Thermochimica Acta, 109 (1987) 343–351
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF $Eu_2(SO_4)_3 \cdot 8H_2O$ STUDIED BY LOW TEMPERATURE HIGH-RESOLUTION LUMINESCENCE SPECTROSCOPY

JAMES F. LYNCH

Department of Chemistry, Seton Hall University, South Orange, NJ (U.S.A.)

CLIFFORD J. SACHS and HARRY G. BRITTAIN

Squibb Institute for Medical Research, New Brunswick, NJ (U.S.A.)

(Received 27 May 1986)

ABSTRACT

The thermal decomposition in air at temperatures up to 1450 °C of hydrated europium sulfate has been studied by high-resolution luminescence spectroscopy, X-ray powder diffraction, differential thermal analysis (DTA), and thermogravimetric analysis (TGA). Information regarding the number of europium(III) species present in a particular material can be deduced from the fine structure within the europium(III) emission bands. Determination of the site symmetry of the europium(III) emitting species can be deduced from a complete analysis of the luminescence spectra. The application of this method has shown the presence of a multitude of partially dehydrated species in materials where the more conventional thermal analysis methods predict the presence of only pure anhydrous material. The data indicate the presence of an intermediate assumed to be $Eu_2O(SO_4)_2$. The presence of this intermediate has been suggested before, though never actually observed. Complete decomposition to $Eu_2O_2SO_4$ occurs by 800 °C and finally to Eu_2O_3 by 1150 °C.

INTRODUCTION

The thermal decomposition of rare earth sulfates has attracted much attention over the years, since thermal decomposition has been shown to be a feasible preparative route to the dioxysulfate and oxide [1]. Both materials have been shown to exhibit interesting physical properties, particularly their unique luminescence characteristics [2,3].

The thermal dehydration/decomposition of europium(III) sulfate octahydrate has been studied previously by conventional thermal analysis techniques (DTA, TGA) [4–8]. Cumulatively, these studies revealed that hydrated europium(III) sulfate decomposes via the following scheme:

$$Eu_2(SO_4)_2 \cdot 8H_2O \rightarrow Eu_2(SO_4)_3 + 8H_2O \quad (1)$$

$$Eu_2(SO_4)_3 \rightarrow Eu_2O_2(SO_4) + SO_2 + 0.5O_2 \quad (2)$$

$$Eu_2O_2(SO_4) \rightarrow Eu_2O_3 + SO_2 + 0.5O_2 \quad (3)$$

0040-6031/87/$03.50

Utilizing high-resolution luminescence spectroscopy a more complete understanding of the thermal decomposition of hydrated europium(III) sulfate may be obtained. Luminescence spectroscopy has a clear advantage over conventional thermal analysis techniques in that it can monitor the presence of multiple species simultaneously within a particular material. Thus, one may qualitatively assess material purity. From analysis of the fine structure within the luminescence spectrum, two types of information are available: (1) the number of spectroscopically non-equivalent europium(III) species may be ascertained, and (2) the site symmetry of these species may be deduced provided the origin of each emission band is known. One advantage of luminescence spectroscopy over X-ray diffraction is the ability to obtain structural information on micro-crystalline materials. In the present work, we have combined all the techniques mentioned to gain a more complete understanding of the thermal decomposition pathways associated with hydrated europium(III) sulfate.

EXPERIMENTAL

The $Eu_2(SO_4)_3 \cdot 8H_2O$ was obtained from the Research Chemical Corporation at 99.9% purity and was used as received.

Thermal decomposition of $Eu_2(SO_4)_3 \cdot 8H_2O$ was achieved by placing the samples in quartz tubes and calcining these open tubes in a tube furnace (Lindbergh, model 59545). The samples were fired for 4 h at 100, 225, 300, 350, 400, 525, 600, 730, 800, 1000, 1150, 1300, or 1450°C. The tube furnace was held isothermally at the desired temperature (±1°C). After 4 h of isothermal calcination the quartz tube was evacuated to ca. 5 Torr and sealed. The samples were then cooled to 77 K and secured at the entrance slit of the luminescence monochromator. Maintaining the samples at liquid nitrogen temperatures while scanning the luminescence spectra greatly enhanced the resolution of the emission bands.

