

Photophysical Properties of New Terbium (III) Organophosphonates

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Abstract This paper reports on the synthesis, characterization and photophysical properties of the Tb³⁺ organophosphonates, TbH(O₃PR)₂, methylphosphonate (R = CH₃), ethylphosphonate (R = C₂H₅), propylphosphonate (R = C₃H₇), and phenylphosphonate (R = C₆H₅). The layered Tb³⁺ organophosphonates were characterized by X-ray diffraction, IR spectroscopy, TG and elemental analysis. The interlayer distances of the Tb³⁺ organophosphonates evaluated by the X-ray diffractogram were 9.50 Å for TbH(O₃PCH₃)₂, 12.18 Å for TbH(O₃PC₂H₅)₂, 14.84 Å for TbH(O₃PC₃H₇)₂ and 15.20 Å for TbH(O₃PC₆H₅)₂. The Tb³⁺ luminescence data revealed highly green emissive materials when they were excited at 368 nm, where the characteristic ⁵D₄ → ⁷F_J (J = 6, 5, 4 and 3) transitions of Tb³⁺ were observed at 488, 543, 585 and 619 nm, respectively. The lifetime of the Tb³⁺ ⁵D₄ → ⁷F₅ transition (λ_{exc} = 368 nm and λ_{em} = 543 nm) for the Tb³⁺ organophosphonates was evaluated from the decay curves, which values were of 2.88, 2.22, 2.14 and 2.59 ms, respectively for TbH(O₃PCH₃)₂, TbH(O₃PC₂H₅)₂, TbH(O₃PC₃H₇)₂ and TbH(O₃PC₆H₅)₂. TG analysis revealed that these materials are thermally highly stable, with no water

molecule in their composition, which makes them potential luminophores.

Keywords Organophosphonates · Rare earth · Terbium · Luminescence

Introduction

Low temperature reaction strategies, where soluble or volatile molecular precursors are snapped together, are available to solid-state chemists to design supramolecular solids [1,2]. Although many of the solid-state materials have been discovered accidentally, rational synthesis is now playing an increasing important role [3], as rationally designed supramolecular solids cannot be made in a high-temperature solid-phase reaction from refractory precursors.

The layered metal phosphonate salts are organic/inorganic materials in which the structure is directed by choice of metal and reaction conditions while the nature of the interlayer region depends on the organic moiety [4]. Metal organophosphonates have the general formula M_xH(O₃PR)_z, where R is an organic group covalently bonded to the phosphorous atom [5]. The two-dimensional nature of these compounds allows introduction of the different chemical species within the solid network, creating changes in the host lattice. Therefore, their internal structure can, in principle, be tailored in order to obtain new materials with desired and regulated properties [6].

Alberti *et al.* reported the synthesis of a new class of organic/inorganic lamellar materials [7]. The synthesis and structural characterization of metallic phosphonates, with general formula LnH(RPO₃)₂, where Ln = La, Sm and Ce, was reported by Cao *et al.* [8]. The rare-earth phosphonates studied were structurally related to the Ca(RPO₃H)₂ and Zr(RPO₃)₂.

