

Synthesis of inorganic-organic composite phosphors with lanthanide complexes embedded in fibrous clays

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This paper concerns with the synthesis and the luminescence spectra of lanthanide complexes of Eu(III) and/or Eu(II) or Tb(III) ions which are embedded into fibrous palygorskite and sepiolite clays in which the magnesium ion are ion exchanged with lanthanide ions. The He-Cd laser excitation photoluminescence of the present complexes without organic ligands exhibit the deferration effects. The phosphors with light harvesting ligands such as benzophenone derivatives and 1,10-phenanthroline give the fairly strong visible luminescence by UV-A light excitation with a LED black light in a light room under fluorescent lamps. Further, the temperature dependent phosphors with benzophenone derivatives exhibit the stronger luminescence with increasing the temperature over 100 °C.

Key words: Eu(III), Eu(II), Tb(III) complexes, Inorganic-organic composite, Fibrous clays, Luminescence spectra.

Introduction

Attapulgite or palygorskite is a fibrous clay mineral of hydrated magnesium aluminum silicate in nature, of which an inorganic-organic nanocomposite with indigo dye has been famous for Maya blue in view of the tremendous exposure robustness [1]. Embedding luminescent lanthanide ions in the analogous magnesium silicate clay mineral, sepiolite, as well as the palygorskite is expected to improve the stabilities and even luminescent properties of the lanthanide complexes, overcoming the disadvantage of the simple lanthanide complexes alone. However, there are only a few reports [2–4] of fibrous clay-based lanthanide composites, pursuing stable luminescent composites with palygorskite-based ternary europium complexes where a tris (β -diketonato) europium complex was covalently coupled onto modified attapulgites through a ligand exchange reaction or assembled by ion-pairing interactions.

In this article, the preparation of lanthanide complexes of Eu(III) and/or Eu(II) or Tb(III) ions are described, which are embedded into palygorskite and sepiolite clays in which the magnesium ion are ion exchanged with lanthanide ions. This is the first example of the lanthanide complexes embedded in the clay through ion-exchange which interacts directly with the clay moiety unlike the reported composites with the

far distant arrangement between the clays and the lanthanide complexes. Some unprecedented luminescence properties in the present new inorganic-organic composite phosphors will be reported.

Experimental

Fibrous clays, Attagel 40(attapulgite or palygorskite) and PangelAD (sepiolite), were provided by Omi Mining Co. LTD. The light harvesting ligands, 1,10-phenanthroline (phen) and 4,4'-dimethoxybenzophenone (DMBP) were purchased from Wako Chemicals. The lanthanide salts, $\text{Eu}_2(\text{NO}_3) \cdot 6\text{H}_2\text{O}$, $\text{Tb}_2(\text{NO}_3) \cdot 6\text{H}_2\text{O}$ and EuCl_2 were purchased from Sigma-Aldrich.

Crude Attagel 40 and Pangel AD contain calcium carbonate as impurity. In order to remove it, concentrated hydrochloric acid or EDTA was used. Since the treatment with EDTA is easier than that with conc.HCl, EDTA was used as follows. The suspension of 1 g of the clay in 0.08 M $\text{Na}_2\text{H}_2\text{EDTA}$ aqueous solution (80 ml) was stirred at 80 °C for 2 h. This was filtered and washed with ion-exchanged water. The purified clays were designated as Attagel-40-*H* for the conc. HCl treatment and Attagel-40-*E* and PangelAD-*E* for the EDTA treatment. The ICP analysis showed that 0.4% of calcium ion in the PangelAD is reduced to < 0.05% in the PangelAD-*E*. The iron in the clay-*E* was removed as follows. The suspension of 1g of Attagel 40-*E* or Pangel AD-*E* in 0.15 M oxalic acid (40 ml) was stirred at 80 °C for 2 h. This was filtered and washed with ion-exchanged water. The deferrated clays were denoted as the Attagel40-EO or PangelAD-EO. The ICP analysis

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showed that 2.4 w/w % of iron in the Attagel 40-*E* and 0.34 w/w % of iron in the PangelAD-*E* was removed to 1.5 w/w % in the AttagelAD-*EO* and 0.10 w/w % in the PangelAD-*EO*.

