.

As complicated as the data appear, the spectra of NH_4F-precipitated EuF_3 actually seem to consist of a superposition of some new Eu(III) emission (best illustrated as band sequence C in Fig. 3) on top of the hydrated EuF_3 characteristic spectra. This observation would therefore imply that the mixed Eu(III) salt precipitated via the NH_4F route actually produces a mixture of products. The makeup of the hydrated fluoride actually isolated was found to depend critically on the procedures chosen for the cleanup and washing of the materials.

The sequence of bands labelled E in Fig. 3 corresponds to NH_4F-precipitated EuF_3, which has been extensively washed with ethanol. The observed spectral features are practically superimposable with those of EuF_3 prepared by HF precipitation. It may be concluded from these results that the ethanol washing process removes the coprecipitated NH_4F, and as a result the Eu(III) ion exhibits the site symmetry characteristic of the hydrated trifluoride. Since the thermal studies have indicated that ethanol still remains in the product, the luminescence data indicate that this solvent also does not interact with the Eu(III) ion at the inner coordination sphere.

Thermal decomposition of NH-precipitated EuF$_3$

The effect of thermal treatment of EuF$_3$ prepared by HF precipitation is shown in Figs. 4 and 5. Materials heated at 200, 350, and 450°C correspond

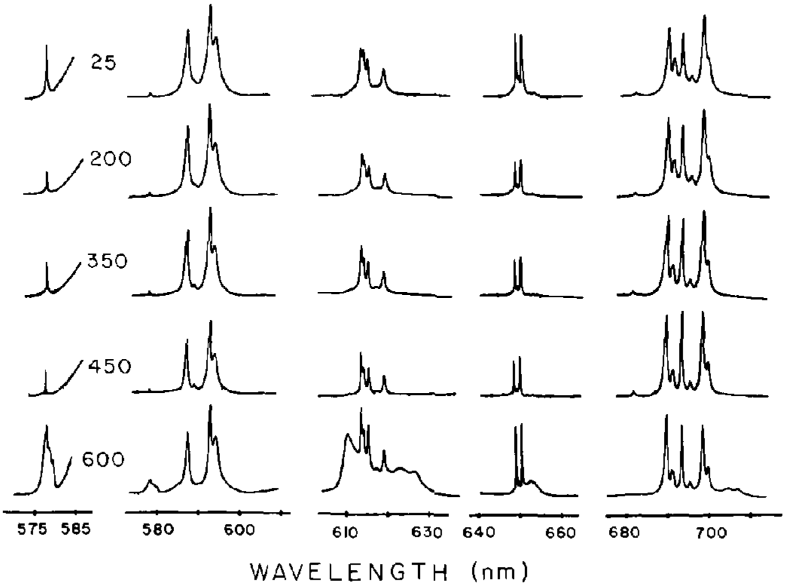

Fig. 4. Luminescence spectra of hydrated europium fluoride as obtained by precipitation with aqueous HF. The luminescence transitions illustrated are the 0–0 (575–585 nm), 0–1 (580–610 nm), 0–2 (610–630 nm), 0–3 (640–660 nm), and 0–4 (680–710 nm). Calcination temperatures are given immediately next to the 0–0 band.

