

Manganese and iron-doped yttrium borate as an excellent multifunctional inorganic material

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https://creativecommons.org/licenses/by/ 4.0/ **ABSTRACT:** Manganese and iron-doped π -YBO₃ have been synthesized using a modified epoxide-mediated gel method. The PXRD pattern evaluated the formation of the desired phase and the structural changes. EDS spectra determined the elemental analysis of undoped and doped samples. Raman spectra observed the stretching and bending modes of B-O bonds. The direct band gaps for doped samples were 1.47 and 2.07 eV, respectively, lower than the band gap value of 5.81 eV for π -YBO₃. The green and blue indigo emission bands were observed in the photoluminescence spectra. Doped samples showed good magnetic properties as they are antiferromagnetic and ferromagnetic at low temperature (T = 5 K) M-H plot and SQUID measurement. An indigenously built Sawyer-Tower circuit is used to measure ferroelectric hysteresis. Photodegradation studies of RhB were conducted under UV-visible irradiation.

KEYWORDS: borate; sol-gel; magnetic; photocatalytic; ferroelectric; phosphor

1. Introduction

Transition metal borates have recently attained enormous attention due to their significant properties and potential applications^[1–3]. Transition metal borates can be classified into metal orthoborates and metal oxyborates. The metal-rich oxyborates, containing six coordinated metal ion of mixed valence and trigonal planar BO₃^{3–} unit, adopts two warwickite and pinakiolite type structure^[4], and the metal: borate ratio of warwickite is 2:1. In contrast, pinakiolite type has a ratio of 3:1. The mixture of divalent and trivalent metal ions, the composition $M_2^{II}M^{III}OBO_3$ and $M_2^{II}M^{III}O_2BO_3$, where metals are iron, cobalt and manganese, can cause the formation of homometallic oxyborates and mixed valence in solid state. The known homometallic oxyborates are manganese oxyborates (Mn_2OBO_3 and $Mn_2^{II}Mn^{III}O_2BO_3$), iron oxyborates (Fe_2OBO_3 and $Fe_2^{II}Fe^{III}O_2BO_3$) and cobalt oxyborates (Co_2OBO_3 and $Co_2^{II}Co^{III}O_2BO_3$) which adopt warwickite and pinakiolite structure^[4–7].

The name warwickite is applied to an unusual family of orthorhombic minerals having space group *Pnma* and ideal composition ($M_2O_3BO_3$ (M = Mn^{2+} , Fe^{3+} , Mg^{2+} , Ti^{4+} , and Al^{3+})), warwickite structure was first investigated by Takeuchi et al. in 1950 having composition (Mg,Fe)_{1.5} $Ti_{0.5}OBO_3$ ^[4]. Mg_2InBO_5 belongs to the category of M_3BO_5 , having a ludwigite structure with a space group of *Pbam*. The M_3BO_5 (where M can be divalent ions such as Mg^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} or tri- and tetravalent ions as Al^{3+} ,

