

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Crystal structure

4.1.1 Different preparation method of $\text{PbBi}_2\text{Nb}_2\text{O}_9$

The materials were synthesized using three different preparation techniques, namely the Sol-gel, Hydrothermal, and Molten salt methods. The crystalline structures of the materials obtained from each method were examined using X-ray diffraction (XRD), and the corresponding patterns are presented in Figure 4.1. The XRD results indicate that all synthesized samples exhibited diffraction peaks that are in good agreement with the standard crystalline structure of PBNO (JCPDS No. 86-1333), confirming the successful formation of the target phase regardless of the preparation method.

Although all samples showed similar phase compositions, noticeable differences were observed in the intensity and sharpness of the diffraction peaks, reflecting variations in crystallinity. The sample prepared via the Molten salt method displayed the highest peak intensities and the sharpest diffraction patterns, suggesting superior crystallinity. This was followed by the Hydrothermal method, while the Sol-gel method exhibited relatively broader and less intense peaks, indicating a lower degree of crystallinity.

The morphological characteristics of the synthesized materials were further investigated using scanning electron microscopy (SEM), as shown in Figure 4.2. The SEM images support the XRD findings, revealing that the Molten salt-derived material possessed well-defined, densely packed plate-like structures, consistent with its high crystallinity. In contrast, the Hydrothermal method resulted in uniformly distributed spherical particles that tended to aggregate into clusters. Meanwhile, the Sol-gel-prepared

material exhibited a largely amorphous morphology with an interconnected network-like structure, leading to the formation of voids within the material.

The photocatalytic performance of the materials prepared by each method was evaluated using methylene blue (MB) degradation under irradiation, as illustrated in Figure 4.3. Interestingly, despite its lower crystallinity, the Sol-gel-derived material demonstrated the highest photocatalytic activity, achieving complete degradation of MB within 60 minutes. In comparison, the materials synthesized via the Molten salt and Hydrothermal methods exhibited lower degradation efficiencies of 74% and 76%, respectively. These results suggest that factors such as surface area, porosity, and structural defects play a significant role in enhancing photocatalytic performance. Consequently, the Sol-gel preparation method was selected for further investigation in this study.

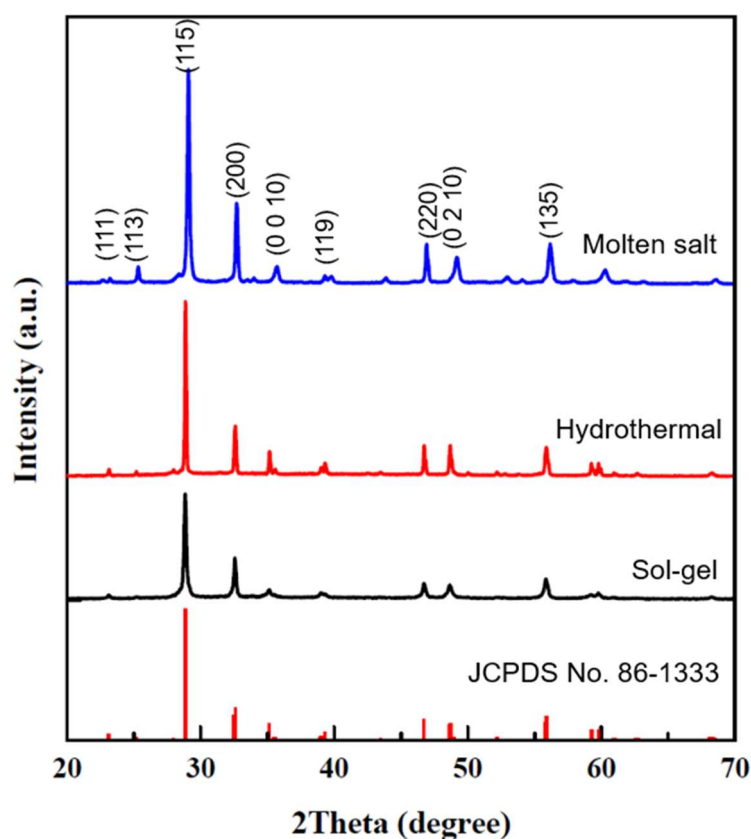


Figure 4.1 XRD patterns of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ at different preparation methods Sol-gel (a), Hydrothermal (b) and Molten salt (c).

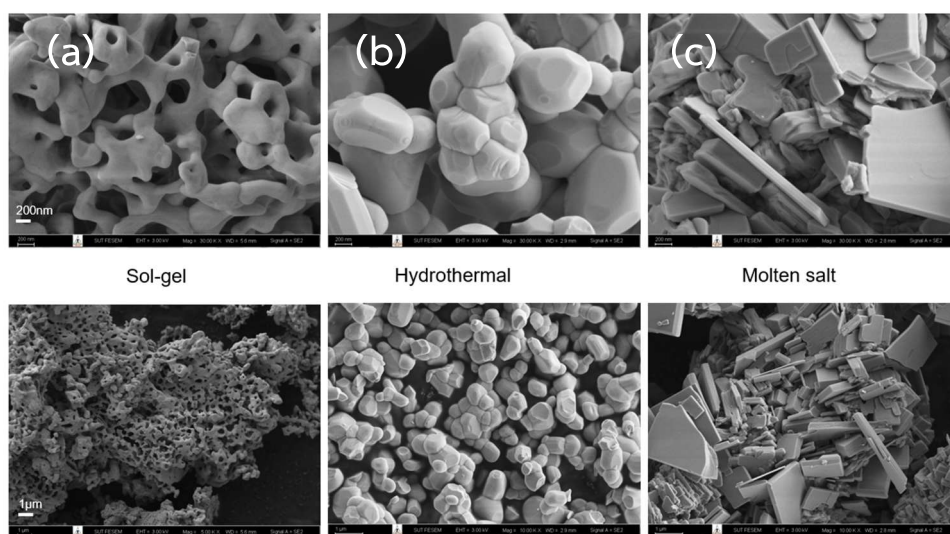


Figure 4.2 SEM images of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ at different preparation methods Sol-gel (a), Hydrothermal (b) and Molten salt (c).

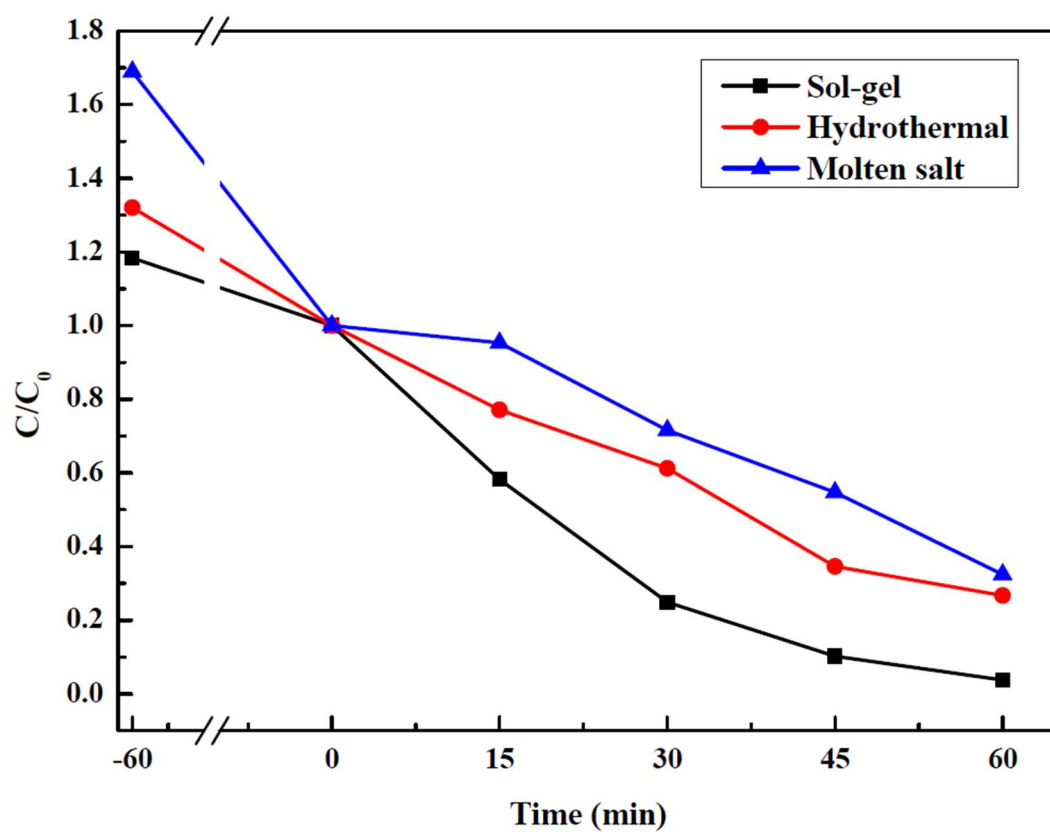


Figure 4.3 Photocatalytic degradation of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ at different preparation methods.

4.1.2 Sol-Gel method by various calcination temperature

The preparation of PBNO using the Sol-gel method was further investigated by varying the calcination temperature in order to obtain a crystal structure most suitable for photocatalytic applications. Calcination was carried out at 650°C, 700°C, 750°C, and 800°C, and the resulting crystalline structures were analyzed by X-ray diffraction (XRD), as shown in Figure 4.4.

The XRD patterns indicate that all samples exhibited diffraction peaks characteristic of the Aurivillius-type structure of PBNO (JCPDS No. 86-1333). This layered structure is composed of alternating Bi_2O_2 layers and NbO_6 double-perovskite slabs stacked along the c-axis, with Pb atoms incorporated within the NbO_6 slabs. The crystal structure belongs to the orthorhombic space group $A2_1am$, with lattice parameters of $a = 5.4960 \text{ \AA}$, $b = 5.4960 \text{ \AA}$, and $c = 25.5500 \text{ \AA}$.