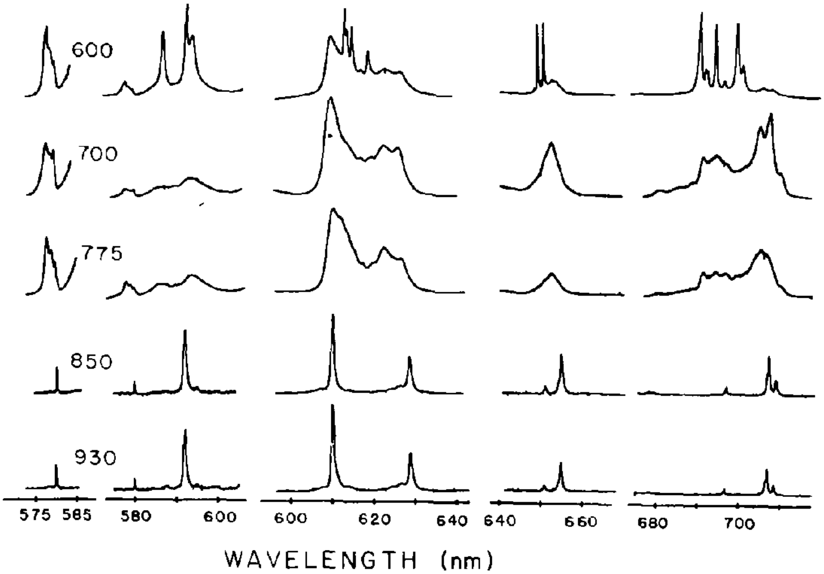

Fig. 5. Additional luminecence spectra of hydrated europium fluoride as obtained by precipitation with aqueous HF.

to various stages of the dehydration process. A comparison of the spectra obtained at each decomposition temperature reveals that sharpening of the peaks and increases in resolution accompany the loss of lattice water. At a calcination temperature of 450°C the observed spectral features are superimposable with those of the anhydrous EuF_3, and we conclude that the dehydration process is complete at this temperature. This result is consistent with the results obtained by more conventional thermal techniques. While the TG results indicated the presence of two different types of hydration water, the luminescence data indicate that neither of these interacts strongly with the Eu(III) ion.

However, while the 450°C spectrum is exceedingly similar to that of anhydrous EuF_3, features in the 0–4 transition indicate that some decomposition to the oxyfluoride has already begun to take place. This process becomes much more important for material heated under isothermal conditions at 600°C, and one now finds that the spectra become exceedingly complicated. The 0–0 band region contains at least 4 peaks, thus indicating the presence of multiple species being present in the sample. Material calcined at 700 and 775°C loses much of the Eu(III) sharp-line character, which suggests the production of a sizeable number of amorphous species. Such spectral alterations could only accompany profound changes in the inner coordination sphere of the Eu(III) ion.

In materials calcined at 850°C the spectra simplify greatly, and a spectral pattern characteristic of Eu(III) oxyhalide compounds is observed [11]. This particular line shape is also found in materials calcined at 930°C, and must correspond to the presence of EuOF. The crystal structure of EuOF is considerably different from that of EuF_3 [12], and the nature of the Eu(III) crystal field is also considerably changed. For instance, while the 0–0 transition of anhydrous EuF_3 is observed at 5784 A, the same band is found at 5800 A in EuOF.

Thermal decomposition of NH_4F-precipitated EuF_3

The TG results discussed in a preceding section indicated that occluded ammonium fluoride played an important role in minimizing EuOF formation during the calcination process. The luminescence spectra of the starting materials indicated that coprecipitated NH_4F was capable of influencing the inner coordination sphere of the Eu(III) ion, and it was anticipated that luminescence studies on the thermal decomposition products would provide additional information on the role of this material. The 0–0 through 0–4 transitions for two samples of hydrated EuF_3 prepared by NH_4F precipitation are shown in Figs. 6 and 7. As mentioned earlier, both contained nonstoichiometric amounds of NH_4F, with sample C containing more than sample D.

As the calcination of NH_4F-precipitated EuF_3 proceeds, a slight splitting of the 0–0 transition is noted. This feature is most noticeable in the data of

