

# Porous Nanosheets and Excellent Charge Carrier Dynamics in $\text{Ag}^+$ -Doped $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ Aurivillius-Phase Layered Perovskite for Enhanced Visible-Light Photocatalytic Activity

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The new Aurivillius layered perovskite compounds,  $\text{Ag}_x\text{Na}_{0.5-x}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  (AGBNO), were successfully synthesized using a hydrothermal technique followed by conventional, microwave-assisted, and acid-assisted ion exchange procedures. The formation of these compounds was evidenced by several techniques. A single-phase crystal structure was identified by XRD patterns, and expanded lattice parameters were revealed by crystal structure refinement. Chemical composition was verified by EDS, XPS, and ICP-OES analyses. Bandgap energies remained similar to the parent  $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  host material.  $\text{Ag}^+$  incorporation significantly enhanced photocatalytic performance for Rhodamine B degradation under visible light, which was attributed to the intrinsic catalytic properties of  $\text{Ag}^+$  as a noble metal cation. The variations in photocatalytic

activities among the series of  $\text{Ag}^+$ -doped samples produced were associated with differences in morphology, specific surface area, and charge carrier dynamics. The AGBNO sample prepared via acid-assisted ion exchange exhibited the highest photocatalytic efficiency, which was attributed to its highly porous nanosheet morphology, largest surface area, and excellent charge carrier dynamics, including high initial charge carrier concentration, optimal lifetime, high charge mobility, efficient charge separation, and transfer. Overall, this study demonstrates the potential of designing Aurivillius-phase layered perovskite photocatalysts with enhanced activity for wastewater remediation and environmental applications through noble metal cation doping.

## 1. Introduction

The rapid growth of the industrial sector has resulted in a rise in environmental pollution from the effluent wastewater produced. Photocatalysis is a promising green technology that can remediate a variety of pollutants using renewable solar

energy. Semiconducting photocatalysts function by absorbing ultra-bandgap energy light, creating charge carriers capable of forming radicals that degrade such pollutants.<sup>[1]</sup>

The design of efficient materials for achieving high photocatalytic efficiency remains a significant challenge. Perovskites have been extensively investigated as photocatalysts for wastewater

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treatment and air pollutant removal.<sup>[2–5]</sup> Due to their tendency to form visible light active bandgaps, Bi-based perovskites have attracted significant attention. Among various crystal structures, Aurivillius Bi-based compounds exhibit a unique crystal structure composed of  $(A_{n-1}B_nO_{3n+1})^{2-}$  pseudo-perovskite slabs and  $(Bi_2O_2)^{2+}$  layers, where  $n$  represents the number of  $BO_6$  layers.<sup>[6]</sup> The spontaneous polarization between these ionic layers facilitates the separation of photo-induced electron-hole pairs,<sup>[7]</sup> which is a critical step in the photocatalytic process. For the simplest structure with  $n = 2$ , compounds such as  $A_{0.5}Bi_{2.5}Nb_2O_9$ , where  $A = Na^+, Li^+$  and  $K^+$ , have shown potential as photocatalysts due to these intrinsic properties.<sup>[8,9]</sup> Typically, the A-site cation can be mono-, di- or trivalent, including  $Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Bi^{3+}$  and  $Ln^{3+}$ .<sup>[10,11]</sup> The choice of A-site cation significantly influences the local environment within the perovskite-like layer, affecting the polarizability and enabling them to behave as piezoelectric, ferroelectric, and dielectric materials.<sup>[11–14]</sup> Consequently, selecting the appropriate A-site cation, along with doping with other cations, is a key consideration for designing more efficient photocatalysts. The photocatalytic activities of these materials are strongly influenced by their crystal structures. For instance, the sizes of divalent A-site cations, such as  $Ca^{2+}, Sr^{2+}$  and  $Ba^{2+}$ , impact the rearrangement of  $NbO_6$  octahedra in  $ABi_2Nb_2O_9$ , which in turn affects the mobility of free charge carriers.<sup>[6,15]</sup> However, the incorporation of noble metal cations, particularly  $Ag^+$ , into the A-site of  $A_{0.5}Bi_{2.5}Nb_2O_9$  has remained unexplored. To date, only one Aurivillius Bi-based perovskite containing  $Ag^+$ ,  $Bi_5AgNb_4O_{18}$ , has been reported in the literature.<sup>[16,17]</sup>  $Ag^+$  is of particular interest due to its unique electronic properties, which allow it to form a shallower valence band, reducing band gap energy, thus enhancing light absorption, and it can also act as an electron trap to improve charge carrier separation.<sup>[18–21]</sup> This presents an opportunity to further explore the role of noble metal cations in Aurivillius-phase layered perovskites in modifying the electronic structure, enhancing charge transfer, and improving photocatalytic activity.