The suspension of 1 g of the purified clay in 25 ml water was mixed with 50 mg of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5 w/w% for the clay). The mixture was stirred at 80 °C for 2 h. This was filtered and washed with water. The ICP analysis showed that the clays contained about 1 w/w % of Eu^{3+} ion. These europium containing clays are designated as Attagel40-*E*: Eu^{3+} 5% or PangelAD-*E*: Eu^{3+} 5% and Attagel40-*EO*: Eu^{3+} 5% or PangelAD-*EO*: Eu^{3+} 5%. For the Tb^{3+} complexes, the similar procedures were made with use of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ instead of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. For the divalent europium ion-exchanged clays, europium(II) chloride(EuCl_2) and methanol were used instead of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and water, respectively. In order to remove oxygen in the solution of the flask, 12 ml of methanol containing 1 g of PangelAD-*E* was boiled under N_2 gas bubbling. To the methanol solution was added 20 mg of EuCl_2 under N_2 gas bubbling at room temperature. After the mixed solution was heated at 80 °C for 2 h, the clay was filtered and dried.

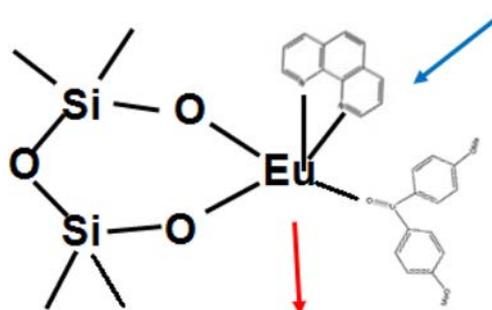
To the suspension of 0.1 g of clay-*E*: Eu^{3+} 5% or clay-*EO*: Eu^{3+} 5% in 3 ml ethanol was added 0.01 g of the ligand(10w/w% of the clay). The mixture was heated with stirring at about 80 °C and dried. After then, the resulted compound was dried at 150 °C in an electric oven. These are denoted as ligand@Attagel40-*E*: Eu^{3+} 5% or ligand@PangelAD-*E*: Eu^{3+} 5% and ligand@ Attagel 40-*EO*: Eu^{3+} 5% or ligand@PangelAD-*EO*: Eu^{3+} 5%. The CHN and ICP analysis for phen10%·dmbp20%@Attagel40-*E*: Eu^{3+} 5% gave the similar chemical formula before and after the calcination at 150 °C. Calcd for dmbp·phen@ $\text{Mg}_{7.9}\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 28\text{H}_2\text{O}:\text{Eu}_{0.1}$: C, 18.99; H,2.71; N, 1.27; Mg, 8.79; Eu, 0.69.

Found for dmbp·phen@PangelAD-*E*: Eu^{3+} 5%(before heating) : C, 18.58; H,2.39; N, 1.25; Mg, 9.46; Eu, 0.68. Found for dmbp·phen@PangelAD-*E*: Eu^{3+} 5%(after heating) : C, 18.35; H,2.51; N, 1.21; Mg, 9.60; Eu, 0.69.

The photoluminescence was measured in a powdery state by an excitation source of He-Cd Laser (325 nm, 20 mW) excitation with a photomultiplier (Hamamatsu R980) and a monochromator (JASCO CT25C). The luminescence spectra were measured in a powdery state by a Hitachi F-4500 fluorophotometer. Temperature dependent luminescence spectra were recorded in a powdery state using a fluorometer FP-6500 (JASCO, Japan) equipped with a temperature-changing cell holder Unispeks (UNISOKU, Japan). X-ray photoelectron spectroscopy were measured by a KRATOS AXIS 165 X-ray photoelectron spectrometer.

Results and Discussion

After exchanging with magnesium ions in the clay, lanthanide ion is coordinated through oxygen atoms of the silicate as shown in Scheme 1, as if the silicate is a



Scheme 1.

bidentate ligand as investigated for the retention of uranium and europium ion onto sepiolite by the spectroscopic and modeling techniques.⁵

The coordinated ligands act for the antenna effect like Scheme 1.

The chemical constitution of the clay

The ICP and/or CHN analysis showed that the chemical formula of PangelAD-*E*: Eu^{3+} 5% and dmbp·phen@PangelAD-*E*: Eu^{3+} 5% is $\text{Mg}_{7.9}\text{Si}_{12}\text{O}_{50}\text{H}_{44} (\text{Eu}_{0.1})$ or $\text{Mg}_{7.9}(\text{Eu}_{0.1})\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 28\text{H}_2\text{O}$ and dmbp·phen@ $\text{Mg}_{7.9}\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 28\text{H}_2\text{O}:\text{Eu}_{0.1}$, respectively, assuming $\text{Mg}_8\text{Si}_{12}\text{O}_{50}\text{H}_{44}$ for the PangelAD-*E* neglecting the small impurity. This means that one europium ion is exchanged

