Preparation and Characterization of Layered Compound Zirconium Bis(monohydrogenphosphate) Intercalated with Rare Earth Complex

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Abstract: Layered compound zirconium bis(monohydrogenphosphate)(α-ZrP) intercalated with rare earth complex Eu(DBM)$_3$phen was prepared. The pre-intercalation of *p*-methoxyaniline into α-ZrP makes the interlayer separation large enough to exchange PMA with europium complex, thus, the luminescent assembly was prepared. This was confirmed by X-ray diffraction, UV-visible spectra and elemental analysis. The fluorescence spectra and lifetime of the assembly were also presented.

Keywords: Layered compound, rare earth complex, luminescence.

Rare earth organic complexes usually exhibit intense narrow band emission *via* an energy transfer from the ligands to the central rare earth ions under UV excitation. Although rare earth complexes, especially for the complex with β-diketone, have strong luminescence, their photostability and thermal stability are not very good enough for the phosphor. Therefore, the key problem related to rare earth complex is to try to find a suitable matrix material to trap them. Inorganic solid matrixes are promising host materials due to their good optical, thermal and chemical stability. In fact, so far rare earth complexes have already been encapsulated in or adsorbed on such host materials as Langmuir-Blodgett films, SiO$_2$ matrix derived from sol-gel process and some kinds of zeolites[1-3]. But there have been no reports on the intercalation of rare earth complex into the layered compounds. Zirconium bis(monohydrogenphosphate) (α-ZrP) is a layered compound with good photo and thermal stability[4]. In this work, our main aim is to synthesize a new assembly intercalated with rare earth complex using the layered compound α-ZrP as the host material. The synthesis mainly includes the modification of α-ZrP with *p*-methoxyaniline(PMA) and intercalation of europium complex with dibenzoylmethane (DBM) and 1, 10-phenanthroline (phen) Eu(DBM)$_3$phen. The preparation and characterization are presented in the following section.

α-ZrP and HBF$_4$ were first added to ethanol solution with the molar ratio of F$^-$ to Zr^{4+} of 6.6. The mixed solution was stirred for 24 h at room temperature. The precipitate was filtered and washed with ethanol, then added to the ethanol solution of PMA, and stirred

for another four weeks. The precipitate was washed with the mixed solvents of ethanol/acetone and dried in the air. So the *p*-methoxyaniline-preintercalated compound (α-ZrP·2PMA) was obtained. For the synthesis of the assembly, Eu(DBM)$_3$phen was first dissolved into DMF, then α-ZrP·2PMA was added to the above solution with the mass ratio of α-ZrP·2PMA to rare earth complexes being 10/1. The mixture was stirred for one week at room temperature, filtered and washed with chloroform until the rare earth complex absorbed on the surface of α-ZrP was totally washed off. The resultant assembly was dried at room temperature and stored in a desiccator for future measurements. .

Since the interlayer separation in the α-ZrP is small, α-ZrP need to be modified firstly. PMA can react with α-ZrP *via* Brønsted acid base reactions to give an intercalation compound α-ZrP·2PMA. When this compound was mixed with rare earth complex, an ion-exchange reaction between PMA and the rare earth complex will occur. Figure 1 shows the X-ray diffraction patterns of α-ZrP·2PMA and rare earth complexes assembly. As shown in **Figure 1**, some new phases were formed with the interlayer separation of 21.02 Å owing to the intercalation of Eu(DBM)$_3$phen, and the concomitant disappearance of α-ZrP·2PMA at 20.25 Å. Compared to α-ZrP·2PMA, the interlayer separation is enlarged by 0.77 Å. Considering the interlayer separation of α-ZrP is 7.5 Å[5], the interlayer separation of the assembly is 13.5 Å, which accords to the diameter of Eu(DBM)$_3$phen.

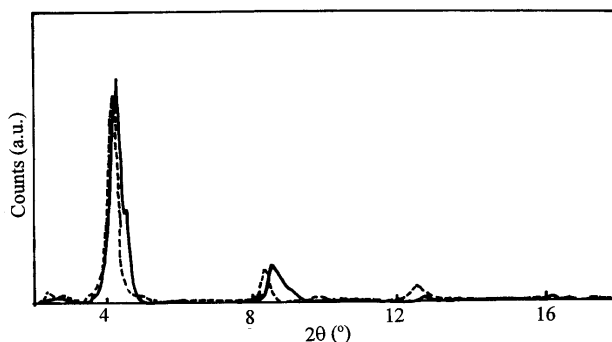**Figure 1**. XRD patterns.
— α-ZrP·2PMA;   ---- assembly.

