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Preparation, thermal decomposition and lifetime of Eu(III)-phenanthroline complex doped xerogel

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Abstract

The main purpose of this work is proposing a new method of using non-isothermal formal kinetics analysis to predict the lifetime of luminescent complex materials. The Eu(III)-phenanthroline complex doped xerogel has been in situ synthesized by a catalyst-free sol–gel method. The photoluminescence spectra and TG curves of the xerogel verify the formation and decomposition of Eu(III)-phenanthroline complex in xerogel. The decomposition of the xerogel formally occurs in three steps. The Friedman and FWO isoconversional methods and multivariate non-linear regression method are used for formal kinetic analysis. The overall decomposition process below 800 °C is fitted by three-step consecutive reaction. The best fitted model for each step is F_n (n order reaction, the corresponding function $f(\alpha)$ is $(1-\alpha)^n$). Correlation coefficient is 0.99956. The lifetime values of xerogel at different temperatures are predicted based on non-isothermal kinetic models by the 5% decomposition of europium organic complex.

Keywords: Formal kinetics; Thermal decomposition; Multivariate non-linear regression; Lifetime; Europium complex doped xerogel

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1. Introduction

Great interest has been attracted to the properties of lanthanide organic complexes since Lehn [1] proposed that luminescent lanthanide organic complexes could act as efficient Light Conversion Molecular Device (LCMD). Most of those researches are interested in the synthesis and luminescence properties of materials; however, there is only limited research on the lifetime of luminescence lanthanide complexes [2–4], which are the main hindrance to their application. Kinetic analysis of thermal analysis data, an important tool for estimating the thermal stability and shelf life of drugs [5], has been used to make kinetic analysis and predictions of lifetime of lanthanide organic complexes [2–4].

It is difficult to express exactly the concentration profile in the solid particle. Simplified models of reactant/product interface movement in hypothetical bodies must be introduced in the kinetic analysis. Thus, traditional force-fitting kinetic analysis methods are likely to conceal the kinetic complexity [6]. Consequently, the available kinetic information is physically meaningless. So more attention should be drawn to the formal kinetic analysis [7], in which the reaction rate is an empirical function of time and temperature, and the real reaction mechanism is not essential. Real reaction steps are often put together to one formal step, so n (order of reaction) can show arbitrary values. Its main goal is the precise mathematical description of the complete range of reaction and based on this to get reliable predictions.

For practical application, luminescence lanthanide organic complexes are often doped into different matrices [8–10]. Eu(III)-phenanthroline complex $[\mathrm{Eu(phen)_2}^{3+}]$ doped xerogel is an important system and has attracted much research attention [8,9]. In this work, the $[\mathrm{Eu(phen)_2}^{3+}]$ doped xerogel was used as an example and a new method of using non-isothermal formal kinetics to predict the lifetime of luminescent materials was proposed.

2. Kinetic consideration

The combination of isoconversional methods and non-linear regression analysis is probably the best way for a formal kinetic

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analysis of processes in solids [7,11]. Model-free isoconversional methods allow for evaluating Arrhenius parameters without choosing the reaction model. These methods are based on the isoconversional principle that states that the reaction rate at a constant extent of conversion is only a function of the temperature [12].

$$\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)_\alpha}{\mathrm{d}T^{-1}} = -\frac{E_\alpha}{R} \tag{1}$$

(Henceforth, the subscript α indicates the values related to a given extent of conversion).

From Eq. (1), the differential isoconversional method of Friedman [13] and the integral isoconversional methods of Flynn and Wall [14] and Ozawa [15] can be obtained at Eq. (2) and Eq. (3), respectively

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\alpha = \mathrm{Const} - \frac{E_\alpha}{RT} \tag{2}$$

$$\ln(\beta) = \mathrm{Const} - \frac{E_\alpha}{RT_\alpha} \tag{3}$$

The conclusion by some that model fitting is a poor approach is largely due to improper use of model fitting, such as fitting a single heating rate or multiple heating rates separately [16]. Compared to the single curve analysis, the quality of fitting models simultaneously to multi-thermal history data diminishes considerably for the non-applicable reaction types, so the distinguishability between the individual reaction types improves drastically [17]. Multivariate non-linear regression is based on multiple heating rates, making the assumption that the parameters of the model are identical for measurements at all heating rates [17]. It has recently attracted much interest [11,18].

