

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials and reagents

The following materials and reagents were used as starting materials: lead nitrate ($\text{Pb}(\text{NO}_3)_2$) (99%, KemAus), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) ($\geq 98\%$, CARLO ERBA Reagents), ammonium niobate oxalate hydrate ($\text{C}_4\text{H}_4\text{NNbO}_9 \cdot \text{H}_2\text{O}$) (99.99%, Aldrich), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) (99.5%, CARLO ERBA Reagents), cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (99.5%, ACROS ORGANICS), ammonium solution (NH_4OH) (30%, CARLO ERBA Reagents), nitric acid (HNO_3) (69.5%, CARLO ERBA Reagents) and hydrogen peroxide (H_2O_2) (30%, CARLO ERBA Reagents).

3.2 Sample preparation

$\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBNO) was prepared by sol-gel method. Starting materials including $\text{Pb}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{C}_4\text{H}_4\text{NNbO}_9 \cdot \text{H}_2\text{O}$ and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$. The compounds are dissolved in a solution containing 30 mL of 30% H_2O_2 aqueous solution. The solution is stirred at 400 rpm for 5 minutes to ensure uniform mixing of the precursors. 2 mL of 6M HNO_3 is added to the mixture. The mixture is then heated at 65°C for an hour. Then, the pH of the solution is adjusted to around 6.5 by slowly adding NH_4OH to obtain a yellow solution. This step must be careful control of pH to ensure the desired chemical reaction occur. The precursor solution undergoes a transformation, turning into a resin-like gel. The obtained gel is dried by heating at 120°C for 24 hours. This step removes excess solvent and helps in the formation of a solid material. Then, the dried gel was preheated at 300°C for 2 hours to remove organic compounds and calcined at different temperatures. In this work, it was calcined at 650°C , 700°C , 750°C and 800°C for 4 hours.

Synthesis Ce-doped of $\text{PbBi}_{2-x}\text{Ce}_x\text{Nb}_2\text{O}_9$. The general synthesis steps are similarly as the PBNO preparation method. The main difference being the introduction $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as a dopant to replace some of the bismuth ions. The starting materials include $\text{Pb}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (to provide cerium ions for doping), $\text{C}_4\text{H}_4\text{NNbO}_9 \cdot \text{H}_2\text{O}$ and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$. The cerium nitrate hexahydrate was calculated in a ratio corresponding to the desired Ce doping level, $x = 0.02, 0.05, 0.08, 0.2, 0.5$ and 0.8 respectively.

3.3 Characterizations

3.3.1 X-ray diffraction (XRD) and structure refinement

X-ray diffraction (XRD) was employed to analyze the structural characteristics of the synthesized materials. This technique was used to obtain detailed information regarding the crystal structure, phase composition, and crystallinity of the samples. Prior to measurement, the obtained powders were finely ground and carefully packed into a standard sample holder to ensure a flat and homogeneous surface.

The XRD patterns were recorded using a Bruker D2 Phaser diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Data collection was carried out over a 2θ range of 10° to 70° , with a step size of 0.02° and a scan speed of 0.2 s per step . These measurement conditions were selected to achieve sufficient resolution for phase identification and structural analysis.

The recorded diffraction patterns were subsequently analyzed and compared with standard reference data obtained from the Physical Sciences Data-Science (PSDS) database to identify crystalline phases and evaluate phase purity. Structural refinement and detailed analysis were conducted based on the indexed diffraction peaks to assess any structural changes induced by compositional modification.

3.3.2 Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX).

Scanning electron microscopy (SEM) was employed to examine the surface morphology, particle distribution, and particle size of the synthesized materials at the

microscale. SEM observations were carried out using a JEOL JSM-6010LV scanning electron microscope. The measurements were conducted under an accelerating voltage of 20 kV with a working distance of 9.9 mm, which provided sufficient resolution and contrast for morphological analysis.

Energy-dispersive X-ray spectroscopy (EDS) was used in conjunction with SEM to perform qualitative and quantitative elemental composition analysis of the samples. The EDS measurements were conducted using an Oxford Instruments X-Max detector with an active area of 50 mm², enabling elemental mapping and area analysis. This technique was applied to confirm the presence and distribution of constituent elements in the samples and to verify the successful incorporation of dopant elements within the photocatalyst structure.

3.3.3 X-ray photoelectron spectroscopy (XPS).

X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemical composition and electronic states of the constituent elements in the synthesized materials. The measurements were carried out at the Thailand Center of Excellence in Physics (ThEP), Chiang Mai University.

XPS spectra of all samples were collected using an AXIS Ultra DLD X-ray photoelectron spectrometer (Kratos Analytical Ltd., Manchester, England) equipped with a monochromatized Al K α X-ray source (photon energy = 1486.6 eV). During data analysis, the binding energy scale was calibrated by referencing the C 1s peak at 284.8 eV, which originates from adventitious carbon on the sample surface. This calibration ensured accurate determination of the binding energies and reliable comparison of chemical states among the samples.