The principal diffraction peaks were detected at 2θ values of 23.1°, 25.1°, 28.8°, 32.5°, 35.1°, 39.3°, 46.7°, 48.7°, and 55.9°, which were indexed to the (111), (113), (115), (200), (0010), (119), (220), (0210), and (135) crystallographic planes, respectively.

Based on the analysis of the diffraction peaks, impurity phases were detected in the samples calcined at 650°C and 700°C, as evidenced by additional peaks that were not present in the standard pattern. In contrast, the samples calcined at 750°C and 800°C exhibited diffraction patterns that matched well with the standard PBNO structure, indicating the formation of a single-phase, highly crystalline material. Consequently, the PBNO sample calcined at 750°C was selected for further study, as phase purity was achieved at a lower calcination temperature, thereby reducing energy consumption compared to calcination at 800°C.

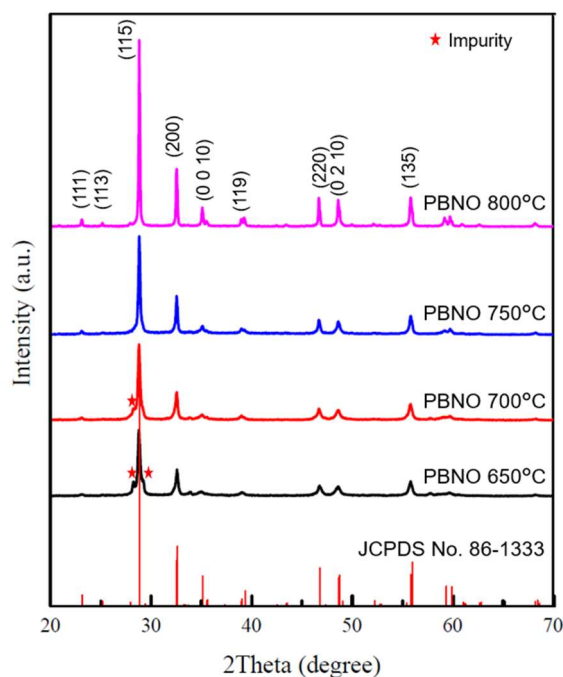


Figure 4.4 XRD patterns of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ at temperatures of 650°C, 700°C, 750°C and 800°C.

4.2 Ce-doped

4.2.1 Crystal structure of Ce-doped obtained samples

$\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$ ($x = 0.00, 0.05, 0.20$, and 0.50) samples were synthesized using the Sol-gel method, and their crystalline structures were characterized by X-ray diffraction (XRD), as presented in Figure 4.5a. The XRD results show that the diffraction peaks of all samples could be indexed to the Aurivillius-type structure of PBNO (JCPDS No. 86-1333), which crystallizes in the orthorhombic space group $A2_1am$.

For the compositions with $x = 0.00$ and $x = 0.20$, the XRD patterns exhibited a single-phase Aurivillius two-layer structure without any detectable secondary phases, indicating successful incorporation of Ce into the PBNO lattice at these doping levels. In contrast, for the samples with $x = 0.05$ and $x = 0.50$, additional diffraction peaks were observed, suggesting the formation of unidentified impurity phases and indicating that phase stability was disrupted at these compositions.

As shown in Figure 4.5b, an enlarged view of the diffraction patterns in the 2θ range of 28.0° – 33.0° highlights the reflections corresponding to the (115) and (200) crystallographic planes. With increasing Ce content, a noticeable shift of the (115) diffraction peak toward lower 2θ values was observed, while the (200) peak shifted toward higher 2θ values. These opposite peak shifts indicate changes in the lattice spacing and confirm that Ce incorporation significantly influences the unit cell parameters of $\text{PbBi}_2\text{Nb}_2\text{O}_9$, as summarized in Table 4.1.

During the calcination process, partial oxidation of Ce^{3+} to Ce^{4+} is known to occur. The substitution of Pb^{2+} ions (ionic radius = $1.49 \text{ \AA}$, coordination number (CN) = 12) by smaller Ce^{4+} ($1.14 \text{ \AA}$, CN = 12) and/or Ce^{3+} ($1.34 \text{ \AA}$, CN = 12) ions results in a contraction of the lattice parameters a and b . This contraction is attributed to the shrinkage of the NbO_6 octahedra within the perovskite slabs. Conversely, as confirmed by additional characterization discussed later, charge compensation and cation redistribution lead to the partial occupation of Bi^{3+} sites (ionic radius = $1.17 \text{ \AA}$, CN = 8) by larger Pb^{2+} ions ($1.29 \text{ \AA}$, CN = 8), which contributes to lattice expansion along the c -axis.

Furthermore, the reduction in octahedral size and the associated lattice strain induce distortion within the ab plane, causing the crystal structure to become increasingly orthorhombic as the Ce concentration increases. This structural distortion was quantitatively evaluated using the orthorhombicity ratio, $|(a - b)/(a + b)|$, and the calculated values are provided in Table 4.1.

Local structural changes in the samples were investigated using Fourier-transform Raman (FT-Raman) spectroscopy. The spectra were recorded in the wavenumber range of 1100 – 50 cm^{-1} in order to analyze vibrational modes associated with the crystal structure. The observed Raman bands were predominantly associated with the orthorhombic phase of the PBNO compound, confirming consistency with the structural information obtained from XRD analysis.

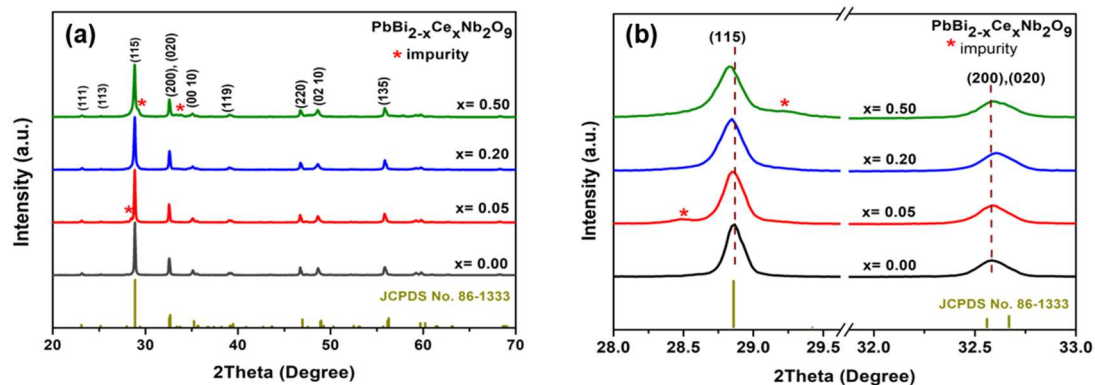


Figure 4.5 XRD patterns (a) and their close-up (b) of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$ ($x = 0.00, 0.05, 0.20$, and 0.50).

Table 4.1 Cell Parameters, Cell Volumes (V), and degree of distortion in terms of the orthorhombicity ratio ($| (a - b) / (a + b) |$).

Composition (x)	Cell parameter ($\text{\AA}$)			Cell Volume; V ($\text{\AA}^3$)	$ (a - b) / (a + b) $
	a	b	c		
0.00	5.495 (2)	5.497 (1)	25.539 (2)	771.4 (3)	1.82×10^{-4}
0.05	5.492 (6)	5.496 (1)	25.540 (1)	770.9 (1)	3.64×10^{-4}
0.20	5.488 (1)	5.494 (1)	25.582 (3)	771.3 (1)	5.46×10^{-4}
0.50	5.486 (2)	5.488 (2)	25.586 (4)	770.3 (4)	1.82×10^{-4}

For the Aurivillius-type structure, Raman modes located below 200 cm^{-1} were attributed to lattice vibrations involving the Bi_2O_2 layers and the vibrations of heavy A-site cations within the perovskite blocks. These low-frequency modes are highly sensitive to distortions and cation substitutions occurring in the layered structure. In contrast, the Raman modes appearing above 200 cm^{-1} were assigned to the bending and stretching vibrations of the BO_6 octahedra in the perovskite slabs, which provide direct information about octahedral connectivity and local symmetry.

To obtain quantitative information on the vibrational behavior, the Raman spectra were deconvoluted using Lorentzian fitting, as illustrated in Figure 4.6. The extracted peak positions are summarized in Table 4.2. Variations in peak positions and

intensities reflect changes in bond lengths, bond angles, and local lattice distortions, thereby providing insight into the structural modifications induced by compositional variation.

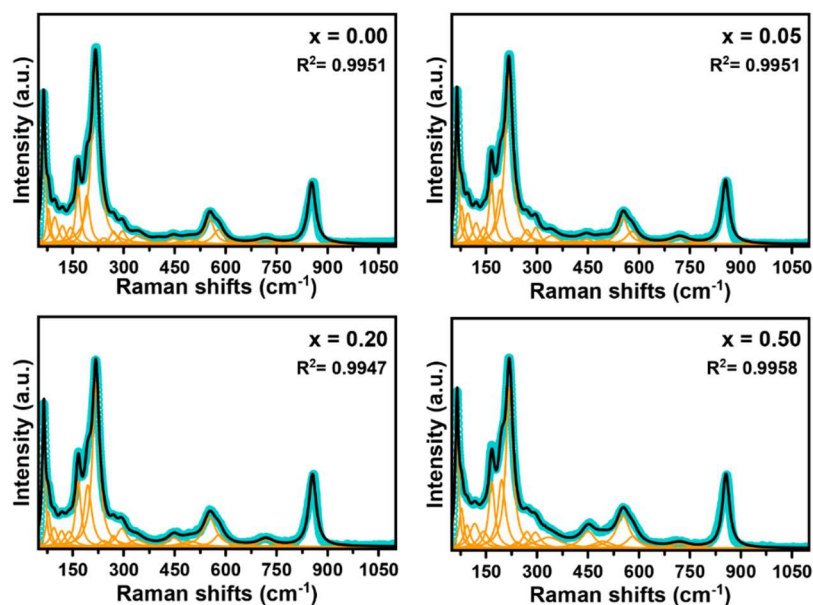


Figure 4.6 The fitted FT-Raman of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$ ($x = 0.00, 0.05, 0.20$, and 0.50).

