Contents lists available at ScienceDirect





Journal of Luminescence

journal homepage: http://www.elsevier.com/locate/jlumin

Luminescence of undoped and Ce-doped hexagonal BiPO₄

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ARTICLE INFO

Keywords: Bismuth phosphate Hexagonal structure Cerium Defect Luminescence Excitation wavelength

ABSTRACT

Undoped and Ce-doped hexagonal BiPO₄ were synthesized by a precipitation method and characterized on their structure, Ce spatial distribution and chemical state, together with detailed luminescence spectroscopy investigation through systematic variation of the excitation wavelength (λ_{exc}) over the broad range 250–460 nm combined with radioluminescence measurements and extensive literature review. Up to five distinct emission bands were observed, depending on λ_{exc} and on the presence or not of the activator. The host presented three emission bands: the 350 nm (3.54 eV) band was ascribed to a defect, the 405 nm (3.06 eV) band was ascribed to metal-to-metal charge transfer (MMCT), and the 570 nm (2.18 eV) band was ascribed to the Bi³⁺ $^{3}P_{1} \rightarrow ^{1}S_{0}$ transition. The presence of Bi³⁺ ions perturbed by oxygen vacancies in the coordination polyhedron at varying distances to the Bi³⁺ ions created states with lower energies than the states of unperturbed Bi³⁺. Ce-incorporation led to the creation of two partially superimposing bands at about 445 nm (2.79 eV) and 490 nm (2.53 eV). Strong interaction between Ce³⁺ and the host was observed. These results led to enhanced understanding of the intrinsic and extrinsic luminescence of this material that presents considerable controversy in the literature.

1. Introduction

Bismuth phosphate (BiPO₄) presents three polymorphs, depending on the temperature: hexagonal (5.54 g/cm³) up to about 473–523 K, low-temperature monoclinic (6.83 g/cm³) up to about 873–973 K, and high-temperature monoclinic (6.22 g/cm³) up to 1270 K [1–3]. Among them, the hexagonal structure is of particular interest to this work. It can be described in terms of alternating BiO₈ polyhedra and PO₄ tetrahedra forming chains along the c-axis. In this structure, there are three chemical formulas in the unit cell, and there is only one crystallographic site for Bi³⁺. The large ionic radius of the Bi³⁺ ions allows for the substitution with rare earth ions and thus of optical activation of the host. Indeed, BiPO₄ has been doped and co-doped with rare earths aiming at diverse technological applications [4-8]. The high density and the capacity of being doped with rare earths make this material attractive as scintillator. The most common scintillator activators are Ce³⁺ and Pr³⁺ due to their fast allowed 4f-5d transition. Recently, BiPO4 was doped with Pr ions and its luminescence investigated. Those authors reported red emission due to the 4f-4f transitions, while not observing the 5d-4f transition of Pr^{3+} [8].

On the other hand, limited work has been carried out on the luminescence of undoped and Ce-doped BiPO₄. The majority of the reports on Ce-doped BiPO₄ focused on co-doping it with other rare earths to promote energy transfer from Ce to the other rare earth towards enhanced luminescence. Table 1 summarizes a literature survey on the luminescence of undoped and Ce-doped BiPO₄ [9–20], where conflicting results were observed. This can be illustrated by the emission of Ce³⁺ in hexagonal BiPO₄ that was reported within a broad spectral region, from 352 nm to 459 nm. The lack of consistency among the different reports showed the intrinsic luminescence of the host and of Ce³⁺ in BiPO₄ are still not well understood.

Additional interest in this material rises from its photocatalytic properties and within this context the relevance of understanding the response of BiPO₄ to ultraviolet light, including photoionization, photoluminescence and energy transfer processes [16,21–24]. This work aims at providing insight into the nature of the luminescence of undoped and Ce-doped hexagonal BiPO₄ based on detailed spectroscopy investigation and comparison with other Bi-based oxides towards paving the way for future technological applications of this material.

2. Experimental procedures

Powders of undoped $BiPO_4$ and 5 mol% Ce-doped $BiPO_4$ with Ce substituting for Bi were synthesized via a precipitation method. In a

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https://doi.org/10.1016/j.jlumin.2020.117626

Received 22 July 2020; Received in revised form 25 August 2020; Accepted 28 August 2020 Available online 2 September 2020 0022-2313/© 2020 Elsevier B.V. All rights reserved.

Table 1

Literature survey of the luminescence of Ce-doped (top layer of Table 1) and undoped (bottom layer of Table 1) BiPO₄. The column 'Emissions in this work' quotes the peak positions of the bands observed in this work under the same excitation wavelength, or closest excitation wavelength when indicated. Good matches of the peak position of the other report with this work were underlined. Some measurements were reported at low temperatures, as indicated, otherwise room temperature was assumed. * Values obtained after spectral analysis.

