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Microwave Synthesis and Characterization of Europium Complexes with Cinnamic Acid and Phenanthroline[1]

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Abstract—We report here the synthesis and characterization of a host of Eu(Phen)L_3 with cinnamic acid (C_6H_5CH = CHCOOH, HL) and phenanthroline (Phen), and employing microwave radiation, where the microwave radiation is used just for the uniform heating of the reaction mixture. Its IR absorption spectra, scanning electron microscopy (SEM), and fluorescence spectra were studied. The results show that the particles of Eu(Phen)L_3 phosphors are basically spherical in shape, with good dispersing. The mean particle size is 1–2 μm. The excitation spectrum is a broad band and the main peak is at 320.0 nm. Moreover, excitation peak at 396.0 nm was found in the excitation spectrum. The emission spectrum shows that Eu(Phen)L_3 has narrow emission peaks. The emission peaks are ascribed to Eu^{3+} ions transition from ^5D_J (J = 0) to ^7F_J (J = 1, 2, 4). However, the strongest main emission peak locates at 614.0 nm, which corresponds to the electric dipole transition of Eu^{3+}($^5D_0 \longrightarrow {}^7F_2$).

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INTRODUCTION

The rare-earth cinnamate coordinate compounds were studied [1] in the past several decades. However, no report is available on the synthesis and characterization of ternary solid coordinate compounds of cinnamic acid and phenanthroline with rare-earths and employing microwave radiation. The most notable effect of microwave radiation is the heating effect. In microwave heating, unlike in conventional heating, heat is generated within the material itself instead of external heat being supplied. As a result of this internal and volumetric heating, thermal gradients and flow of heat during microwave processing are quite different from those observed in conventional heating. The present paper describes the preparation of Eu(Phen)L_3 (HL – cinnamic acid, Phen – phenanthroline) through the reaction of cinnamate and phenanthroline with europium nitrate employing microwave radiation. Its IR absorption spectra, scanning electron microscopy (SEM), and fluorescence spectra were studied.

EXPERIMENTAL

Europium nitrate was prepared by the reaction of europium oxide (purity 99.95%) with nitric acid, cinnamic acid (AR), phenanthroline (AR), ethanol (AR) and deionized water, et al.

Synthesis of compounds. All europium nitrates were prepared by dissolving europium oxide (purity 99.95%) in nitric acid and then heated to remove extra HNO_3. An HL and Phen mixed solution was prepared by dissolving 3 mmole of HL and 1 mmole of Phen in 30 ml of ethanol. The mixed solutions of 3 mmole of HL and 1 mmol of Phen was added to europium nitrate under stirring. After the mixed solutions finished, the appropriate amount of 6 M $NH_3 \cdot H_2O$ was added, and pH was adjusted to 6–7. At last, the contents of the beaker were exposed to microwave irradiation in a microwave oven, operating at an electric power of 600 W for 20 min, the temperature in the microwave oven was recorded constant at 333 K by means of setting parameter, cooling to room temperature, and filtering. The products were washed with deionizal water and dried for 2 h at 353 K.

Measurement methods. The IR spectra of compounds were recorded on a AVATAR370 FTIR spectrophotometer in a form of KBr pellets. The fluorescence spectra were taken on a HI-TACH F–4500 fluorescence photometer. The morphology of the samples was observed using SEM.

RESULTS AND DISCUSSION

FTIR spectra of HL, Phen, and Eu(Phen)L_3 were given in Fig. 1a–1c. In the coordination compounds, the asymmetric and symmetric stretching vibrations of carboxylate group ($\nu_{as}(COO^-)$ and $\nu_s(COO^-)$) appear in the region of 1639–1642 and 1401–1420 cm^{-1}, respectively. Stretching vibration peak of the carboxyl group is located at 1683 cm^{-1}, and the $\delta(OH^-)$ with ν(CO) coincidence vibration gives absorption at 1285 and 944 cm^{-1}