3.3.4 UV-Visible spectrophotometer.

UV-Visible diffuse reflectance spectroscopy (DRS) was employed to investigate the optical properties of the synthesized materials. The measurements were carried out using an Agilent UV-Vis-NIR spectrophotometer (Cary 60 UV-Vis) operating in double-beam mode. The diffuse reflectance spectra (%R) were recorded over a

wavelength range of 200–800 nm, which covers both the ultraviolet and visible regions of the electromagnetic spectrum.

The obtained reflectance data were analyzed using the Kubelka–Munk function, which is commonly applied to convert diffuse reflectance measurements into an equivalent absorption coefficient. The Kubelka–Munk function is expressed as:

$$F(R) = \frac{(1-R)^2}{2R} \quad (3.1)$$

where R represents the measured reflectance, defined as the ratio of the reflectance of the sample to that of the reference standard ($\%R_{\text{sample}}/\%R_{\text{standard}}$).

The optical band gap energy (E_g) of the samples was determined by extrapolating the linear region of the Tauc plot, constructed by plotting $(F(R)h\nu)^{1/2}$ as a function of the photon energy ($h\nu$). This method is based on the assumption of an indirect allowed electronic transition and provides an estimation of the band gap energy from the intersection of the extrapolated linear portion with the photon energy axis.

3.3.5 Photoluminescence (PL).

Photoluminescence (PL) spectroscopy was employed to investigate the optical emission properties and charge carrier recombination behavior of the synthesized materials. PL is a phenomenon in which photons are emitted from a material following the absorption of higher-energy photons. This process occurs when electrons are excited from lower energy states to higher energy states upon photon absorption and subsequently relax back to lower energy states, accompanied by photon emission. The emitted photons typically possess lower energy (longer wavelength) than the absorbed photons due to non-radiative energy losses within the material.

Prior to measurement, the obtained powder samples were carefully packed into a suitable sample holder and placed into the measurement chamber. The PL spectra were recorded using a HORIBA Scientific Fluoro Max-Plus spectrofluorometer with an excitation wavelength (λ_{ex}) of 315 nm. The recorded PL spectra were used to evaluate the recombination efficiency of photogenerated electron–hole pairs, where

lower PL intensity generally indicates suppressed radiative recombination and improved charge carrier separation in the photocatalyst.

3.3.6 X-ray adsorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) was employed as a powerful analytical technique to investigate the electronic and local structural properties of the synthesized materials. This technique is based on the interaction between incident X-rays and matter and is widely used in chemistry, physics, materials science, and biology for probing the local atomic environment. XAS is particularly suitable for studying complex materials such as nanoparticles, semiconductors, and superconductors, as it provides element-specific information independent of long-range crystallinity.

A typical XAS spectrum can be divided into two main regions: the X-ray Absorption Near-Edge Structure (XANES) and the Extended X-ray Absorption Fine Structure (EXAFS), as illustrated in Figure 3.1. The XANES region, located near the absorption edge, provides information related to the oxidation state, coordination geometry, and electronic structure of the absorbing atom. In contrast, the EXAFS region, which extends beyond the absorption edge, yields quantitative information on the local atomic structure, including interatomic distances, coordination numbers, and structural disorder around the absorbing atom.

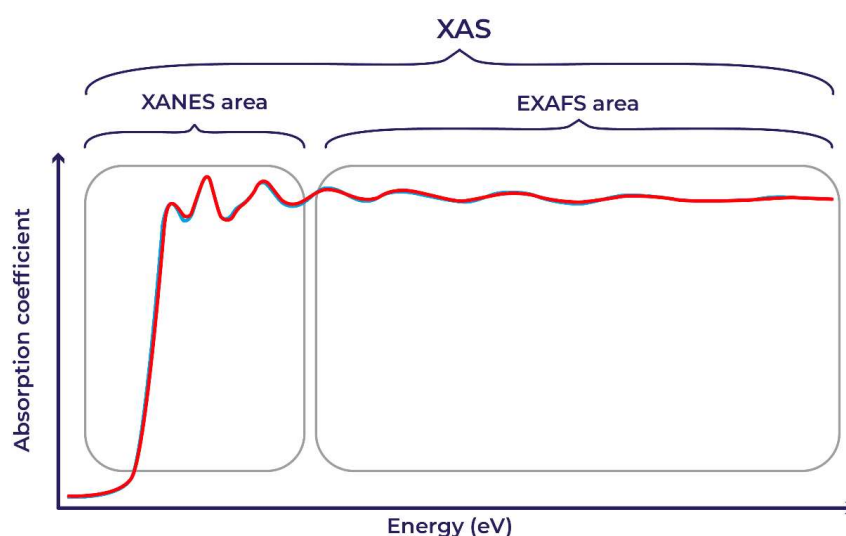


Figure 3.1 XANES and EXAFS region within XAS (Kartashov, Chernov, Polyanichenko and Butakova, 2021).