	Crystallographic phase	Excitation (nm)	Emission (nm)	Emissions in this work (nm)	Ref.
Ce-doped	Hexagonal	275	352	<u>342</u> , ~450, ~605 ($\lambda_{exc} = 270$ and 280 nm)	[9]
	Hexagonal	360	437	441	[<mark>10</mark>]
	Hexagonal	417	459	513 ($\lambda_{\rm exc} = 420 \text{ nm}$)	[11]
	Hexagonal	-	410	-	[12]
	High-temperature monoclinic	363	396, <u>427</u> *	441	[15]
Undoped	Hexagonal	250	~440, ~490	$\overline{350}$, 550 ($\lambda_{\rm exc} = 260$ nm)	[17]
	Hexagonal	-	468	-	[16]
	Hexagonal	355	<u>470</u> , 535, 607*	~ 418 ($\lambda_{\rm exc} = 350$ and 360 nm)	[20]
	High-temperature monoclinic	225 (8 K)	480, ~ <u>550</u>	$350, 550 \ (\lambda_{\text{exc}} = 260 \text{ nm})$	[18]
		310 (8 K)	<u>480,</u> ~ <u>550</u>	379, 412, 620	
	High-temperature monoclinic	300 (8 K)	428, 477, <u>605</u> *	352, <u>408</u> , <u>610</u>	[19]
	High-temperature monoclinic	260 (8 K)	475, ~600 (8 K)	350, 550	[13]
	High-temperature monoclinic	302 (8 K)	<u>450,</u> ~ 600 (8 K)	352, $\overline{408}$, $\underline{610}$ ($\lambda_{\rm exc} = 300 \text{ nm}$)	[14]

typical synthesis, stoichiometric amounts of the precursors, 4.75 mmol (2.3041 g) Bi(NO₃)₃·5H₂O (Acros Organics, 99.999%), 0.25 mmol (108.6 mg) Ce(NO₃)₃·6H₂O (Beantown Chemical, 99.99%), and 5 mmol (660.3 mg) (NH₄)₂HPO₄ (Acros Organics, 99%) were mixed in a beaker. Simultaneously, 15 mmol (1.1859 g) NH₄HCO₃ (Alfa Aesar, 99%) was dissolved in 50 mL ultrapure 18.2 M Ω water provided by a Thermo Scientific Barnstead Smart2Pure water purification system based on 0.2 μ m particle and reverse osmosis filtering of prefiltered water under stirring at room temperature. The NH₄HCO₃ solution was slowly dropped into the precursor mixture under vigorous stirring, and the new solution stirred at room temperature for 1 h followed by centrifugation, several steps of washing with deionized water and ethanol, and drying at 80 °C overnight. Undoped bismuth phosphate was synthesized with the same procedure above using 5 mmol (2.4254 g) Bi(NO₃)₃·5H₂O and 5 mmol (660.3 mg) (NH₄)₂HPO₄.

X-ray diffraction (XRD) measurements were executed with a Rigaku Ultima IV X-ray diffractometer with Cu K α radiation (40 kV, 40 mA) with 2 θ scans from 10° to 80° at a rate of 0.5°/min.

Raman scattering spectroscopy was executed with a Horiba LabRAM HR Evolution confocal microscope equipped with an 800 mm focal length spectrograph and an air-cooled (-60 °C) back-illuminated deepdepleted 1024 × 256 pixels CCD detector. A 100 mW 532 nm laser, 50% neutral density filter, 50x magnification objective, and 1800 groves/mm diffraction grating were used in the measurements. Spectra corresponded to the average of eight 10 s-long scans. The spectra were corrected by the pre-recorded instrument-specific response to a calibrated white light source, namely the intensity correction system (ICS).

Scanning electron microscopy (SEM) was executed with a Hitachi SU6600 variable pressure electron microscope operated at 10 kV. Energy dispersive X-ray spectroscopy (EDX) mapping was executed with an Oxford Instruments X-Max detector (resolution at 5.9 KeV = 129 eV). The AZTEC software was used for data analysis.

X-ray photoelectron spectroscopy (XPS) was executed using a Physical Electronics PHI VersaProbe III Scanning ESCA Microprobe. A monochromatic Al Ka (1486.7 eV) X-ray source was used in these measurements, with the 100 μ m diameter X-ray beam (25 W, 2 kV) impinging at a 45° to the normal of the surface of the sample. High resolution scans of the Bi *4f*, P *2p* (3 sweeps), and Ce *3d* (5 sweeps) lines were obtained using 69 eV pass energy, 0.125 eV step size, and 50 ms dwell time/step. Spectra were calibrated to the carbon signal at 284.8 eV.

Photoluminescence emission (PL) and excitation (PLE) measurements were executed using an Edinburgh Instruments FLS-1000 spectrofluorometer equipped with a 450 W Xe lamp, dual monochromators for emission and excitation, respectively, and a Hamamatsu R928P photomultiplier tube. The number of detected photons was automatically corrected by the instrument's software for the background and spectral differences in excitation intensity and detection sensitivity. If needed, spectra obtained with excitation wavelengths lower than 320 nm were smoothed by the Savitzky-Golay filter using a first order polynomial to fit successive sub-sets of adjacent data points that corresponded to a 10 nm range. This procedure essentially eliminated noise from the spectra without affecting their shape.

