*Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 2, 347–350*

# PREPARATION, THERMAL DECOMPOSITION AND LIFETIME OF EUROPIUM TRIS(DIBENZOYLMETHANATO)PHENANTHROLINE COMPLEX DOPED XEROGEL

*J.-H. Hong*[1,2]*, J. Min*[1]*, G.-H. Guo*[1] *and K.-L. Zhang*[1,3,4]*

[1]College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China
[2]Faculty of Material Sience and Chemical Engineering, China University of Geosciences, Wuhan 430074, China
[3]Centre of Nanoscience and Nanotechnology Research, Wuhan University, Wuhan 430072, China
[4]Institute of Chemistry and Chemical Industry, Wuhan University, Wuhan 430072, China

The Eu tris(dibenzoylmethanato)phenanthroline complex doped xerogel has been synthesized by a catalyst-free sol-gel roure. The non-isothermal kinetic analysis is calculated by Friedman isoconversional method and multivariate non-linear regression method. The overall decomposition process below 600°C is fitted by an Fn model (*n* order reaction), corresponding to the dehydration of the matrix, and a two-step consecutive reaction of Cn model (*n* order autocatalytic reaction), corresponding to the decomposition of organic complex. Correlation coefficient is 0.99986. The lifetime values of xerogel, defined as the 5% decomposition of europium organic complex, indicate that the xerogel can find application at near room temperature.

***Keywords:*** *europium complex doped xerogel, lifetime, multivariate non-linear regression, non-isothermal kinetics, thermal decomposition*

## Introduction

Great interest has been attracted to the properties of lanthanide organic complexes since Lehn [1] proposed that luminescent lanthanide organic complexes can act as efficient Light Conversion Molecular Device (LCMD). Organic complexes usually have too low thermal and mechanical resistances to be directly used as luminescent materials. Some groups have focused their interest on embedding luminescent complexes into matrices such as sol–gel glasses [2], polymers [3] and inorganic–organic hybrid materials [4].

Most of those researches are interested in the synthesis and luminescence properties of materials; however, there is only limited research on the thermal kinetics and lifetime of luminescence lanthanide complexes, 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 [6–9]. However, traditional force-fitting kinetic analysis methods based on single heating-rate data are likely to conceal the kinetic complexity and even not applicable [10]. The model-free isoconversional methods and model-fitting methods that use multiple heating rates data have been verified to be particularly successful in correctly describing the multi-step kinetics in the simulated data.

For practical application, luminescence lanthanide organic complexes are often doped into different matrices. In this work, the Eu tris(dibenzoylmethanato) phenanthroline [Eu(DBM)$_3$phen] complex doped xerogel was in situ synthesized and its photoluminescence and non-isothermal kinetics were studied. The lifetime at different temperatures were predicted by the fitted non-isothermal kinetic models.

## 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% $EuCl_3\cdot nH_2O$, 9 mol% dibenzoyl methane and 3 mol% 1,10-phenanthroline ethanol solution 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 gellation. After aging at 40°C for one week, the gel was dried at 80°C for 10 h.

Photoluminescence excitation and emission spectra and fluorescence lifetimes were recorded at room temperature with a Hitachi F-4500 fluorescence

---

* Author for correspondence: klzhang@whu.edu.cn

*1388–6150/$20.00*

*Akadémiai Kiadó, Budapest, Hungary*
*Springer, Dordrecht, The Netherlands*

spectrophotometer equipped with a 450 W xenon lamp as the excitation source.

Thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTG) were performed on a Netzsch STA449C thermal analyzer. Experiments were carried out in static air, at heating rates of 2, 5, 10°C $\text{min}^{-1}$. The sample mass used in all TA runs was kept at about 6 mg.

## Results and discussion

### *Photoluminescence and thermal decomposition*

Photoluminescence excitation and emission spectra of xerogel are shown in Figs 1 and 2, respectively. The sharp peak centered at 466 nm in excitation spectrum is attributed to $^7F_0\rightarrow^5D_2$ *f–f* transition of $Eu^{3+}$ ion. The broad and strong excitation band at about 220 to 450 nm is attributed to the excitation of organic ligand, which indicates the efficient energy transfer from ligands to europium ions. Three bands associated to $^5D_0\rightarrow^7F_i$ ($i$=0–2) spin forbidden *f–f* transitions of $Eu^{3+}$, respectively, can be observed in emission spectrum. In the emission spectrum, the splitting of $^5D_0\rightarrow^7F_2$ transition is similar to that of pure Eu(DBM)$_3$phen complex [11]. All the emitted light is emitted through the $Eu^{3+}$ ion. There is no evidence for emission from the triplet state of the dibenzoyl methane or phenanthroline. The decay curve of the xerogel can be fitted with a single exponential function and the lifetime is 435 µs, which is similar to that obtained by Zhao [11]. All these indicate the formation of Eu(DBM)$_3$phen complex in xerogel.

