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Materials Chemistry and Physics 87 (2004) 44–48
MATERIALS CHEMISTRY AND PHYSICS
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Luminescent sol–gel thin films based on europium-substituted heteropolytungstates

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Received 15 December 2003; received in revised form 4 March 2004; accepted 5 April 2004

Abstract

Polyester thin films containing europium-substituted heteropolytungstate were obtained on quartz plate by the sol–gel method. The films exhibited the characteristic emission bands of the europium ion. The red to orange intensity ratio (R:O) of Eu^{3+} in the films increased as compared to the corresponding heteropolytungstate solids. The fluorescence lifetime of europium is shorter in the thin film than in the heteropolytungstate solid. The results indicated that the formation of europium-substituted heteropolytungstate/polyester thin film has great effect on the luminescence of europium-substituted heteropolytungstate.

Keywords: Luminescence; Sol–gel; Europium; Polyoxometalate

1. Introduction

Rare earths have long been known for their characteristic luminescence properties. They have widely been used in cathodoluminescent display phosphor screens, liquid lasers, electroluminescent devices and as probe ions in biochemistry because of their high quantum yields of the emission, large Stokes shifts, long decay times and narrow emission bands [1–3]. Europium and terbium have attracted more attention because of their excellent luminescent characters. Europium complexes with β-diketones, aromatic carboxylic acids, crown-ethers and cryptates exhibit high color purity and strong fluorescent intensity due to the efficient energy transfer from organic ligands to the europium ion (the so-called antenna effect) through the triple state. In addition, ligands play an important role in protecting the europium ion from its environment (residual water or solvent molecules, etc.). This shielding effect considerably reduces the non-radiative de-activation process, which arises from coupling with the lattice vibrations and concentration quenching [4]. However, application of these organic complexes in optical devices is very limited due to their low thermal and mechanical resistance. Polyoxometalates are a distinct class of multinuclear complexes with interesting optical, electric and magnetic properties. Rare earth-substituted polyoxometalates have been found exhibiting excellent luminescence properties and have been proved to be good candidates to fabricate hybrid organic/inorganic luminescent materials [5–7]. Recently, much attention has been directed to the sol–gel method in the preparation of optical materials containing rare earths because it offers the possibility of controlling the micro- and macrostructure of the optically transparent matrix [8]. However, conventional silica matrix tends to crack during the drying period. To improve the mechanical strength of the gels, we accommodate rare earth-substituted polyoxometalates into polymer matrix instead of silica matrix. In addition, polymer matrix provides different environment of rare earths through interaction with complexes.

In the present study, europium-substituted heteropolytungstates were incorporated into citric acid (CA)/polyethylene glycol (PEG) matrices by sol–gel method. Esterification of citric acid occurs readily in the presence of PEG at moderate temperature (100–150 °C). As citric acid has three carboxylic acid groups, branched polyesters may be obtained. During the process of polyesterification of CA and PEG, europium-substituted heteropolytungstates were entrapped in the gel polyester. The luminescent properties, lifetimes of thin films were studied with respect to the corresponding pure complexes.

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doi:10.1016/j.matchemphys.2004.04.016

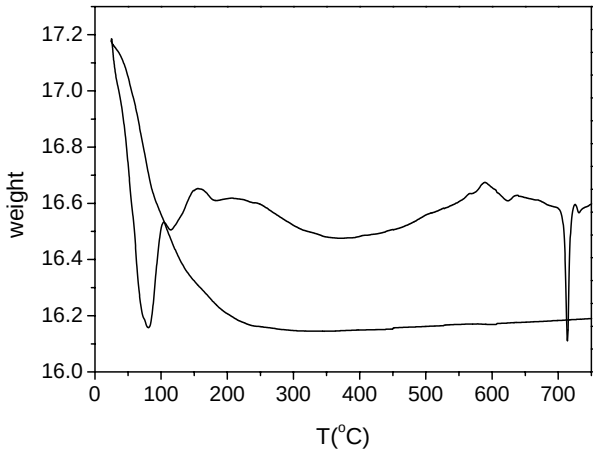

Fig. 1. TG–DTA figure of the $EuSiW_{11}$ powder.