XAS measurements were conducted at two beamlines of the Synchrotron Light Research Institute (SLRI), Thailand, in order to accommodate the wide range of absorption edge energies corresponding to the constituent elements of the samples. For Ce L₃-edge and Nb L₃-edge analyses, XAS spectra were collected in fluorescence mode at Beamline 8, covering a photon energy range of 2–6 keV. Measurements at the Pb L₃-edge and Bi L₃-edge were performed at Beamline 1.1W using a combination of transmission and fluorescence modes, with photon energies ranging from 13–19 keV.

The acquired XAS data were processed and analyzed using the ATHENA and ARTEMIS software programs within the Demeter package. These programs were utilized for background subtraction, normalization, and fitting of the XANES and EXAFS regions to extract reliable electronic and structural parameters.

3.4 Photocatalytic test

Photocatalytic performance was evaluated through the reduction of methylene blue (MB) using a solar simulation lamp as the light source. An aqueous MB solution with an initial concentration of 20 ppm was employed as a representative organic dye pollutant. For each experiment, 50 mg of photocatalyst was dispersed in 50 mL of the MB solution, resulting in a catalyst loading of 1 g/L.

Prior to light irradiation, the suspension was magnetically stirred at 400 rpm in the dark for 1 h to establish adsorption–desorption equilibrium between the MB molecules and the photocatalyst surface. This dark adsorption step ensured that subsequent changes in MB concentration were attributed solely to photocatalytic reactions rather than physical adsorption.

After the adsorption equilibrium was achieved, the suspension was irradiated under simulated solar light. During irradiation, 5 mL aliquots of the suspension were withdrawn at predetermined time intervals. The solid photocatalyst was then separated from the collected samples by centrifugation to obtain clear supernatant solutions.

The concentration of MB in the supernatant was determined by measuring the absorbance at the maximum absorption wavelength ($\lambda_{\text{max}} = 664 \text{ nm}$) using a UV–visible

spectrophotometer. The photocatalytic degradation efficiency was calculated using Equation (3.2):

$$\% \text{degradation} = [(C_0 - C_t) / C_0] * 100 \quad (3.2)$$

where C_0 is the initial concentration of MB.

C_t is the concentration of MB after irradiation at time t .

3.5 Computational details

To clarify the effect of Ce doping on the electronic properties of the $\text{PbBi}_2\text{Nb}_2\text{O}_9$ structure (PBNO), we conducted first-principles calculations using density functional theory (DFT) with spin polarization, utilizing the Vienna Ab initio Simulation Package (VASP 6.3) (Kresse and Furthmüller, 1996). The interaction between core ions and electrons was modeled using the projector-augmented wave (PAW) method (Kresse and Joubert, 1999), while the exchange-correlation functional was described using the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) functional (Perdew, Burke and Ernzerhof, 1996).

All structures were performed the optimization with energy and force convergence criteria set at 10^{-6} eV and 0.02 eV/Å, respectively. All calculations were performed using valence-electron wavefunctions of O $2s^2 2p^4$, Nb $4s^2 4p^6 4d^4 5s^1$, Ce $4f^1 5s^2 5p^6 5d^1 6s^2$, Pb $5d^{10} 6s^2 6p^2$ and Bi $5d^{10} 6s^2 6p^3$ expanded in a plane-wave basis with energy cutoff of 500 eV. Additionally, k-points sampling of $6 \times 6 \times 1$ and $13 \times 13 \times 1$ grids were employed using the Monkhorst-Pack meshes (Monkhorst and Pack, 1976) for optimization and electronic density of state (DOS) calculation, respectively.

3.6 References

Kartashov, O. O., Chernov, A. V., Polyanichenko, D. S., & Butakova, M. A. (2021). XAS Data Preprocessing of Nanocatalysts for Machine Learning Applications. *Materials*. 14(24), 7884.

- Kresse, G., & Furthmüller, J. (1996). Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science*. 6(1), 15-50. doi:10.1016/0927-0256(96)00008-0.
- Kresse, G., & Joubert, D. (1999). From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B*. 59(3), 1758-1775. doi:10.1103/PhysRevB.59.1758.
- Monkhorst, H. J., & Pack, J. D. (1976). Special points for Brillouin-zone integrations. *Physical Review B*. 13(12), 5188-5192. doi:10.1103/PhysRevB.13.5188.
- Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. *Physical Review Letters*. 77(18), 3865-3868. doi:10.1103/PhysRevLett.77.3865.