Table 4.2 Assignment of Raman active modes of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$.

$\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$				assignment
$x = 0.00$	$x = 0.05$	$x = 0.20$	$x = 0.50$	
64.37	64.59	64.77	64.68	Bi_2O_2 rigid layer mode
165.61	165.99	166.29	166.78	Perovskite layer A-site ion
218.67	218.44	218.27	217.88	Torsional bending of BO_6
552.83	552.54	552.93	552.76	Asymmetric B-O stretching (apical oxygen atoms)
853.15	854.59	855.45	855.87	Symmetric B-O stretching (equatorial oxygen atoms)

At a frequency of approximately 64 cm^{-1} , a vibrational mode associated with the motion of the Bi_2O_2 layers parallel to the z-axis was observed. Compared to undoped $\text{PbBi}_2\text{Nb}_2\text{O}_9$, this mode exhibited a slight shift toward higher frequencies with increasing Ce content. This frequency shift is indicative of partial occupation of Pb^{2+} ions within the Bi_2O_2 layers, which modifies the local bonding environment. The frequency of this vibrational mode is governed by the effective mass of the vibrating cation and the strength of the metal–oxygen (M–O) bond. Although Bi^{3+} and Pb^{2+} possess similar atomic masses (209 amu for Bi^{3+} and 207 amu for Pb^{2+}), Bi–O bonds exhibit a lower bond dissociation energy (337 kJ/mol) than Pb–O bonds (382 kJ/mol). Consequently, the partial replacement of Bi^{3+} by Pb^{2+} within the Bi_2O_2 layers results in an increase in bond strength, leading to a shift of the vibrational mode toward higher wavenumbers.

In addition, a high-intensity Raman band located at approximately 165 cm^{-1} , which is associated with vibrations of A-site cations within the perovskite-like layers, was observed to shift toward higher frequencies as the Ce content increased. This behavior is attributed to variations in the A–O bond strength resulting from the substitution of Ce ions, which possess stronger Ce–O bonding (795 kJ/mol), for Pb^{2+} ions. The enhanced bond strength leads to stiffer lattice vibrations and consequently higher Raman frequencies.

The counter-motion vibrations of the NbO_6 octahedra were identified by Raman bands located at approximately 217 cm^{-1} , 552 cm^{-1} , and 854 cm^{-1} . The vibrational mode at 217 cm^{-1} was assigned to the bending vibration of the NbO_6 octahedra and is commonly regarded as a sensitive indicator of octahedral distortion. With increasing Ce concentration, this mode exhibited a shift toward higher wavenumbers, suggesting an increase in the distortion of the NbO_6 octahedra induced by Ce substitution. This observation is in good agreement with previously reported studies on doped Aurivillius-type materials.

The Raman band observed at approximately 552 cm^{-1} was attributed to the asymmetric stretching vibration of Nb–O bonds involving the terminal oxygen atoms, while the band at approximately 854 cm^{-1} originated from the symmetric stretching vibration of Nb–O bonds along the z-axis of the crystal lattice. These vibrations correspond to oxygen atoms located along the centerline of the NbO_6 octahedra. As shown in Figure 4.7a, the band associated with the symmetric Nb–O stretching mode shifted progressively toward higher wavenumbers with increasing Ce content. This shift indicates a shortening of the Nb–O bond length, which is influenced by the incorporation of Ce ions at the A-site of the perovskite-like layers.

According to the empirical relationship proposed by Hardcastle, the Nb–O bond distance ($R_{\text{Nb-O}}$) can be correlated with the Raman stretching frequency using the following equation (4.1):

$$R_{\text{Nb-O}} = 0.5217 \ln(25922/\mathbf{V}) \quad (4.1)$$

where $\mathbf{V}$ represents the Raman stretching frequency in units of cm^{-1} . The calculated bond lengths, shown in Figure 4.7b, indicate that the Nb–O bond lengths associated with equatorial oxygen atoms decrease systematically with increasing Ce content, whereas the Nb–O bond lengths corresponding to apical oxygen atoms remain nearly unchanged. Furthermore, the reduction in equatorial Nb–O bond lengths is consistent with the FT-IR results (Figure 4.7c) and XRD analysis, and it supports the observed decrease in the lattice parameters within the ab plane. This behavior is attributed to the contraction of the NbO_6 octahedra resulting from Ce-induced structural distortion.

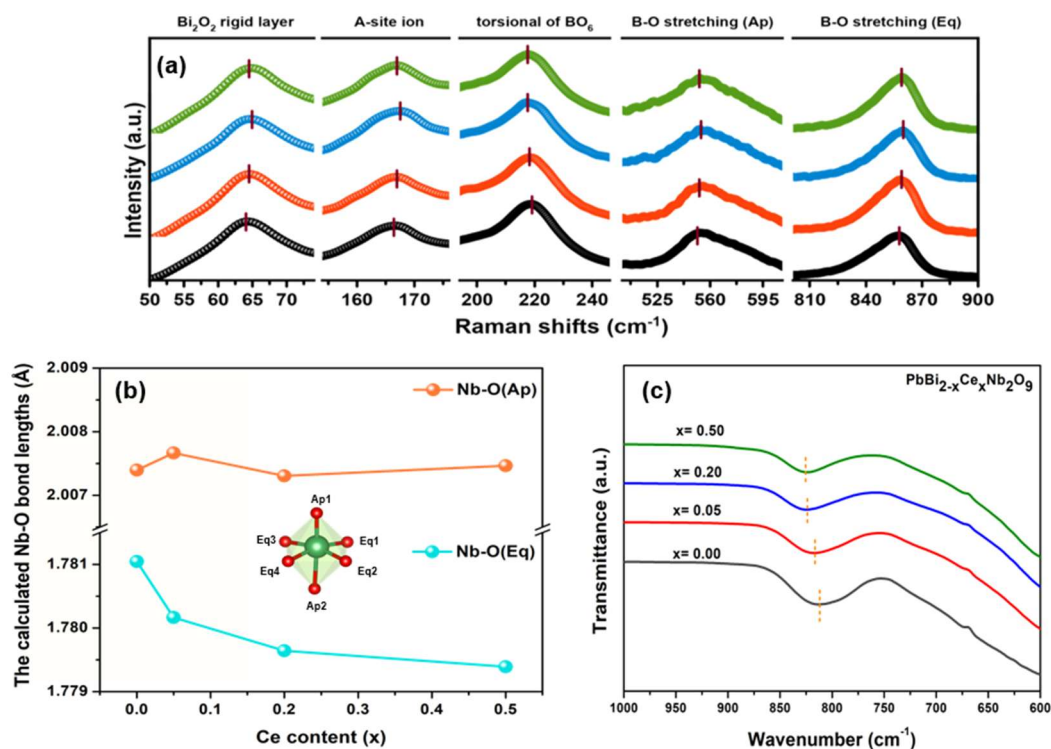


Figure 4.7 The FT-Raman spectra (a), the calculated Nb–O bond lengths (b) and FT-IR spectra (c) of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$ ($x = 0.00, 0.05, 0.20$, and 0.50).

4.2.2 Morphology and surface area

The structural characteristics of PBNO and Ce-doped PBNO samples were examined using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDS). The SEM images reveal that the morphology of PBNO is irregular and is significantly influenced by the incorporation of Ce, as shown in Figure 4.8. With increasing Ce concentration, a noticeable change in particle morphology and crystallinity was observed.

For the undoped PBNO sample, the SEM image (Figure 4.8a) reveals a porous microstructure composed of interconnected pores, which is favorable for mass transport. At the nanoscale, the HRTEM image (Figure 4.8b) shows well-defined lattice fringes with an interplanar spacing of approximately 0.27 nm, corresponding to the

(200) and (020) crystal planes of PBNO. This observation indicates the presence of a well-ordered crystalline structure. The corresponding SAED pattern (Figure 4.8c) exhibits sharp and discrete diffraction spots, confirming the single-crystalline nature of the PBNO sample. The measured angle of approximately 90° between the (200) and (020) diffraction spots is consistent with the theoretical value expected for an orthorhombic crystal structure, further validating the structural integrity of the undoped PBNO.

In contrast, the $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ sample exhibits a markedly different morphology, as shown in Figure 4.8d. The SEM image reveals the formation of larger, well-defined grains, accompanied by the presence of small particles distributed on the surface of the grains. This morphological evolution suggests that Ce incorporation influences nucleation and grain growth during the synthesis process. HRTEM analysis of these small surface particles (Figure 4.8e) reveals lattice spacings of approximately 0.31 nm and 0.27 nm, which can be indexed to the (115) and (200) crystallographic planes, respectively. These results indicate that the Ce-doped sample retains the Aurivillius-type crystal structure at the nanoscale, despite the observed changes in morphology.

The SAED pattern obtained from the $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ sample (Figure 4.8f) exhibits concentric diffraction rings rather than discrete spots, which is characteristic of a polycrystalline structure and indicates a reduction in crystallinity compared to the undoped PBNO sample. Nevertheless, EDS elemental mapping (Figure 4.8g) confirms that Pb, Bi, Ce, Nb, and O are uniformly distributed throughout the $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ sample, demonstrating successful and homogeneous incorporation of Ce into the PBNO lattice.