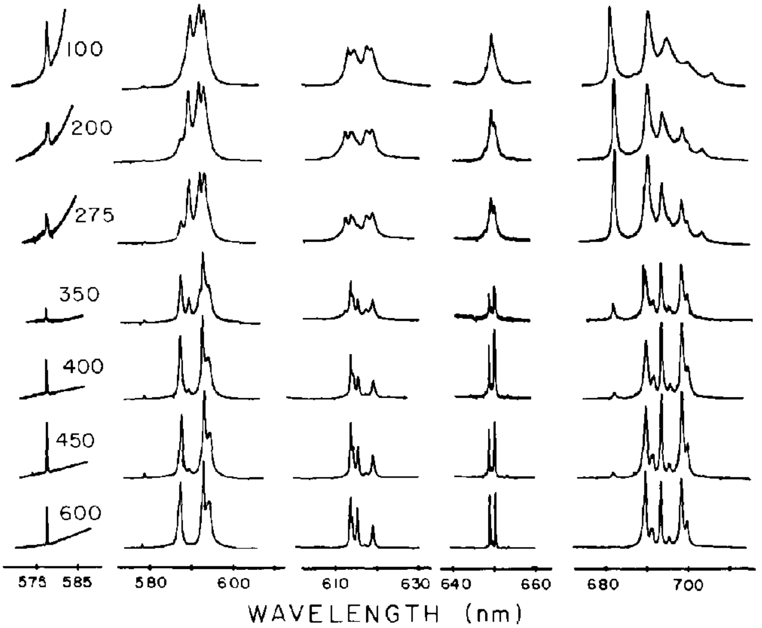

Fig. 6. Luminescence spectra of hydrated europium fluoride as obtained by precipitation with aqueous NH_4F (preparation C). The luminescence transitions illustrated are the 0–0 (575–585 nm), 0–1 (580–610 nm), 0–2 (610–630 nm), 0–3 (640–660 nm), and 0–4 (680–710 nm). Calcination temperatures are given immediately next to the 0–0 band.

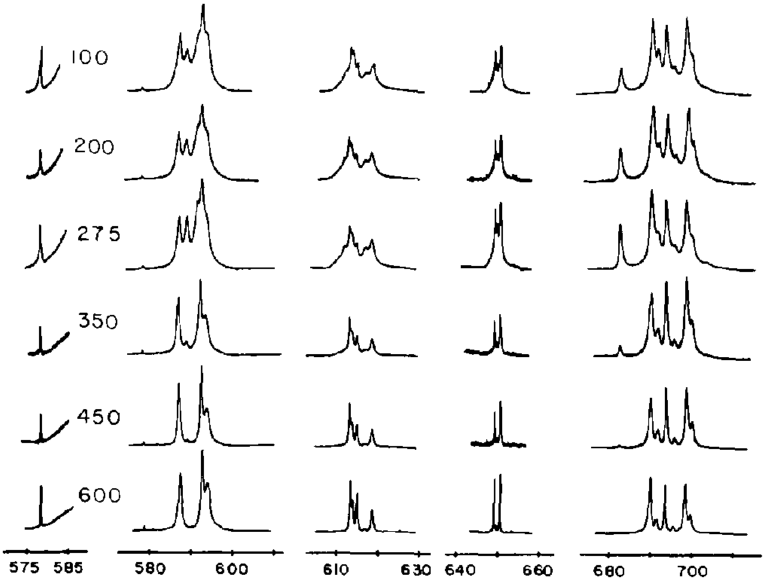

Fig. 7. Luminescence spectra of hydrated europium fluoride as obtained by precipitation with aqueous NH_4F (preparation D).

Fig. 6, and clearly indicates the presence of two compounds at the 200 and 275°C calcination temperatures. One of these corresponds to simple hydrated EuF_3, and the other corresponds to EuF_3 perturbed by the NH_4F. Once the dehydration is complete, the splitting in the 0–0 transition disappears. The firing out of the NH_4F is evident in the other transitions, which continue to change at successively higher calcination temperatures. These changes finally cease for material fired at 600°C, and at this firing temperature anhydrous EuF_3 apparently free from EuOF contamination is obtained. The diagnostic 0–4 transition at 6814 A (found only for the double salt) was observed to be present at all calcination temperatures below 600°C.

One interesting feature noted during the calcination of the NH_4F-precipitated EuF_3 materials was that the normally white calcination products were colored gray until all traces of NH_4 F were burned out. Normally, the gray coloration was observed until all traces of the 6814 A 0–4 peak were lost. While this coating did not affect the spectral distribution, it did greatly reduce the emission quantum yield of the Eu(III) ion, and resulted in a few poor signal/noise ratios.

Heating of NH_4F-precipitated material at higher temperatures than 600°C did not result in the production of EuOF, as long as the heating was not performed in air. The spectral results indicate that the water is removed prior to the NH_4F, and clearly one cannot produce EuOF from a completely anhydrous EuF_3. These observations contain important implications for the dehydration mechanism, and these will be commented on in a later section.