 V^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Ga^{3+} , Mn^{4+} , Sn^{4+} , Ge^{4+} , Zr^{4+} and Ti^{4+}) belongs to oxyborate family having ludwigite type structure has already been studied in the past. These all materials such that the cations (transition metal ions) are distributed over four crystallographic distinct octahedral sites, but in some cases, two different atoms can occupy the complementary sites^[8,9]. Rare earth ortho-borates show excessive polymorphism, where most structures have explicitly been determined. The following is a survey of previous work^[10-13]. Levin et al.^[14] 1961 described the vaterite type- orthoborate π -REBO₃ (RE: Y, Nd, Sm-Lu). The structure of π -REBO₃ was proposed to be hexagonal with a coordination number greater than three. A new phase μ -YBO₃ was proposed, which was isostructural with vaterite form and possibly in a pseudohexagonal phase. Newnham et al.^[15] considered two hexagonal structures of π -YBO₃, one distorted with the space group of $P6_3/mmc$ and the other ordered with a space group of $P6_3/mcm$). In both structures, rare earth ions were coordinated with eight oxygen atoms, forming a distorted cube. Spectroscopic techniques such as IR, NMR and Raman studies of π -ortho-borates confirmed the tetrahedral coordination of boron in the $B_3O_9^-$ ring^[16-20]. The hexagonal space group P6c2 at low temperatures was proposed by Bradley et al.^[21], and at high temperatures, it described the P6₃22 space group. In 1977, the pseudohexagonal model for π -YBO₃ orthoborate was proposed by Morgan et al.^[13], and it favoured the psuedowollastonite-type structure over the vaterite type. In 1997, Chadeyron et al.^[22] restudied the structure of π -YBO₃ using single-crystal diffraction techniques where hexagonal cell, a =3.776 Å and c = 8.806 Å with space group of P_{6_3}/m was observed. Ren et al.^[23] introduced two other space groups for π - and μ -REBO₃, where π -YBO₃ was identified as a sub cell of a rhombohedral structure. In this way, a fully ordered structure in the rhombohedral space group R32 was accomplished. The study results of Cohen-Adad et al.^[24] in 2000 were consistent with all possible hexagonal space groups P6₃/mmc, *P6c2*, *P6₃/mcm* and *P6₃/m*, while the best agreement could be accounted for in *P6c2*. For μ -GdBO₃, hexagonal space group P6₃22 was assumed. Lin et al.^[12] surveyed the powder data of the Y_{0.92}Er_{0.02}BO₃ sample by neutron diffraction, and it was found that a monoclinic structure was observed with space group of C2/c for both low- and high-temperature. In 2008, Hosokawa et al.^[25] presented the space group $P6_3/m$ for orthoborate powder synthesized by gyrothermal reaction, which was previously determined by Chadeyron et al.^[22]. We know that literature has yet to be published on doping transition metals in YBO₃. The use of the sol-gel process is quite beneficial for creating superior materials. The result of the sol-gel method is an improvement in the processing of traditional materials and their properties, as well as the synthesis of new materials. Due to its low-temperature nature, the organic-inorganic hybrids sol-gel technique is beneficial for creating high-performance liquid chromatography. The following benefits of the sol-gel technique are Easy procedure, the creation of highly pure products, the efficiency of synthesis is very high, more thorough surface coverage, the creation of low-cost and high-quality materials, etc.^[26]. In the present study, transition metal doped YBO₃ has been synthesized by epoxide gel route. Following this, photoluminescence, magnetic, ferroelectric, and photocatalytic properties have been studied thoroughly. In the present study, transition metal doped YBO_3 has been synthesized by epoxide gel route. Following this, photoluminescence, magnetic, ferroelectric, and photocatalytic properties have been studied thoroughly.

2. Experimental

2.1. Synthesis

To synthesize π -YBO₃, YCl_{3.6}H₂O (99.9%, Sigma Aldrich), H₃BO₃ (99.9%, BDH) and Propylene Oxide (99%, Alfa Aesar, Massachusetts) as the starting materials, we dissolved 0.3056 g (1 mmol) of YCl_{3.6}H₂O in 5 mL of absolute ethanol and 0.061 g of H₃BO₃ (1 mmol), and constantly stirred the

mixture at room temperature. Then, we added 0.69 mL (10 mmol) of propylene oxide drop by drop while stirring the solution. After a few minutes of ultrasonication, the mixture produced a colourless xerogel. We calcined the samples in a muffle furnace at 900 °C for 4 h, with the heating rate set to 20 °C/min. Finally, we allowed the samples to cool naturally to room temperature by turning off the furnace^[27].

Use 0.0192 g (10 mmol) MnCl_{2.4}H₂O (99%, Alfa Aesar), 0.0410 g (10 mmol) Fe(NO₃)_{3.9}H₂O (98%, CDH), 0.281 g (0.9 mmol) YCl_{3.6}H₂O and 0.061 g H₃BO₃ with 0.69 mL (10 mmol) of propylene oxide to produce xerogels of composition of Y_{0.90}M_{0.10}BO₃ (M = Mn²⁺ and Fe²⁺) following the same procedure described for the synthesis of π -YBO₃.