Radioluminescence (RL) measurements were executed using a customer-designed Freiberg Instruments Lexsyg Research spectrofluorometer equipped with a Varian Medical Systems VF-50J X-ray tube with a tungsten target. The X-ray source was coupled with an ionization chamber for continuous irradiation intensity monitoring. The light emitted by the sample was collected by a lens and converged into an optical fiber connected to an Andor Technology Shamrock 163 spectrograph coupled to a cooled (-80 °C) Andor Technology DU920P-BU Newton CCD camera (spectral resolution was *ca.* 0.5 nm/pixel). RL measurements were executed under continuous X-ray irradiation (40 kV, 1 mA) at room temperature. Relative luminosity was determined using Bi₃Ge₄O₁₂ powder (BGO; Alfa Aesar, 99.9995% (metals basis), Puratronic) as reference. Powders filled *ca.* 8 mm diameter 0.5 mm deep cups thus allowing for relative RL intensity comparison between different samples.

3. Results and discussion

The structure of the powders was investigated by XRD and Raman scattering spectroscopy measurements whose results are shown in Figs. 1 and 2, respectively. XRD results revealed single phase hexagonal structure, in agreement with JCPDS card 45-1370. Doping with cerium substituting for bismuth did not affect the structural arrangement, in agreement with the small difference in ionic radii of 2.3% between eightfold Bi3+ (1.17 Å) and Ce3+ (1.143 Å) [25]. Raman scattering spectroscopy results shown in Fig. 2 confirmed the powders to have hexagonal structure [16,26]. No significant differences were found between the spectra of undoped and Ce-doped BiPO₄ confirming XRD results that the incorporation of 5 mol% Ce did not affect the structure of the host. Further, all bands matched their respective positions reported in Refs. [16,26] within up to about $\pm 6 \text{ cm}^{-1}$. The vibrational modes could be grouped in three sets: the 202 cm^{-1} band being related to the O-Bi-O symmetric bending mode, the bands between about 350 and 650 cm⁻¹ related to ν_2 (405 and 448 cm⁻¹ bands) and ν_4 (472, 550, and 587 cm^{-1} bands) PO₄ bending modes, and the bands between 900 and 1150 cm⁻¹ to ν_1 symmetric (968 cm⁻¹ band) and to ν_3 antisymmetric (1054 $\rm cm^{-1}$ band) $\rm PO_4$ stretching modes.

Fig. 3A illustrates a typical SEM image of BiPO₄:Ce powder obtained in secondary electron mode where aggregates of particles with a broad range of sizes were observed. The same region was mapped by scanning EDX for the intensity of the Bi M α 1, Ce L α 1, P K α 1, and O K α 1 X-ray lines



Fig. 1. XRD diffractograms of undoped and 5 mol% Ce-doped $BiPO_4$, together with JCPDS card 45–1370 shown as the bar plot.



Fig. 2. Raman scattering spectra of undoped and Ce-doped hexagonal $BiPO_4$. The spectra are vertically shifted to facilitate visualization.

(Fig. 3B–E). These results revealed Ce to be uniformly distributed within the grains, further demonstrating $BiPO_4$ to be a good host for cerium ions and possibly for other rare earths. Other regions of the sample were also probed, and similar results were obtained.

In addition to the spatial distribution, the chemical state of cerium ions is particularly important since only Ce³⁺ ions are luminescent. Representative XPS measurements are shown in Fig. 4, where high energy resolution spectra of the Bi 4f (Fig. 4A), P 2p (Fig. 4B), and Ce 3d (Fig. 4C) lines are presented. The Bi 4f spectrum was composed of two doublets at 165.3 eV (4 $f_{5/2}$) and 160.0 eV (4 $f_{7/2}$) in agreement with the presence of Bi-O bonds [27]. The P 2p peak was located at 133.4 eV in agreement with the presence of the phosphate group [27,28]. The value of full width at half maximum (FWHM) = 1.74 eV confirmed the existence of only one chemical species of P-O. The slight asymmetry of this peak was due to the superposition of the unresolved $2p_{3/2}$ and $2p_{3/2}$ doublet [28]. The XPS results on Bi and P further supported the XRD and Raman scattering results, confirming the formation of BiPO₄. The Ce 3d XPS spectrum presented overlapping sets of doublets, where the envelope onset was located at about 880 eV. The complex peaks were assessed qualitatively based on the shape of the peak envelope to identify the presence of Ce^{3+} . These results were consistent with the presence of Ce 3+ state (peaks U', U_o, V', and V_o marked in red in Fig. 4) [29]. Importantly, the absence of Ce^{4+} was demonstrated by the lack of any lines at binding energies around 916 eV (U^m peak) and 898 eV (V^m



Fig. 3. SEM/EDX results of BiPO₄:Ce: A) SEM image obtained in secondary electron mode, B) EDX map of Bi M α 1 line, C) EDX map of Ce L α 1 line, D) EDX map of P K α 1 line, and E) EDX map of O K α 1 line.