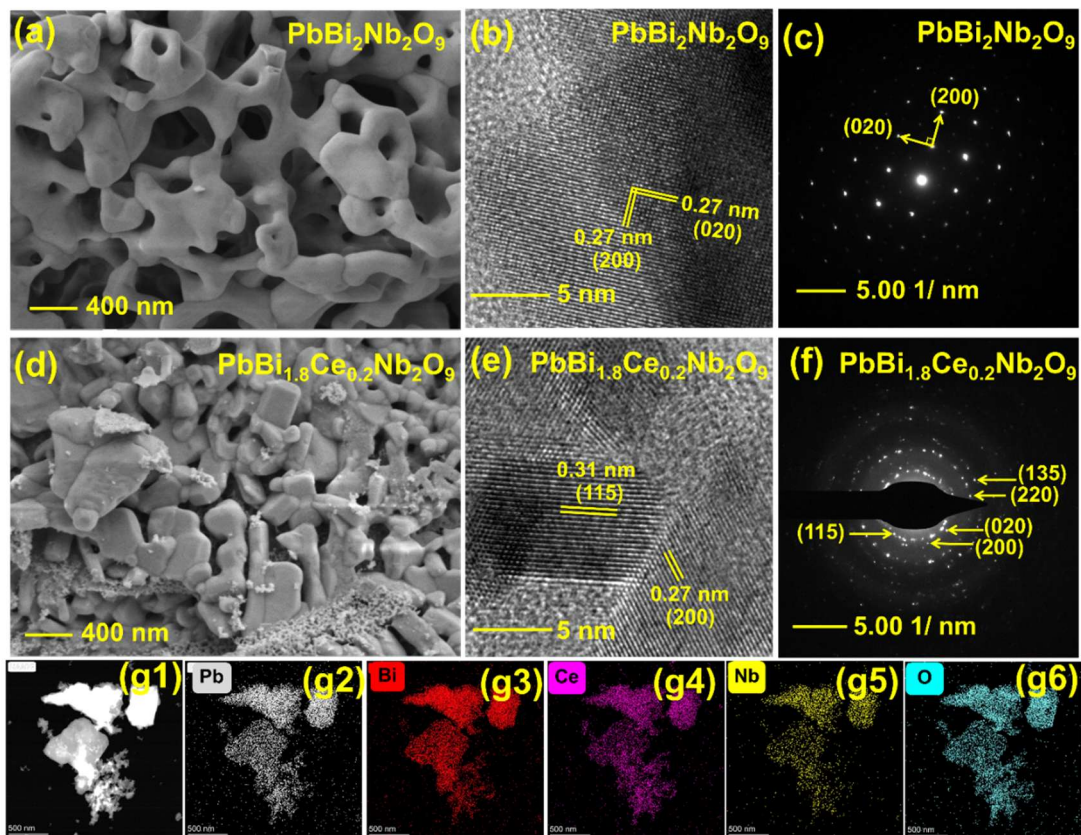


Figure 4.8 SEM (a and d), HRTEM (b and e), SAED pattern (c and f) of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$, and EDS of $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ (g1–g6).

The specific surface areas of all samples were determined using the Brunauer–Emmett–Teller (BET) method based on nitrogen adsorption–desorption measurements. The corresponding N_2 adsorption–desorption isotherms are presented in Figure 4.9. A noticeable increase in the specific surface area was observed for the Ce-doped samples compared to the undoped PBNO sample.

The enhancement in surface area suggests that the incorporation of Ce significantly alters the morphology and surface texture of PBNO. This morphological modification is consistent with the microstructural changes observed in the SEM and HRTEM analyses, where Ce doping was shown to promote grain growth accompanied by the formation of surface-attached nanoparticles and microstructural heterogeneity.

As a result, an increased number of exposed surface sites is generated, despite the observed reduction in long-range crystallinity.

From a photocatalytic perspective, the increase in specific surface area is particularly advantageous, as it provides a larger number of active sites for the adsorption of reactant molecules and facilitates more effective interaction between the photocatalyst surface and incident light. Consequently, the enhanced surface area induced by Ce substitution is expected to contribute positively to the photocatalytic performance of PBNO by improving reactant accessibility and promoting surface-mediated photocatalytic reactions.

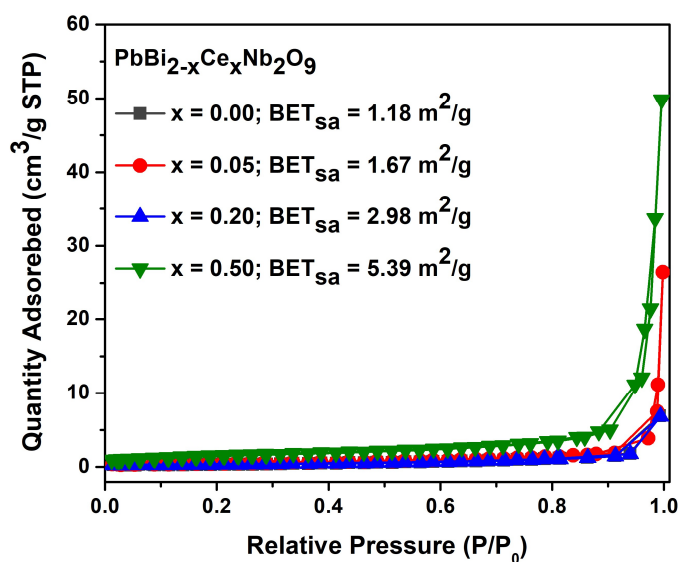


Figure 4.9 Nitrogen adsorption–desorption isotherm and surface area of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$.

4.2.3 Electronic band structure and band gap energy

The electronic band structure and band gap energy, which are strongly influenced by ion substitution and play a crucial role in determining photocatalytic activity, were investigated using optical absorption data obtained from UV–visible diffuse reflectance spectroscopy (UV–vis DRS), as shown in Figure 4.10a. The optical band gap energies were estimated by extrapolating the linear region of the Kubelka–

Munk plots of $[F(R)h\nu]^{1/2}$ versus photon energy ($h\nu$), assuming an indirect allowed electronic transition. In this analysis, $F(R)$ represents the Kubelka–Munk function, defined as $F(R) = (1 - R)^2 / 2R$, where R corresponds to the reflectance ratio of the sample relative to the standard reference.

The calculated band gap energies of all samples are summarized in Figure 4.10b. A systematic reduction in band gap energy was observed upon Ce doping, accompanied by enhanced light absorption in the visible region. This red-shift in the absorption edge indicates that Ce incorporation effectively extends the optical response of PBNO toward longer wavelengths. As a result, improved utilization of visible light is enabled, which is expected to enhance photocatalytic performance, as materials with narrower band gaps generally exhibit higher photocatalytic efficiency under visible-light irradiation.

In addition to experimental optical analysis, the influence of Ce doping on the electronic structure was further elucidated through density of states (DOS) calculations. The calculated DOS of pure PBNO is shown in Figure 4.10c, while that of Ce-doped PBNO is presented in Figure 4.10d. For the undoped PBNO, the DOS exhibits symmetric distributions between spin-up and spin-down states, indicating a non-magnetic electronic character. The valence band maximum (VBM) was found to be predominantly composed of O 2p states, whereas the conduction band minimum (CBM) mainly consists of Nb 4d states.

In contrast, the DOS of Ce-doped PBNO exhibits asymmetry in the conduction band region, reflecting modifications to the electronic structure induced by Ce incorporation. Although the VBM remains dominated by O 2p states, the CBM is now contributed by both Nb 4d and Ce 4f states. The introduction of Ce-derived electronic states near the CBM leads to a reduction in the band gap energy by lowering the CBM energy level. This downward shift of the CBM is attributed to the hybridization and interaction between Nb 4d and Ce 4f orbitals, which alters the electronic band alignment.