2.2. Characterization

A high-resolution Bruker D-8 Advanced X-ray diffractometer was used to record the powder X-ray diffraction (PXRD) patterns. The obtained PXRD data was subjected to structure refinement via the Le Bail method, which used TOPAS3 software. Renishaw spectrometer was adopted to record the Raman spectra using a microscope system operating with an Nd: YAG laser ($\lambda = 532$ nm). Diffuse reflectance spectra were collected for the samples on a Perkin-Elmer Lambda-35 UV-visible spectrophotometer with an attached integrating sphere, taking BaSO₄ as the reference transformed to absorbance via selecting KM Function to perform this. The conventional excitation and emission spectral measurements of the samples were performed adopting Horiba Jobin Yvon Fluorolog-modular spectrofluorometer at room temperature with a continuing-wave xenon lamp source and Cary Eclipse Fluorescence Spectrophotometer G9800AA. Low-temperature magnetic measurements were recorded using MPMS (Magnetic Properties Measurement System) Excel manufacturing quantum design USA in temperatures ranging between 5 to 320 K under an applied field of ±1 Tesla. Magnetization measurements were performed using a vibrating sample magnetometer (Magnetic Properties Measurement System excel manufacturing quantum design USA) at 5 K and 300 K under an applied field of ±7 Tesla. An indigenously built Sawyer-Tower circuit was used to measure the ferroelectric hysteresis, and a lock-in amplifier drove the circuit. Further, a photodegradation study of dye molecules was done in the presence of a catalyst in an immersion type, in-house fabricated reactor under UV-visible radiation adopting a 125 W capacity mercury vapour lamp (Philips, India). A solid sample (50 mg) was added to a 10 µM aqueous solution of RhB (pH \sim 7) dye, formed by adopting double distilled water. Firstly, the suspension was stirred under the dark for almost 20 min to attain equilibrium, then turned on the UV-visible radiation and shined on the suspension. A 5-6 mL quantity of aliquots was withdrawn periodically from the reaction mixture. Then, solutions were centrifuged, and the concentration of the solution was obtained by measuring the absorbance at $\lambda max = 556$ nm for (Rh-B) using a UV-visible spectrometer (Shimadzu UV-1601).

PXRD patterns of 10% manganese and iron-doped π -YBO₃, were compared with those of pure π -YBO₃, in **Figure 1**. The xerogel is amorphous, and the calcined product exhibited reflections that matched well with hexagonal π -YBO₃, regarding position and intensity profile (JCPDS File No. 83-1205).

The PXRD pattern of this sample was successfully refined using the Le-Bail method in the $P6_3/m$ space group. The resulting lattice parameters were a = 3.7756 (15) and c = 8.8138 (25) with no uncounted reflections^[15,16,22,25]. The crystallite size (D) was estimated to be 27 nm using Scherrer's formula D = 0.89 λ/β Cos θ , (where λ is the wavelength of the X-ray, θ is the diffraction angle, and β is half peak width). The



Figure 1. PXRD patterns of product calcination of xerogels from the attempts to make π -YBO₃, manganese and iron doped π -YBO₃, samples. Inset showing the EDS spectra.

doped samples showed peaks only about hexagonal π -YBO₃, with no additional reflections and a systematic shifting of the diffracted peaks toward higher 20 values was observed. From the Le-Bail refinement of the PXRD pattern, we derived unit cell constants of a = 3.7701 (18) and c = 8.8025 (11) Å for the manganese-doped sample, a = 3.7616 (20) and c = 8.8011 (18) Å for the iron-doped sample (**Figure 2**). This suggests the inclusion of smaller-sized manganese (0.83 Å) and iron (0.78 Å) for Y³⁺ in six-fold coordination. The crystallite size of π -YBO₃, increased with the doping of transition metal ions, with crystallite sizes of 36 nm and 38 nm deduced for the manganese and iron-doped samples, respectively. EDS analysis of the π -YBO₃ sample showed that approximately 21%, 22%, and 63% of Y, B, and O were present in the sample, respectively, which was close to the expected ratio of 1:1:3. For the doped samples, 10% manganese and iron were confirmed to be present about the amount of yttrium.



Figure 2. Le-Bail refinement of (a) π-YBO₃, (b) π-Y_{0.90}Mn_{0.10}BO₃ and (c) π-Y_{0.90}Fe_{0.10}BO₃.

Raman spectra of Mn^{2+} and Fe^{2+} doped π -YBO₃ samples have been compared with π -YBO₃, in **Figure 3**. Translations of Y³⁺, B₃O₉ units and vibrational modes of B₃O₉ units within the structure contribute to the bands visible between 180 and 250 cm⁻¹. Moreover, the existence of B₃O₉ rings was

attributed to the bands present at 414 and 513 cm⁻¹. B-O-B bending of the BO₄ units and B₃O₉⁹⁻ borate ring deformation modes were visible at 615 and 839 cm⁻¹. Stretching vibration of tetrahedral BO₄ groups exists as a part of the B₃O₉⁹⁻ ring displayed as a band at 1006 cm^{-1[27-29]}. All the Raman peaks shifted toward lower values for Mn²⁺ and Fe²⁺ doped samples, confirming their incorporation.