2. Experimental

2.1. Synthesis and characterization of $K_mEu(XW_{11}O_{39})_2{\cdot}nH_2O$ (X = Si, Ge, B) complexes

$K_{13}Eu(SiW_{11}O_{39})_2{\cdot}28H_2O$ ($EuSiW_{11}$), $K_{13}Eu(GeW_{11}O_{39})_2{\cdot}25H_2O$ ($EuGeW_{11}$) and $K_{15}Eu(BW_{11}O_{39})_2{\cdot}22H_2O$ ($EuBW_{11}$) were prepared according to references [9,10]. The molecular formulas of the products were confirmed on the basis of elemental analysis, IR and TG–DTA analysis.

Fig. 1 represented the thermal decomposition of $EuSiW_{11}$. $EuSiW_{11}$ decomposed in three consecutive steps. The first mass loss occurred in the temperature range of 25–95 °C with the loss of 4.5% of the material, the second mass loss took place in the temperature range of 97–147 °C with 1.5% loss, and the third mass loss took place in the temperature range of 150–280 °C with 1.0% loss. The DTA plot showed four distinct endothermic peaks, three of which at 80, 115 and 183 °C corresponded to the loss of water molecule, the other one at 714 °C corresponded to the melting of $EuSiW_{11}$. Fig. 2 showed the IR spectrum of $EuSiW_{11}$. The IR spectrum of $EuSiW_{11}$ had four regions [11], which corresponded to metal–oxygen oscillations including Si–O stretching (1008.6 cm^{-1}), W–O stretching (951.9 cm^{-1}), and W–O–W stretching (900–600 cm^{-1}).

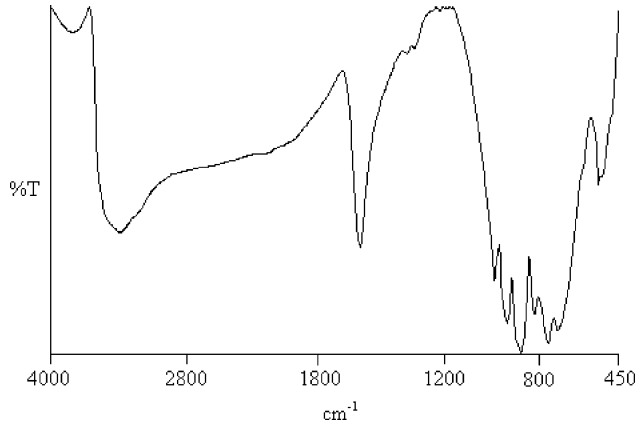

Fig. 2. IR spectra of the $EuSiW_{11}$ powder.

2.2. Thin film preparation

Appropriate amounts of $K_mEu(XW_{11}O_{39})_2{\cdot}nH_2O$ ($EuXW_{11}$) (X = Si, Ge, B) were dissolved in the aqueous solution of citric acid and polyethylene glycol (molecular weight 10,000). The molar ratio of $EuXW_{11}$, citric acid and polyethylene glycol was 1:2:0.5. A little excess portion of polyethylene glycol was to guarantee the esterification of the three carboxylic acid groups of citric acid. The mixture was stirred for about 3 h at room temperature. A homogeneous transparent solution was obtained and it was dip-coated on a quartz plate. The coating was dried in a drying oven for 3 h at 150 °C and the resulting thin film was stored in a desiccator for further measurements.

2.3. Measurements

The TG–DTA measurements were made with a SDT2960 thermal analyzer. IR spectra were recorded on a Nicolet 170 spectrophotometer using KBr pellets. UV–vis spectra were recorded on a Tu-1901 spectrophotometer. Luminescence spectra were measured on a Spex FL-2T2 spectrophotometer using xenon lamp as excitation source. Luminescence lifetime of Eu^{3+} was recorded on a Spex 1934D-phosphorescence spectrophotometer.

