

Preparation and Characterization of New Lanthanide materials: Layered Double Hydroxide Intercalated by Luminescent Polyoxometalate Anions with Dawson-like $[\text{Eu}(\text{H}_2\text{O})_3(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ and Keggin-like $[\text{Eu}(\text{H}_2\text{O})_2(\text{PW}_{11}\text{O}_{39})]^{4-}$

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Abstract

Dawson-like $[\text{Eu}(\text{H}_2\text{O})_3(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ and Keggin-like $[\text{Eu}(\text{H}_2\text{O})_2(\text{PW}_{11}\text{O}_{39})]^{4-}$ were first isolated and x-ray crystallized in our group. We are interested in synthesizing new lanthanide materials by incorporating the title polyoxometalates (POMs) anions into layered double hydroxides (LDHs). The pillaring of $\text{Mg}_3\text{Al-LDH}$ by the title POM anions were accomplished by ion exchange reaction of the LDH-hydroxide and adipate precursors with the POM anions at refluxing temperature. The structural, textural and luminescence properties of the POM-incorporated compounds were elucidated based on PXRD, FTIR, BET N_2 adsorption/desorption studies, Raman, Fluorescence and solid state NMR spectroscopies. The Raman and Fluorescence studies showed that the title LDH materials are potential useful as luminescence sensors.

Key words: Layered double hydroxide, lanthanide, polyoxometalate anions, luminescence.

1. INTRODUCTION

Layered double hydroxides (LDHs) are the only known family of layered materials with permanent positive charge on the layers [1]. Such LDHs may be used as precursors of pillared layered structures which can be tailored-made by modification of the host structure chemical composition or by chemical or structural modification of the guest species domains [2]. Currently, LDHs pillared by polyoxometalates anions have attracted considerable attentions as a potentially important class of catalytically active, microporous materials [1,3-5]. Owing to the diversity in approaches to the design of these nanoscale materials, a wide range of structural, chemical, electronic, ionic, optical, and magnetic applications are possible [2].

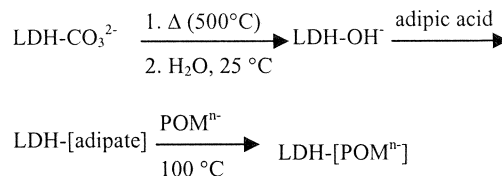
Lanthanide derivatives of the monovacant, lacunary Wells-Dawson and Keggin polyoxoanion ligands have attracted great interest because of their potential

applications in catalysis, medicine and nuclear waste treatment. In particular, europium complexes have generated interest because of their structural and luminescence properties, connected with their potential use in lasers and luminescent materials.

Up to now and to the best of our knowledge, very few papers concerning the intercalation of europium complexes into the LDHs have been reported. In our group, we successfully isolated and x-ray crystallized Dawson-like $[\text{Eu}(\text{H}_2\text{O})_3(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ (1) and Keggin-like $[\text{Eu}(\text{H}_2\text{O})_2(\text{PW}_{11}\text{O}_{39})]^{4-}$ (2). We extend our prior efforts with the aims of creating composite materials as novel photoluminescent materials and catalysts.

In this paper, we exchanged polyoxometalate 1 and 2 into "expanded" $\text{Mg}_3\text{Al-LDH}$ -adipate material at refluxing temperatures following the method of Yun and Pinnavaia [1]. The synthetic route was illustrated in Scheme 1.

The structural, textural and luminescence properties of the pillared products were examined based on PXRD, FTIR, N_2 adsorption/desorption studies, Raman, Fluorescence, and solid state NMR spectroscopies.



Scheme 1. Synthetic routes to prepare LDH-POMⁿ⁻

2 EXPERIMENTAL

2.1 Materials preparation

$\text{K}_7[\text{Eu}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]$ (1) The $\text{K}_{10}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})$ was prepared by literature method [6]. The lacunary $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]$ (5 g, 1.017mmol) was dissolved in 50 ml of 0.5 M sodium acetate buffer at pH = 5.5 at 70°C to form a clear solution. EuCl_3 (1.2 g, 3.08

mmol) was dissolved in a minimum amount of water and added dropwise to the stirring $K_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]$ solution. KCl (5 g,) was added to the reaction mixture, and the clear solution was cooled in the refrigerator. After 2 h, a white precipitate formed, which contained a small impurity of the 1:2 sandwich complex, according to ^{31}P NMR spectroscopy. The precipitate was dissolved in 50 ml of sodium acetate buffer at pH 5.5 at 70°C , and 1.5 mL of 1.0 M EuCl_3 was added, followed by the addition of 3 g of KCl. The clear solution was cooled to 0°C . A white precipitate formed after a few hours and was collected and was collected and recrystallized twice from hot water at 70°C . Crystallization of **1** gives a dimeric form $[\text{Eu}(\text{H}_2\text{O})_3(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{14-}$, see Figure 1 [7].