All luminescence spectra were obtained on a high resolution emission spectrometer constructed in our laboratory. Samples were excited by the 350 nm output (50 mW) of an argon ion laser, and the emission was analyzed at 2 cm^{-1} resolution by a 1 m grating monochromator (Spex, model 1704). The emission was detected by a cooled (−20°C) EMI 9558B photomultiplier tube (S-20 response).

The thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer (TGS-1) instrument over the temperature range from room temperature to 900°C in static air. Differential thermal analysis (DTA) was carried out on a DuPont 900 analyzer over the temperature range from room temperature to 900°C under static air conditions. The heating rate in both analyses was 10°C min^{-1}.

The X-ray powder diffraction data were collected on a Philips APD-3720

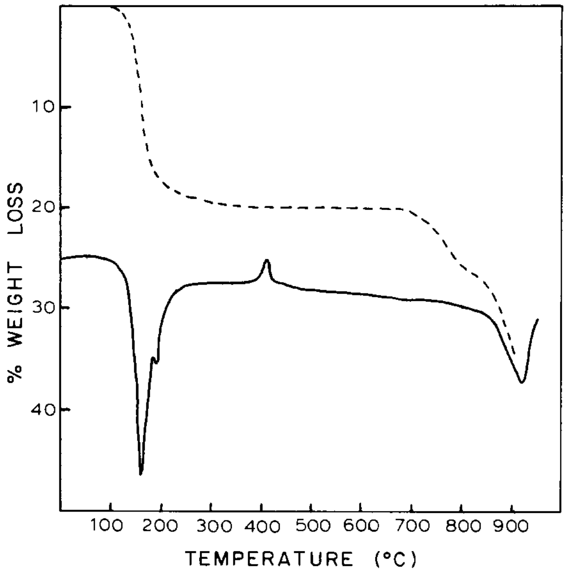

Fig. 1. Thermogravimetric (dashed trace) and differential scanning calorimetric (solid trace) scans of hydrated europium sulfate.

XRD system, with an XRG 3100 X-ray generator operating at the Cu $K\alpha$ (1.54056 Å) line. The θ–2θ scan technique was employed with a scan range of 2–75°. This instrument is equipped with an automatic θ compensating slit.

RESULTS AND DISCUSSION

Thermal analysis

The thermal dehydration/decomposition behavior of commercially available europium(III) sulfate octahydrate was initially investigated up to 900°C by TGA and DTA. Figure 1 contains the thermograms of $Eu_2(SO_4)_3 \cdot 8H_2O$.

The weight loss due to dehydration of $Eu_2(SO_4)_3 \cdot 8H_2O$ begins to occur at 100°C and is not complete until 400°C. From DTA there appear to be two forms of water of crystallization, but from TGA there seems to be only one form. This is not disturbing, however, since it has been shown that depending on reaction conditions, i.e. heating rate, sample size, etc. [1], both forms can be observed. The weight loss due to dehydration was found to be 20.0%, consistent with the 19.6% expected. The additional weight loss is probably due to residual surface water not expelled during the drying process.

The dehydration step yields anhydrous $Eu_2(SO_4)_3$ which is thermally stable up to 675°C. However, DTA shows a small exothermic peak centered at 400°C [4]. This exothermic reaction has no corresponding weight loss associated with it, and therefore, must be due to a lattice rearrangement [9]. Thus, dehydration of $Eu_2(SO_4)_3 \cdot 8H_2O$ appears to yield a genuine anhydrous $Eu_2(SO_4)_3$ existing in a metastable state capable of conversion to a more stable form, with a corresponding release of energy in the form of heat.

