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Thermal decomposition of $LaC_2O_4Cl \cdot 3H_2O : Eu^{3+}$: a high-resolution luminescence spectroscopy study

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Abstract

The thermal decomposition of Eu^{3+}-doped lanthanum oxalato-chloride trihydrate, $LaC_2O_4Cl \cdot 3H_2O : Eu^{3+}$, was monitored by high-resolution photoluminescence spectroscopy and X-ray powder diffraction. By studying the fine structure of the luminescence spectra, information from the structure of the intermediate phases, e.g. the number of sites, was obtained for each compound. The splitting of the spectral lines can also reveal the similarities between the different phases. Examination of the luminescence spectra showed the presence of a well defined anhydrous oxalato-chloride form before decomposition to oxychloride and, finally, to the oxide. The evolution of the crystal field effect in these compounds is discussed. The results of the analysis of the luminescence spectra are compared to the information obtained from X-ray powder diffraction. The use of combined TG/DTG and quadrupole mass spectrometry (QMS) is also reported.

INTRODUCTION

The thermal decomposition of rare earth oxalato-chlorides, $REC_2O_4Cl \cdot 3H_2O$, has attracted much attention over the years as it has been shown to be an easy and feasible route to the corresponding oxychlorides and oxides [1]. The latter materials have interesting physical properties; in particular, they and their related materials (i.e. rare earth oxybromides) have found wide applications as commercial phosphors [2].

The thermal decomposition of lanthanum oxalato-chloride trihydrates has been studied previously by conventional TG/DTG and DTA techniques [1,3–9]. According to these studies the thermal decomposition of $LaC_2O_4Cl \cdot 3H_2O$ proceeds via the following scheme

$$LaC_2O_4Cl \cdot 3H_2O \rightarrow LaC_2O_4Cl + 3H_2O \quad (1)$$

$$LaC_2O_4Cl \rightarrow LaOCl + CO + CO_2 \quad (2)$$

$$2LaOCl \rightarrow La_2O_3 + Cl_2 \quad (3)$$

In addition to the general decomposition scheme presented above, the existence of some intermediate hydrated phases (e.g. a monohydrate phase)

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has been suggested on the grounds of the TG/DTG analysis [3]. However, no detailed identification of these phases has been published.

In the present work, high-resolution luminescence spectroscopy is used in combination with and complemented by X-ray powder diffraction in order to achieve a more profound understanding of the thermal decomposition of $LaC_2O_4Cl \cdot 3H_2O$. It is our aim to demonstrate that luminescence spectroscopy has a clear advantage over conventional TG/DTG and X-ray powder diffraction methods in that it can be used to indicate the presence of multiple species within the sample studied. This extra possibility results from the analysis of the fine structure of the sharp RE^{3+} luminescence transitions. Three types of information are available: the number of lines may ascertain the presence of non-equivalent RE^{3+} species; the site symmetry of each RE^{3+} species can be deduced; and the magnitude of the splitting of the spectral lines can be used to analyse the strength of the crystal field effect and to compare it with those of known splitting patterns [10]. One of the additional advantages of luminescence spectroscopy over X-ray diffraction is that it also provides structural information on microcrystalline materials.

EXPERIMENTAL

Preparation of $LaC_2O_4Cl \cdot 3H_2O$

The rare earth oxalato-chloride samples were obtained as microcrystalline powders by a slow (a few days) crystallisation from a highly acidic (HCl(aq)) solution of the corresponding oxalates [11]. For optical luminescence measurements, the $LaC_2O_4Cl \cdot 3H_2O$ samples were doped with Eu^{3+} ion (nominally 1.5 mol%). Due to the low Eu^{3+} content and the slight differences in solubility of different RE salts, a random, uniform distribution of the Eu^{3+} ion in the lanthanum site was assumed.

Thermoanalytical measurements

The thermogravimetric analyses were carried out using a Perkin–Elmer TGA7 thermogravimetric analyser of the Perkin–Elmer 7 Series Thermal Analysis system in a dynamic air atmosphere with a heating rate of 2.5 °C min^{-1}. For the QMS measurements a Leybold–Heraeus INFICON IQ 200 quadrupole mass spectrometer was employed.