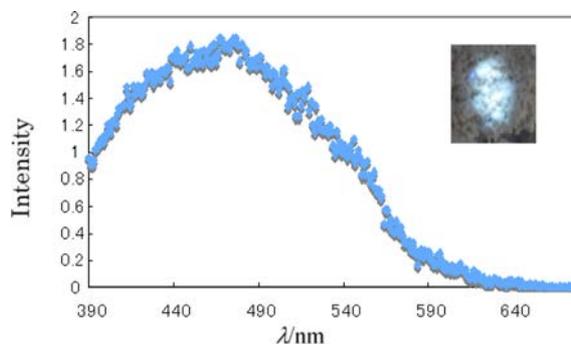


Fig. 1. He-Cd laser excitation (325 nm) Photoluminescence of Attagel40-H. Insert shows the naked-eye blue luminescence.

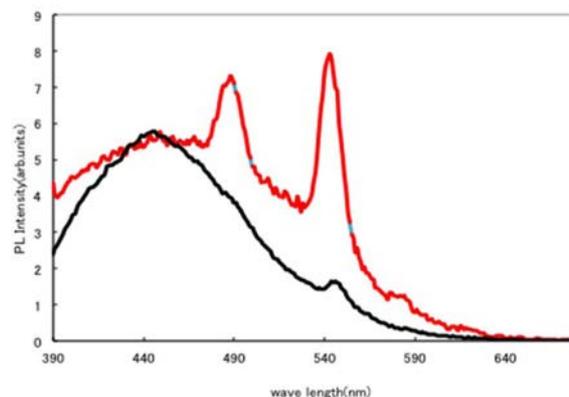


Fig. 2. He-Cd laser 325 nm excitation photoluminescence spectra of Attagel40-*H*: Tb^{3+} 5% (black) and dmf treated Attagel40-*H*: Tb^{3+} 5% (red).

with one of 80 magnesium ions in ten units of $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4$, whereas each one ligand is incorporated within one of the unit.

The photoluminescence of the palygorskite and sepiolite

He-Cd laser 325 nm excitation for Attagel40-*H* gave a broad luminescence peak around 440 nm, the blue light being viewed by naked eyes as in Fig. 1. This is due to the photoluminescence from the energy oxygen defected semiconductor level in the Attagel40. The photoluminescence spectra of Attagel40-*H*: Tb^{3+} gave a weak $^5\text{D}_4 \rightarrow ^7\text{F}_5$ peak in the 4f-4f transitions region around 540 nm, whereas after the suspension in *N,N*-dimethylformamide (dmf) was evaporated to dryness, clear peaks were observed as Fig. 2, suggesting the disappearance of the vibrational quenching due to the aqua ligands for the former complex as a result of the displacement of the aqua ligand to dmf.

The deferration effect of the clay on the luminescence

The luminescence in the 4f-4f transitions of deferrated phen@attagel40-*EO*: Eu^{3+} at 615 nm (Fig. 3) and phen@attagel40-*EO*: Tb^{3+} (Fig. 4) around 490-600 nm become stronger by about eight times than undeferrated phen@attagel40-*E*: Eu^{3+} and phen@attagel40-*E*: Tb^{3+} . This may be because the iron quenching effect is reduced as a result of the decrease of the iron content of 2.4% in the

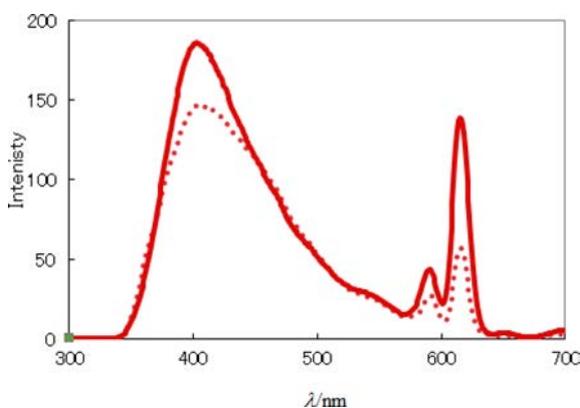


Fig. 3. Luminescence spectra of phen@Attagel40-*EO*: Eu^{3+} (solid line) and phen@Attagel40-*E*: Eu^{3+} (dotted line) with excitation of 280 nm.

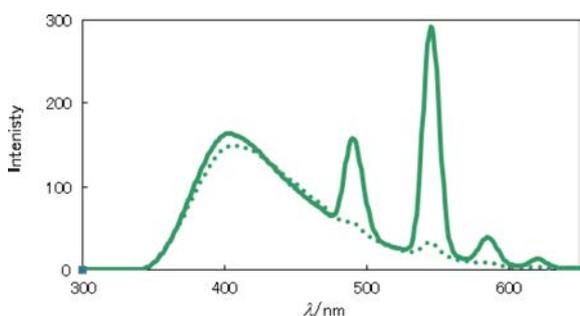


Fig. 4. Luminescence spectra of phen@Attagel40-*EO*: $\text{Tb}^{3+}5\%$ (solid line) and phen@Attagel40-*E*: $\text{Tb}^{3+}5\%$ (dotted line) with excitation of 280 nm.