Anhydrous $Eu_2(SO_4)_3$ begins to decompose at 675°C. The weight loss associated with this decomposition is interrupted at 795°C, however, by the presence of a shoulder. This is thought to be due to the formation of the unstable oxydisulfate before decomposition to the more stable dioxysulfate occurs [10]. The weight loss associated with this point of inflection is 25.7%. This is significantly lower than the 30.0% weight loss expected for oxydisulfate formation. The discrepancy is attributed to the simultaneous decomposition of the unstable oxydisulfate to the dioxysulfate before all the oxydisulfate has been formed.

TGA studies by Nathans and Wendlandt [4], have shown that anhydrous $Eu_2(SO_4)_3$ begins to decompose to $Eu_2O_2(SO_4)$ at 870°C, with no indication of an intermediate being formed. The dioxysulfate begins to decompose to the oxide at 1180°C. Oxide formation has been shown to be complete by 1300°C [4].

Luminescence / X-ray diffraction studies

The luminescent $^5D_0$ level of Eu(III) is populated upon excitation by light of the near-UV region. Emission from this excited state occurs to the various ^7F_J levels of the ground state. To simplify matters, we will label the various states by their defining J quantum numbers. It was found that the most useful europium(III) transitions for our purposes were the 0–0 (580 nm), 0–1 (595 nm), 0–2 (615 nm), 0–3 (650 nm) and 0–4 (690 nm). Emission from the $^5D_1$ to the $^7F_3$ level was observed in some samples. This transition has been observed previously by Porcher et al. [11]. Since no crystal field can split the 0–0 band, the number of 0–0 lines is a direct count of the number of spectroscopically non-equivalent europium(III) species present in the sample. If complete resolution of all components within the fine structure is possible, then a comparison of the observed number of emission bands for the 0–J transitions with published selection rules [12] enables a determination of the site symmetry of the Eu(III) ion.

In Fig. 2, the 77 K spectra of the 0–0, 0–1 and 0–2 band regions for the stock $Eu_2(SO_4)_3 \cdot 8H_2O$ are shown. The two low intensity emission bands within the 0–0 region indicate that Eu(III) occupies two types of site. It is immediately apparent from the low intensity of these 0–0 emission bands that the two Eu(III) emitting species must occupy sites of fairly high symmetry.

The space group for the europium sulfate octahydrate was previously

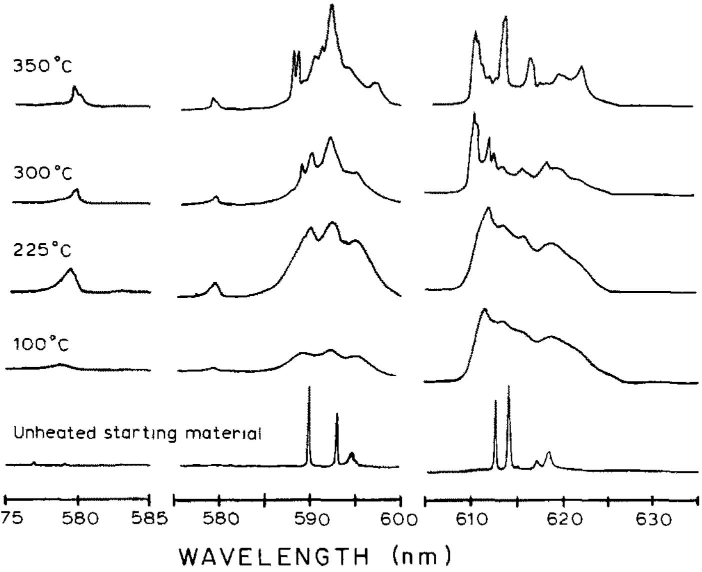

Fig. 2. Luminescence spectra obtained for hydrated europium sulfate, and for material heated over the 100–350 °C calcination range. The 575–585 nm interval corresponds to the Eu(III) 0–0 transition region, the 575–600 nm interval to the 0–1 transition region, and the 605–635 nm interval to the 0–2 transition region. The intensity scales are arbitrary, and are roughly normalized to indicate comparable peak heights.

found to be monoclinic, i.e. $C2/c$ [7]. Therefore, the point symmetry can only be C_2, $C_{1h}(C_S)$, or C_{2h}. The observed spectrum corresponds well with these possible symmetries though complete resolution of all bands was not possible and therefore a point symmetry could not be assigned.