X-ray powder diffraction

The powder diffraction patterns were obtained with a Philips PW 1800 series powder diffractometer system (with Cu K_α radiation) in the 2θ range between 5 and 60 °.

Optical measurements

The luminescence of the $LaC_2O_4Cl \cdot 3H_2O:Eu^{3+}$ powder samples was measured under UV, argon ion and dye laser excitation at ambient and liquid nitrogen temperatures (300 and 77 K, respectively). The global UV excitation was achieved with radiation from a 200 W mercury lamp centred with wide band filters around 300 nm to correspond to the strongly absorbing charge transfer band of the Eu^{3+} ion. The argon ion laser line at 476.5 nm was used to excite only the three lowest ^5D_J ($J = 0, 1,$ and 2) levels of the Eu^{3+} ion.

The selective excitation of the lowest excited ^5D level, $^5D_0$, near 580 nm, was achieved with a Spectra Physics 375 continuous wave rhodamine 6G dye laser (line width 0.7 cm^{-1}) pumped by a Spectra Physics 2016 argon ion laser. The luminescence was dispersed by a 1 m Jarrell–Ash Cerny–Turner-type monochromator and was detected by a Hamamatsu R374 photomultiplier. The resolution of the equipment was better than 1.0 cm^{-1}. The $^5D_0 \rightarrow {}^7F_{0-2}$ transitions between 575 and 645 nm were considered in detail.

Crystal structures

We have recently determined the crystal structure of $PrC_2O_4Cl \cdot 3H_2O$ which is isomorphous with the corresponding lanthanum compound [11]. This compound crystallises in the monoclinic system with $P2_1/n$ ($Z = 4$) as the space group. The crystallographic point symmetry of the Pr site is very low, C_1. In contrast to this, the oxychlorides of lighter REs (La–Er, Y) have a tetragonal structure: space group $P4/nmm$ and $Z = 2$ [12]. The RE site symmetry is higher than in the oxalato-halide case, C_{4v}. The final decomposition product La_2O_3 has a structure of highest symmetry in the whole system with $P\bar{3}m1$ ($Z = 1$) as space group and C_{3v} as the symmetry of the La site [13].

RESULTS AND DISCUSSION

Thermal analysis

According to TG/DTG analysis the decomposition of $LaC_2O_4Cl \cdot 3H_2O:Eu^{3+}$ starts at 200 °C with dehydration and proceeds to the anhydrous $LaC_2O_4Cl:Eu^{3+}$ (Fig. 1, upper curve). In contrast with previous studies [3], no other intermediate phases were observed. This presents, however, no serious problems, as it has been shown for other samples that the experimental conditions, e.g. heating rate, sample size, sample crystal size, atmosphere, etc., can have a tremendous effect on TG/DTG curves [14]. Therefore, great attention was paid to the choice of experimental