3. Results and discussion

3.1. UV spectra

The UV spectra of $K_mEu(XW_{11}O_{39})_2$ ($EuXW_{11}$) (X = Si, Ge, B) solutions and $EuXW_{11}$/polyester films are measured. Two major bands corresponded to the characteristic O → W transitions of heteropolytungstates are observed both in the spectra of $EuXW_{11}$ solutions and in the spectra of $EuXW_{11}$/polyester films. Fig. 3 illuminates the UV spectra of the $EuSiW_{11}$ solution and the $EuSiW_{11}$/polyester film. $EuSiW_{11}$ solution shows characteristic absorption bands of $EuSiW_{11}$ at 199 and 250 nm, which correspond to the $O_d \rightarrow W$ and $O_{b,c} \rightarrow W$ charge transitions, respectively. In the $EuSiW_{11}$/polyester film, characteristic absorption bands of $EuSiW_{11}$ can be observed and the peaks are red shift to 202 nm ($O_d \rightarrow W$) and 255 nm ($O_{b,c} \rightarrow W$), respectively. From the facts above, we can conclude that $EuSiW_{11}$ has been successfully incorporated in the polyester film. The same phenomena can be observed in the absorption spectra of $K_mEu(XW_{11}O_{39})_2$ (X = Ge, B) and their polyester films. UV data of $EuXW_{11}$ solution and $EuXW_{11}$/polyester films are listed in Table 1. Differences between the UV spectra of $EuXW_{11}$ solution and $EuXW_{11}$/polyester films can be attributed to the interactions between $EuXW_{11}$ and polyester

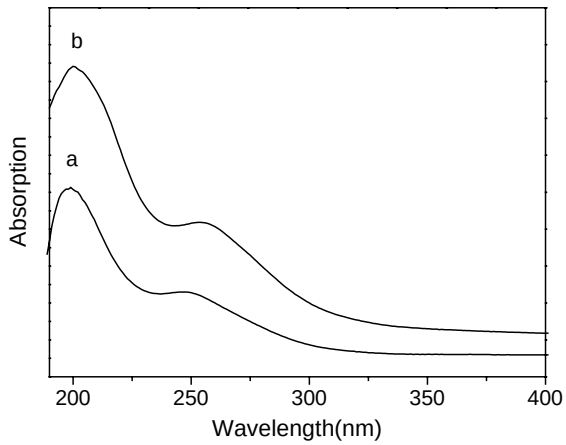

Fig. 3. UV spectra of the $EuSiW_{11}$ solution (a) and the $EuSiW_{11}$/polyester film (b).

Table 1
UV data of $EuXW_{11}$ solutions and $EuXW_{11}$/polyester films (X = Si, Ge, B)

	$O_d \rightarrow W$ transition	$O_{b,c} \rightarrow W$ transition
$EuSiW_{11}$ solution	199	250
$EuSiW_{11}$/PE film	202	255
$EuGeW_{11}$ solution	198	252
$EuGeW_{11}$/PE film	203	255
$EuBW_{11}$ solution	197	250
$EuBW_{11}$/PE film	202	254

matrix, which influence the O → W charge transitions of europium-substituted heteropolytungstates.

3.2. Excitation and emission spectra of $EuSiW_{11}$/polyester film and $EuSiW_{11}$ solid

Fig. 4 shows the excitation spectra of the $EuSiW_{11}$ solid (solid line) and the $EuSiW_{11}$/polyester film (dash line). The excitation spectrum of the $EuSiW_{11}$ solid consists of characteristic peaks of Eu^{3+} at 362, 376, 381, 385, 395, 417 and 465 nm, which correspond to $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5G_4$, $^7F_0 \rightarrow {}^5G_3$, $^7F_0 \rightarrow {}^5G_2$, $^7F_0 \rightarrow {}^5L_6$, $^7F_0 \rightarrow {}^5D_3$ and $^7F_0 \rightarrow {}^5D_2$ transitions, respectively. Nevertheless, the excitation spectrum of the $EuSiW_{11}$/polyester film differs greatly from that of the $EuSiW_{11}$ solid. The $EuSiW_{11}$/polyester film shows a strong wide band from 210 to 270 nm with a maximum peak at 250 nm and some weak characteristic peaks of Eu^{3+}. The wide band is assigned to ligand-to-metal charge transfer (LMCT) band, which has a close relationship with the luminescence of the complex. The difference between the spectrum of the $EuSiW_{11}$ solid and the $EuSiW_{11}$/polyester film indicates that the energy transfer process is different in different states of the complex. In the excitation spectrum of the $EuSiW_{11}$ solid, there are only sharp excited lines of Eu^{3+} and no charge transfer band could be found. This shows that the luminescence of the $EuSiW_{11}$ solid was mainly contributed by the excitation of Eu^{3+}. This kind of excitation could hardly result in efficient luminescence of the complex [12]. In $EuSiW_{11}$, Eu^{3+} is coordinated by two SiW_{11} groups through eight oxygen atoms forming an Archimedian antiprism. The extent of the delocalization of the d^1 electron in SiW_{11} ligand is great at room temperature. As a result, the energy excitated into SiW_{11} can hardly transfer to Eu^{3+} effectively, but falls back to the ground state by the non-radiative transition. That is why we cannot observe the LMCT band in the $EuSiW_{11}$ solid. However, an intense LMCT band of $EuSiW_{11}$ ($\lambda_{max} = 250$ nm) emerges in the $EuSiW_{11}$/polyester film, which indicates that the energy can be effectively transferred to Eu^{3+} in the $EuSiW_{11}$/polyester film. The formation of the $EuSiW_{11}$/polyester film reduces the delocalization of the d^1 electron in SiW_{11} ligand. The energy level of LMCT band of $EuSiW_{11}$ differs from before the entrapment of $EuSiW_{11}$ in polyester. Strengthened interaction between the energy level of Eu^{3+} and LMCT band of $EuSiW_{11}$ makes possible the energy transfer from ligands to rare earths.