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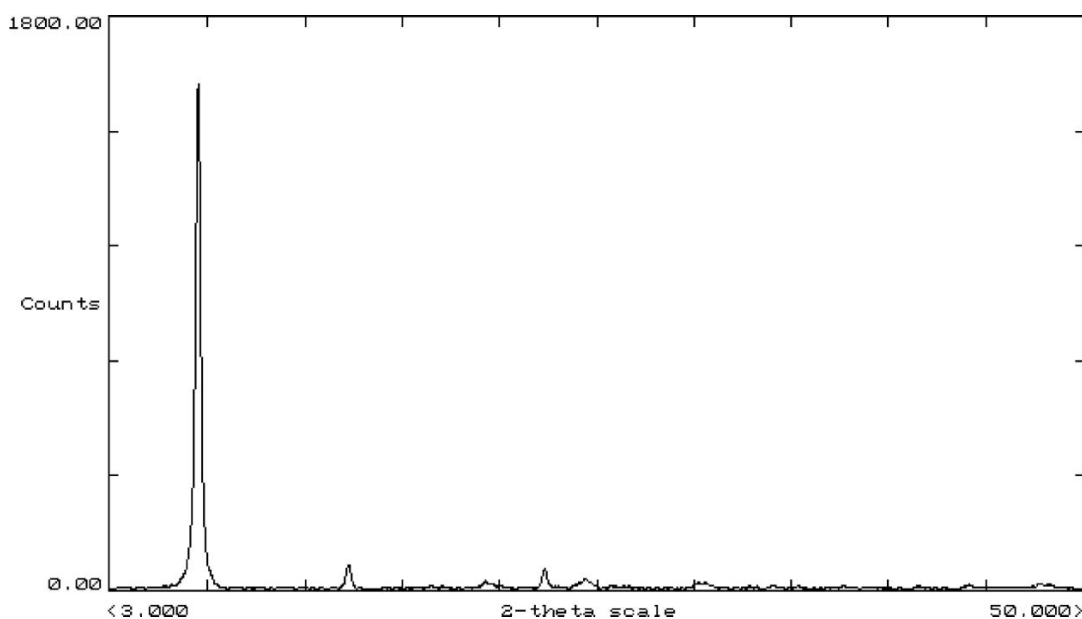


Fig. 1 X-ray diffraction pattern of the Tb^{3+} ethylphosphonate, $\text{TbH}(\text{O}_3\text{PC}_2\text{H}_5)_2$

The luminescent properties of lanthanide ions and its interactions with many different environments, such as vitroceraamics, zeolites, Langmuir–Blodgett films, silica gel, hourglass and supramolecular devices have been studied [8–16]. Lanthanide organophosphonates are promising luminescent systems for this kind of research, as in their organic–inorganic layered structure lanthanide atoms could be located at different distances from each other by using pre-established size of organic radical, which intercalates them. Besides, lanthanides organophosphonates are promising luminescent systems because they present rigid and non-hygroscopic structure. In this paper, we report the synthesis, characterization and photoluminescent study of the following Tb^{3+} organophosphonates, $\text{TbH}(\text{O}_3\text{PR})_2$, methylphosphonate ($\text{R} = \text{CH}_3$), ethylphosphonate ($\text{R} = \text{C}_2\text{H}_5$), propylphosphonate ($\text{R} = \text{C}_3\text{H}_7$) and phenylphosphonate ($\text{R} = \text{C}_6\text{H}_5$).

Experimental

The Tb^{3+} organophosphonates, $\text{TbH}(\text{O}_3\text{PR})_2$, where $\text{R} = \text{CH}_3$, C_2H_5 , C_3H_7 and C_6H_5 were prepared by combining an aqueous solution of TbCl_3 with an aqueous-ethanolic solution of the respective phosphonic acid. In the case of phenylphosphonate, 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 $\sim 70^\circ\text{C}$ in air. The crystallites of $\text{TbH}(\text{O}_3\text{PR})_2$, where $\text{R} = \text{CH}_3$, C_2H_5 , C_3H_7 and C_6H_5 , were characterized by IR and luminescence spectroscopy. DTA/TGA as well as elemental and X-ray powder diffraction analysis were also carried out. Emission and excitation spectra were obtained

in a spex fluorolog II spectrophotometer. Luminescence lifetime measurements were done as well using a 1934 D model spectrophotometer coupled to the spex at room temperature. IR spectra of the samples in a KBr disk were taken on a BOMEN model 102 spectrometer. An TGA 2050 Du Pont from TA Instruments was used to obtain thermogravimetric analyses, where an oxygen flux of $90 \text{ mL}\cdot\text{min}^{-1}$ was used and the heating rate was $15^\circ\text{C}\cdot\text{min}^{-1}$ until 900°C , using a platinum suport. X-ray powder diffraction patterns were obtained with a Siemens D-5000 diffractometer using CuK_2 radiation. Elemental analyses were performed in a CHNS analyzer EA 1108 from Fisions Instruments.