3. Experimental

The starting materials for preparation of the silica are tetraethoxysilane (TEOS), absolute ethanol and deionized water. They were mixed at the ratio of c_{TEOS}:c_{ethanol}:c_{water} = 1:4:4. The preparation process was under neutral pH condition, no acid or base added. The sol was stirred for 1 h at room temperature, and then with continuous stirring, 3 mol% $\mathrm{EuCl_3}\cdot n\mathrm{H_2O}$, and 6 mol% 1,10-phenanthroline ethanol solutions were added into the sol. The molar ratio of c_{TEOS}:c_{ethanol} of the final sol is 1:8, and the pH is 6–7. The mixed solution was vigorously stirred for 1 h and subsequently kept in a sealed Petri dish at 40 °C until the onset of gellation. After aging at 40 °C for 1 week, the gel was dried at 80 °C for 10 h. The xerogel was heated at 200 °C or 450 °C for 5 h, respectively.

Photoluminescence excitation and emission spectra and fluorescence lifetimes were recorded at room temperature with a Hitachi F-4500 fluorescence spectrophotometer equipped with a 450 W xenon lamp as the excitation source.

Simultaneous TG-DTA measurements were performed on a Netzsch STA 449C thermal analyzer. Experiments were carried out in static air, at heating rates of 1, 5, 10 and 20 °C/min. The sample is the xerogel after heated at 200 °C, and the mass was kept at about 6 mg.

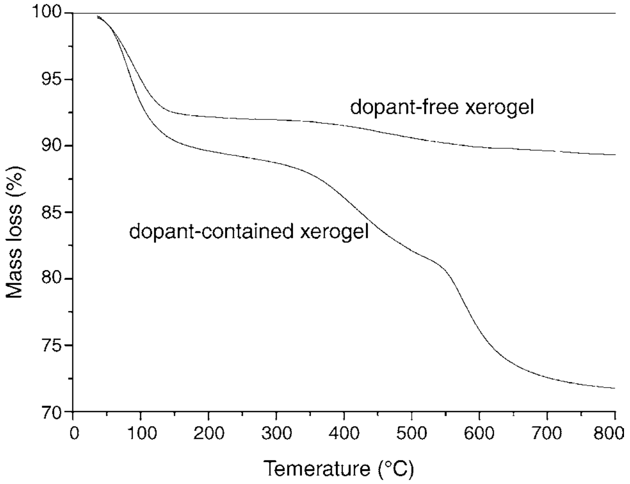

Fig. 1. The TG curves of the undoped and the complex doped xerogel at 20 °C/min in air.

4. Results and discussion

4.1. Thermal decomposition

The thermal decomposition TG curve of an undoped sample is compared to that of the doped xerogel in Fig. 1. It is observed that the thermal decomposition of the undoped sample has two steps. The mass loss below 250 °C is resulted from the absorbed water of xerogel during the storage, and that above 300 °C is ascribed to the decomposition of silanol. The thermal decomposition of the doped xerogel below 800 °C occurs in three steps. The first step (below 250 °C) has a mass loss of about 11%, also resulted from the absorbed water of xerogel during the storage. The second and the third step (above 250 °C) both have a mass loss of about 9%, corresponding to the decomposition of a phenanthroline ligand and a little silanol. It is assumed that the final products after decomposition at 800 °C are $\mathrm{SiO_2}$ and $\mathrm{SiO_2/Eu_2O_3}$ for undoped sample and complex doped xerogel respectively, then their mass loss above 250 °C relative to the mass retained are 3.0% and 24.3%. So the experimental mass loss for europium complex is 21.3%, which is close to the theory value 20.4% of the decomposition of doped $\mathrm{Eu(phen)_2Cl_3}$ complex to $\mathrm{Eu_2O_3}$ [8]. TG/DTG/DTA curves of xerogel at a heating rate of 20 °C/min in air are shown in Fig. 2. It is shown that the decomposition of the third step is exothermic, which indicates the oxidation of some ligands. TG curves of the thermal decomposition of xerogels in air at four heating rates are shown in Fig. 3. The mass loss is almost independent of the heating rates.

