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Eu^{3+} and Tb^{3+} organophosphonates: synthesis, characterization and luminescent properties

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Abstract

This paper reports the results for the synthesis, characterization and photophysical properties of $EuH(O_3PR)_2$ and $TbH(O_3PR)_2$ ($R=CH_3$ or C_6H_5). The Eu^{3+} luminescence data revealed highly red emissive materials where the characteristic transitions $^5D_0 \rightarrow {}^7F_J$ ($J=1$, 2, 3, and 4) of Eu^{3+} were observed when they were excited at 378 nm. The lifetime ($\lambda_{EXC}=378$ nm) for $EuH(O_3PC_6H_5)_2$ ($\lambda_{EM}=614.5$ nm) is 1.95 ms and for $EuH(O_3PCH_3)_2$ ($\lambda_{EM}=610.5$ nm) is 1.75 ms. Tb^{3+} compounds presented a highly green luminescence when excited at 368 nm due to the Tb^{3+} $^5D_4 \rightarrow {}^7F_J$ ($J=6$, 5, 4, and 3) transitions. The Tb^{3+} lifetime ($\lambda_{EXC}=368$ nm, $\lambda_{EM}=544$ nm) for $TbH(O_3PC_6H_5)_2$ is 2.59 and 2.88 ms for $TbH(O_3PCH_3)_2$. The emission spectra of the solids resulting from TGA/DTA showed a Eu^{3+} $^5D_0 \rightarrow {}^7F_1$ transition more intense than the $^5D_0 \rightarrow {}^7F_2$ one. The decrease in the 0→2/0→1 ratio from 2.92 to 0.503 for $EuH(O_3PCH_3)_2$ and from 3.19 to 0.881 for $EuH(O_3PC_6H_5)_2$, is consistent with a higher symmetry around Eu^{3+}. © 1998 Elsevier Science S.A.

Keywords: Luminescence; Phosphonates; Terbium; Europium

1. Introduction

Solid-state materials with appropriate physical and chemical properties for useful technological applications are often the aim of the researchers. Although many of these materials have been discovered by accident, rational synthesis is now playing an increasing important role [1]. Rationally designed supramolecular solids cannot be made in a high-temperature, solid-phase reaction from refractory precursors. However, low-temperature reaction strategies where soluble or volatile molecular precursors are snapped together are available to solid state chemists [2,3]. The layered metal phosphonate salts are organic/inorganic materials in which the structure is directed by the choice of metal and reaction conditions. The nature of the interlayer region depends on the organic moiety. The synthesis and preliminary structural characterization of a new family of metal phosphonates, $LnH(O_3PR)_2$, where Ln=La, Sm and Ce, were also reported by Mallouk and co-workers [4].

Many different environments such as vitroceramics, zeolites, Langmuir-Blodgett films, silica gel, hourglass and supramolecular devices have been used as hosts to study the interaction of lanthanide ions by luminescence methods [5–14]. Lanthanide organophosphonates are promising luminescent systems for this kind of research, since in their organic–inorganic layered structure lanthanide atoms could be located at different distances within each other by using pre-established size of the organic radical, which intercalates them. In this communication, we report the results for the synthesis, characterization and luminescence studies of Eu^{3+} and Tb^{3+} organophosphonates, $EuH(O_3PR)_2$ and $TbH(O_3PR)_2$ ($R=CH_3$ or C_6H_5).

2. Experimental

The Eu^{3+} and Tb^{3+} organophosphonates, $EuH(O_3PR)_2$ and $TbH(O_3PR)_2$ ($R=CH_3$ or C_6H_5) were prepared by combining an aqueous solution of $EuCl_3$ or $TbCl_3$ with an aqueous–ethanolic solution of the respective phosphonic acid. In the case of phenylphosphonates an aqueous solution of 0.10 M NaOH was added dropwise while the mixture was vigorously stirred. The resulting white precipitate in its mother liquor was kept at ~70°C for 10 days. The precipitate was filtered, washed with water and

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ethanol, and dried at 70°C in air. Crystallites of $EuH(O_3PR)_2$ and $TbH(O_3PR)_2$ ($R=CH_3$ or C_6H_5) were studied by IR and luminescence spectroscopy. DTA/TGA as well as elemental and X-ray powder diffraction analysis were carried out. Emission and excitation spectra were obtained in a SPEX Fluorolog II spectrofluorometer. Luminescence lifetime measurements were done as well using a 1934D model spectrophosphorometer coupled to the SPEX at room and liquid nitrogen temperature. IR spectra of the samples in a Nujol mull were taken on a Nicolet 5ZDX FT-IR spectrometer. An SDT 2690 simultaneous DTA/TGA apparatus from TA Instruments was used to obtain thermogravimetric analyses, where an oxygen flux of 100 ml min^{-1} was used and the heating rate was 10°C min^{-1} until 1000°C. X-ray powder diffraction patterns were obtained with a UNIVERSAL XZG-4C diffractometer using Cu Kα radiation. Elemental analyses were performed by the Chemistry Institute of the University of São Paulo.