Figure 2 shows the UV spectra of α-ZrP·2PMA, Eu(DBM)$_3$phen and the corresponding assembly, respectively. The spectrum of the (Eu(DBM)$_3$phen has two absorption peaks located at 348 nm and 385 nm, while the assembly has also two absorption at λ=360 nm and 381 nm. α-ZrP·2PMA has almost no absorption in the region from 300 nm to 600 nm. In addition, the spectrum profiles of Eu(DBM)$_3$phen and of the corresponding assembly are very similar. This also indicates that Eu(DBM)$_3$phen is intercalated into α-ZrP.

Figure 2. UV-visible spectra.
— α-ZrP·2PMA; ---- Eu(DBM)$_3$phen; —·— assembly.
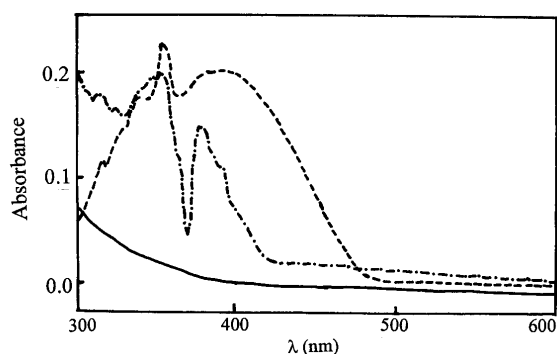
Figures **3A** and **3B** show the excitation and emission spectra of the assembly and the corresponding pure rare earth complex. Both of the emission spectra exhibit the characteristic emission of Eu^{3+} arising from the transition $^5D_0\rightarrow^7F_J$ (J=0,1,2,3,4), with the transition $^5D_0\rightarrow^7F_2$ red emission as the dominant group. This strongly suggests that an efficient energy transfer from the ligands to Eu^{3+} can take place not only in the pure rare earth complex but also in the complex intercalated into a layered compound. Compared to the pure rare earth complex, the excitation spectrum of the assembly shows a blue shift and the emission spectrum exhibits fewer splits.

Figure 3. Excitation and emission spectra.
A. Eu(DBM)$_3$phen; B. the assembly.
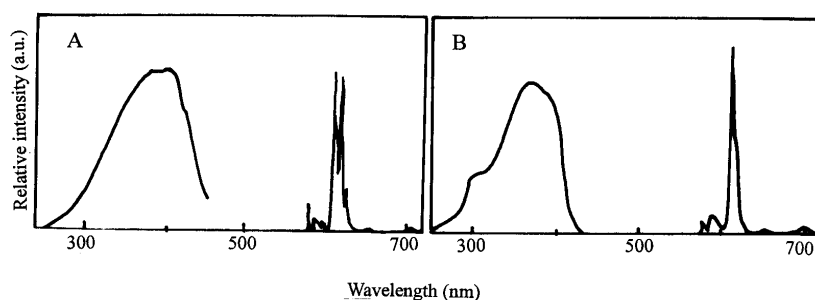
The differences in the luminescence spectra can be explained as follows. As we know, the spectral shift is related to the polarity of the fluorophore surrounding environment. When the rare earth complex is intercalated into α-ZrP, the polarity of its surrounding is increased. According to Lippert equation[6], the fluorophore will have a larger Stokes' shift. Therefore, for Eu(DBM)$_3$phen, the excitation spectrum will have a blue shift. Since the intensity of transition $^5D_0\rightarrow^7F_2$ is strongly dependent on the Eu^{3+} surrounding due to its electric-dipole character while $^5D_0\rightarrow^7F_1$ emission intensity is independent of the surrounding, the ratio of 0–2/0–1 emission intensity will give us

valuable information about environment changes around Eu^{3+}. The decrease in the 0−2/0−1 ratio from 14.0 in the pure complex to 8.8 in the assembly is consistent with a high symmetry around Eu^{3+} ion in the assembly. So fewer emission lines were observed in the luminescence spectrum of the assembly.

The fluorescence decay curves of Eu^{3+} related to the transition $^5D_0 \rightarrow ^7F_2$ emission for the pure $Eu(DBM)_3$phen and the corresponding assembly were measured. The fluorescence times are 608 μs in the former and 768 μs in the latter, respectively. The relatively rigid matrix structure of the assembly inhibits the vibration of the ligands around Eu^{3+}, and leads to longer luminescence lifetime of Eu^{3+} in the assembly than that of the corresponding pure complex.

The content of Eu^{3+} in the assembly was measured by ICP-AES, and the content of $Eu(DBM)_3$phen in the assembly was calculated to be 6.71 %. On the other hand, the relative luminescent intensity of the assembly is appropriately 40 % that of the corresponding pure $Eu(DBM)_3$phen, suggesting that the unit molecule of the rare earth complex in the assembly can give stronger luminescence than the corresponding pure complex powder.

Acknowledgments

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