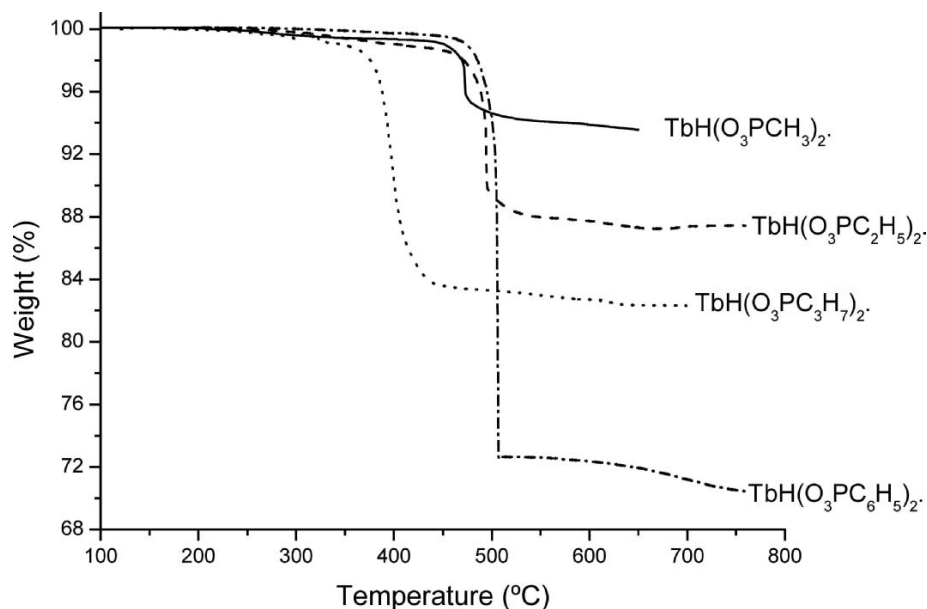
Results and discussion

X-ray diffractogram presented in Fig. 1 as illustration, was used to obtain the interlayer distances of the organophosphonates.

The values of interlayer distances were of 9.50 \AA for $\text{TbH}(\text{O}_3\text{PCH}_3)_2$, 12.18 \AA for $\text{TbH}(\text{O}_3\text{PC}_2\text{H}_5)_2$, 14.84 \AA for $\text{TbH}(\text{O}_3\text{PC}_3\text{H}_7)_2$ and 15.20 \AA for $\text{TbH}(\text{O}_3\text{PC}_6\text{H}_5)_2$. The elemental analysis resulted in 6.90% C (calc. = 6.55), and 2.03% H (calc. = 1.88) for $\text{TbH}(\text{O}_3\text{PCH}_3)_2$, 12.81% C (calc. = 12.85), and 2.69% H (calc. = 2.92) for $\text{TbH}(\text{O}_3\text{PC}_2\text{H}_5)_2$, 17.83% C (calc. = 18.23), and 3.75% H (calc. = 3.82) for $\text{TbH}(\text{O}_3\text{PC}_3\text{H}_7)_2$ and 30.53% C (calc. = 29.67), and 2.35% H (calc. = 2.29) for $\text{TbH}(\text{O}_3\text{PC}_6\text{H}_5)_2$. These experimental results are in agreement with the theoretical data. This indicates that the organophosphonate compositions correspond to the empirical formula of $\text{MH}(\text{RPO}_3)_2$.

The synthesized compounds show a high thermal stability. The TG curves of Tb^{3+} organophosphonates are presented

Fig. 2 TG curves of Tb³⁺ methyl, TbH(O₃PCH₃)₂, ethyl, TbH(O₃PC₂H₅)₂, propyl, TbH(O₃PC₃H₇)₂ and phenyl TbH(O₃PC₆H₅)₂ phosphonates



for illustration in Fig. 2. These curves show a plateau that goes to about 500°C.