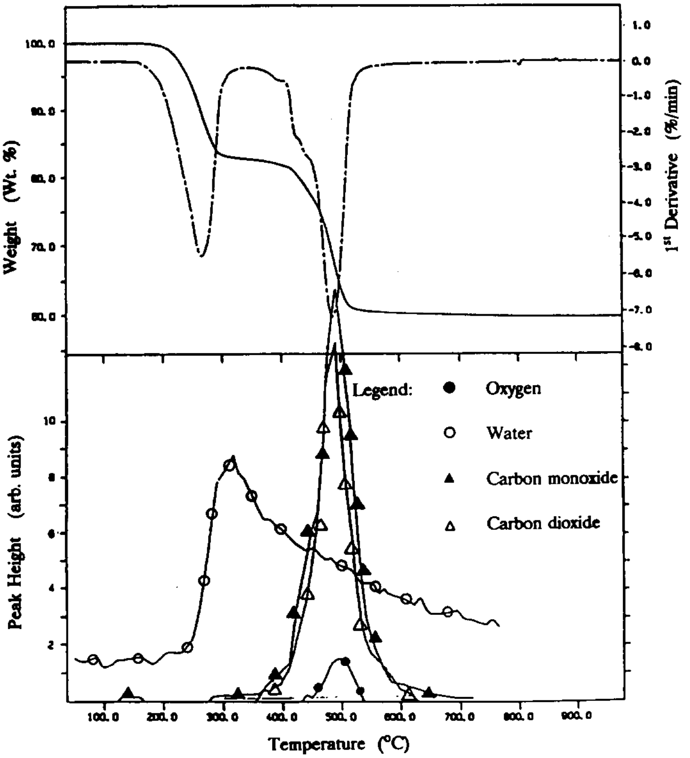

Fig. 1. The TG, DTG and QMS (quadrupole mass spectrometry) curves for the thermal decomposition of $LaC_2O_4Cl \cdot 3H_2O$ in air with a heating rate of 2.5 °C min^{-1}.

conditions. With a slow heating rate, i.e. 2.5 °C min^{-1}, and small sample sizes, i.e. only a few milligrams, the thermal decomposition should proceed uniformly with no local retardation of the decomposition reaction resulting in the appearance of extra phases. The single dehydration step obtained by TG/DTG analysis is further supported by the results of a simultaneous quadrupole mass spectroscopic (QMS) analysis which shows an even build-up of H_2O evolution corresponding to the mass number 18 (Fig. 1, lower curve).

The anhydrous LaC_2O_4Cl is thermally stable up to 420 °C, above which it is converted to the corresponding oxychloride, $LaOCl:Eu^{3+}$. The rather extended stability range of LaC_2O_4Cl (some 150 degrees) makes feasible the isolation of the product for luminescence and X-ray diffraction studies. The decomposition of the anhydrous oxalato-chloride appears to take place in at least two steps, according to the DTG curve. The possible intermediate compounds include an oxycarbonatochloride, $(LaO)_3C_2O_4Cl$, but as no clear phase formation can be observed in the TG curve, this cannot be verified. Nor can the QMS data help because, although there is a definite peak at mass number 28 corresponding to carbon monoxide, this may also result from the cleavage of CO_2. An alternative to the presence of intermediate phases for this decomposition step is that the reaction occurs through several different kinetic paths. The latter seems to offer a more plausible explanation due to the instability of the possible intermediate phases, e.g. $(LaO)_3C_2O_4Cl$.

Lanthanum oxychloride ($LaOCl:Eu^{3+}$) is stable up to the utmost temperature limit of the equipment available to us and, accordingly, no information on the formation of the final decomposition product, lanthanum oxide $La_2O_3:Eu^{3+}$ could be obtained. However, it has been shown earlier that La_2O_3 forms at considerably higher temperatures [15].

Luminescence and X-ray powder diffraction studies

In most solid phases, the luminescence of the Eu^{3+} ion originates mainly from the electronic transitions from the $^5D_0$ level to the ground multiplet ^7F_J ($J = 0, 1, \ldots, 6$) (Fig. 2 [16]). These transitions result in very sharp emission lines in the visible spectral range from 575 to 850 nm. In some cases [17,18], emission from higher ^5D_J ($J = 1$–3) levels has also been observed. Because the $^5D_0$ and $^7F_0$ levels cannot be split by any interaction, apart from nuclear spin, into more than one crystal field sublevel (c.f.) the number of $^5D_0 \rightarrow {}^7F_0$ transition(s) is a direct count of the different species of Eu^{3+} ions present in the material studied. In addition to the information on the different species, some information on the nature of the surroundings of the Eu^{3+} ion, i.e. site symmetry and interactions with neighbouring atoms, can also be extracted from the c.f. fine structure of the other $^5D_0 \rightarrow {}^7F_J$ transitions [10]. The number of lines, as well as the selection rules regulating the former play an important role. If the entire spectral fine structure could be resolved, it would enable the determination of the point symmetry of the Eu^{3+} site.

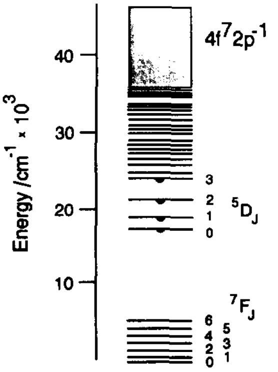

Fig. 2. The energy level scheme of the Eu^{3+} ion in crystalline solids. The levels marked with a filled semi-circle are luminescent.