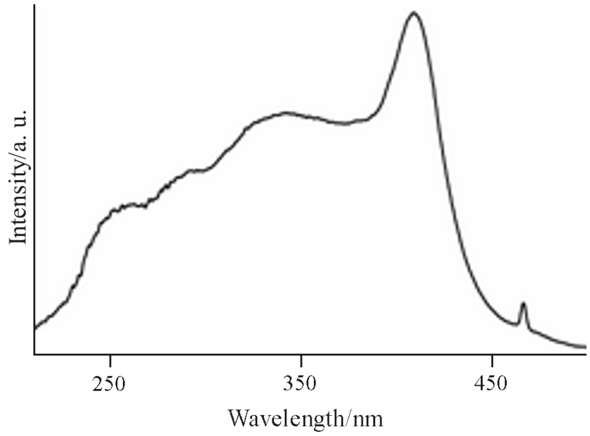

**Fig. 1** Photoluminescence excitation spectrum (monitored at 612 nm) of xerogel

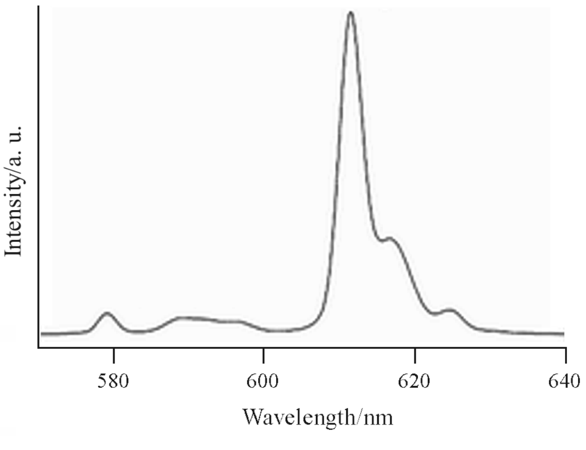

**Fig. 2** Photoluminescence emission spectrum (excited at 410 nm) of xerogel

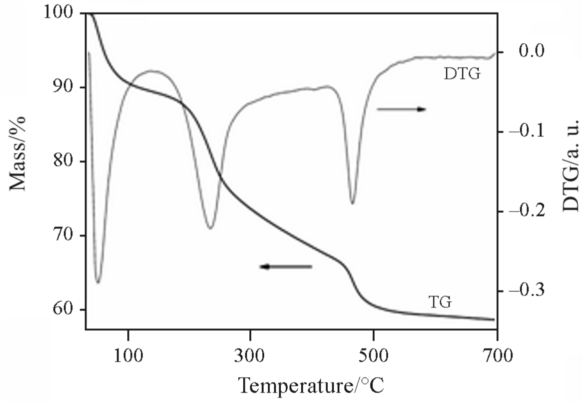

**Fig. 3** TG/DTG curves of xerogel at a heating rate of 2°C $\text{min}^{-1}$ in air

TG and DTG curves of the thermal decomposition of xerogel at a heating rate of 2°C $\text{min}^{-1}$ in air are presented in Fig. 3. It can be seen from TG curves that the thermal decomposition of xerogel below 700°C occurs in three steps. The mass loss of the first step (below 150°C) is about 11%, resulted from the loss of adsorbed water and silanol. The DTG peaks of the second and the third steps are about 240 and 460°C, corresponding to the fastest decomposition rates of the two steps. According to the knowledge of thermal stability of both organic ligands, the second step is ascribed to the decomposition of dibenzoyl methane, and the third step is that of phenanthroline. The overall mass loss of both steps (150–500°C) is about 30%, corresponding to the decomposition of europium organic complex.

### *Kinetics*

For the prediction of the lifetime of europium organic complex doped xerogel, the thermal kinetics is studied.

#### Estimation of the activation energy *E* of dehydration

For kinetic analysis, model-free isoconversional methods allow for evaluating Arrhenius parameters without choosing the reaction model. The dependence of E on the extent of conversion assists in both detecting multi-step processes and drawing certain mecha-