Figure 3. Raman spectra of undoped and doped π -YBO₃.

UV-visible spectra of Mn^{2+} and Fe^{2+} doped π -YBO₃ are presented in **Figure 4**. The band centred at 235, 360, 402 and 498 nm for the manganese doped samples corresponded to transitions from ${}^{6}A_{1g}(S)$ to ${}^{4}A_{1g}(F)$, ${}^{4}T_{2g}(D)$, ${}^{4}E_{g}(D)$ and ${}^{4}T_{1g}(G)$, respectively^[30]. On the other hand, the broad band centred at 534 nm and 885 nm for the iron doped π -YBO₃ corresponded to ${}^{5}A \rightarrow {}^{5}E$ and ${}^{6}A_{1} \rightarrow {}^{4}T_{1}$ (⁴G) transitions of iron, respectively^[31].



Figure 4. UV-visible spectra for (a) π -Y_{0.90}Mn_{0.10}BO₃ and (b) π -Y_{0.90}Fe_{0.10}BO₃.

The direct band gaps for Mn^{2+} and Fe^{2+} doped samples, calculated using Tauc plot $((\alpha h\nu)^2 (eV/cm)^2 versus h\nu (eV))$, were 1.47 and 2.07 eV, respectively. They were lower than the value of 5.81 eV for

 π -YBO₃. Pure π -YBO₃ was off-white, whereas brown and reddish-brown colours were acquired by Mn²⁺ and Fe²⁺ doped samples (**Figure 5**). PL spectra of Mn²⁺ and Fe²⁺ doped π -YBO₃ have been presented in **Figure 6(a)**. Blue indigo emissions at 412, 438 and 454 nm were observed for the Fe²⁺ doped sample^[32]. The green emission band in the region of 500 nm to 630 nm was assigned to the ⁶A_{1g} (⁶S) \rightarrow ⁴T_{1g} (⁴G) transition of Mn²⁺ doped π -YBO₃^[33].



Figure 5. Bandgap estimation for π -YBO₃ (Black), π -Y_{0.90}Mn_{0.10}BO₃ (Red) and π -Y_{0.90}Fe_{0.10}BO₃ (Blue).



Figure 6. (a) PL spectra of π -Y_{0.90}Mn_{0.10}BO₃ and π -Y_{0.90}Fe_{0.10}BO₃ and (b) CIE coordinate of colour intensity of Mn²⁺ doped π -YBO₃.

The CIE 1931 XY coordinate plot for the Mn^{2+} doped sample as per their emission maxima has been presented in **Figure 6(b)**, which fell in the green region.

3. Magnetic properties

In **Figure 7(a)**, the Magnetic properties of π -Y_{0.90}Mn_{0.10}BO₃ have been investigated at 200 K. The sample exhibited a hysteresis loop with an immense coercivity value (H \approx 31.5 K Oe), indicating ferromagnetic solid ordering^[34]. The magnetic susceptibility of the sample was studied in zero field-cooled (ZFC) and field-cooled (FC) conditions. The ZFC measurements revealed antiferromagnetic ordering with a Neel temperature (T_N) of 108 K. Below T_N, the sample showed antiferromagnetic

behaviour, while above T_N , it showed paramagnetic behaviour. On the other hand, FC measurements showed ferromagnetic behaviour below Curie temperature (TC \approx 171 K), indicating the existence of large domains in the same direction. These results provide important insights into the magnetic properties of π -Y_{0.90}Mn_{0.10}BO₃ at 200 K.



Figure 7. (a) and **(c)** show the magnetization versus magnetic field for π -Y_{0.90}Mn_{0.10}BO₃ and π -Y_{0.90}Fe_{0.10}BO₃. **(b)** and **(d)** represent the variation of magnetic susceptibility with temperature under zero field and at an applied field of 1000 Oe for π -Y_{0.90}Mn_{0.10}BO₃ and π -Y_{0.90}Fe_{0.10}BO₃.