4.2. Photoluminescence properties

Photoluminescence excitation and emission spectra of xerogel are shown in Fig. 4. The sharp peak centered at 466 nm in the excitation spectrum is attributed to $^7F_0 \rightarrow {}^5D_2$ f–f transition of $\mathrm{Eu^{3+}}$ ion. The broad and strong excitation band at about 210–410 nm is attributed to the excitation of organic ligand, which indicates the efficient energy transfer from ligands to

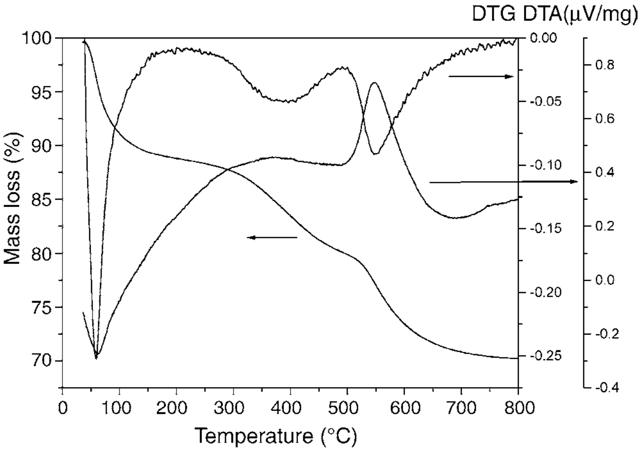

Fig. 2. TG/DTG/DTA curves of xerogel at a heating rate of 20 °C/min in air.

europium ions. Five bands associated to $^5D_0 \rightarrow {}^7F_i$ ($i = 0$–4) spin forbidden f–f transitions of Eu^{3+}, respectively, can be observed in the emission spectra. Almost all the emitted light is emitted through the Eu^{3+} ion, since there is little luminescence between 400 and 500 nm, which is correspond to the emission from the triplet state of phenanthroline. All these indicate the formation of $Eu(phen)_2{}^{3+}$ complex in the xerogel after heated at 200 °C for 5 h. After heated at 450 °C for 5 h, the luminescence intensity excited from the organic ligands decreases and the fine structure of $^5D_0 \rightarrow {}^7F_2$ transition disappears, indicating the partial decomposition of Eu(III)-phenanthroline complex.

4.3. Kinetics analysis

4.3.1. Estimation of the activation energy E

Both Friedman and FWO methods are applied to calculate the dependence of E on α (fractional mass loss), and the calculated values of the apparent activation energy at different extent of conversion are presented in Fig. 5.

According to Fig. 5, the apparent activation energies calculated by Friedman and FWO methods are very close. So these activation energies are reliable and close to the real values. Three steps can be distinguished from the dependence of E on extent of conversion α, and the average values of each step are listed in Table 1. The region between the first

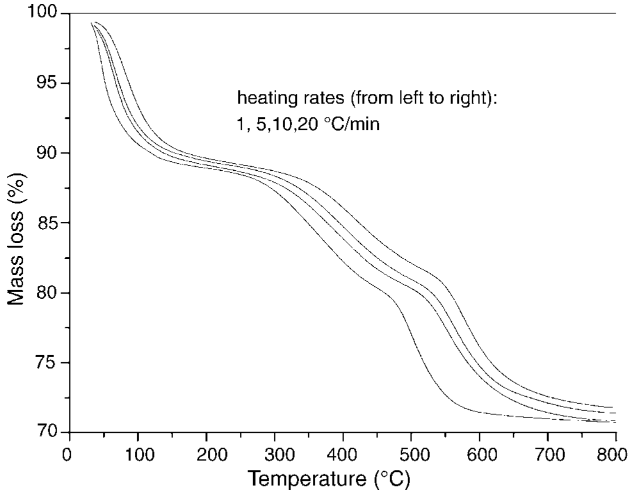

Fig. 3. TG curves of xerogel at different heating rates in air. Heating rates are 1, 5, 10 and 20 °C/min (from left to right).