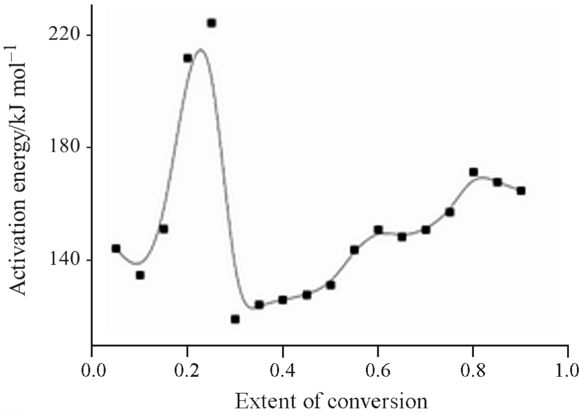

**Fig. 4** Calculated apparent activation energies using the Friedman method plotted *vs.* the extent of conversion

nism conclusions [10]. The activation energies calculated with isoconversional methods act as initial values for multivariate nonlinear regression process [12]. In this work, Friedman [13] method is 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. 4. The apparent activation energy of each step is about 150, 120 and 160 kJ mol$^{-1}$

Determination of the kinetic model

Multivariate non-linear regression method [12] (Netzsch Thermokinetics) is applied to determinate the most-probable kinetic model. 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 [12]. Compared to the single curve analysis, the quality of fit diminishes considerably for the non-applicable reaction types [12]. So the distinguish ability between the individual reaction types improves drastically. In addition, there are no limitations with respect to the complexity of the model, and consequently it can be applied to multi-step reactions. We have previously studied the kinetics of thermal decomposition with model-free isoconversional methods and multivariate non-linear regression [14].

In this work, three dynamic measurements run at heating rates of 2, 5 and 10°C min$^{-1}$ are brought together during the analysis. Since no apparent relation between the dehydration and the decomposition of organic complex, a three-step composite reaction is selected as follows:

$$A \rightarrow B$$

$$C \rightarrow D \rightarrow E$$

16 commonly used models [12] were tested, and models with a high correlation coefficient and similar *E* values with that calculated by isoconversional method were the most-probable models. In this work, the most-probable models are Fn for A→B, Cn for C→D and D→E. The corresponding function $f(\alpha)$ of Fn, *n* order reaction, is $(1-\alpha)^n$; $f(\alpha)$ of Cn, *n* order autocatalytic reaction, is $(1-\alpha)^n(1+K_{cat}\alpha)$. The fitted curves are shown in Fig. 5 and the fitted kinetic parameters are listed in Table 1. Correlation coefficient is 0.99986.

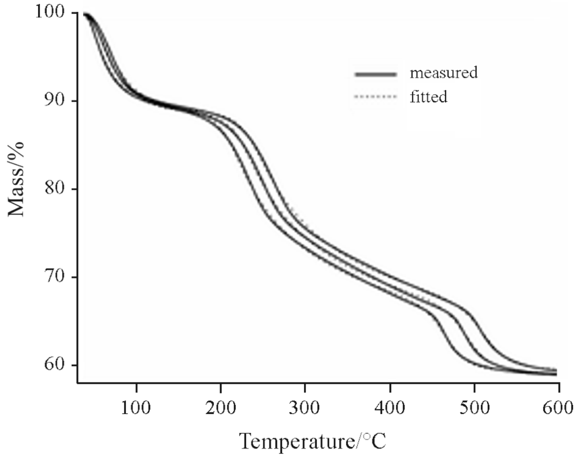

**Fig. 5** Measured and fitted TG curves of xerogel at different heating rates in air. Heating rates are 2, 5 and 10°C min$^{-1}$ (from left to right)

**Table 1** Fitted kinetic parameters of xerogel resulting from multivariate non-linear regression (heating rate 2, 5 and 10°C min$^{-1}$). Correlation coefficient is 0.99986. C→D step takes up 74.5% of the overall decomposition of organic complex

| Reaction step and model | $E$/kJ mol$^{-1}$ | $A$/s$^{-1}$ | $n$ | $K_{cat}$ |
|---|---|---|---|---|
| A→B Fn | 160.5 | $3.0\cdot10^{23}$ | 6.4531 | 0.00 |
| C→D Cn | 115.6 | $7.4\cdot10^{8}$ | 9.4128 | 18.38 |
| D→E Cn | 160.4 | $1.3\cdot10^{8}$ | 1.5620 | 6.619 |

*E* – activation energy, *A* – preexponential factor, *n* – reaction order, $K_{cat}$ – catalysis constant

As presented in Table 1, the activation energy of each step is close to that calculated by Friedman method. The C→D step takes up about 3/4 of the overall decomposition of organic complex, corresponding to the decomposition of 3 parts of dibenzoyl methane ligand.