The zero field-cooled (ZFC), and field cooled (FC) samples showed significant differences at low temperatures in the curve. This could be due to an inhomogeneous mixture of ferromagnetic and antiferromagnetic ordering in the sample and frustration in the lattice. Similar magnetic behaviour has been reported in the literature^[35,36]. **Figure 7(c)** shows iron-doped samples' magnetization versus magnetic field. A small hysteresis loop suggests the presence of antiferromagnetic ordering in the sample at 300 K^[37]. The magnetic susceptibility of π -Y_{0.90}Fe_{0.10}BO₃ under ZFC and FC conditions has been presented in **Figure 7(d)**. For Fe²⁺ doped π -YBO₃, the magnetic susceptibility was increased with a decrease in temperature from 320 K and exhibited a small cusp at around 141 K, indicating the presence of antiferromagnetic ordering. Below 133 K, magnetic susceptibility was again increased and exhibited a curve around 21.2 K before falling rapidly as the temperature approached 5 K. The cooled (FC) plot showed similar behaviour above 21.2 K temperature. The bifurcation in both ZFC and FC curves above 141 K might be due to the anisotropy in the system, which appeared well above T_N^[38,39]. The ZFC/FC bifurcation also exhibited local spin or anti/ferromagnetic domain growth clustering. Such bifurcation behaviour was noticed for Fe₃BO₃ in the literature^[40].

The magnetic moment value for the manganese doped sample was plotted with a temperature range of 5 K to 300 K (**Figure 8**). Magnetic moment increased with temperature up to 74 K and showed a decreasing trend. The magnetic moment (μ_{eff}) values were 5.74 BM at 74 K, corresponding to the +2-oxidation state of manganese. This was due to the orientation of domains at low temperatures, which became random at room temperature^[41]. For the iron-doped sample, the magnetic moment increased with temperature. At room temperature, it was found to be 4.81 BM, corresponding to the only value of Fe²⁺ (d⁶ configuration, 4 unpaired electrons).



Figure 8. Magnetic moment versus temperature plot for manganese and iron, doped π -YBO₃.

3.1. Ferroelectric properties

The combine P-E loops of Mn^{2+} and Fe^{2+} doped sample at 7 V/cm potential have been shown in **Figure** 9. It was observed that π -YBO₃ doped with Mn^{2+} exhibited ferroelectric polarization, with $P_r \approx 9.52 \times 10^{-2} \mu$ C/cm² as the P-E loop's remnant polarisation value. The iron-doped sample also displayed ferroelectric polarization, with a remnant polarization value of 1.90×10^{-1} at zero electric fields^[37,42].



Figure 9. Ferroelectric hysteresis loop (P-E) curve for π -Y_{0.90}Mn_{0.10}BO₃ and π -Y_{0.90}Fe_{0.10}BO₃ at 7 V/cm.

3.2. Photocatalytic properties

The catalytic role of π -Y_{0.90}Mn_{0.10}BO₃ and π -Y_{0.90}Fe_{0.10}BO₃ for the photodegradation of RhB dye solution was studied. Temporal changes in absorbance maxima at $\lambda = 549$ nm (for RhB dye) in the presence of undoped and doped samples after shining with UV-visible radiation have been shown in **Figure 10(a–c)**.

The reduction in intensity of absorbance maxima confirmed their catalytic role in the presence of these samples. Approximately 57%, 93% and 87% of dye was observed to degrade in 90 min of exposure with undoped and doped samples, respectively (**Figure 10(d**)). The concentration of dye was computed using the expression,

$$C = C_0 \exp\left(-kt\right)$$

C—concentration of dye at time *t*, *C*₀—concentration at *t* = 0 min, *k*—rate constant and *t*—time in minutes. Pseudo-first-order rate constants (*k*) for these experiments employing π -YBO₃, π -Y_{0.90}Mn_{0.10}BO₃ and π -Y_{0.90}Fe_{0.10}BO₃ as catalysts were 9.16 × 10⁻³, 3.01 × 10⁻² and 2.54 × 10⁻² min⁻¹, whereas in the absence of catalyst (photolysis experiments), observed rate constant was found 5.14 × 10⁻⁴ min⁻¹ (**Figure 10(e)**). The excitation of electrons from the valance band (VB) to the conduction band (CB) and generation of electron-hole (*e*⁻ – *h*⁺) pairs is predicted due to the narrow bandgap^[28].