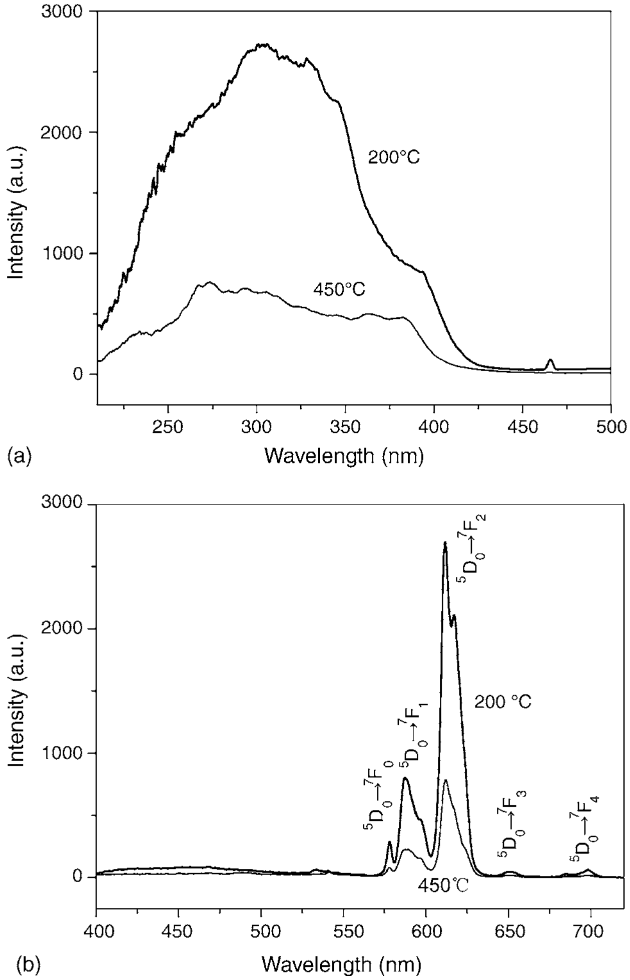

Fig. 4. (a) Photoluminescence excitation (monitored at 611 nm) and (b) emission spectra (excited at 297 nm) of xerogel.

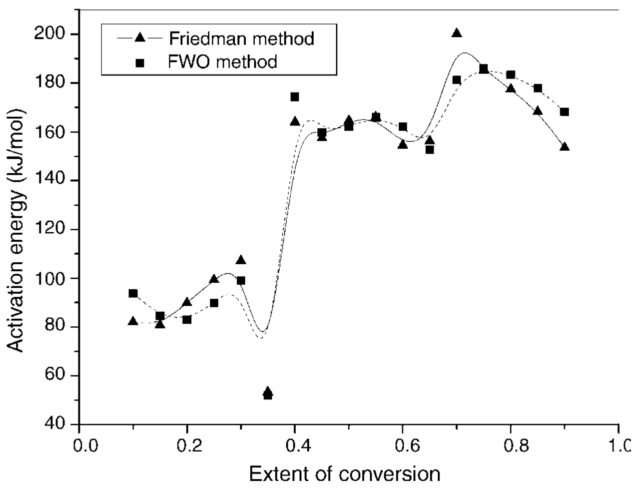

Fig. 5. Calculated apparent activation energies using the Friedman and FWO methods plotted against the extent of conversion.

Table 1
Average-activation energies E at different reaction steps calculated by Friedman and FWO methods

Zone of extent of conversion	0.1–0.3	0.4–0.65	0.70–0.90
Average E			
Friedman method	91.9	160.5	176.9
FWO method	90.0	162.8	179.3

step and the second step (α close to 0.35) has relatively large error.