### *The prediction of lifetime*

According to the fitted models, the isothermal decomposition behavior, also the lifetime, at different temperatures can be predicted. The isothermal decomposition behavior at different temperatures is shown in Fig. 6. The drastic mass loss at the beginning is corresponding to the dehydration. After that is the decomposition of organic complex. In this work, the lifetime

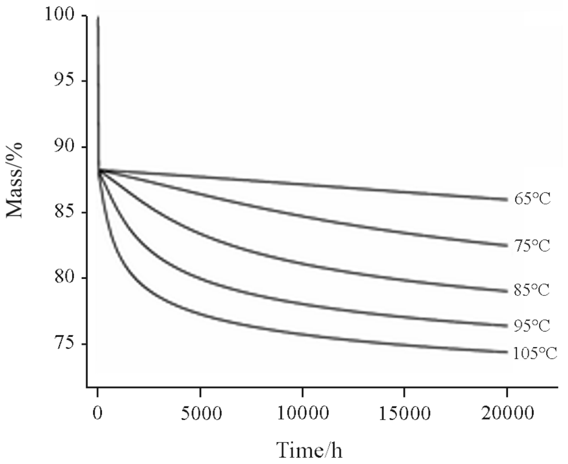

**Fig. 6** The isothermal decomposition behavior of xerogel at different temperatures

**Table 2** The lifetime values of xerogel at different temperatures

| *T*/°C | Lifetime/h | *T*/°C | Lifetime/h |
|---|---|---|---|
| 65 | 16650 | 90 | 982 |
| 70 | 9150 | 95 | 585 |
| 75 | 5100 | 100 | 353 |
| 80 | 2900 | 105 | 215 |
| 85 | 1675 | 110 | 133 |

of xerogel is defined as the 5% decomposition of luminescent europium complex. According to Fig. 6, there is about 12% mass loss at the short beginning time, due to the dehydration. The mass retained after the decomposition of europium organic complex is about 58%. The 5% of the decomposition of organic complex is the mass loss of 1.5% in the TG curve, so the lifetime of organic complex doped xerogel is predicted at the mass retained of 86.5%. The lifetime values of xerogel at different temperatures are listed in Table 2. It is observed that the xerogel can find application at near room temperature, and at higher temperature, the lifetime is very sensitive to the minor change of temperature.

## Conclusions

The decomposition of the xerogel occurs in three steps. With multivariate non-linear regression method, the overall decomposition process below 600°C is fitted by two independent routes: The one is the dehydration (Fn model), and the other is a two-step consecutive reaction (both steps are Cn model). The lifetime values of xerogel at different temperature (predicted by the 5% decomposition of europium organic complex) indicate that the xerogel can find application at near room temperature, and at higher temperature, the lifetime is very sensitive to the minor change of temperature.

## Acknowledgements

We gratefully acknowledge that this work was supported by National Natural Science Foundation of China (20071026).

## References

1 J. M. Lehn, Angew. Chem. Int. Edit. Engl., 102 (1990) 1347.
2 S. Bucella, P. Riello, B. F. Scremin, P. Calvelli, R. Polloni, A. Speghini, M. Bettinelli and A. Benedetti, Opt. Mater., 27 (2004) 249.
3 D. M. Wang, J. H. Zhang, Q. Lin, L. S. Fu, H. J. Zhang and B. Yang, J. Mater. Chem., 13 (2003) 2279.
4 V. Bekiari, G. Pistolis and P. Lianos, Chem. Mater., 11 (1999) 3189.
5 G. T. Long, S. Vyazovkin, N. Gamble and C. A. Wight, J. Pharm. Sci-US., 91 (2002) 800.
6 C. R. S. Morais, A. G. Souza and P. A. Santa-Cruz, J. Alloy Compd., 344 (2002) 101.
7 M. E. de Mesquita, L. S. Barreto, M. L. Santos and R. O. Freire, J. Non-cryst. Solids, 351 (2005) 394.
8 J.-J. Zhang, R.-F. Wang and H.-M. Liu, J. Therm. Anal. Cal., 66 (2001) 431.
9 J.-J. Zhang, R.-F. Wang, S.-P. Wang, H.-M. Liu, J.-B. Li, J.-H. Bai and N. Ren, J. Therm. Anal. Cal., 79 (2005) 181.
10 S. Vyazovkin, Thermochim. Acta, 355 (2000) 155.
11 D. Zhao, W. P. Qin, C. F. Wu, G. S. Qin, J. S. Zhang and S. Z. Lü, Chem. Phys. Lett., 388 (2004) 400.
12 J. Opfermann, J. Therm. Anal. Cal., 60 (2000) 641.
13 H. L. Friedman, J. Polym. Sci. Part C, 6 (1963) 183.
14 K. L. Zhang, J. H. Hong, G. H. Cao, D. Zhan, Y. T. Tao and C. J. Cong, Thermochim. Acta, 437 (2005) 145.

Received: September 1, 2005
Accepted: June 14, 2006

DOI: 10.1007/s10973-005-7306-3