There is essentially no weight loss below this temperature. The decomposition of the organic moiety begins at 500°C. This stability is related to the distance of the organic groups, inhibiting the dissociation routes by collision. Phosphonates are more resistant to the temperature than phosphates. This could be ascribed to the fact that the dissociation route in phosphates are similar to elimination in esters, while in phosphonates, the decomposition occur through the hemolytic scission of the P–C bond [17]. The weight loss in percentage for the organophosphonates was calculated from the thermal analysis data and the values were of 5.80, 12.00, 15.16 and

26.20%, respectively for TbH(O₃PCH₃)₂, TbH(O₃PC₂H₅)₂, TbH(O₃PC₃H₇)₂ and TbH(O₃PC₆H₅)₂ samples. The theoretical values, considering the loss of carbons and hydrogens, were of 5.80, 12.00, 15.16 and 26.20%, respectively for TbH(O₃PCH₃)₂, TbH(O₃PC₂H₅)₂, TbH(O₃PC₃H₇)₂ and TbH(O₃PC₆H₅)₂. The experimental weight loss is smaller than the theoretical weight loss for all the samples. This behavior has also been observed before for another layered materials [17–19]. In this work, the weight loss is different from that expected for the theoretical values. This fact can be ascribed to the presence of different process occurring simultaneously during the phosphonates decomposition, which are the pyrolysis of the organic group and its

Fig. 3 Absorption spectra of the Tb³⁺ organophosphonates in the IR region

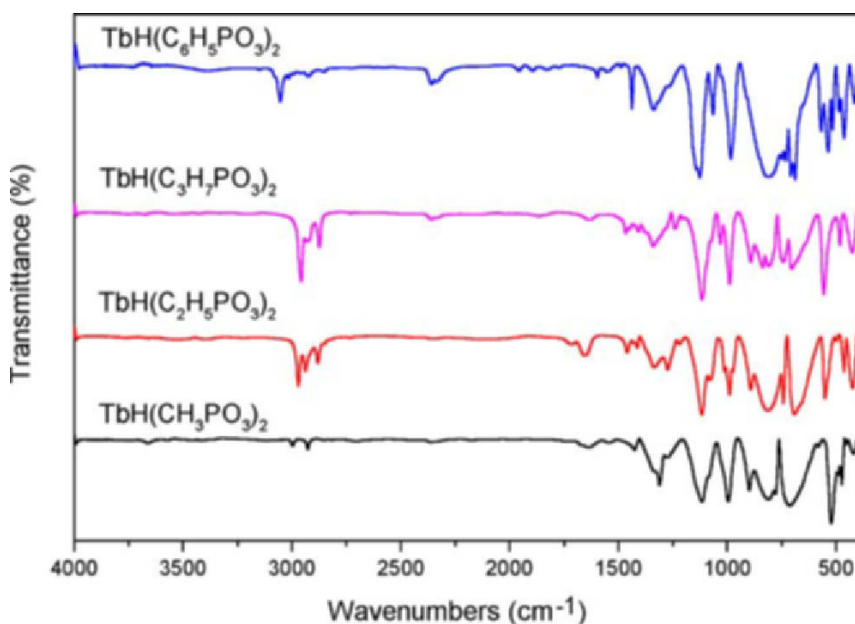
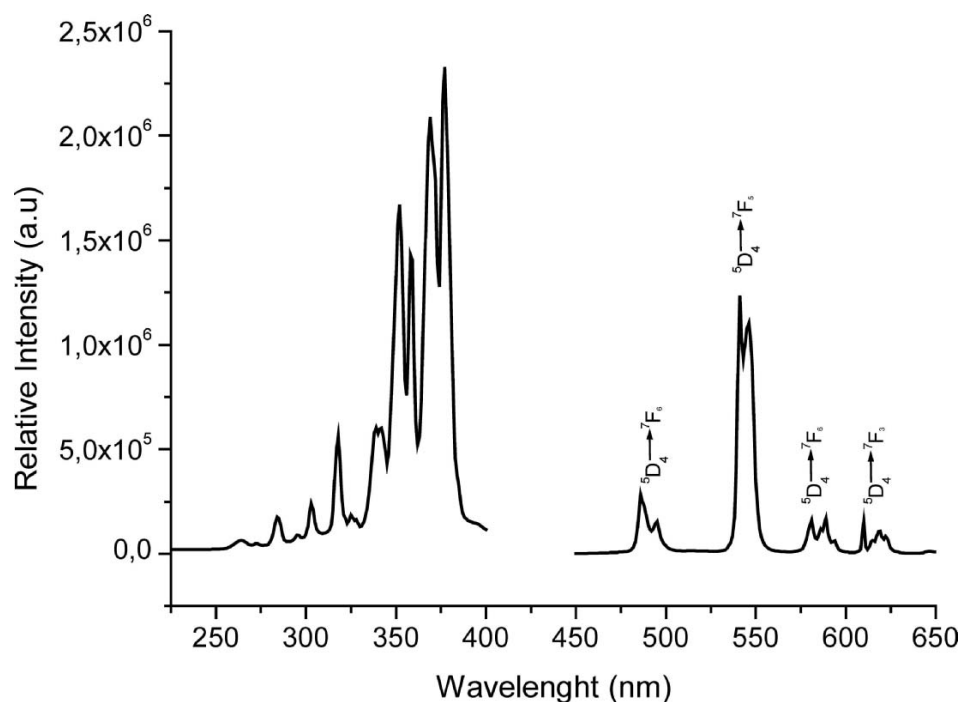