Fig. 4. High energy resolution XPS spectra: A) Bi 4f, B) P 2p, and C) Ce 3d where the peak positions related to Ce3+ are marked in red.

peak) [29]. Nevertheless, it is noted that while unlikely photoreduction of Ce⁴⁺ to Ce³⁺ has been previously reported under long exposures or intense beams [30,31]. However, compared to those papers, the relatively low number of five beam sweeps used in this work significantly reduced beam exposure. Additionally, the 69 eV pass energy and the 0.125 eV step size used in this work minimized radiation damage due to intensity or dwell time. Further, the focused beam down to 100 μ m diameter of our instrument provided higher sensitivity to the sample allowing for less exposure time and reduced beam damage compared to other instruments. Based on all of these important experimental modifications and the information provided about photoreduction from cited papers, we are confident our experimental conditions provided an accurate reading of the sample regarding the chemical state of Ce.

PL of BiPO₄(:Ce) was complex, with up to five distinct emission bands observed depending on the excitation wavelength (λ_{exc}) and on being or not doped with Ce. Fig. 5 summarizes PL results by presenting the peak position of all emission bands as functions of λ_{exc} , where open symbols correspond to undoped BiPO₄ and solid symbols to Ce-doped BiPO₄. Representative spectra from both undoped and Ce-doped BiPO₄ are presented in Figs. 6–14. First, the intrinsic luminescence of undoped BiPO₄, the host, is presented and discussed followed by the discussion of the effects of incorporation of Ce³⁺.

Undoped BiPO₄ presented up to three bands, depending on $\lambda_{\text{exc.}}$. Under high energy excitation, typically within 250 nm (4.96 eV) and 300 nm (4.13 eV), two bands were observed at around 350 nm, henceforth referred to as '350 nm' (3.54 eV) band, and around 570 nm (2.18 eV), henceforth referred to as '570 nm' band (Fig. 6). The 350 nm band was narrow with FWHM ~0.4 eV, and relatively weak. Its shift to higher wavelengths observed for $\lambda_{\text{exc}} > 300$ nm (Fig. 5) was attributed to the progressive decrease of its intensity combined with the proximity of the growing and much more intense band at about 400 nm. The excitation spectrum of 350 nm band is shown in Fig. 7 where a relatively weak band centered at about 300 nm (4.13 eV) mounted on the onset of the 350 nm band was observed. The Stokes shift of the 350 nm band was



Fig. 5. Peak position of all emission bands as functions of λ_{exc} , where open symbols correspond to undoped BiPO₄ and solid symbols to Ce-doped BiPO₄.



Fig. 6. PL spectra of undoped BiPO₄ for 280 nm $\leq \lambda_{exc} \leq$ 340 nm.



Fig. 7. PLE spectra of undoped (black lines) and Ce-doped (red lines) BiPO₄ for $\lambda_{em} = 350$ nm, 420 nm, 444 nm, and 495 nm.



Fig. 8. PLE spectra of undoped (black lines) and Ce-doped (red lines) BiPO₄ for $\lambda_{\rm em}=575$ nm and 600 nm.



Fig. 9. Spectra obtained by taking the difference between the PL spectra of undoped and Ce-doped BiPO₄ excited at $\lambda_{exc} = 400$ nm (Fig. 9AA) and 460 nm (Fig. 9B).

estimated to be 0.59 eV. The 570 nm band was broad, with FWHM = 1.2 eV. It shifted to higher wavelengths for higher λ_{exc} , as discussed in detail below. The excitation spectra of 570 nm band are illustrated in Fig. 8 for monitoring at emission wavelengths $\lambda_{em} = 575$ nm and 600 nm. Both spectra were essentially identical. They presented an excitation band at around 280 nm (4.43 eV) and a broad band within about 350–550 nm, peaked around 460 nm (2.70 eV) and with a shoulder at around 400 nm (3.10 eV). The Stokes shift of band 570 nm was estimated to be 2.25 eV. Fig. 9 shows two spectra obtained by taking the difference between the PL spectra of undoped and Ce-doped BiPO₄ excited at $\lambda_{exc} = 400$ nm (Fig. 9AA) and 460 nm (Fig. 9B). The spectra showed a broad band centered at 595 nm and 610 nm for higher λ_{exc} , respectively. As can be seen in Fig. 5 and as it will be discussed later, the 570 nm band was not



Fig. 10. PL spectra of undoped BiPO₄ for 340 nm $\leq \lambda_{exc} \leq$ 460 nm.



Fig. 11. PL spectra of Ce-doped BiPO₄ for 280 nm $\leq \lambda_{exc} \leq$ 340 nm.



Fig. 12. PL spectra of undoped (black lines) and Ce-doped (red lines) BiPO₄ for $\lambda_{\rm exc} = 280$ nm, 300 nm, and 340 nm.

observed in Ce-doped BiPO₄ for $\lambda_{exc} > \sim$ 340 nm. These results confirmed that excitation in the broad PLE band shown in Fig. 8 resulted in the emission from 570 nm band shifted to higher wavelengths.

Under $\lambda_{exc} = 290$ nm (4.28 eV) and higher wavelengths, a band at



Fig. 13. PL spectra of Ce-doped BiPO₄ for 340 nm $\leq \lambda_{exc} \leq$ 460 nm.