$\text{K}_4[\text{Eu}(\text{H}_2\text{O})_2(\text{PW}_{11}\text{O}_{39})]$ (2) The $\text{K}_7\text{PW}_{11}\text{O}_{39}$ was prepared by literature methods [6]. To a solution of $\text{EuCl}_3\cdot 6\text{H}_2\text{O}$ (1.32 g, 3.6 mmol) in 25 mL of 0.2 M sodium acetate buffer at pH = 4 at 50°C was added slowly with vigorous stirring $\text{K}_7(\text{PW}_{11}\text{O}_{39})$ (2.12 g, 0.72 mmol). After the solution has been stirred at this temperature (50°C) for 20 min, KCl (0.5 g) was added, the reaction mixture was allowed to cool to room temperature and filtered. Addition of a threefold excess of ethanol to the cooled filtrate yielded a precipitate, which was collected by filtration. The precipitate was dissolved in 50 mL of sodium acetate buffer at pH 4 at 50°C , the clear solution was cooled in the refrigerator, after two days, the colorless crystals was formed. (yield: 1.2 g, 56.7% based on $[\text{PW}_{11}\text{O}_{39}]^{7-}$). The x-ray quality crystal was selected from the bulk crystals. Figure 2 shows the crystal structure of the polymeric form of **1** [8].

The pillaring of Mg_3Al LDH by the title POM anions were accomplished by ion exchange reaction of the LDH-hydroxide and -adipate precursors with the POM anions at refluxing temperature. The pillaring materials were prepared by a modification of the literature methods [1, 9].

2.2 Physical measurements

Powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku diffractometer, using $\text{CuK}\alpha_1$ (0.154 nm) x-rays: typically run at a voltage 40 kV and current of 30 mA. Steady-state emission and excitation spectra were acquired using a SPEX Fluorolog- $\tau 2$ spectrofluorimeter. Raman spectra were excited with laser radiation of wavelength 488 nm from a Coherent Innova 200 argon-ion laser. The excitation power was maintained at 100 mW and the Raman scattering was collected and dispersed by a Spex 1877, 0.6-meter spectrometer. A cooled (140 K) Spex Spectrum-1 CCD camera was coupled to the spectrometer and used as the detector. The FTIR

spectra of the samples pressed in KBr pellets were obtained at a resolution of 8 cm^{-1} between 4000 and 400 cm^{-1} on a Perkin-Elmer 1625 series FTIR spectrometer, using 64 sample scans and 64 background scans.

3. RESULTS AND DISCUSSION

Crystal Structures In the solid state the $[\text{Eu}(\text{H}_2\text{O})_3(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ (**1**) (Figure 1) is a dimer where the Eu is bound to the four oxygen atoms in the cap vacancy of the Dawson-like polyanion and to three water molecules and to a terminal tungsten oxygen of another $(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})^{10-}$ unit. The luminescence spectroscopy and ^{183}W NMR show good evidence that $[\text{Eu}(\text{H}_2\text{O})_3(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]_2^{14-}$ in aqueous solution dissociate into a monomeric species wherein the Eu is bound to four water molecule and one $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ moiety [7]. The size of this monomeric form is 10Å and 20Å for the minor and major dimensions, respectively. In the solid state, $[\text{Eu}(\text{H}_2\text{O})_2(\text{PW}_{11}\text{O}_{39})]^{4-}$ (**2**) (Figure 2) is a polymer where the Eu is bound to the four oxygen atoms in the cap vacancy of the Keggin-like polyanion and to two water molecules and to a terminal tungsten oxygen of another $\text{PW}_{11}\text{O}_{39}^{7-}$ unit. Both ^{31}P NMR and ^{183}W NMR show good evidence that $[\text{Eu}(\text{H}_2\text{O})_2(\text{PW}_{11}\text{O}_{39})]_2^{8-}$ in aqueous solution dissociate into a monomeric species [8]. The size of this monomeric form is 10Å .

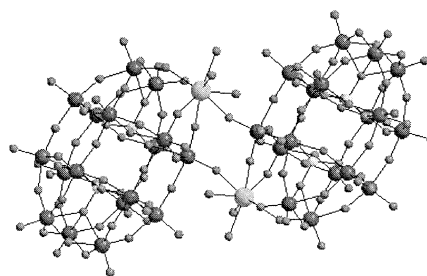


Figure 1: Dimeric form of $[\text{Eu}(\text{H}_2\text{O})_3(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ (**1**)

Incorporation into Mg_3Al -LDH To facilitate the incorporation of bulky polyoxoanions **1** and **2** into the LDH layers, adipic acid was used in the synthesis to expand the interlayer distances from about 8.0Å to 12.9Å , which is anticipated to be sufficiently large to allow the **1** or **2** to be incorporated into the “expanded” layers. The IR of the composite Mg_3Al -

4 CONCLUSIONS

Analyses of other growth characteristics in these systems, such as the dependence of step speed and critical size on supersaturation show that numerous and fundamentally different mechanisms are responsible for the observed modifications of growth morphology and dynamics including: 1) Step-blocking due to impurity pinning, 2) Changes in equilibrium activity, a_e , and strain-induced step retardation due to impurity incorporation, 3) Alterations of the orientational dependence of step-edge energy, and 4) Blocking of kink-sites. However, in all cases, the basis for growth modification is a modulator-crystal interaction that is dominated by step-specific binding at the step edges on existing crystal faces. Thus the appearance of new facets or pseudo facets does not appear to be the result of thermodynamic stabilization of the new facets, but rather a direct manifestation of kinetic limitations to step motion imposed on the steps of the pre-existing facets.

5 ACKNOWLEDGMENTS

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