4.3.2. *Determination of the kinetic model*

Multivariate non-linear regression method is applied to formal kinetic analysis. Four dynamic measurements run at heating rates of 1, 5, 10 and 20 °C/min are brought together during the analysis. According to Fig. 3 and the activation energy dependence obtained by isoconversional methods, the overall decomposition process below 800 °C formally occurs in three steps. So it is fitted by three-step consecutive reaction. A region is set for the activation energy of each step according to the apparent activation energies calculated by Friedman and FWO methods. The scaling values for three steps are 90–92, 160–163 and 176–180 kJ/mol, respectively. The best fitted model for each step is F_n (n order reaction). Correlation coefficient is 0.99956. The corresponding function $f(\alpha)$ of F_n is $(1-\alpha)^n$, and the kinetics parameters of each step are listed in Table 2.

4.4. *The prediction of lifetime*

According to the fitted models, the isothermal decomposition behavior and the lifetime at different temperatures can be predicted. From the isothermal prediction, it is obtained that the drastic mass loss corresponding to the dehydration is about 10.85% and the mass retained after the complete decomposition of organic complex is about 70.66%. Since the decomposition of luminescent lanthanide complex is in agreement with the decrease of the luminescent intensity [8], the decomposition of the doping complex can be used as an indicator of the lifetime of the xerogel. Referring to the estimating of shelf life of drugs [5], in this work, the lifetime of xerogel is defined as the 5% decomposition of luminescent europium complex, corresponding to the mass retained of about 88.22% in the TG curve. The lifetime values of xerogel at different temperatures are listed in Table 3. It is observed that at temperatures listed in Table 3, the lifetime is very sensitive to the minor change of temperature.

Table 2
Fitted kinetic parameters of xerogel resulting from multivariate non-linear regression (heating rate 1, 5, 10 and 20 °C/min) with the assumption of consecutive reaction $A \rightarrow B \rightarrow C \rightarrow D$

Reaction step	E (kJ/mol)	lg A	n
$A \rightarrow B$	91.9 ± 4.3	12.28 ± 0.69	5.3 ± 0.2
$B \rightarrow C$	160.1 ± 7.5	10.74 ± 0.66	6.4 ± 0.5
$C \rightarrow D$	179.9 ± 5.2	8.87 ± 0.35	1.5 ± 0.1

Each step is fitted by F_n model. Correlation coefficient is 0.99956.

Table 3
The lifetime values of xerogel at different temperatures

T (°C)	Lifetime (h)
160	13100
165	7890
170	4810
175	2960
180	1840
185	1160
190	736
195	472
200	305
205	200

5. Conclusions

The Eu(III)-phenanthroline complex doped xerogel has been in situ synthesized by a catalyst-free sol–gel method. The TG curves and luminescence spectra indicate the formation of $Eu(phen)_2^{3+}$ complex in xerogel after heated at 200 °C and the partial decomposition after heated at 450 °C. The decomposition of the xerogel occurs in three steps. The apparent activation energies calculated by Friedman and FWO methods are very close, and the concrete values for three steps are about 90–92, 160–163 and 176–180 kJ/mol, respectively. With multivariate non-linear regression method, the overall decomposition process below 800 °C is fitted by three-step consecutive reaction of F_n. The fitted n, E and lg A of the first step are 5.3 ± 0.2, 91.9 ± 4.3 and 12.28 ± 0.69 kJ/mol; those of the second step are 6.4 ± 0.5, 160.1 ± 7.5 and 10.74 ± 0.66 kJ/mol; those of the final step are 1.5 ± 0.1, 179.9 ± 5.2 and 8.87 ± 0.35 kJ/mol. The lifetime values of xerogel at different temperature (predicted by the 5% decomposition of europium organic complex) indicate that the xerogel may find application at temperature below about 200 °C, and at this temperature zone, the lifetime is very sensitive to the minor change of temperature.

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