Fig. 14. PL spectra of undoped (black lines) and Ce-doped (red lines) BiPO₄ for $\lambda_{\text{exc}} = 350$ nm, 370 nm, 400 nm, and 460 nm.

about 405 nm (henceforth referred to as '405 nm' band (3.06 eV)) was clearly observed (Figs. 6 and 10). It co-existed with bands 350 nm and 570 nm up to $\lambda_{\text{exc}} = 320$ nm (3.88 eV), and up to about $\lambda_{\text{exc}} = 350$ nm (3.54 eV), its emission wavelength remained unchanged. For higher λ_{exc} it continuously shifted to higher wavelengths, as shown in Figs. 5 and 10, when its peak intensity decreased dramatically to 20-30% of the peak intensity under excitation at 350 nm (3.54 eV). The excitation spectra of this band obtained at $\lambda_{em} = 420$ (2.95 eV), 444 (2.79 eV), and 495 nm (2.51 eV) are shown in Fig. 7. For $\lambda_{em} = 420$ nm (2.95 eV) and 444 nm (2.79 eV), the spectra were essentially the same with a single band centered at 355 nm (3.49 eV), yielding a Stokes shift of 0.43 eV. For $\lambda_{em} = 495$ nm (2.51 eV), in addition to the band at 355 nm (3.49 eV), a weak band at 280 nm (4.43 eV) and broad shoulder starting around 380 nm (3.26 eV) and extending with decreasing intensity to higher wavelengths were also observed. As it shifted to higher wavelengths, the Stokes shift of the 405 nm band slightly decreased: from 0.55 eV for λ_{exc} = 370 nm (3.35 eV) and $\lambda_{\rm em}$ = 443 nm (2.80 eV) to 0.40 eV for $\lambda_{\rm exc}$ = 460 nm (2.70 eV) and $\lambda_{em} = 538$ nm (2.30 eV), simultaneously with a decrease in emission intensity.

The top of the valence band of hexagonal $BiPO_4$ is composed by the overlap of the dominant O 2p orbital and the Bi 6s orbital, while the bottom of the conduction band is mostly formed by Bi 6p with minor contribution of O and P 2p orbitals, according to density-functional theory (DFT) calculations [20]. In previous experimental works, the

band gap of hexagonal BiPO₄ was estimated to be within 3.71 eV (334 nm) and 4.6 eV (270 nm), depending on the morphology and synthesis conditions [16,17,32–34]. The above fact together with the observation of an excitation band centered at 280 nm (4.43 eV; *cf.* Fig. 7) suggested the band gap of the material being reported in this work to be within ~4.5–4.6 eV. Consequently, energetic photons like λ_{exc} < 270 nm (>4.59 eV) were expected to cause photoionization and the promotion of electrons to the conduction band. Once in the conduction band, electrons could migrate and recombine at available luminescence centers, explaining why 350 nm and 570 nm bands luminesce under high energy photons. It has been shown that hexagonal BiPO₄ presents photocatalytic properties [16], suggesting a semiconductor character for this material and supporting the present argument of electron mobility in the conduction band.

Overall, in Bi-based compounds, broad emission bands and large Stokes shifts are expected where there is great asymmetry in the coordination polyhedron surrounding the Bi³⁺ ion [35]. This is illustrated in Table 2, where a literature survey of Stokes shift values of the Bi^{3+} emission in Bi-based oxides, and particularly in Bi-based phosphates, is shown [36–42]. Bi^{3+} ions in hexagonal BiPO₄ are coordinated to eight oxygen ions [1] with Bi-O distances ranging from 2.369 Å to 2.896 Å [43]. Since all compounds listed in Table 2 had Stokes shift larger than 1.57 eV, with their Stokes shift ranging from 1.57 to 2.5 eV, while none having FWHM as narrow as 0.4 eV (their FWHM values were within about 0.8 and 1 eV), and all having emission peak at 459 nm or higher wavelengths, it seemed unlikely that the 350 nm band could be assigned to the ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ transition. Moreover, in many Bi-free phosphates with several different structures, namely cubic, orthorhombic and monoclinic, intrinsic emission within 310 nm (4.00 eV) and 385 nm (3.22 eV) was reported [44-47] suggesting luminescent defects to be commonly formed in metal phosphates. Accordingly, the 350 nm (3.54 eV) band in hexagonal BiPO₄ was tentatively ascribed to a defect emission. On the

Table 2

Literature survey of the Stokes shift of Bi^{3+} emission in Bi-based compounds together with relevant information, including the oxygen coordination around Bi^{3+} , Stokes shift, emission band full width at half maximum (FWHM), and the excitation and emission peak positions in both nm and eV. Some measurements were reported at low temperatures, as indicated, otherwise room temperature was assumed. LN = liquid nitrogen temperature. The results on $BiPO_4$ are from this work.