Attagel40 to 1.5% after treating with oxalic acid. However, for the PangelAD-*E*: Eu^{3+} and PangelAD-*EO*: Eu^{3+} without organic ligands, the reverse deferration effect on the He-Cd laser excitation photoluminescence was observed as Fig. 5. The reason for the reverse phenomenon is not clear, even though 0.4% of the iron content of the PangelAD-*E* (sepiolite) reduced to 0.13% after deferration.

Comparison of the luminescence between the divalent and trivalent Eu complexes

The ICP analysis and X-ray photoelectron spectroscopy (XPS) showed that about 0.4% of Eu ion was contained

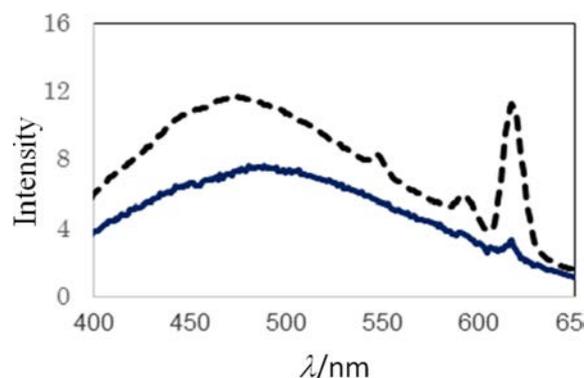


Fig. 5. He-Cd laser 325 nm excitation photoluminescence spectra of PangelAD-*E*: $\text{Eu}^{3+}5\%$ (broken line) and PangelAD-*EO*: $\text{Eu}^{3+}5\%$ (solid line).

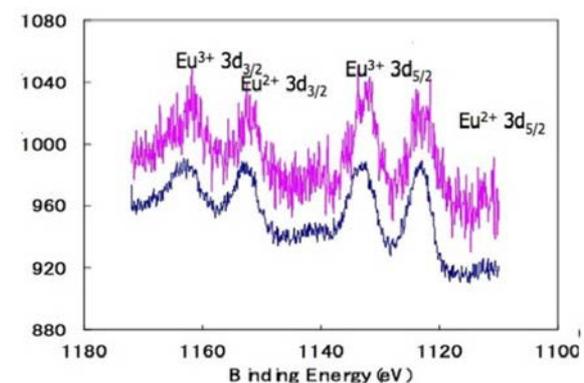


Fig. 6. X-ray photoelectron spectroscopy of Attagel40-*E*: $\text{Eu}^{2+}2\%$ for 3d electrons showing the existence of Eu^{3+} and Eu^{2+} upper red line after 80 days.

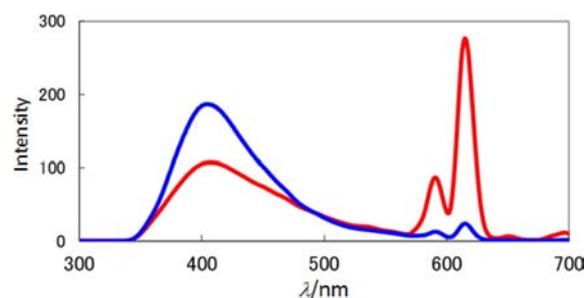


Fig. 7. Luminescence spectra of trivalent Eu^{3+} complex, phen@Attagel40-*E*: Eu^{3+} (Blue line) and divalent Eu^{2+} complex, phen@Attagel40-*E*: $\text{Eu}^{2+}, \text{Eu}^{3+}$ (Red line)].

with about equal amount of Eu^{2+} and Eu^{3+} , showing the oxidation of half of Eu^{2+} to Eu^{3+} during the preparation. This is stable in the air with about 5% decrease of divalent Eu^{2+} peaks even after 80 days as shown in Fig. 6, though Eu^{2+} is easily oxidized in aqueous solutions⁶. In order to evaluate the luminescence intensity, the ratio ($I_{615}/I_{400-450}$) of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ luminescence intensity of at 615 nm in the 4f-4f transitions to that at 400-450 nm in the intraligand triplet-singlet emission are compared with each other. The larger the ratio, the brighter the phosphors become to naked eyes. The divalent $\text{dmbp} \cdot \text{phen}@\text{PangelAD-E:Eu}^{2+}$ gives $I_{615}/I_{450} = 2.8$, which is much stronger than the former trivalent $\text{dmbp} \cdot \text{phen}@\text{PangelAD-E:Eu}^{3+}$ $I_{615}/I_{450} = 0.1$ as Fig. 7, even though the content of the Eu ion in the latter is smaller by about half than that of the former Eu^{3+} ion. This may be affected by the existence of divalent Eu^{2+} ion.