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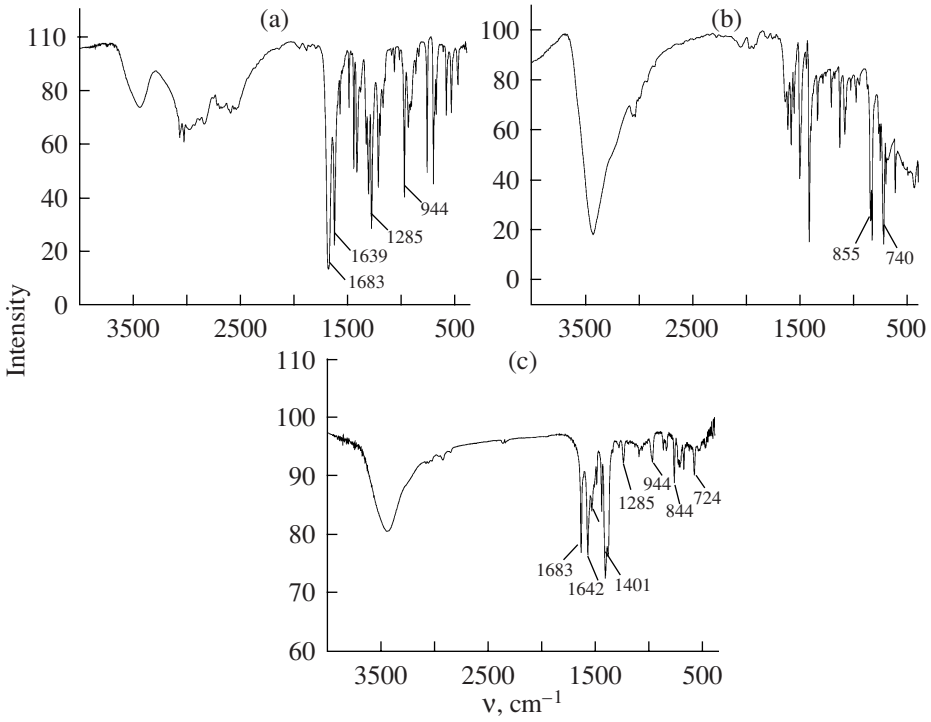

Fig. 1. FTIR spectra of HL (a), Phen (b), and Eu(Phen)L_3 (c).

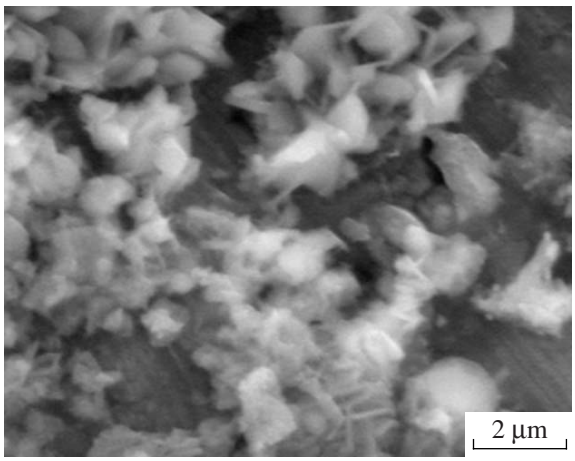

Fig. 2. Scanning electron microscopy of Eu(Phen)L_3.

for that in cinnamic acid. These facts show that cinnamate coordinates to the rare-earth ions in the compounds. The *ν*(C=C) and *ν*(C=N) stretching vibration peaks appear at 1619 and 1588 cm^{-1}, respectively, in phenanthroline. These bands shifted to about 1578 and 1569 cm^{-1} in the coordination compounds. It shows that the coordination bonds have formed between the rare-earth ions and nitrogen atom in phenanthroline [2]. In addition, from the IR spectra of the complexes it can also be seen that the vibration frequency of 1650 cm^{-1} belonging to the phenyl ring of 1.10-phenanthroline becomes weaker than that of free Phen. The out-of-plane bending vibrations of the hydrogen atoms on the phenyl ring of Phen decrease from 855 and 740 to 844 and 724 cm^{-1}, indicating that Phen participates in the coordination.