Compound	l Bi coordination	Stokes shift (eV)	FWHM (eV)	Excitation/ Emission	Ref.
Bi ₂ Ga ₄ O ₉	5	2.05	-	285/530 nm (4.35/2.34eV) (LN)	[39]
Bi ₂ Al ₄ O ₉	5	1.75	-	290/490 nm (4.28/2.53eV)	[38]
	6	2.2		270/517 nm (4.6/2.4eV) (280K)	[41]
Bi ₄ Ge ₃ O ₁₂	6	2.5	-	253/517 nm (4.90/2.40eV)	[40]
		2.25		270/528 nm (4.6/2.35eV) (270K)	[41]
		2.3			[42]
Bi ₂ Ge ₃ O ₉	6	2.5	-	253/517 nm (4.9/2.4eV) (120K)	[41]
BiPO ₄	8	2.25	1.2	280/570 nm (4.43/2.18 eV)	this work
BiZn ₂ PO ₆	9	2.13	0.83	272/510 nm (4.56/2.43eV)	[<mark>36</mark>]
BiCd ₂ PO ₆	9	1.57	0.97	306/500 nm (4.05/2.48eV)	[36]
BiMg ₂ PO ₆	10	2.25/2.08	0.89	265/510 nm (4.68/2.43eV)	[36,37]

other hand, the values of the emission peak wavelength, emission band FWHM, and Stokes shift of the 570 nm band were in agreement with the values reported from other Bi-based materials, as summarized in Table 2, and in agreement with the expected effects of highly distorted nature of the BiO₈ polyhedra on Bi³⁺ luminescence [35]. Consequently, the 570 nm band was ascribed to the ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ transition, a transition made allowed by spin-orbit coupling of levels ${}^{3}P_{1}$ and ${}^{1}P_{1}$ [35,36].

In addition to the Bi³⁺ interconfigurational transition discussed above, Bi^{3+} luminescence related to metal-to-metal charge transfer (MMCT) is commonly reported [48]. There are many possible energy configurations involving MMCT and the ${}^{3}P_{1} \leftrightarrow {}^{1}S_{0}$ transition, depending on the position of their energy states in relation to the bottom of the conduction band [48]. The similarities between the 405 nm and 570 nm bands in terms of excitation spectral range suggested a related origin. Given the attribution of 570 nm band to the ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ transition, the 405 nm band was attributed to MMCT. As stated before, in hexagonal BiPO₄, Bi³⁺ ions are coordinated with eight oxygens with varying distances from 2.369 Å to 2.896 Å [43]. The presence of oxygen vacancies alters the chemical environment of Bi³⁺ ions and thus its electronic transitions. Moreover, since there are four distinct Bi-O distances in hexagonal BiPO₄, a variety of 'perturbed' Bi^{3+} are expected to exist. It is proposed that perturbed Bi³⁺ ions create states with energies lower than those of unperturbed Bi³⁺ ions and are responsible for the emission shifted to lower energies (higher wavelengths) in relation to the 405 nm and 570 nm bands. A similar proposition was suggested to explain the origin of the band at 517 nm (2.40 eV) in Bi₄Ge₃O₁₂ [49]. From $\lambda_{\text{exc}} =$ 350 nm (3.54 eV) to higher wavelengths, the 405 nm band continuously shifted to higher wavelengths (Figs. 5 and 10), while the shift of 570 band followed a similar behavior for $\lambda_{exc} \ge 270$ nm (4.59 eV) (Figs. 5 and 9). This proposition found support in the presence of a broad shoulder in the PLE spectra of band 405 nm when monitored at high wavelengths, as illustrated in Fig. 7 for $\lambda_{em} = 495$ nm (2.51 eV). The shoulder started at ~380 nm (~3.26 eV) and extended to higher wavelengths. The PLE shoulder was interpreted as being originated from a variety of perturbed Bi³⁺ configurations with lower energy states than the excitation band of unperturbed Bi³⁺ observed at 355 nm (3.49 eV). Also, the emission intensity of perturbed Bi^{3+} was considerably weaker (~3–5x less) than that of unperturbed Bi3+ ions, in agreement with the expected lower number of Bi³⁺ ions neighboring an oxygen vacancy. It is worthy of note that this shoulder matched the spectral region of the broad excitation band in the PLE spectra of the 570 nm band (Fig. 8). These results mutually support the hypothesis that perturbation of Bi³⁺ ions created a distribution of states with lower energy when compared to unperturbed Bi³⁺ ions.

In order to interpret the two partially superimposing excitation bands at 400 nm (3.10 eV) and 460 nm (2.70 eV) observed in the PLE spectra of 570 nm band, we considered the Bi-O distances in hexagonal BiPO₄: 2.896 Å, 2.561 Å, 2.418 Å, and 2.369 Å [43]. Since the dispersion of the three shortest Bi-O distances to the respective 2.449 Å average was $\pm ~0.1$ Å, the Bi-O distances were tentatively separated in two groups: 2.896 Å and 2.449 Å. Further, assuming oxygen vacancies occurred for all Bi-O distances, each Bi-O distance group with oxygen vacancies was assumed to contribute to the creation of perturbed Bi³⁺ states and ascribed to one of the excitation bands, 400 nm and 460 nm.

Finally, the results summarized in Table 1 were compared with the results reported in this work. Overall, the peak positions in those reports matched with the positions observed in this work for the same or closest λ_{exc} , as can be seen in Table 1. While the number of bands reported for undoped BiPO₄ varied from one to three, their positions were about the same regardless if hexagonal or high-temperature monoclinic. Bands around 350 nm [9,15], 480 nm [10–20] and 600 nm [13,14,18–20] were consistently reported in agreement with the defect and perturbed Bi³⁺ bands found in this work.