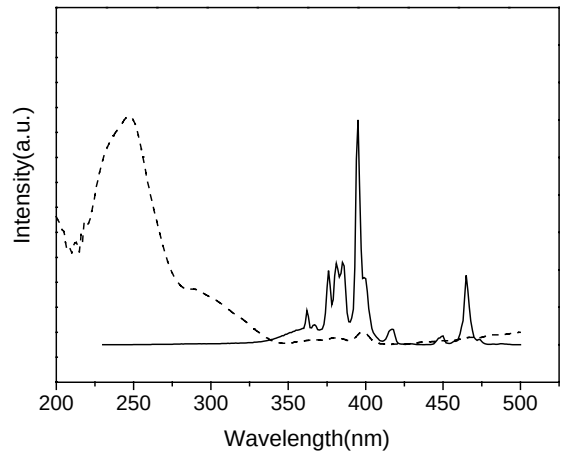

Fig. 4. Excitation spectra of the $EuSiW_{11}$ solid (solid line) and the $EuSiW_{11}$/polyester film (dash line).

The emission spectra of the $EuSiW_{11}$ solid (solid line) and the $EuSiW_{11}$/polyester film (dash line) excited at 395 and 250 nm, respectively, are shown in Fig. 5. Both of the solid and the film exhibit characteristic emission of Eu^{3+} ion, which originates from $^5D_0$ excited state of Eu^{3+} and terminates at ^7F_j ($j = 0$–4) ground state. It is obvious that the transitions correspond to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ are much stronger than those correspond to $^5D_0 \rightarrow {}^7F_j$ ($j = 0$, 3, 4). The $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition and its intensity varies with the crystal field strength acting on Eu^{3+} ions. As to the $^5D_0 \rightarrow {}^7F_2$ transition, it is an electric dipole transition and is extremely sensitive to chemical bonds in the vicinity of the Eu^{3+} ion. The possibility of $^5D_0 \rightarrow {}^7F_2$ transition will increase drastically if the site symmetry of Eu^{3+} ion decreases. As a result, the intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ transition to $^5D_0 \rightarrow {}^7F_1$ transition has been widely used as an indicator of Eu^{3+} site symmetry. In the $EuSiW_{11}$ solid, the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions split into two peaks at 592, 594 nm

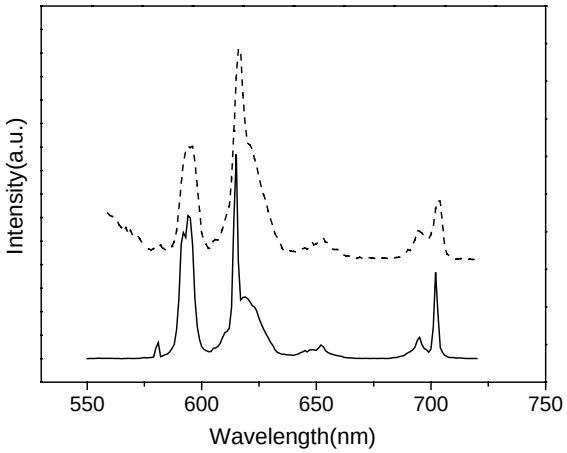

Fig. 5. Emission spectra of the $EuSiW_{11}$ solid (solid line) and the $EuSiW_{11}$/polyester film (dash line).

