

CHAPTER V

CONCLUSIONS

In this study, $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBNO) and Ce-doped $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ photocatalysts were successfully synthesized and systematically investigated to elucidate the effects of preparation methods, calcination temperature, and Ce substitution on structural, electronic, and photocatalytic properties.

The influence of synthesis routes on PBNO revealed that all preparation methods (Sol-gel, Hydrothermal, and Molten salt) produced the desired Aurivillius-type PBNO phase. However, significant differences in crystallinity, morphology, and photocatalytic performance were observed. Although the Molten salt method yielded the highest crystallinity, the Sol-gel-derived PBNO exhibited superior photocatalytic activity toward methylene blue (MB) degradation. This enhancement was attributed to its porous morphology, higher surface area, and defect-rich structure, highlighting that photocatalytic efficiency is not governed solely by crystallinity but also by surface and microstructural characteristics. Consequently, the Sol-gel method was selected for further optimization.

Calcination temperature played a critical role in phase formation and purity. PBNO samples calcined at 750 °C and 800 °C exhibited single-phase Aurivillius structures, while impurity phases were present at lower temperatures. The sample calcined at 750 °C was identified as optimal, achieving high phase purity with reduced energy consumption.

Ce substitution was found to significantly modify the crystal structure, lattice distortion, and electronic properties of PBNO. XRD and Raman analyses confirmed that Ce was successfully incorporated into the PBNO lattice at moderate doping levels ($x = 0.20$), inducing lattice contraction in the *ab*-plane, expansion along the *c*-axis, and increased orthorhombic distortion due to NbO_6 octahedral deformation. Excessive or insufficient Ce doping led to secondary phase formation and structural instability.

Morphological and surface analyses demonstrated that Ce incorporation altered grain growth behavior and increased specific surface area, providing more accessible active sites for photocatalytic reactions. Despite a reduction in long-range crystallinity, Ce-doped samples exhibited improved surface heterogeneity favorable for photocatalysis.

Optical and electronic structure investigations revealed that Ce doping effectively narrowed the band gap and extended light absorption into the visible region. Density of states calculations showed that Ce 4f states contributed to the conduction band minimum, lowering its energy and enhancing visible-light responsiveness. XPS and XAS analyses confirmed the coexistence of $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox pairs without altering the oxidation states of Pb, Bi, or Nb, indicating that Ce primarily modifies the electronic environment rather than inducing host lattice redox reactions.

Photocatalytic performance evaluation demonstrated that $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ exhibited the highest activity, achieving approximately 2.6 times higher MB degradation efficiency than pristine PBNO under alkaline conditions (pH 12). Kinetic analysis confirmed pseudo-first-order behavior, while cycling tests demonstrated excellent stability and reusability. Photoluminescence and time-resolved PL studies revealed that optimal Ce doping significantly suppressed electron-hole recombination by introducing efficient charge trapping and transfer pathways.

Reactive species trapping experiments and band edge calculations confirmed that photogenerated holes (h^+) and hydroxyl radicals ($\cdot\text{OH}$) were the dominant active species responsible for MB degradation, while dissolved oxygen played a minor role. The band structure analysis validated that the valence band positions were sufficiently positive to generate $\cdot\text{OH}$ radicals, in agreement with experimental observations.

Overall, the enhanced photocatalytic performance of $\text{PbBi}_{1.8}\text{Ce}_{0.2}\text{Nb}_2\text{O}_9$ arises from the synergistic effects of band gap narrowing, improved visible-light absorption, efficient charge carrier separation via $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couples, increased surface area, and optimized band edge positions. This work demonstrates that controlled Ce substitution is an effective strategy for improving the photocatalytic efficiency of Aurivillius-type perovskite oxides and provides valuable insights for the rational design of high-performance visible-light-driven photocatalysts for environmental remediation.