Thermal decomposition of ethanol-washed, NH_4F-precipitated EuF_3

The relationship between NH_4F content and calcination trends was probed further through a luminescence study of the decomposition of EuF_3

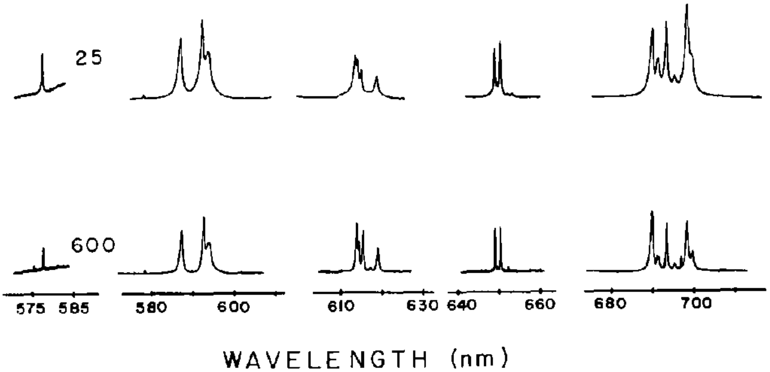

Fig. 8. Luminescence spectra of hydrated europium fluoride as obtained by precipitation with aqueous NH_4F, and then washed extensively with ethanol. The luminescence transitions illustrated are the 0–0 (575–585 nm), 0–1 (580–610 nm), 0–2 (610–630 nm), 0–3 (640–660 nm), and 0–4 (680–710 nm). Calcination temperatures are given immediately next to the 0–0 band.

prepared by NH_4F precipitation, but which was thoroughly washed with ethanol as part of the purification procedure. The TG results indicated that the material lacked weight losses characteristic of both NH_4F and the high-temperature water, and that the formation of EuOF was greatly inhibited.

The luminescence spectra obtained at the normal program of calcination temperatures were not found to vary significantly, and examples of this behavior may be found in Fig. 8. One may note the complete lack of evidence for NH_4F occlusion in the spectra; for instance, there is no 6814 A peak in the 0–4 band region for the starting material. The bands simply sharpen into those associated with anhydrous EuF_3 during the calcination process, and no formation of EuOF is apparent. The very large stability region for anhydrous EuF_3 (as noted in the TG results) is confirmed through the luminescence data.

DISCUSSION

The luminescence and TG results allow one to deduce important information regarding the properties of the starting materials, and the decomposition pathways associated with each of these. The most important conclusion available from the TG results was that two kinds of hydration water appear to exist in hydrated EuF_3, and that these may be differentiated through the temperatures at which each is lost. The luminescence results clearly demonstrated that either type of water was present at the inner coordination sphere of the Eu(III) ion. In all hydrated EuF_3 materials investigated during the present work, loss of low-temperature water appeared to be possible. This low-temperature water did not appear to be capable of leading to EuOF formation.

The EuF_3 precipitated by aqueous HF also was found to contain water which was lost at significantly higher temperatures. The luminescence data indicated that during the loss of this water, formation of the EuOF compound commenced. When the high-temperature water could be removed, the formation of EuOF was greatly inhibited. This latter hydration type could only be removed by replacement by another species, which could be either NH_4F or ethanol. These materials could both be dehydrated at relatively low temperatures, yielding anhydrous EuF_3 which was observed to be essentially free from EuOF contamination.

The present study has shown that luminescence spectroscopy may be used as a valuable addition to conventional thermal techniques. With the use of Eu(III) as a probe ion, detailed information can be obtained on the nature of the species existing at various calcination temperatures. The great advantage of luminescence spectroscopy is that all intermediates present in a given material may be simultaneously observed. Normally, each species will exhibit a characteristic series of line shapes which may be used for qualitative identification. Thus, one could in principle use a combination of conventional thermal methods together with luminescence spectroscopy (and using Eu(III) as the probe ion) to follow the thermal decomposition pathways of a given material completely. Further work along these lines is now being pursued in our laboratory.

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