Fig. 4 Excitation ($\lambda_{em} = 544$ nm) and emission spectra ($\lambda_{exc} = 368$ nm) of the $TbH(O_3PC_3H_7)_2$



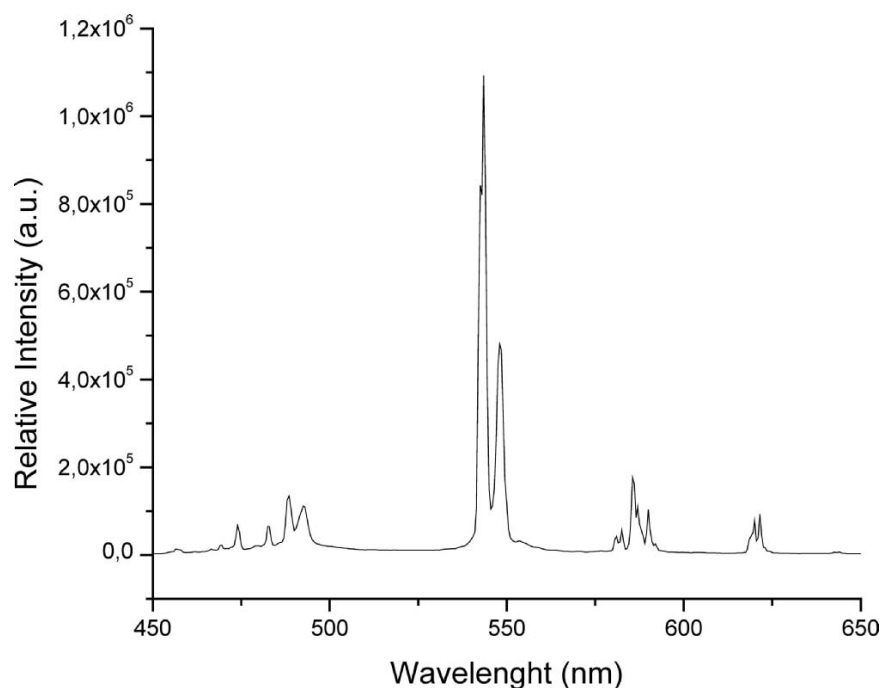
oxidation. The phosphonate oxidation will probably result in a pyrophosphate like $Ln_2(P_4O_{13})$ [20].