3. Results and discussion

Unit cell parameters and elemental composition of the Eu^{3+} and Tb^{3+} organophosphonates are in agreement with Mallouk and co-workers' [4] data for La^{3+}, Sm^{3+}, and Ce^{3+} methyl- and phenylphosphonates. They found an interlayer distance of 9.6 Å for $LaH(O_3PCH_3)_2$, where C and H compositions were 7.40 and 2.09%, respectively, while $LaH(O_3PC_6H_5)_2$ showed an interlayer distance of 15.6 Å, and 31.77% C and 2.46% H. According to our results, $EuH(O_3PCH_3)_2$ presented an interlayer distance of 9.45 Å, 7.12% C (calc.=7.04) and 1.98% H (calc.=2.07), and $TbH(O_3PCH_3)_2$ showed an interlayer distance of 9.50 Å, 6.65% C (6.90% calc.) and 1.88% H (2.03% calc.). $EuH(O_3PC_6H_5)_2$ presents an interlayer distance of 15.4 Å, 29.89% C (calc.=30.99) and 2.42% H (calc.=2.39), and $TbH(O_3PC_6H_5)_2$ showed an interlayer distance of 15.2 Å, 29.67% C (30.53% calc.) and 2.29% H (2.35% calc.).

Eu^{3+} and Tb^{3+} organophosphonates presented strong red and green emissions, respectively, when excited by a UV lamp. The excitation and emission spectra of the europium methylphosphonate, $EuH(O_3PCH_3)_2$, and europium phenylphosphonate, $EuH(O_3PC_6H_5)_2$, are presented in Fig. 1a and Fig. 1b, respectively. The Eu^{3+} emission spectra presented the characteristic transitions $^5D_0 \rightarrow {}^7F_J$ (where $J=1$, 2, 3, and 4) of Eu^{3+} when excited at 378 nm. The intensity maximum at 610.5 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} (Fig. 1a) is noticed for the $EuH(O_3PCH_3)_2$ emission spectrum, while the intensity maximum for the $EuH(O_3PC_6H_5)_2$ emission spectrum (Fig. 1b), due to the same $^5D_0 \rightarrow {}^7F_2$ transition, appears at 614.5 nm. Excitation spectra for both $EuH(O_3PCH_3)_2$ and $EuH(O_3PC_6H_5)_2$ compounds at the left side of Fig. 1a and Fig. 1b, respectively, present almost the same feature. Both spectra have maximum excitation bands at 378 nm. Some difference is noticed, however. The $EuH(O_3PC_6H_5)_2$ spectrum presents a broader excitation band near 300 nm than the $EuH(O_3PCH_3)_2$ spectrum. This broad band is probably related to some interaction between the phenyl ring and Eu^{3+} in the $EuH(O_3PC_6H_5)_2$ compound, compared to the methyl group in the $EuH(O_3PCH_3)_2$ one. This band could be ascribed to light absorption by the phenyl groups or to a charge transfer band. Fig. 2 shows excitation and emission spectra of (a) terbium methylphosphonate ($TbH(O_3PCH_3)_2$) and (b) terbium phenylphosphonate ($TbH(O_3PC_6H_5)_2$). These compounds showed the characteristic Tb^{3+} emission when excited at 368 nm due to the $^5D_4 \rightarrow {}^7F_J$ transitions ($J=6$, 5, 4, and 3). Both spectra show an emission maximum at 544 nm, ascribed to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+}. Excitation spectra of both Tb^{3+} compounds presented excitation maxima at 368 nm.

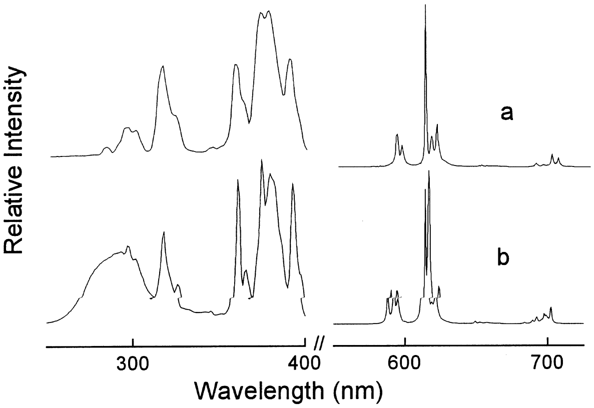

Fig. 1. Excitation and emission spectra ($\lambda_{EXC}=378$ nm) of Eu^{3+} methylphosphonate (a) $EuH(O_3PCH_3)_2$ ($\lambda_{EM}=610.5$ nm) and phenylphosphonate (b) $EuH(O_3PC_6H_5)_2$ ($\lambda_{EM}=614.5$ nm).