The incorporation of Ce into $BiPO_4$ led to changes in the luminescence behavior, with the appearance of partially superimposing bands peaked at about 445 nm (2.79 eV) and 490 nm (2.53 eV) simultaneously to the decrease of the 570 nm band intensity (Fig. 11). Interestingly, at $\lambda_{exc} = 290$ nm (4.28 eV) all five bands were observed simultaneously in Ce-doped BiPO₄. The difference in energy between the 445 nm (2.79 eV) and 490 nm (2.53 eV) bands, $\Delta E = 0.26$ eV, was compatible with the expected spin-orbit coupling split of the ground state of Ce³⁺ into levels ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ [50]. These bands were observed within the excitation spectral range from about 260 nm (4.77 eV) to 330 nm (3.76 eV), and besides some fluctuation probably due to the proximity to other bands, their positions were not sensitive to λ_{exc} (Fig. 5). The maximum intensity of the 445 nm and 490 nm bands was estimated to be under $\lambda_{exc} = 300$ nm (4.13 eV), yielding a Stokes shift of 1.65 eV. Spectra from the undoped (black lines) and Ce-doped (red lines) for representative λ_{exc} values are compared in Fig. 12, confirming that 445 nm and 490 nm bands were only observed in Ce-doped BiPO₄. As per the above, they were attributed to Ce³⁺ ions and henceforth referred to as 'Ce bands'.

Fig. 13 complements Fig. 11 by showing the emission spectra of Cedoped BiPO₄ for 340 nm (3.65 eV) $\leq \lambda_{exc} \leq 460$ nm (2.70 eV). A single broad band shifted to higher wavelengths for higher λ_{exc} , with the behavior of the peak position as a function of λ_{exc} shown in Fig. 5. Noticeable was the absence of 570 nm band. A comparison between emission spectra of undoped and Ce-doped BiPO₄ for selected λ_{exc} is presented in Fig. 14. For $\lambda_{exc} \leq 380$ nm (3.26 eV), a small difference in peak position occurred with Ce-doped BiPO₄ spectra being peaked at slightly higher wavelengths. For $\lambda_{exc} > 380$ nm, while their peak position matched, the spectra of undoped BiPO₄ presented a relatively more intense contribution at wavelengths higher than the peak position. As illustrated in Fig. 9, this difference was due to a relatively weak contribution of perturbed 570 nm band in the spectra of undoped BiPO₄.

The excitation spectra of Ce-doped BiPO₄ monitored at $\lambda_{em} = 420$ nm, 444 nm, and 495 nm are shown in Fig. 7 (red lines), together with those of undoped BiPO₄ (black lines). For 420 nm (2.95 eV) $\leq \lambda_{em} \leq$ 495 nm (2.51 eV), in addition to the excitation band centered at around 355 nm (3.49 eV) that dominated the spectra of undoped BiPO₄, the spectra of Ce-doped BiPO₄ presented a relatively weak excitation around 300 nm (4.13 eV). They also presented a progressively more intense excitation band at higher wavelengths ($\lambda_{exc} > \sim 380$ nm). This band had already developed into a well-shaped band peaked at 400 nm (3.10 eV) that dominated the spectrum for $\lambda_{em} = 495$ nm (2.51 eV). For $\lambda_{em} = 575$ nm (2.16 eV) and higher λ_{em} values, as illustrated in Fig. 8 (cf. red spectra), the excitation spectra of Ce-doped BiPO₄ were dominated by a band peaked at 405 nm (3.06 eV) with a shoulder at around 300 nm (4.13 eV). The weak excitation around 300 nm suggested Ce^{3+} to compete against the 350 nm band whose excitation was also centered around 300 nm. In fact, as shown in Fig. 11, the 350 nm band was not observed in Ce-doped BiPO₄ for $\lambda_{exc} \ge 300$ nm. As shown in Figs. 5, 11 and 13, excitation for $\lambda_{exc} \geq 340$ nm did not yield Ce³⁺ luminescence. Consequently, the excitation bands at 355 nm and 405 nm were not related to Ce³⁺, with the 355 nm excitation band already ascribed to the 405 nm emission band, and the excitation at around 400 nm to perturbed 570 nm band.