Figure 3 presents the absorption spectra of the Tb^{3+} organophosphonates in the IR region. The characteristic set of bands in the 1300 – 900 cm^{-1} region is due to the different P–OR stretching vibrations of the phosphonate groups.

The presence of a band at 1312 cm^{-1} is attributed to P–CH₃ stretching vibration in the terbium methylphospho-

nate spectrum, while in the europium ethylphosphonate spectrum a band characteristic of the P–C₂H₅ at 1081 cm^{-1} . The bands in the 2995 – 2922 cm^{-1} region are ascribed to the $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ in the Tb^{3+} methyl, ethyl and propylphosphonates. The band at 3052 cm^{-1} is due to the $\nu(C-H)$, and those between 1485 and 1437 cm^{-1} are related to the $\nu(C=C)$ vibration of the aromatic ring in the Tb^{3+} phenylphosphonate. The C–C axial deformation of the Tb^{3+}

Fig. 5 Emission spectra, $\lambda_{exc} = 368$ nm, of the reference compound (Gd_2O_3/Tb)



methyl, ethyl and propylphosphonates results in weak bands, which are observed in the 1200–800 cm^{-1} range of the IR spectra, almost in the same region where the P–OR stretching vibrations of the phosphonate groups were observed. No broad band in the 3300–3000 cm^{-1} region, confirming the absence of water in these materials [19,21–23].

Figure 4 presents the emission and excitation spectra of the Tb^{3+} organophosphonates. The transitions between the energy levels of the $4f^8$ configuration of the Tb^{3+} ion are observed in the excitation spectra. It was noticed that only the $\text{TbH}(\text{O}_3\text{PC}_6\text{H}_5)_2$ spectrum presented a broad but not so intense band at around 278 nm when the emission was set at 545 nm. This band was ascribed to the energy transfer from the phenyl group to the Tb^{3+} ion. The more intense excitation band observed at 368 nm in all the excitation spectra is due to the $^7\text{F}_6 \rightarrow ^5\text{G}_5$ transition of the Tb^{3+} ion. The emission spectra of the Tb^{3+} , when excited at 368 nm, present the characteristic bands of the Tb^{3+} ion. The bands relating to the $\text{Tb}^{3+} \ ^5\text{D}_4 \rightarrow ^7\text{F}_6, ^5\text{D}_4 \rightarrow ^7\text{F}_5, ^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions are observed respectively at 488, 543, 585 and 619 nm. The $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of the Tb^{3+} ion at around 543 nm is the more intense band and is responsible for the characteristic green emission of these compounds. This material has a strong emission, which is compared with the intensity of the reference compound $\text{Gd}_2\text{O}_2\text{S}/\text{Tb}$, Fig. 5.

The lifetime of the $\text{Tb}^{3+} \ ^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition ($\lambda_{\text{exc}} = 368$ nm and $\lambda_{\text{em}} = 543$ nm) for the Tb^{3+} organophosphonates was evaluated from the decay curves, and its values were 2.88, 2.22, 2.14 and 2.59 ms, respectively for $\text{TbH}(\text{O}_3\text{PCH}_3)_2$, $\text{TbH}(\text{O}_3\text{PC}_2\text{H}_5)_2$, $\text{TbH}(\text{O}_3\text{PC}_3\text{H}_7)_2$ and $\text{TbH}(\text{O}_3\text{PC}_6\text{H}_5)_2$. These lifetimes are relatively high compared to different Tb^{3+} complexes. The monoexponential features of the Tb^{3+} organophosphonates decay curves indicate only one kind of Tb^{3+} emission site in these materials.

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