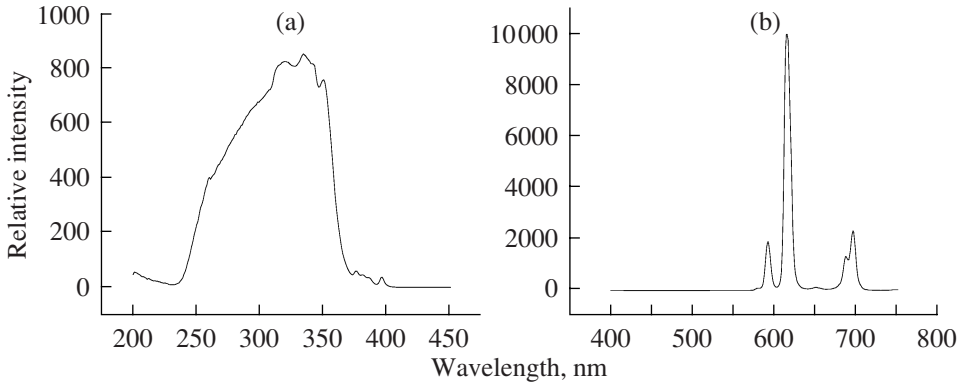

Fig. 3. Excitation (a) and emission (b) spectra of Eu(Phen)L_3.

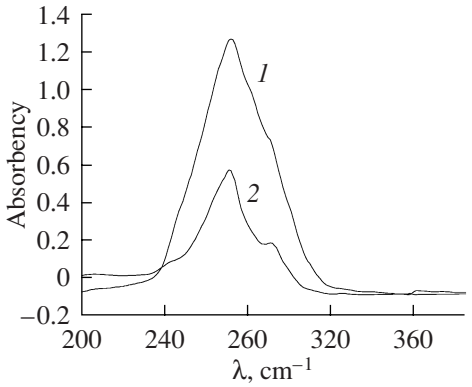

Fig. 4. UV spectra of the Eu(Phen)L_3 complex (*1*) and Phen ligand (*2*).

The micrographs of Eu(Phen)L_3 are shown in Fig. 2. We highlight here that the particles of Eu(Phen)L_3 phosphors are basically spherical in shape, with good dispersing. The mean particle size is 1–2 μm. Such spherical morphology of particles is highly desirable in phosphors as it reflects directly on the luminescence behavior.

The excitation and emission spectra of Eu(Phen)L_3 at room temperature are given in Fig. 3. The excitation spectrum is a broad band and the main peak is at 320.0 nm. Moreover, excitation peaks at 396.0 nm was found in the excitation spectrum, which corresponds to $^7F_0 \longrightarrow {}^5L_6$ absorption of Eu^{3+} ion. The emission spectrum shows that Eu(Phen)L_3 has narrow emission peaks when Eu(Phen)L_3 is excited by 320 nm at UV-light. The emission peaks are ascribed to Eu^{3+} ions transition from ^5D_J ($J = 0$) to ^7F_J ($J = 1, 2, 4$), the emission peaks locate at 592.0, 614.0, and 699.0 nm, which correspond to $^5D_0 \longrightarrow {}^7F_1$, $^5D_0 \longrightarrow {}^7F_2$, and $^5D_0 \longrightarrow {}^7F_4$ transitions of Eu^{3+} ion, respectively. However, the strongest main emission peak locates at 614.0 nm, which corresponds to electric dipole transition of Eu^{3+} ($^5D_0 \longrightarrow {}^7F_2$) induced by the lack of inversion symmetry at the Eu^{3+} site [3]. It shows that the lowest excitation state energy level of Eu^{3+} ion and the triplet state energy level of the ligand match well with each other. The absorbing energy of the ligand is effectively transfered to Eu^{3+} ion. Thus, its luminescence intensity is very high. The excitation spectrum (Fig. 3) consists of a symmetric and broad band, ranging from 240 to 400 nm (λ_{max} = 320 nm) with some small peaks superimposed with the band. The corresponding emission spectrum only contains $^5D_0 \longrightarrow {}^7F_J$ ($J = 0, 1, 4$) transition lines of Eu^{3+} as compared to [4]. The differences can be the size effect.

Figure 4 shows the UV-absorption spectra peaks of free ligand (Phen) and complex (Eu(Phen)L_3) in the same concentration (1×10^{-5} mol/l) in a CH_2Cl_2 solution. Absorption energy of the complex mostly comes from that the ligands in Eu(Phen)L_3 show typical absorptions peaks of 1.10-Phen.

Thus, the Eu(Phen)L_3 phosphors were prepared using a microwave oven operated at a power of 600 W. It is in the experimental that the microwave synthesis

can provide a product without sintering, as well as good homogeneous distribution of the dopant. In view of energy saving synthetic method, an ideal system is the one where the heating eases spontaneously as quickly as the reaction is complete. The system proposed in this study could be the case.

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