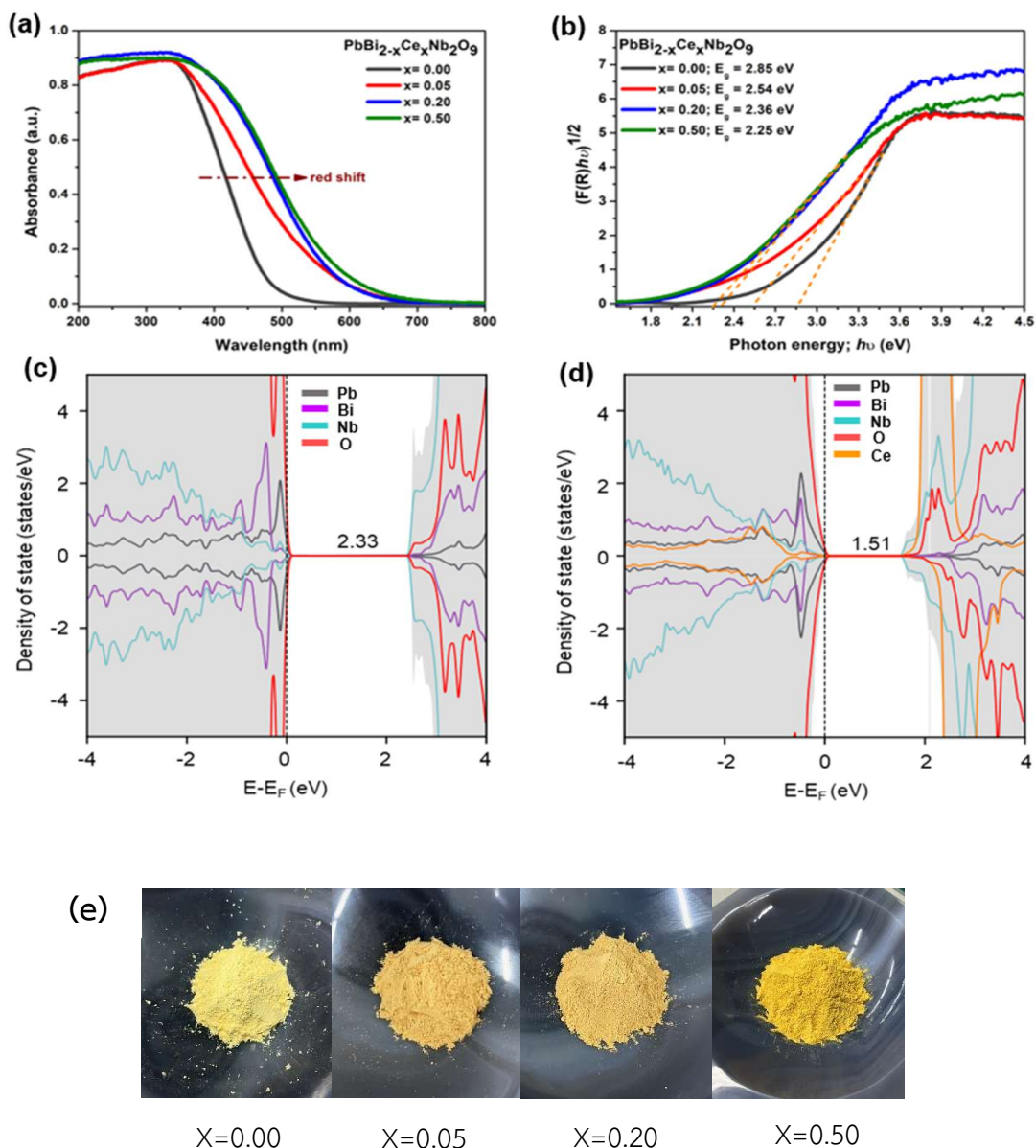


Figure 4.10 UV-vis absorption spectra (a) and Kubelka–Munk plot (b) of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$ ($x = 0.00, 0.05, 0.20$, and 0.50). The density of state (DOS) of (c) pure and (d) Ce-doped $\text{PbBi}_2\text{Nb}_2\text{O}_9$. The colour of obtained photocatalysts (e).

Furthermore, a detailed analysis of the band structure reveals changes in orbital hybridization at the valence band edge in the Ce-doped samples, as shown in Figure 4.11a–b. In particular, variations in Pb orbital contributions at the VBM were observed. These changes are associated with modifications in the local coordination

environment, including variations in Pb–O bond lengths and bond angles at both the original Pb sites and substituted Bi sites. Such structural distortions, induced by Ce doping and cation redistribution, enhance orbital overlap and further influence the electronic band structure. These observations highlight the strong coupling between lattice disorder, cation substitution, and electronic structure in Ce-doped PBNO.

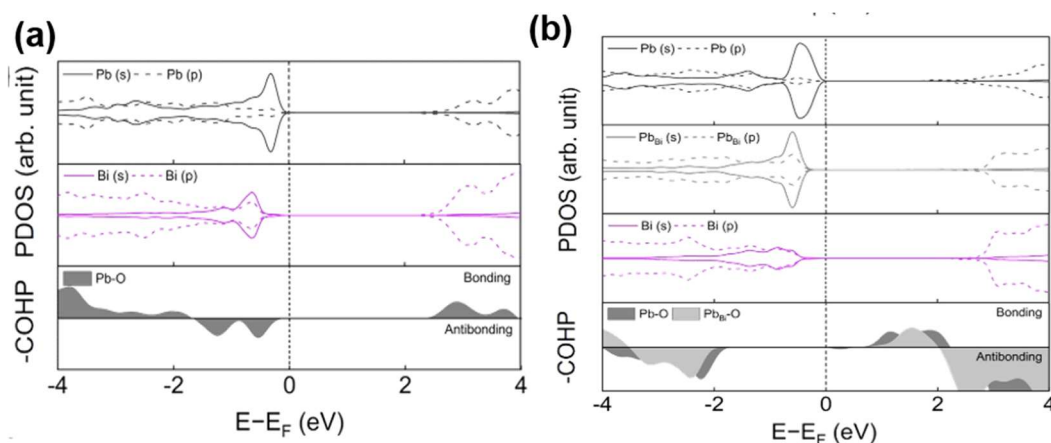


Figure 4.11 Projected electronic density of states (PDOS) of s and p orbital of Pb and Ce and crystal orbital Hamilton populations (COHP) for Pb–O and Pb_{Bi}–O of (a) pure and (b) Ce-doped PbBi₂Nb₂O₉.

4.2.4 Chemical state

The chemical states and elemental compositions of the samples with $x = 0.00$ and $x = 0.20$ were analyzed by X-ray photoelectron spectroscopy (XPS). The survey XPS spectra, as shown in Figure 4.12a, confirm the presence of Pb, Bi, Nb, and O elements in the undoped PbBi₂Nb₂O₉ sample, while additional characteristic peaks corresponding to Ce are observed in the Ce-doped sample, indicating the successful incorporation of Ce into the PBNO lattice.

The high-resolution Ce 3d core-level XPS spectrum of the $x = 0.20$ sample is presented in Figure 4.12b. The spectrum was deconvoluted into ten characteristic peaks, revealing the coexistence of Ce³⁺ and Ce⁴⁺ oxidation states. The peaks labeled as v , v'' , v''' , u , u'' and u''' are recognized as fingerprints of Ce⁴⁺ species, whereas

the remaining peaks are attributed to Ce^{3+} species, in agreement with previously reported studies (Soni et al., 2018) (Yang et al., 2020). The absence of Ce 3d signals in the undoped PBNO sample further confirms that Ce is exclusively introduced through doping.

The high-resolution Bi 4f spectrum (Figure 4.12c) exhibits two prominent peaks corresponding to Bi $4f_{7/2}$ and Bi $4f_{5/2}$ with binding energies in the ranges of 159.14–159.44 eV and 164.44–164.75 eV, respectively. These values are characteristic of Bi^{3+} species and indicate that the valence state of Bi remains unchanged after Ce doping. Similarly, the Pb 4f spectrum (Figure 4.12d) displays Pb $4f_{7/2}$ and Pb $4f_{5/2}$ peaks at binding energies consistent with Pb^{2+} , confirming the preservation of the Pb oxidation state. The Nb 3d core-level spectrum (Figure 4.12e) shows Nb $3d_{5/2}$ and Nb $3d_{3/2}$ peaks located at 206.62–206.79 eV and 209.37–209.56 eV, respectively, which are characteristic of Nb^{5+} species, indicating that the Nb oxidation state is also maintained upon Ce incorporation.

The O 1s spectrum (Figure 4.12f) was deconvoluted into three distinct components. The peak at lower binding energy is assigned to lattice oxygen (O_L), the intermediate peak corresponds to surface-adsorbed oxygen species (O_{ads}), and the peak at higher binding energy is attributed to molecularly adsorbed water ($\text{O}_{\text{H}_2\text{O}}$) on the surface. A slight shift of the O 1s peak toward lower binding energies was observed for the Ce-doped sample compared to the undoped PBNO. This shift is attributed to changes in the local electronic environment resulting from the incorporation of mixed-valence $\text{Ce}^{3+}/\text{Ce}^{4+}$ ions, which alter the ionicity and electronic polarizability of the metal–oxygen bonds within the lattice.

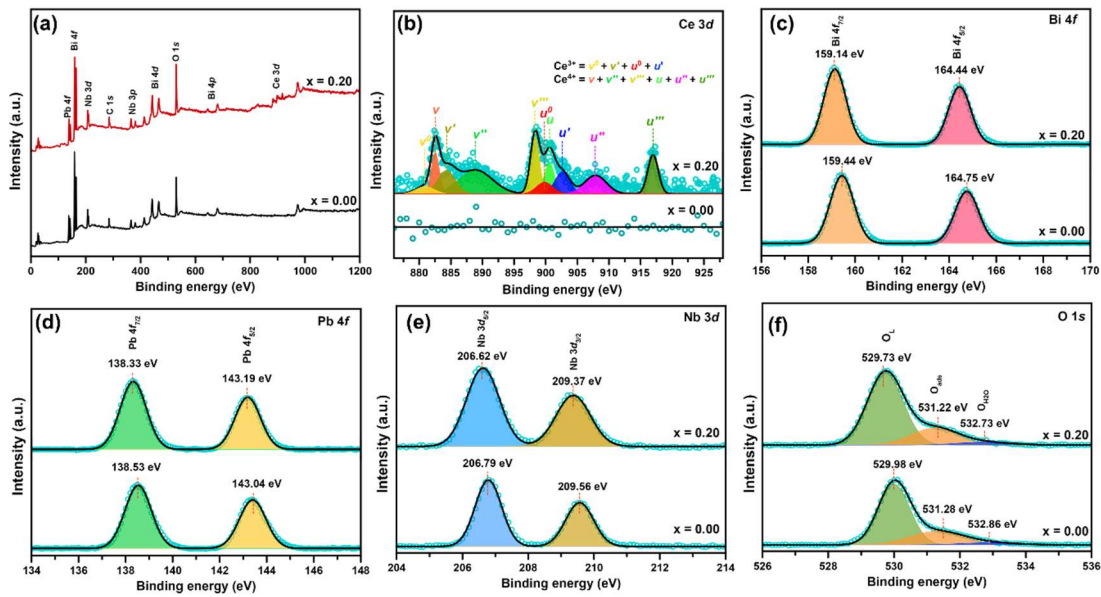


Figure 4.12 XPS spectrum:(a) survey spectra, and high-resolution spectrum of (b) Ce 3d, (c) Bi 4f, (d) Pb 4f, (e) Nb 3d, and (f) O 1s of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$ ($x = 0.00$, and 0.20).

The chemical-state information obtained from XPS analysis can be further corroborated and complemented by X-ray absorption spectroscopy (XAS), which provides insight into the bulk electronic structure and local coordination environment of the constituent elements. While XPS is a surface-sensitive technique probing the top few nanometers of the material, XAS offers element-specific information representative of the bulk, thereby enabling a comprehensive understanding of the oxidation states and electronic structure of Ce-doped PBNO (Watts J, 2003).

The XPS results reveal the coexistence of Ce^{3+} and Ce^{4+} species in the Ce-doped PBNO sample, as evidenced by the deconvolution of the Ce 3d core-level spectrum. This mixed-valence behavior is consistent with the XAS spectra at the Ce L₃-edge (Figure 4.13d), where characteristic absorption features corresponding to both Ce^{3+} and Ce^{4+} states are typically observed (Mullins, 2015). In XAS, the presence of multiple white-line features and changes in edge intensity and shape reflect variations in the Ce 4f occupancy, thereby confirming the mixed-valence nature of Ce within the PBNO lattice.