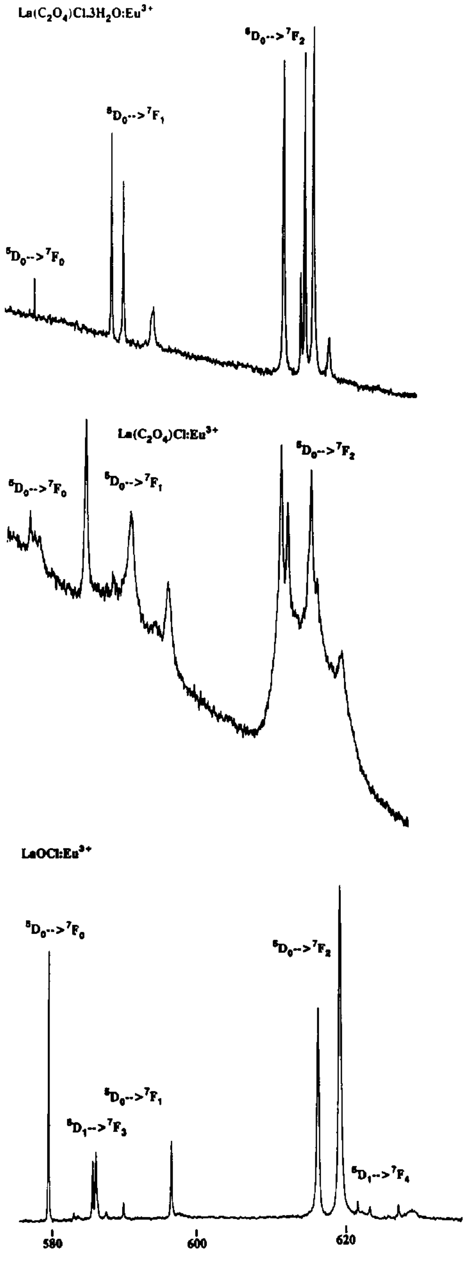

Fig. 3. The luminescence spectra of the Eu^{3+} ion in $LaC_2O_4Cl \cdot 3H_2O$, LaC_2O_4Cl and LaOCl under Ar laser excitation at 77 K.

From the characteristic zones of the Eu^{3+} luminescence in the three materials considered here, $LaC_2O_4Cl \cdot 3H_2O : Eu^{3+}$, $LaC_2O_4Cl : Eu^{3+}$ and $LaOCl : Eu^{3+}$ (Fig. 3), it is immediately clear that in each matrix the Eu^{3+} ion occupies only a single, well-defined site (the number of $^5D_0 \rightarrow {}^7F_0$

TABLE 1

The X-ray powder diffraction patterns of LaC_2O_4Cl and $LaC_2O_4Cl \cdot 3H_2O$

LaC_2O_4Cl			$LaC_2O_4Cl \cdot 3H_2O$		
2θ (°)	d (Å)	I/I_{100} (%)	2θ (°)	d (Å)	I/I_{100} (%)
15.63	5.67	100	10.99	8.05	30
17.52	5.06	70	15.35	5.77	40
21.08	4.21	95	17.57	5.04	10
23.47	3.79	40	22.00	4.04	20
25.65	3.54	55	32.36	2.76	15
28.42	3.14	30	33.20	2.70	100
29.53	3.02	40	36.57	2.46	15
30.94	2.89	35	37.65	2.39	20
31.71	2.82	40	44.78	2.02	15
33.77	2.65	50	51.39	1.78	15
34.91	2.57	40	53.38	1.72	10
37.58	2.39	75	56.94	1.62	85
39.98	2.25	65			
44.94	2.01	40			
47.20	1.92	40			
57.35	1.61	25			

transitions is always one). In addition, the high intensity of these transitions implies that the symmetries of the Eu^{3+} sites are relatively low, i.e. C_s, C_n or C_{nv} [19]. The resolved c.f. fine structure of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions indicates the presence of a maximum of $2J+1$ lines for each transition for $LaC_2O_4Cl \cdot 3H_2O : Eu^{3+}$ and $LaC_2O_4Cl : Eu^{3+}$, whereas the number of lines for $LaOCl : Eu^{3+}$ is considerably less.