In summary, the above observations indicated competition and energy transfer between the several luminescence centers in hexagonal BiPO₄(:Ce): the intrinsic defect, Ce^{3+} , Bi^{3+} and perturbed Bi^{3+} ions. Accordingly, Ce³⁺ and the intrinsic defect competed for excitation around 300 nm. Inspection of PLE spectra of 405 nm and 570 nm bands showed absorption around 280 nm from unperturbed Bi³⁺ and over a combined broad range within *ca*. 330-550 nm from perturbed Bi³⁺ that could absorb the emissions of the intrinsic defect and of Ce³⁺, respectively. RL measurements of undoped and Ce-doped BiPO₄ presented in Fig. 15 provided additional insight into these propositions. The spectra were dominated by emission around 630 nm, resembling the spectrum obtained under $\lambda_{exc} = 280$ nm (Fig. 6), and attributed to the ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ transition involving perturbed Bi3+ ions. Weaker contributions below about 500 nm from the 350 nm and 405 nm bands, including contribution of perturbed Bi³⁺ ions, were also observed. However, no emission from Ce³⁺ was observed, and in fact the spectrum was identical to the



Fig. 15. RL spectra of a) undoped ${\rm BiPO}_4,$ b) Ce-doped ${\rm BiPO}_4$ and c) BGO powder.

one from undoped BiPO₄. At the energies of interest, the cross section for the photoelectric effect goes with the atomic number as $\sim Z^4$ [51] implying that hole creation occurs mostly at Bi sites. The scintillation of activated materials depends on the energy transfer from the host to the activator. This requires mobility of holes in the valence band and electrons in the conduction band, ultimately with radiative recombination of an electron and a hole at the activator site. Materials can be engineered to have efficient charge carrier traps [52]. In BiPO₄, Bi 6s orbitals contribute to the formation of the top of the valence band and Bi 6p orbitals dominate the formation of the bottom of the conduction band [20]. In the case of Ce^{3+} , recombination consists of a two-step energy transfer that involves the capture of a hole by Ce^{3+} followed by the capture of an electron in an excited state of the newly-created Ce⁴⁺ ion [53]. For this to occur efficiently, in addition to the transport of electrons and holes through the host, the probability of capture of holes by Ce³⁺ ions must be high. This probability is dictated by an energy barrier for hole capture that increases with the extent of relaxation energy between the ground state and the Ce^{4+} state. Reasons for the lack of Ce^{3+} scintillation in BiPO₄ could be lower mobility of holes and/or electrons, or a low probability of hole capture by Ce³⁺. Since there is experimental evidence of photoconductivity in $BiPO_4$ under ultraviolet excitation [22, 54,55], we tentatively ascribed the lack of scintillation to the low probability of hole capture by Ce³⁺ ions and the likely localization of holes at Bi sites. This is in part confirmed by the dominance of Bi-related RL showing that radiative recombination occurred at Bi sites, and the relatively large Stokes shift of Ce^{3+} (1.65 eV). The large Stokes shift is indicative of large relaxation between the Ce3+ excited and ground states and thus suggestive of a large energy barrier for hole capture [53]. Without any sample optimization (e.g., thermal treatments or changes in the Ce concentration), the integrated RL output of BiPO₄ and BiPO₄:Ce was estimated to be 0.015% of that of BGO powder.

A literature survey on previous results on the luminescence of Cedoped $BiPO_4$ found few reports (*cf.* Table 1) with, in general, scant analysis. Only hexagonal and high-temperature monoclinic phases have been investigated to date. In all reports of Ce-doped hexagonal BiPO₄, only one band was observed [9–12], while one report on Ce-doped with the high-temperature monoclinic phase reported two bands after spectral analysis with Gaussian bands [15]. While all previous reports on Ce-doped BiPO₄ ascribed the observed emission to Ce³⁺, as expected, we believe this was due to the limited scope of their investigation, sometimes reporting spectra in a narrow spectral region [11]. On the other hand, the results presented in this work are based on a broad and detailed investigation of the effects of λ_{exc} and support different interpretations on the nature of those luminescence bands, as discussed above.

4. Conclusions

Undoped and Ce-doped hexagonal BiPO₄ were synthesized by a precipitation method and characterized on their structure. Ce spatial distribution and chemical state, together with detailed luminescence spectroscopy investigation. Systematic variation of λ_{exc} over the broad range 250-460 nm (2.70-4.96 eV) combined with radioluminescence measurements under X-ray excitation and extensive literature review were used. These results led to enhanced understanding of the intrinsic and extrinsic luminescence of this material that presents considerable controversy in the literature. Up to five distinct emission bands were observed, depending on λ_{exc} and on the presence or not of the activator. The host presented three emission bands: the 350 nm (3.54 eV) band was ascribed to a defect, the 405 nm (3.06 eV) band was ascribed to MMCT, and the 570 nm (2.18 eV) band was ascribed to the Bi $^{3+}$ $^{3}P_{1} \rightarrow {}^{1}S_{0}$ transition. In addition, the presence of Bi³⁺ ions perturbed by oxygen vacancies in the coordination polyhedron at varying distances to the Bi³⁺ ions created states with lower energies than the states of unperturbed Bi³⁺. Ce-incorporation led to the creation of two partially superimposing bands at about 445 nm (2.79 eV) and 490 nm (2.53 eV). Strong interaction between Ce³⁺ and the host was observed. All these observations do not encourage the development of Ce-doped BiPO₄ scintillators.

CRediT author statement

Linyu Pan: Formal analysis, Investigation, Writing - Review & Editing. Kelliann Koehler: Formal analysis, Investigation, Writing - Review & Editing. Luiz G. Jacobsohn: Conceptualization, Methodology, Formal Analysis, Investigation, Resources, Writing - Original Draft, Writing -Review & Editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This material is based upon work by the National Science Foundation under Grant No. 1653016.

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