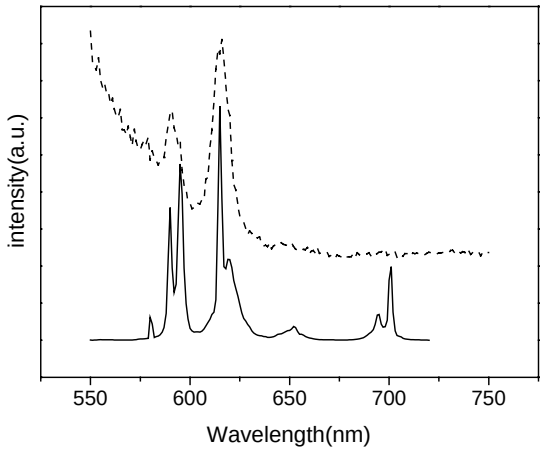

Fig. 6. Emission spectra of the $EuGeW_{11}$ solid (solid line) and the $EuGeW_{11}$/polyester film (dash line).

and 615, 619 nm, respectively. The emission peak at 581 nm corresponds to the $^5D_0 \rightarrow {}^7F_0$ symmetric forbidden emission and the peak at 651 nm is due to the $^5D_0 \rightarrow {}^7F_3$ transition. The splitting peaks at 694–701 nm can be assigned to the transition of $^5D_0 \rightarrow {}^7F_4$. However, no splitting was observed in the transition of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ in the $EuSiW_{11}$/polyester film. The relative intensity of the $^5D_0 \rightarrow {}^7F_2$ transition to $^5D_0 \rightarrow {}^7F_1$ transition increased after $EuSiW_{11}$ was incorporated in the polyester film. The ratio of the relative intensity between the $^5D_0 \rightarrow {}^7F_2$ transition and $^5D_0 \rightarrow {}^7F_1$ transition was 1.8 in the $EuSiW_{11}$/polyester film and lower (1.12) in the $EuSiW_{11}$ solid. The $^5D_0 \rightarrow {}^7F_2$ transition was considered hypersensitive to the site symmetry of Eu^{3+} ion; as a result, the increase of the ratio of the relative intensity of $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ suggested the lower symmetry of Eu^{3+} ion in the $EuSiW_{11}$/polyester film. The distortion of the symmetry may be due to the interaction between the polyester matrix and europium-substituted heteropolytungstates and resulting alteration of the transition energy levels of Eu^{3+}.

3.3. Emission spectra of $EuGeW_{11}$/polyester film and $EuGeW_{11}$ solid

Fig. 6 depicts the emission spectra of the $EuGeW_{11}$ solid (solid line) and the $EuGeW_{11}$/polyester film (dash line). The characteristic emission peaks of Eu^{3+}, which correspond to $^5D_0 \rightarrow {}^7F_j$ ($j = 0$–4) transitions, can be observed both in the $EuGeW_{11}$ solid and in the $EuGeW_{11}$/polyester film.

Nevertheless, obvious differences can be observed in the emission spectrum of the $EuGeW_{11}$/polyester film as compared to that of the $EuGeW_{11}$ solid. In the emission spectrum of the $EuGeW_{11}$ solid, the most intense emissions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ both split into two peaks. However, there is no splitting in the transition of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ in the $EuGeW_{11}$/polyester film. The ratio of the relative intensity between $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transition is higher in the $EuGeW_{11}$/polyester film than in the $EuGeW_{11}$ solid. Such changes are caused by the change of the site symmetry of Eu^{3+}, as have been explained in the emission spectra of the $EuSiW_{11}$ solid and the $EuSiW_{11}$/polyester film.

3.4. Emission spectra of $EuBW_{11}$/polyester film and $EuBW_{11}$ solid

The emission spectra of the $EuBW_{11}$ solid (solid line) and the $EuBW_{11}$/polyester film (dash line) are shown in Fig. 7. Both of them consist of the characteristic emission lines of Eu^{3+}, which correspond to $^5D_0 \rightarrow {}^7F_j$ ($j = 0$–4) transitions. However, there exist differences in the number, the position and the relative intensity of the emission peaks between the spectrum of the $EuBW_{11}$ solid and the $EuBW_{11}$/polyester film. The emissions of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ are the most intense emissions in the spectrum of the $EuBW_{11}$ solid and the $EuBW_{11}$/polyester film. The $^5D_0 \rightarrow {}^7F_2$ (614, 622 nm) and $^5D_0 \rightarrow {}^7F_1$ (592, 595 nm) transitions are split into two peaks in the $EuBW_{11}$ solid. Nevertheless, they are not split in the $EuBW_{11}$/polyester film. Another prominent