Dependence of the luminescence intensity on the ligands

The luminescence intensity for $\text{phen}@\text{PangelAD-E:Eu}^{3+}$ and $\text{dmbp}@\text{PangelAD-E:Eu}^{3+}$ are found to be weaker than that for $\text{dmbp} \cdot \text{phen}@\text{PangelAD-E:Eu}^{3+}$. The ratio I_{615}/I_{400} for the phen complex is 0.1, whereas I_{615}/I_{450} for the dmbp complex is 0.2. In contrast, the ratio I_{615}/I_{450} for the $\text{dmbp} \cdot \text{phen}$ complex is about 4.0, being a strong red phosphor which can be seen by

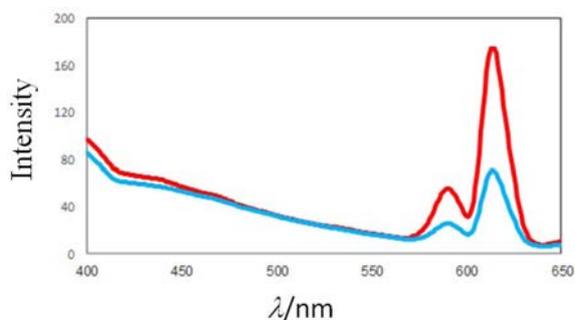


Fig. 8. Luminescence spectra of $\text{dmbpphen}@\text{PangelAD-E:Eu}$ (III) showing the calcination effect at 150 °C for 1 h (Blue: before and Red: after).

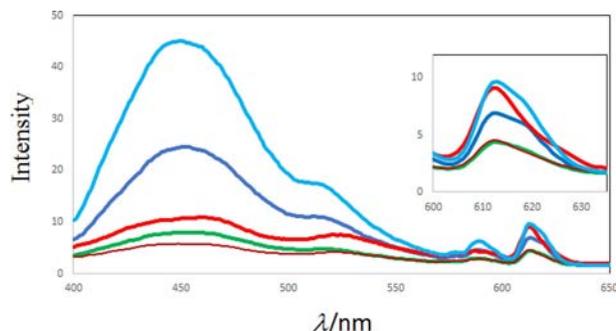


Fig. 9. Temperature dependent luminescence spectra of $\text{dmbp}@\text{PangelAD-E:Eu}^{3+}$ with excitation of 360 nm. From upper to bottom: 30 °C > 50 °C > 120 °C > 80 °C > 100 °C. Insert shows enlarging the 4f-4f transition region.

naked eyes with a 375 nm LED black light in a light room under fluorescent lights.

Calcination effect

The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ luminescence intensity at 615 nm of the $\text{dmbp} \cdot \text{phen}@\text{PangelAD-E:Eu}^{3+}$ increases after calcination at 150 °C for 1 h as shown in Fig. 8.

Temperature dependent luminescence

The temperature dependent luminescence spectra of $\text{dmbp}@\text{PangelAD-E:Eu}^{3+}$ are shown in Fig. 9. This is a weaker emitter ($I_{615}/I_{450} = 0.2$) at 30 °C as mentioned before, but the emitting color becomes red with increasing the temperature, ($I_{615}/I_{450} = 0.5$ at 50 °C; *ca.* 1.0 at 80 ~ 120 °C). The broad intraligand peak at 450 nm become weaker by one tenth, but the sharp ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ peaks around 580 ~ 615 nm decrease by about half from 50 °C to 100 °C. At 120 °C, the former and the latter peaks are stronger than those at 80 °C and 50 °C, respectively. This may be responsible for the interaction among the electronic levels in the clay and the π electron levels in the ligands and/or 4f levels in the Eu^{3+} ion.

Conclusions

The present specific luminescence behavior is considered to be ascribed to the correlation among the semiconductor levels in the clays and the electronic states of the ligands and/or lanthanide ions, probably due to the lanthanide ion directly bonded to the silicate moiety, in contrast of the previously reported cases²⁻⁴ for the covalently bonded lanthanide complexes on an modified palygorskite clay, which is a kind of mixed compounds with no direct bond with silicate moiety.

Acknowledgments

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