The 77 K spectrum of the $Eu_2(SO_4)_3 \cdot 8H_2O$ heated at 100 °C is shown in Fig. 2. The appearance of the broad, low intensity 0–0 band and the considerable peak broadening in the 0–1 and 0–2 band regions, shows that the environment around the Eu(III) emitting species has begun to change. Our thermoanalytical studies on this material show that dehydration is just beginning to occur at 100 °C, however those of Wendlandt and George [5] show no thermal activity between room temperature and 100 °C. Examination of the X-ray powder diffraction patterns of the compound heated at 100 °C, showed this material to be totally amorphous.

As shown in Fig. 2, the luminescence spectra of europium sulfate octahydrate calcined at 225, 300 and 350 °C, show a gradual increase in intensity with calcination temperature. Thermogravimetric analysis indicates that dehydration is occurring throughout this temperature region, and is not complete until 350 °C. Therefore, the increase in luminescence intensity during dehydration has shown that the waters of crystallization are in the inner coordination sphere of the europium(III) emitting species, and the expulsion of these water molecules lowers the site symmetry around that

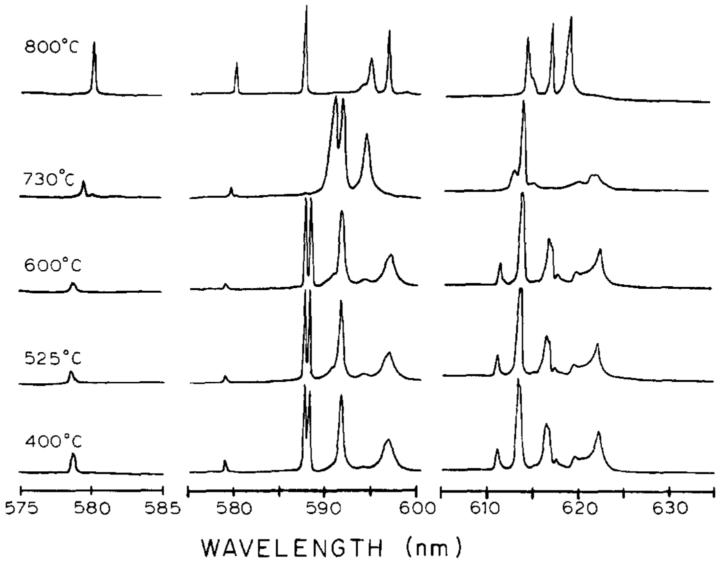

Fig. 3. Luminescence spectra obtained for hydrated europium sulfate heated over the 400–800 °C calcination range. The 575–585 nm interval corresponds to the Eu(III) 0–0 transition region, the 575–600 nm interval to the 0–1 transition region, and the 605–635 nm interval to the 0–2 transition region. The intensity scales are arbitrary, and are roughly normalized to indicate comparable peak heights.

species. The lack of spectral resolution within the emission bands corresponds well with the X-ray powder diffraction data, indicating the existence of several phases throughout this temperature region.

The thermal analysis data show that by 400 °C the material has been completely dehydrated and the more stable form of the anhydrous sulfate has formed. The luminescence spectrum of this material is shown in Fig. 3. It is immediately apparent from the sharp emission behavior, that the site symmetry around the Eu(III) emitting ion has changed as a result of the lattice rearrangement. The X-ray powder diffraction data show, however, that this material is of low crystallinity. This is not disturbing since the single, intense 0–0 emission band at 579 nm in the luminescence spectrum has a shoulder on the low energy side. Thus, there are at least two Eu(III) sites at a temperature where conventional thermal analysis indicates a single species present and X-ray powder diffraction data offers little information.