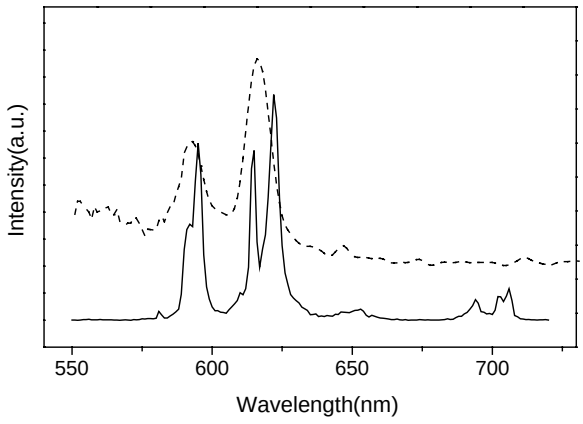

Fig. 7. Emission spectra of the $EuBW_{11}$ solid (solid line) and the $EuBW_{11}$/polyester film (dash line).

difference lies in the increase of the red to orange intensity ratio (R:O) of Eu^{3+} in the film as compared to the solid, which results from the lower site symmetry of Eu^{3+} in the $EuBW_{11}$/polyester film. In addition, there are fewer emissions in the spectrum of the $EuBW_{11}$/polyester film than in the $EuBW_{11}$ solid, which can be explained by the ordered entrapment of $EuBW_{11}$ in the $EuBW_{11}$/polyester film.

3.5. Lifetimes

The fluorescence decay curves of $^5D_0 \rightarrow {}^7F_2$ emission for the $EuSiW_{11}$/polyester film and the $EuSiW_{11}$ solid were measured. Both of the curves were single exponential. The lifetimes of Eu^{3+} were calculated to be 0.76 ms in the polyester film and 2.43 ms in the solid. It was obvious that Eu^{3+} showed shorter lifetime in the polyester film than in the solid, which may result from the intermolecular action between the polyester matrix and inorganic heteropolytungstates. The dimension of the materials may be another reason [13].

4. Conclusion

The hybrid organic/inorganic luminescent films have been successfully prepared by sol–gel method. LMCT band could be observed in the hybrid films, which could not be found in the solid. The films exhibit the characteristic emission bands of the rare earth ion. The emissions of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ split in the solid but not in the polyester film. The ratio of the relative intensity between $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transition increases after europium-substituted heteropolytungstates are incorporated in the polyester film. The lifetime of Eu^{3+} is shorter in the polyester film than in the solid. These results can be ascribed to the intermolecular action between polyester matrix and heteropolytungstates and resulted distortion of the site symmetry of the Eu^{3+} ion in polyester films.

Acknowledgements

The authors are grateful to the Youth Foundation of Hubei University.

References

[1] V. Bekiari, P. Lianos, Adv. Mater. 10 (1998) 1455.
[2] G.E. Buono-core, H. Li, B. Marciniak, Coord. Chem. Rev. 99 (1990) 55.
[3] J. Kido, H. Hayase, K. Hongawa, K. Nagai, Appl. Phys. Lett. 65 (1994) 2124.
[4] L.R. Matthews, E.T. Knobbe, Chem. Mater. 5 (1993) 1697.
[5] J. Wang, H. Wang, L. Fu, F. Liu, H. Zhang, Thin Solid Films 415 (2002) 242.
[6] J. Wang, H. Wang, F. Liu, L. Fu, H. Zhang, Mater. Lett. 416 (2003) 1210.
[7] X.L. Wang, Y.H. Wang, C.W. Hu, E.B. Wang, Mater. Lett. 56 (2002) 305.
[8] N.K. Chaudhury, R. Bhardwaj, B.M. Murari, Curr. Appl. Phys. 3 (2003) 177.
[9] R.D. Peacock, T.J.R. Weakley, J. Chem. Soc. (A) (1971) 1836.
[10] S.A. Zubairi, S.M. Ifzal, A. Malik, Inorg. Chim. Acta 22 (1977) 29.
[11] S. Lis, J. Alloys Compd. 300–301 (2000) 88.
[12] G. Blasse, G.J. Dirksen, J. Inorg. Nucl. Chem. 43 (1981) 2847.
[13] Y.L. Zhao, D.J. Zhou, G.Q. Yao, C.H. Huang, Langmuir 13 (1997) 4060.