The intensity of the $^5D_0 \rightarrow {}^7F_0$ transition, as well as the number of lines for the other transitions, is in excellent agreement with the crystallographic point symmetries of the Eu^{3+} sites, C_1 and C_{4v} in $LaC_2O_4Cl \cdot 3H_2O$ and LaOCl, respectively. No crystallographic structure data are, however, available for LaC_2O_4Cl. Moreover, the X-ray powder diffraction pattern of the anhydrous salt showed only a few diffuse peaks (Table 1) indicating that this material is nearly completely amorphous. However, a preliminary comparison with the diffraction pattern of $LaC_2O_4Cl \cdot 3H_2O$ presents no resemblance. The amorphous nature of the material can be easily understood because of the drastic structural rearrangements that occur during dehydration due to the direct coordination of all three water molecules to the RE atom in $LaC_2O_4Cl \cdot 3H_2O : Eu^{3+}$ [11]. Even the luminescence efficiency of the anhydrous form is low due to the amorphous nature, with the large surface area creating killer sites for luminescence.

The presence of only one rather intense $^5D_0 \rightarrow {}^7F_0$ transition yields C_s, C_n or C_{nv} for the point symmetry of the La site in LaC_2O_4Cl. This indicates, probably, but of course not invariably, a monoclinic or triclinic structure.

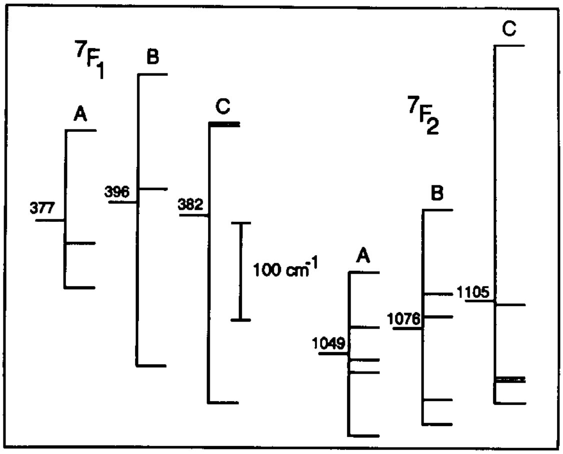

Fig. 4. The crystal field splittings of the $^7F_{1,2}$ levels of the Eu^{3+} ion in $LaC_2O_4Cl \cdot 3H_2O$ (A), LaC_2O_4Cl (B) and LaOCl (C).

The complete lifting of the $2J+1$ degeneracy of the $^7F_{1,2}$ levels and the absence of selection rules also result from a low site symmetry.

The completely different c.f. splittings of the $^7F_{1,2}$ levels in each of the three compounds also indicate naturally different structures (Fig. 4). The remarkable dissimilarity between the luminescence spectra of the anhydrous salt and the oxychloride, obviously results from further structural rearrangements during the decomposition of LaC_2O_4Cl. However, the very large c.f. splittings found in both LaC_2O_4Cl and LaOCl, usually result from strongly anisotropic coordination of the RE site. In LaOCl, the result is a complete separation of the anion (Cl^-) and the complex cation $(LaO)_n^{n+}$ layers [20]. The crystal structure of LaC_2O_4Cl may also be of lamellar type.

CONCLUSIONS

The present work has shown that high-resolution luminescence spectroscopy is an invaluable tool in the identification of the intermediate phases and their possible structures during the thermal decomposition of rare earth materials such as $LaC_2O_4Cl \cdot 3H_2O$. Luminescence spectroscopy has two main advantages over the traditional TG/DTG or X-ray diffraction techniques: the simultaneous observation of several intermediate phases and the derivation of structural data on practically amorphous materials. In this particular study it has been ascertained by TG/DTG and QMS techniques that the dehydration of $LaC_2O_4Cl \cdot 3H_2O$ occurs without intermediate hydrate phases. The Eu^{3+} luminescence was used as a structural probe in the identification of unknown phases. The success of the present work provides a good example of the exploitation of advanced interdisciplinary chemistry in the resolution of problems in material science.

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