Furthermore, the stability of the Pb^{2+} , Bi^{3+} and Nb^{5+} oxidation states inferred from XPS core-level binding energies is supported by XAS measurements at the Pb L_3 -edge, Bi L_3 -edge and Nb L_3 -edge as show in Figure 4.13(a)-(c), respectively. The absence of significant edge shifts or changes in the near-edge structure indicates that the electronic states of these host cations remain largely unaffected upon Ce substitution (Mizoguchi and Woodward, 2004). This agreement between XPS and XAS confirms that Ce substitution does not induce redox changes in the Bi, Pb, or Nb species, but instead primarily affects the local electronic environment through defect formation and orbital hybridization.

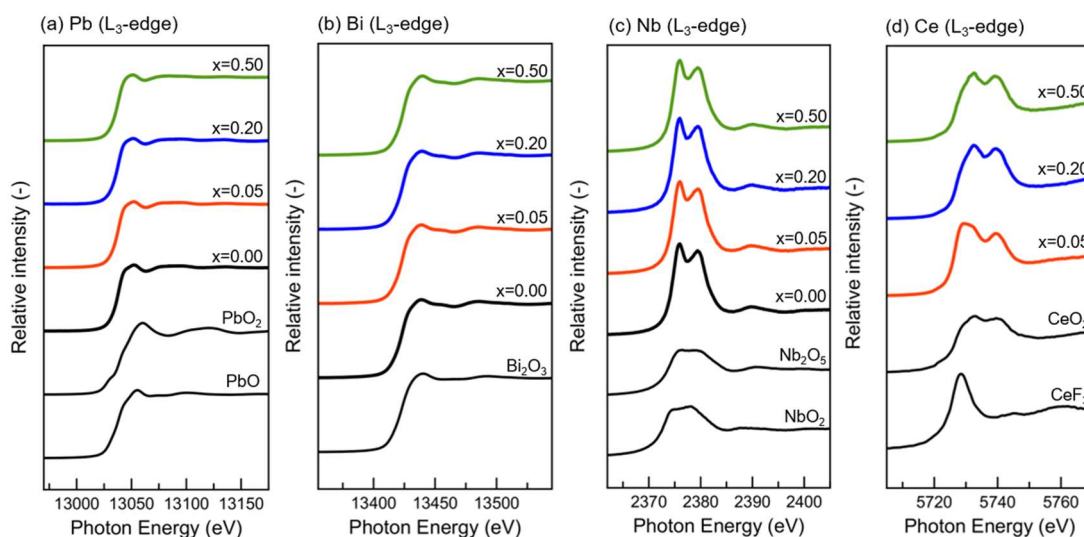


Figure 4.13 XANES spectrum: (a) Pb (L_3 -edge), (b) Bi (L_3 -edge), (c) Nb (L_3 -edge) and (d) Ce (L_3 -edge) of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$ ($x = 0.00, 0.05, 0.20$, and 0.50).

Overall, the combined XPS and XAS analyses demonstrate that Ce incorporation introduces mixed-valence Ce species and modifies the local electronic structure without altering the oxidation states of the host lattice cations. XPS provides direct evidence of surface chemical states and defect-related oxygen species, while XAS confirms the bulk electronic configuration and orbital hybridization effects. This complementary interpretation reinforces the conclusion that the enhanced photocatalytic performance of Ce-doped PBNO arises from the synergistic effects of

mixed-valence Ce, modified metal–oxygen bonding, and electronic band structure tailoring (Zhang, Zhao, Díaz-Somoano, Yang and Zhang, 2018).

4.3 Photocatalytic activity

The photocatalytic performance was evaluated through the degradation of methylene blue (MB) under simulated solar light irradiation, a method commonly used to assess the activity of semiconductor photocatalysts due to the stability and well-defined optical properties of MB (Hoffmann, Martin, Choi and Bahnemann, 1995). Enhanced photocatalytic activity was observed for PBNO at pH 12, which was attributed to the increased generation of hydroxyl radicals ($\cdot\text{OH}$) and improved adsorption of MB molecules under alkaline conditions (Figure 4.14a). Under basic environments, the higher concentration of OH^- ions promote the formation of $\cdot\text{OH}$ radicals, which are recognized as the primary oxidative species responsible for organic dye degradation (Chong, Jin, Chow and Saint, 2010; Herrmann, 1999). Consequently, a basic condition (pH 12) was selected to investigate the influence of Ce substitution on the photocatalytic performance, as illustrated in Figure 4.14b.

In the presence of Ce dopants, the degradation behavior of MB for all samples was analyzed using pseudo-first-order kinetics based on the Langmuir–Hinshelwood model, which is widely applied to heterogeneous photocatalytic reactions at low pollutant concentrations (Linsebigler, Lu and Yates Jr, 1995). The kinetic relationship is expressed by Equation (4.2):

$$\ln(C_0/C) = kt \quad (4.2)$$

where C_0 and C represent the MB concentration at the initial state and at time t , respectively, and k is the apparent rate constant (min^{-1}).

The kinetic analysis derived from the pseudo-first-order model (Figure 4.14c) reveals that an optimal Ce doping level of 0.2 was achieved. The $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$

sample exhibited a photocatalytic efficiency approximately 2.6 times higher than that of pristine PBNO. This enhancement can be attributed to improved charge carrier separation and the suppression of electron–hole recombination induced by appropriate Ce incorporation into the lattice (Zhang and Nosaka, 2014). In contrast, samples with Ce contents of $x=0.05$ and $x=0.50$ demonstrated lower photodegradation efficiencies than pure $\text{PbBi}_2\text{Nb}_2\text{O}_9$. Such deterioration in activity is likely related to the formation of impurity phases or excessive defect states, which act as recombination centers and hinder the photocatalytic process, resulting in reduced photodegradation efficiency (Somorjai, 1977).

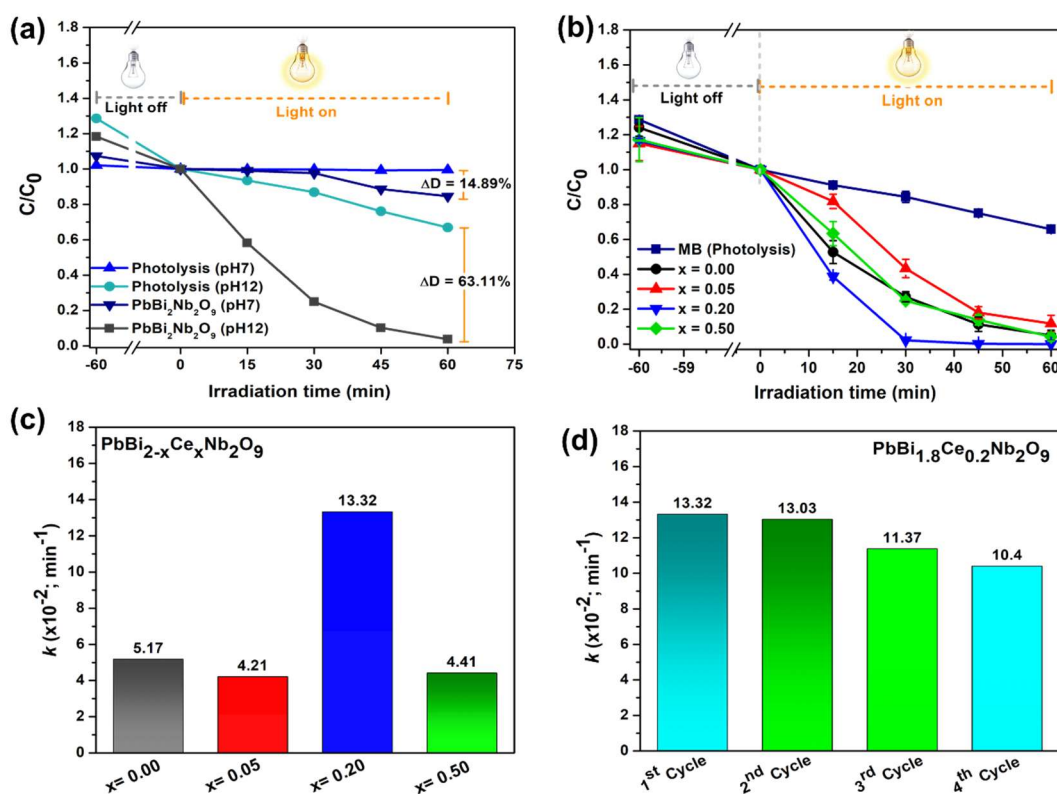


Figure 4.14 Photolysis and photocatalytic activity of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ between pH7 and 12 (a), The photocatalytic activities (b) and the percentages of MB degradation and the rate constants of the apparent pseudo first order reaction (c) at pH12 of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$. Cycling experiment of the photocatalytic degradation MB on $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ (d).

In addition to enhanced photocatalytic activity, $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ exhibited satisfactory cyclic stability. After four successive photocatalytic cycles, approximately 99% MB degradation was achieved within 60 minutes, corresponding to a rate constant of $10.4 \times 10^{-2} \text{ min}^{-1}$, as presented in Figure 4.14d. The retention of high activity over repeated cycles indicates good structural stability and reusability, which are essential for practical photocatalytic applications (Chen and Mao, 2007).

Although variations in band gap energy, morphology, and specific surface area were observed to contribute to the enhanced photocatalytic activity of the Ce-doped samples, these factors alone were insufficient to fully explain the observed performance trends. The efficiency of photogenerated electron-hole pair separation was therefore considered a critical parameter governing the overall photocatalytic behavior of the catalysts. Consequently, photoluminescence (PL) spectroscopy was employed to evaluate the separation efficiency of photogenerated charge carriers in the synthesized samples.