Samples calcined at 525 or 600 °C produce spectra identical to that obtained at 400 °C, as shown in Fig. 3. Also, two minor components at 590.6 and 594.1 nm are observed in the luminescence spectra. X-Ray diffraction patterns of these materials match perfectly with those of the anhydrous sulfate, although trace amounts of a second material are apparent. Thus, in the temperature region where according to thermogravimetric results, there should be essentially pure anhydrous sulfate, luminescence spectroscopy complemented by X-ray diffraction has shown the presence of more than one species.

Heating a sample at 730°C produces a luminescence spectrum completely different from the previous temperatures, and therefore, a new species has been formed. Emission bands appear at 579.3 and 591.4 nm. The small peaks at 590.6 and 594.1 nm observed in the previous spectrum, grow in intensity. All other major components of the previous spectrum disappear, while those of the minor component increase in intensity. This spectrum does not coincide with either the anhydrous sulfate spectrum or the higher temperature dioxysulfate spectrum, $Eu_2O_2SO_4$ (discussed below), and therefore, must be due to oxydisulfate formation, $Eu_2O(SO_4)_2$. This is consistent with the TGA results which indicate the formation of an intermediate phase between the stable anhydrous sulfate and the dioxysulfate, i.e. $Eu_2O_2SO_4$. Previously, the presence of $La_2O(SO_4)_2$ as a possible intermediate in the thermal decomposition of $La_2(SO_4)_3$, was hypothesized but never observed [10]. Trace amounts of a second material are observed in the luminescence spectrum apparently due to dioxysulfate. The X-ray powder diffraction patterns taken of this sample confirm the existence of a single major phase, possessing a diffraction pattern completely different from that of either the lower or higher temperature material. Therefore, the thermal decomposition of anhydrous $Eu_2(SO_4)_3$ to $Eu_2O_2(SO_4)$ is actually a two step process

$$Eu_2(SO_4)_3 \rightarrow Eu_2O(SO_4)_2 + SO_2 + 0.5O_2 \quad (4)$$

$$Eu_2O(SO_4)_2 \rightarrow Eu_2O_2(SO_4) + SO_2 + 0.5O_2 \quad (5)$$

Comparison of the observed 0–0, 0–1, 0–2 emission peaks of the 730°C sample, with those predicted by Forsberg [12], reveals that the emitting Eu(III) species is in either a C_2 or a C_S site symmetry. Since C_s is quite uncommon in Eu(III) luminescence, the emitting Eu(III) ion most likely resides at a site characterized by C_2 symmetry. Thus, the oxydisulfate intermediate has now been observed and a point symmetry assigned. It is important to note the fact that, in the isothermal preparation, there is essentially one species present at 730°C. This suggests that all the anhydrous sulfate is first converted to the oxydisulfate before decomposing to the dioxysulfate with no disproportionation.

Heating the europium sulfate at 800 or 850°C produces a spectrum completely different from that of the previous species. This spectral trace is that of the dioxysulfate, as the X-ray powder diffraction pattern of this compound matches perfectly with that of the dioxysulfate. From Fig. 4 it is observed that calcination at 900 or 1000°C also produces a spectrum identical with that obtained at 800°C. However, calcination at 1150°C produces an entirely different spectrum. This material was confirmed to be Eu_2O_3 by luminescence spectroscopy and X-ray powder diffraction. Though Nathans and Wendlandt [4] show through thermal analysis that the decom-