Catalyst +
$$hv \rightarrow e^- + h^+$$



Figure 10. (a–c) Photocatalytic degradation of RhB under UV-visible irradiation, in presence of π -YBO₃, π -Y_{0.90}Mn_{0.10}BO₃ and π -Y_{0.90}Fe_{0.10}BO₃, (d) Dye degradation plot (Black = photolysis, Royal = π -YBO₃, Red = Y_{0.90}Mn_{0.10}BO₃ and Blue = π -Y_{0.90}Fe_{0.10}BO₃) and (e) ln (C₀/C) plot.

The holes (h^+) generated in the valance band will react with H_2O and hydroxyl anion (OH⁻) acting as electron donors to form hydroxide radical (OH⁻). In the conduction band, electrons will react with electron acceptor species, i.e., oxygen molecule (O₂⁻) leading to the formation of reactive oxygen anion radical (O₂⁻).

Afterwards, reactive hydroperoxyl radical (HO₂) will form. At the end, OH, O_2 , HO₂ radicals will attack the dye molecule, leading to the intermediate with the formation of the final product. Photodegradation of dye through radical mechanism has already been reported in the literature^[28,43].

$$RhB + (OH), (O_2), (HO_2) \rightarrow \text{intermediate} \rightarrow CO_2 + H_2O$$

The comparison study of magnetic and photocatalytic properties of our material with other literature is mentioned in the tabular form (**Table 1**).

To check the stability of our catalyst, we have performed a reusability experiment for the manganese and iron-doped samples (**Figure 11**). The results show that the catalyst degrades the same amount of dye solution until the 4th run. The high degradation of dye and stability is better performed by the manganese-doped sample over iron.

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Compound	Dye	Concentration (M)	Rate constant (min ⁻¹)	Efficiency (%)	Time (min)	Ref.
TiO ₂ (P25)	RhB	2×10^{-5}	5.7×10^{-2}	85	20	[44]
$Co_{0.75}Fe_{2.25}O_4$	RhB	14×10^{-6}	2.41×10^{-1}	54.4	100	[45]
g-C ₃ N ₄	RhB	5×10^{-2}	6.9×10^{-8}	95	320	[46]
Spray deposited ZnO	MB	5×10^{-2}	6.9×10^{-8}	95	60	[47]
$ZnO-ZnWO_4$	Crystal Violet	1×10^{-3}	2.96×10^{-8}	82	160	[48]
ZnO	RhB	4.17×10^{-5}	2×10^{-4}	8	120	[49]
6% Indium ZnO	RhB	4.17×10^{-5}	1.01×10^{-2}	76	120	[49]
γ-MnO ₂	RhB	2×10^{-5}	-	90	270	[50]
$Y_{0.90}Mn_{0.10}BO_3$	RhB	1×10^{-5}	3.01×10^{-2}	93	90	Our work
$Y_{0.90}Fe_{0.10}BO_3$	RhB	1×10^{-5}	2.54×10^{-2}	87	90	Our work

Table 1. Comparison of performance of manganese and iron doped orthoborate catalyst with the other photocatalyst.



Figure 11. (a) Reusability experiment for manganese doped and (b) reusability experiment for iron doped sample.

4. Conclusions

The application of epoxide-mediated gel synthesis of crystalline π -YBO₃, transition metal doped π -YBO₃, has been demonstrated successfully. The PXRD patterns confirmed the inclusion of 10% manganese and iron in π -YBO₃. The optical and PL studies of doped samples have confirmed the presence of manganese and iron. Emission in the green region was observed in the CIE 1931 XY coordination plot for the manganese-containing sample. Magnetic susceptibility versus magnetic field data showed the ferromagnetic and antiferromagnetic behaviour for manganese and iron-doped samples. For doped samples, ferroelectric and at room temperature (300 K) were also observed. The photocatalytic properties of RhB under UV-visible irradiation in the presence of manganese and iron doped π -YBO₃, have been observed.

Author contributions

Conceptualization, PG and MS; methodology, PG; software, PG; validation, PG and MS; formal analysis, PG; investigation, PG; resources, PG; data curation, PG; writing—original draft preparation, PG; writing—review and editing, PG; visualization, PG; supervision, PG; project administration, PG; funding acquisition, MS. All authors have read and agreed to the published version of the manuscript.

Research data policy and data availability statement

The manuscript has associated data in a data repository.

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Conflict of interest

The authors do the work, and have mutual consent to send it as a research paper for review. The authors do not have any conflict of interest.

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