As presented in Figure 4.15a, the Ce-doped samples exhibited significantly lower PL intensities than pristine PBNO, while the main emission peaks remained at similar positions. This observation indicates that radiative recombination was effectively suppressed upon Ce incorporation, suggesting that the separation efficiency of photogenerated electron-hole pairs was enhanced due to the presence of $\text{Ce}^{3+}/\text{Ce}^{4+}$ ions (Huang et al., 2014). Among the investigated compositions, $\text{PbBi}_{1.80}\text{Ce}_{0.20}\text{Nb}_2\text{O}_9$ demonstrated the lowest PL intensity, indicating the highest charge separation efficiency within the series.

The enhanced charge separation observed for the optimally doped sample was attributed to two primary factors. First, the coexistence of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple was found to facilitate reversible electron trapping and release, thereby prolonging the lifetime of charge carriers. Second, lattice distortions induced by Ce substitution, particularly within the NbO_6 octahedra, were shown to generate additional defect states that function as electron-trapping sites (Li, Chen, Zhang and Lv, 2010). These

combined effects contribute to the suppression of electron–hole recombination and promote improved photocatalytic performance.

It is important to note that an optimal Ce doping concentration is required to maximize photocatalytic efficiency (Dai et al., 2016). In the case of $\text{PbBi}_{1.95}\text{Ce}_{0.05}\text{Nb}_2\text{O}_9$, the low Ce content provided limited enhancement in charge separation, while the formation of secondary phases further reduced photocatalytic activity. Conversely, excessive Ce incorporation, particularly in the $\text{PbBi}_{1.5}\text{Ce}_{0.5}\text{Nb}_2\text{O}_9$ composition, resulted in the introduction of a high density of defect states, mainly associated with Ce^{4+} species. These defects acted as recombination centers, thereby accelerating charge carrier recombination and diminishing photocatalytic efficiency (Vento-Lujano and González, 2021).

To further understand the charge carrier dynamics, the time-resolved photoluminescence (TRPL) spectra of pure $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and Ce-doped $\text{PbBi}_{1.80}\text{Ce}_{0.20}\text{Nb}_2\text{O}_9$ were recorded, as shown in Figure 4.15b. The obtained PL decay profiles were satisfactorily fitted using a triple-exponential decay function, which is described by Equation (4.3):

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \quad (4.3)$$

where (τ_i) represents the decay lifetime of the i -th component and A_i represents the corresponding amplitude. The average PL lifetime (τ_{avg}) were estimated with the τ_i and A_i values from the fitted curves data according to equation (4.4):

$$\tau_{\text{avg}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3} \quad (4.4)$$

The detailed fitting parameters are summarized in Table 4.3. A shorter average lifetime (τ_{avg}) was observed for $\text{PbBi}_{1.80}\text{Ce}_{0.20}\text{Nb}_2\text{O}_9$ in comparison with pristine PBNO, indicating the introduction of additional non-radiative decay pathways in the Ce-doped

sample. This behavior was attributed to the rapid transfer of photogenerated electrons from the excited states of the PBNO host lattice to the Ce-related electronic states, which act as efficient electron trapping centers (Sriwichai, Sakulsermsuk, Duangjam, Wetchakun and Wetchakun, 2024).

As a result, enhanced charge carrier separation and accelerated interfacial charge transfer were achieved in the optimally doped sample. These effects facilitate the efficient migration of photogenerated electrons and holes toward the surface-active sites of the photocatalyst, thereby promoting effective interactions with MB molecules and leading to improved photocatalytic performance.

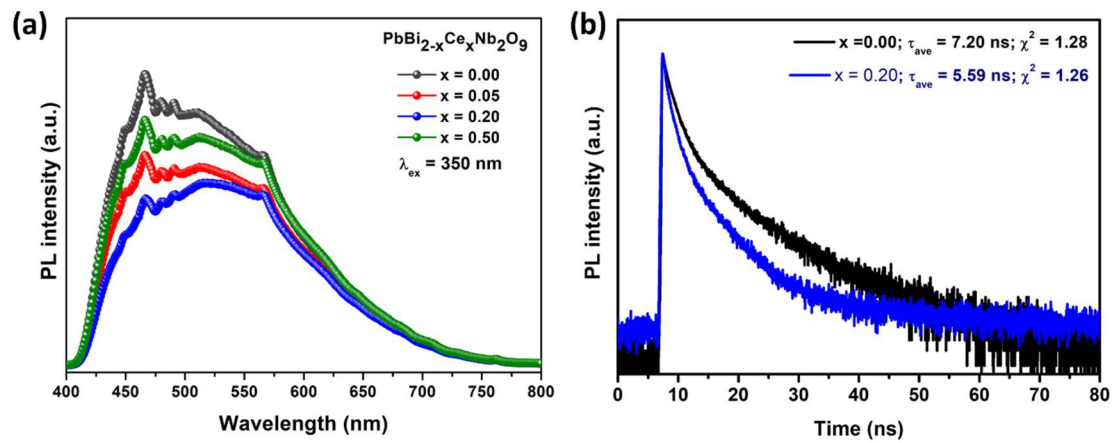


Figure 4.15 PL spectra of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$ (a) and TRPL spectra of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and $\text{PbBi}_{1.80}\text{Ce}_{0.20}\text{Nb}_2\text{O}_9$ (b).

Table 4.3 TRPL fitted data of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$ ($x=0.00$ and $x=0.02$).

Ce content (x)	Lifetime, τ (ns)			Amplitude (%)			average lifetime,	χ^2
	τ_1	τ_2	τ_3	A_1	A_2	A_3	τ_{avg} (ns)	
X=0.00	0.98	2.48	9.83	32.55	41.35	26.10	7.20	1.28
X=0.20	0.49	1.57	6.63	12.26	43.45	44.29	5.59	1.26

To elucidate the generation and contribution of reactive species during the photocatalytic process, potassium iodide (KI) and terephthalic acid (TA) were employed as scavengers for photogenerated holes (h^+) and hydroxyl radicals ($\cdot OH$), respectively. In addition, the influence of dissolved oxygen was evaluated by conducting the photocatalytic reactions under argon (Ar)-saturated conditions. The percentage inhibition of MB degradation over $PbBi_{1.8}Ce_{0.2}Nb_2O_9$ in the presence of various scavengers and under an argon atmosphere is presented in Figure 4.16.

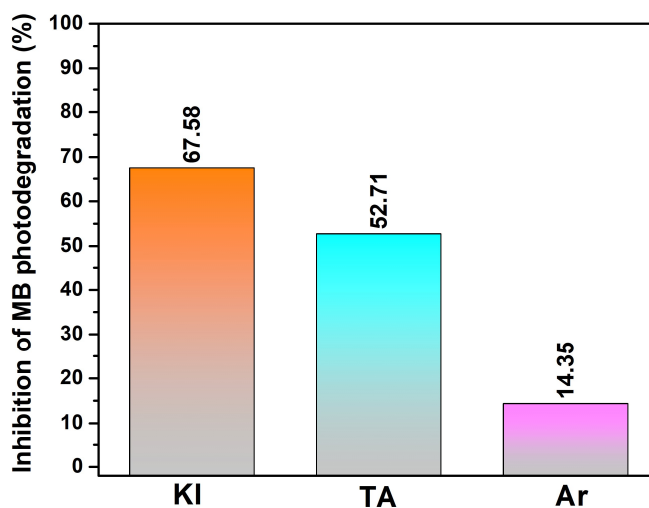


Figure 4.16 Inhibition of MB photocatalytic degradation over $PbBi_{1.8}Ce_{0.2}Nb_2O_9$ in the presence of different scavengers and argon atmosphere relative to the degradation without scavengers and under air atmosphere.

A significant suppression of photocatalytic activity was observed upon the addition of KI and TA, indicating that photogenerated holes (h^+) and hydroxyl radicals ($\cdot OH$) play dominant roles as the primary reactive species responsible for MB degradation. In contrast, only a marginal decrease in photocatalytic efficiency was detected under argon-saturated conditions, suggesting that dissolved oxygen contributes minimally to the overall photocatalytic process. Although dissolved oxygen can act as an electron acceptor and be reduced to form reactive oxygen species such as superoxide radicals ($O_2^{\cdot -}$) and hydrogen peroxide (H_2O_2), its

involvement in the degradation reaction was determined to be secondary compared with that of holes and hydroxyl radicals.

The band potentials of photocatalysts are regarded as critical parameters for determining their redox capabilities under light irradiation. The relative energetic positions of the conduction band (CB) and valence band (VB) edges govern the ability of a photocatalyst to generate reactive oxygen species (ROS), which are essential for the degradation of organic pollutants. To determine the band structure, a combined analysis using X-ray photoelectron spectroscopy (XPS) at the valence band region and UV–vis diffuse reflectance spectroscopy was employed.

The work function (ϕ), defined as the minimum energy required to transfer an electron from the Fermi level (E_F) of a material to the local vacuum level, was estimated using the absolute electronegativity approach (Greiner, Chai, Helander, Tang and Lu, 2012). The absolute electronegativity of a semiconductor was calculated as the geometric mean of the Mulliken electronegativities of its constituent atoms, as expressed by Equation (4.5):

$$\phi = (\chi_A^x + \chi_B^y + \chi_C^z + \cdots)^{1/P} \quad (4.5)$$

where χ denotes the Mulliken electronegativity of each isolated atom, and P represents the total number of atoms in the compound ($P = x + y + z + \cdots$). Based on this method, the work function values were calculated to be 6.14 eV for pristine $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and 6.11 eV for $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$, using the Mulliken electronegativity values of Pb (3.90 eV), Bi (4.69 eV), Ce (3.24 eV), Nb (4.00 eV), and O (7.54 eV) (Liao et al., 2022).