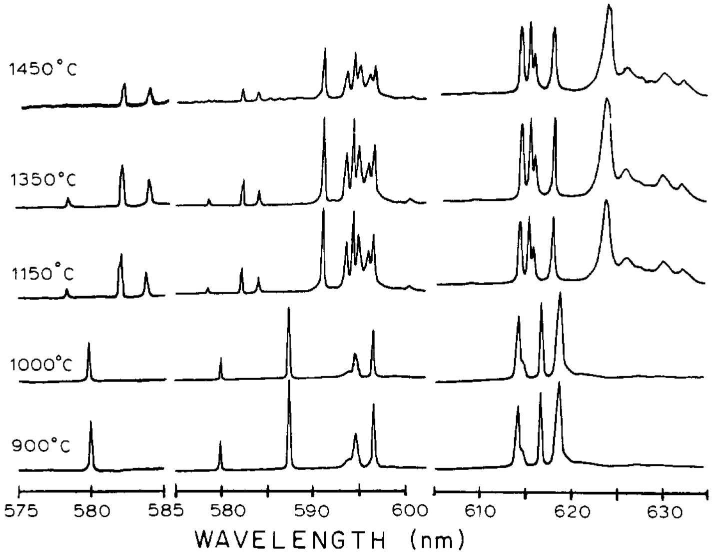

Fig. 4. Luminescence spectra obtained for hydrated europium sulfate, and for material heated over the 900–1450°C calcination range. The 575–585 nm interval corresponds to the Eu(III) 0–0 transition region, the 575–600 nm interval to the 0–1 transition region, and the 605–635 nm interval to the 0–2 transition region. The intensity scales are arbitrary, and are roughly normalized to indicate comparable peak heights.

position of the dioxysulfate to the sesquioxide is not complete until 1300°C, we have shown through luminescence spectroscopy that this decomposition is actually completed by 1150°C. However, this difference is undoubtedly due to the isothermal versus dynamic heating procedures employed.

CONCLUSIONS

High-resolution luminescence spectroscopy has proven to be an invaluable technique in the determination of the thermal decomposition of $Eu_2(SO_4)_3 \cdot 8H_2O$. The ability of luminescence spectroscopy to simultaneously observe many intermediate species present in a given material demonstrates its advantage over the more conventional thermal techniques. Luminescence spectroscopy has the immense advantage over X-ray diffraction techniques in that it can be used to deduce structural information on materials whose crystals are too small to yield good diffraction patterns. An important aspect of the present study is the observation and determination of the site symmetry of the oxydisulfate intermediate. Secondly, this study has shown that all the anhydrous europium sulfate first decomposes to europium oxydisulfate before decomposing to the more stable europium dioxysulfate. Utilizing Eu(III) as an optical probe, luminescence spectroscopy can also be used to gather information on spectroscopically-transparent materials. Further studies in this area are presently being conducted in our laboratory.

ACKNOWLEDGEMENTS

This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, through Grant 13922-AC5.

REFERENCES

1 J.J. Pitha, A.L. Smith and R. Ward, J. Am. Chem. Soc., 69 (1947) 1870.
2 J.W. Haynes and J.J. Brown, J. Electrochem. Soc., 115 (1968) 1060.
3 G. Blasse and A. Bril, Philips Res. Rep., 23 (1968) 461.
4 M.W. Nathans and W.W. Wendlandt, J. Inorg. Nucl. Chem., 24 (1962) 869.
5 W.W. Wendlandt and T.D. George, J. Inorg. Nucl. Chem., 19 (1961) 245.
6 W.W. Wendlandt, J. Inorg. Nucl. Chem., 7 (1958) 51.
7 L. Niinisto, P. Saikkonen and R. Sonninen, The Rare Earths in Modern Science and Technology, Vol. 3, Plenum Press, New York, 1982, p. 257.
8 H.G. Brittain, J. Less-Common Met., 93 (1983) 97.
9 P.D. Garn, Thermoanalytical Methods of Investigation, Academic Press, NY, 1965, p. 32.
10 A.A. Grizik and N. Abdullina, Russ. J. Inorg. Chem., 16 (1971) 965.
11 P. Porcher, D.R. Svoronos, M. Leakela and J. Holsa, J. Solid State Chem., 46 (1983) 101.
12 J.H. Forsberg, Coord. Chem. Res., 10 (1973) 195.