The Eu^{3+} decay curves ($\lambda_{EXC}=378$ nm) for $EuH(O_3PC_6H_5)_2$ ($\lambda_{EM}=614.5$ nm) and $EuH(O_3PCH_3)_2$ ($\lambda_{EM}=610.5$ nm) compounds presented an exponential feature, resulting in long lifetimes of 1.95 and 1.75 ms,

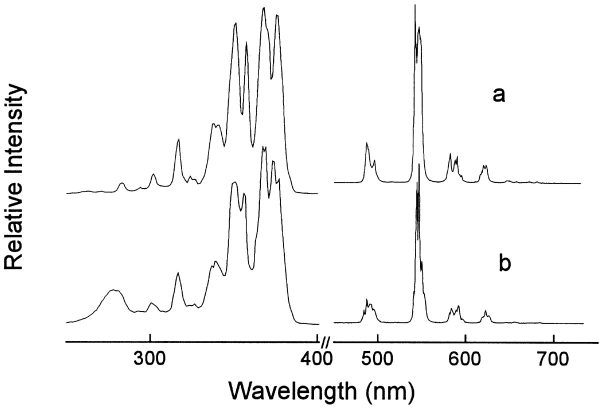

Fig. 2. Excitation ($\lambda_{EM}=544$ nm) and emission spectra ($\lambda_{EXC}=368$ nm) of Tb^{3+} methylphosphonate (a) $TbH(O_3PCH_3)_2$ and phenylphosphonate (b) $TbH(O_3PC_6H_5)_2$.

respectively. The Tb^{3+} decay curves (λ_{EXC}=368 nm) also showed an exponential behavior and the lifetime for $TbH(O_3PC_6H_5)_2$ and $TbH(O_3PCH_3)_2$, both excited at 544 nm, were calculated as 2.59 and 2.88 ms, respectively.

After TGA/DTA, these materials presented an interesting behaviour. The solid residues showed a strong luminescence, and the Eu^{3+} $^5D_0 \rightarrow ^7F_1$ emission band became stronger than the $^5D_0 \rightarrow ^7F_2$ one (see Fig. 3a and Fig. 3b). The intensities of the $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_2$ transitions are strongly dependent on the Eu^{3+} surrounding. The ratio of 0→2/0→1 emission intensity gave us valuable information about Eu^{3+} changes in the environment. The decrease in the 0→2/0→1 ratio after submitting the Eu^{3+} compounds to a 1000°C temperature was from 2.92 for $EuH(O_3PCH_3)_2$ and 3.19 for $EuH(O_3PC_6H_5)_2$ to 0.503 for $EuH(O_3PCH_3)_2$ and 0.881 for $EuH(O_3PC_6H_5)_2$. This fact is consistent with a Eu^{3+} structural change to a higher symmetry in the resulting compounds.

According to TGA/DTA, neither $EuH(O_3PC_6H_5)_2$ nor $TbH(O_3PC_6H_5)_2$ had any water molecule in their structure. Only one weight loss in the thermogravimetric curves was noticed, which did not begin until about 500°C, which was accounted for by removal of the aromatic ring. This is a remarkable stability for organically constituted layers. A weight loss of 31.5% was observed, consistent with a weight loss of 32.65% calculated by assuming a C_6H_5 group. There are some water molecules in the $EuH(O_3PCH_3)_2$ and $TbH(O_3PCH_3)_2$ compounds, according to their thermogravimetric curves. Due to the low weight loss (1%), this water is probably not a structural one, but results from the humidity of the compound. The large weight of the solid residue is consistent with a Eu^{3+} and Tb^{3+} polyphosphate, like $[Ln_2(P_4O_{13})]$, for both methyl- or phenylphosphonates at the end of TGA/DTA (1000°C). Only in this kind of structure is the ratio of lanthanide and phosphorus kept the same as in the initial compounds, which is 1:2. These data are in agreement with the change of lanthanides to a higher symmetry observed through their Eu^{3+} emission spectra, since in the organophosphonates the trivalent metal ions are bonded differently to the oxygens [4], while in the resulting polyphosphate the bonds are all of the same kind.

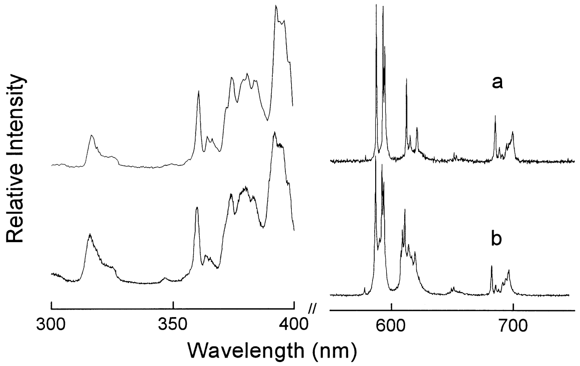

Fig. 3. Excitation and emission spectra of Eu^{3+} methylphosphonate (a) $EuH(O_3PCH_3)_2$ (λ_{EM}=593 nm, λ_{EXC}=393 nm) and phenylphosphonate (b) $EuH(O_3PC_6H_5)_2$ (λ_{EM}=587.8 nm, λ_{EXC}=391 nm) after TGA/DTA (1000°C).

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