The valence band maximum relative to the vacuum level (VBM_{vac}) was determined from valence band XPS spectra (Figure 4.18a and b), which measure the energy difference between the valence band edge and the Fermi level. Subsequently,

the conduction band minimum at the vacuum level (CBM_{vac}) was calculated using Equation (4.6):

$$\text{CBM}_{\text{vac}} = \text{VBM}_{\text{vac}} - E_g \quad (4.6)$$

where E_g represents the optical band gap energy obtained from UV-vis absorption analysis.

To evaluate the photocatalytic redox ability under experimental conditions, the band edge positions referenced to the vacuum level were converted to the reversible hydrogen electrode (RHE) scale using Equation (4.7) (Bard, Faulkner and White, 2022; Trasatti, 1986):

$$E_{\text{RHE}} (\text{V at pH}) = -E_{\text{vac}} (\text{eV}) - [E_0 + (0.059 \times \text{pH})] \quad (4.7)$$

where E_0 is the energy of free electrons on the hydrogen scale, typically taken as 4.44 eV relative to the vacuum level at pH 0.

The relative positions of the valence band maximum and conduction band minimum of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ with respect to both the vacuum scale and the RHE scale at pH 12 are summarized in Table 4.3. Under alkaline conditions (pH 12), the conduction band potentials of both materials were found to be sufficiently negative to enable the reduction of O_2 to H_2O_2 , but not negative enough to promote the formation of superoxide radicals ($\text{O}_2^{\cdot-}$). Meanwhile, the valence band potentials were sufficiently positive to oxidize OH^- ions to generate hydroxyl radicals ($\cdot\text{OH}$) (Nosaka and Nosaka, 2017). These calculated band edge positions are consistent with the experimental results obtained from active species trapping experiments, thereby validating the proposed photocatalytic mechanism (Dou et al., 2023; Nadolska et al., 2022; Sirusy, Ashrafi and Akhond, 2023).

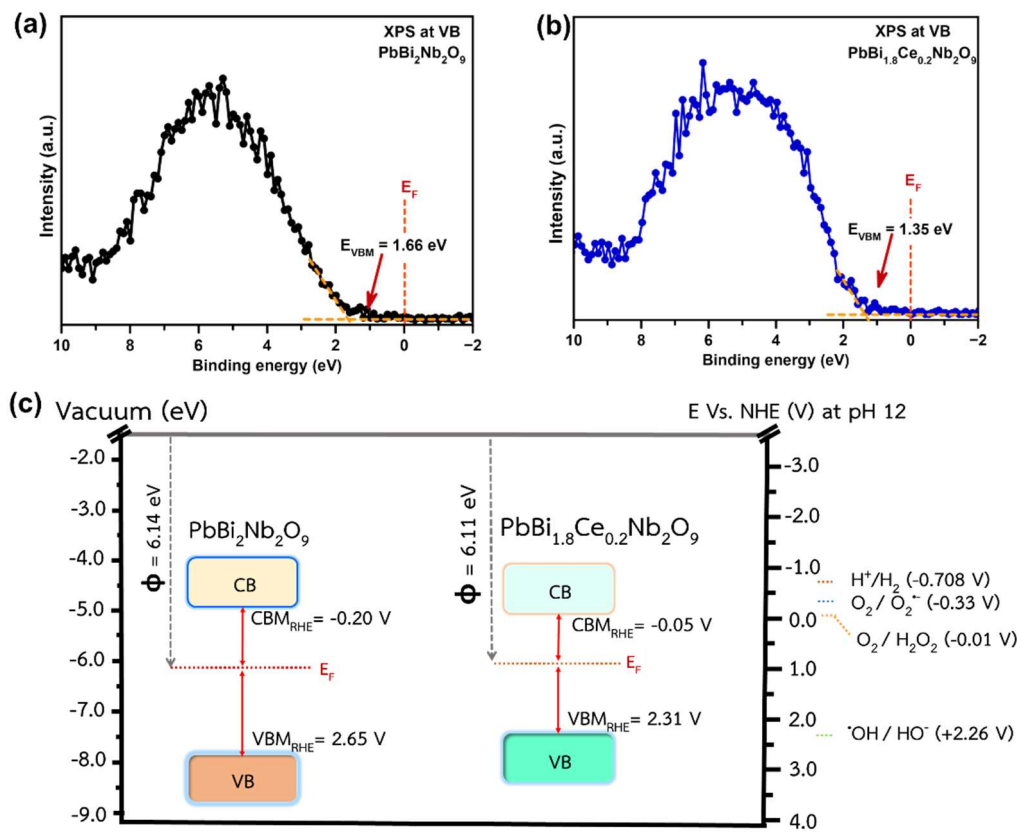


Figure 4.17 XPS at valence band of (a) $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and (b) $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$. Diagram of the band energy (c) of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$.

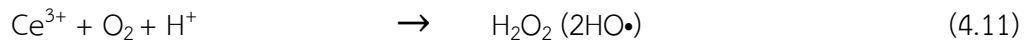
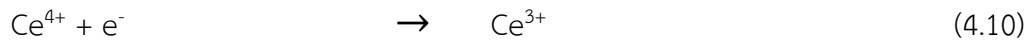
Table 4.4 Band parameters estimated by the calculation of work function (Φ) and the measurement of UV-vis absorption and XPS valence band spectroscopy.

Compound	Φ (eV)	E_{VBM} (eV)	E_g (eV)	VBM_{vac} (eV)	CBM_{vac} (eV)	VBM_{RHE} at pH12 (V)	VBM_{RHE} at pH12 (V)
$\text{PbBi}_2\text{Nb}_2\text{O}_9$	6.14	1.66	2.85	-7.80	-4.95	2.65	-0.20
$\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$	6.11	1.35	2.36	-7.46	-5.12	2.31	-0.05

Accordingly, a photocatalytic reaction mechanism for $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ is proposed based on the experimental results and band structure analysis. As schematically illustrated in Figure 4.18, the incorporation of Ce into the $\text{PbBi}_2\text{Nb}_2\text{O}_9$

lattice is shown to introduce additional electronic energy levels near the bottom of the conduction band, leading to a red shift of the optical absorption edge. As a result, enhanced absorption in the visible light region is achieved, allowing $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ to harvest a broader portion of the solar spectrum. Consequently, an increased number of photogenerated electrons and holes are produced in the conduction band (CB) and valence band (VB), respectively, under light irradiation.

The photocatalytic degradation process of methylene blue (MB) can be described by the following reactions:



Although various modification strategies have been reported to enhance photocatalytic activity, simple Ce substitution within the PBNO lattice provides multiple synergistic advantages. The incorporation of Ce was found to reduce the band gap energy by modifying orbital hybridization, primarily through the elevation of the valence band maximum without introducing harmful deep-level defect states (Chen, Huang, Wu and Lin, 2012). The upward shift and broadening of the valence band improve charge carrier mobility, while the narrowed band gap promotes efficient photocarrier generation under visible light irradiation.

In addition, photogenerated charge carrier recombination is effectively suppressed by Ce-induced lattice distortions and the presence of $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox centers, which function as reversible electron trapping sites (Dai et al., 2016). Photogenerated holes are subsequently transported to the catalyst surface, where they react with surface-adsorbed OH^- ions to generate highly reactive hydroxyl radicals ($\cdot\text{OH}$) that participate directly in pollutant oxidation (Lin, Kurniawan, Valinton, Chen

and Chuang, 2024). Meanwhile, trapped electrons are transferred to surface-adsorbed oxygen molecules, leading to the formation of H_2O_2 , which can further decompose to generate additional $\cdot\text{OH}$ radicals, thereby amplifying the oxidative degradation process (Sheng, Li and Xu, 2014).

Furthermore, the increased specific surface area observed in the Ce-doped samples provides a higher density of active sites for photocatalytic reactions. The combined effects of enhanced light absorption, improved charge separation and transport, increased reactive species generation, and enlarged surface area collectively contribute to an approximately 2.6-fold enhancement in the photocatalytic efficiency of $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$. This improvement is considered significant when compared with other modification strategies previously reported for $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and related photocatalytic materials, as summarized in Table 4.4.

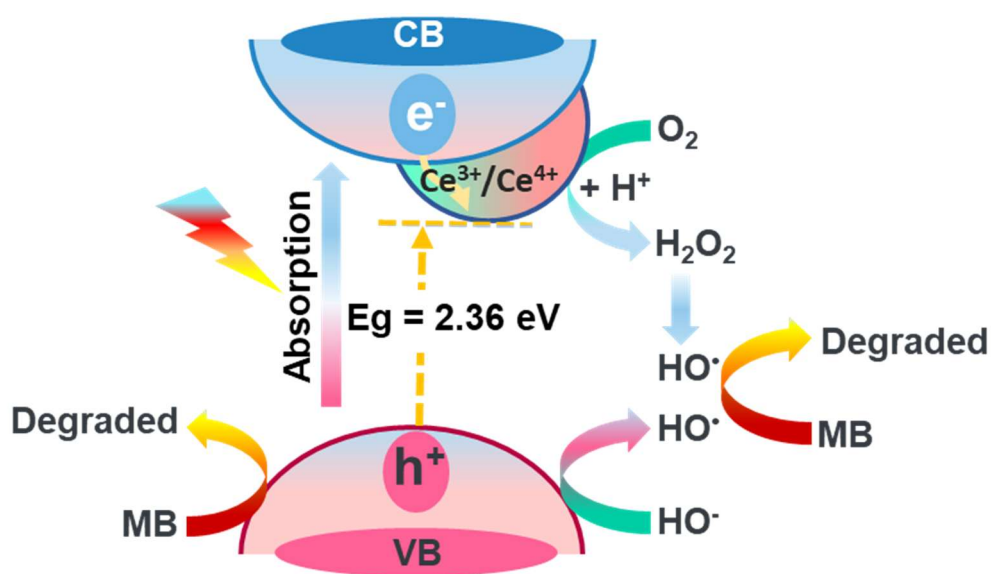


Figure 4.18 Proposed schematic band structures and mechanism of MB photodegradation over the $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ photocatalyst.

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