Here, we present the first report on  $Ag^+$  incorporation into sodium bismuth niobate ( $Ag_xNa_{0.5-x}Bi_{2.5}Nb_2O_9$ ), an Aurivillius Bi-based layered perovskite. The samples were synthesized using a hydrothermal method, followed by ion exchange through conventional, microwave-assisted, and acid-assisted procedures. A systematic investigation was conducted to study the effect of  $Ag^+$  substitution on the crystal structure, chemical composition, physical properties, DFT electronic band structure, optical properties, charge carrier dynamics and photocatalytic performance, where an AGBNO sample prepared via the acid-assisted ion exchange method exhibited the highest photocatalytic efficiency due to its porous nanosheet morphology, high surface area and high initial population of charge carriers formed.

## 2. Experimental Section

### 2.1. Materials

Starting materials used in this study were  $Bi(NO_3)_3 \cdot 5H_2O$  ( $\geq 99\%$ , Sigma-Aldrich),  $C_4H_4NNbO_9$  (99.99%, Sigma-Aldrich),  $AgNO_3$

( $\geq 99\%$ , Carlo Erba),  $NaOH$  ( $\geq 98\%$ , Sigma-Aldrich) and  $HNO_3$  (68–70%, Carl Roth), all of which were used without additional purification.

### 2.2. Sample Preparations

$Na_{0.5}Bi_{2.5}Nb_2O_9$  was prepared using a synthesis method similar to that reported in the literature.<sup>[8,22]</sup> In a general procedure, the precursors were dissolved in separate solvents. Specifically, 1.4552 g (3 mmol) of  $Bi(NO_3)_3 \cdot 5H_2O$  was dissolved in 6 mL of 4 M  $HNO_3$  solution, while 0.8686 g (2.88 mmol) of  $C_4H_4NNbO_9$  was dissolved in 46 mL of deionized water. These solutions were mixed and stirred for 5 min to ensure thorough mixing. Subsequently, 20 mL of 6 M  $NaOH$  solution was added to the mixture, which was then stirred continuously for 30 min. The prepared mixture was transferred to a stainless-steel autoclave lined with Teflon and heated at 180 °C for 36 h in a hot air oven. After the reaction, the product was separated by centrifugation, washed three times with deionized water to remove impurities, and dried overnight at 100 °C. This obtained sample is labelled as ABNO in this work.

To prepare  $Ag_xNa_{0.5-x}Bi_{2.5}Nb_2O_9$ , denoted as AGBNO, silver cations were incorporated into the ABNO sample using ion exchange methods. In a typical preparation, an  $Ag$  ion solution was prepared by dissolving 1.6987 g (10 mmol) of  $AgNO_3$  in 150 mL of deionized water. Subsequently, 1.0000 g (1.1577 mmol) of ABNO was added to the  $Ag$  ion solution and stirred continuously at room temperature for 24 h. The resulting precipitate was collected by centrifugation, thoroughly washed three times with deionized water to remove impurities, and dried overnight at 100 °C. This final product is designated as AGBNO, i.e., the second sample, labelled as AGBNO MIE, was prepared using a microwave-assisted ion exchange method. The preparation of the mixture of ABNO and  $AgNO_3$  solution followed the same procedure as for AGBNO, i.e., However, the mixture was heated using a 110 W microwave for 30 min, and the resulting precipitate was collected, washed and dried in the same manner described above. The third sample, designated as AGBNO AIE, was prepared similarly to AGBNO IE but with 1 M  $HNO_3$  acid used as a solvent for the  $AgNO_3$  solution instead of deionized water.

### 2.3. Sample Characterizations

X-ray diffraction (XRD) patterns were collected using an X-ray powder diffractometer (Rigaku, SmartLab) equipped with  $Cu K_\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation source and operated at 40 kV and 30 mA. The measurement was performed in the range of  $5^\circ \leq 2\theta \leq 80^\circ$  with a step increment of  $0.02^\circ$  and a scanning rate of  $10^\circ \text{ min}^{-1}$ . Lattice parameters were acquired using Le Bail refinement, and crystallite sizes were calculated using Scherrer's equation. A VERTEX 70 Bruker Fourier Transform Infrared Raman Spectrophotometer, equipped with a 1064 nm laser operating at a light intensity of 70–220 mW, was used to acquire Raman spectra over 200 scans. A Carl Zeiss/AURIGA field emission scanning electron microscope and focused ion beam (FE-SEM and FIB), equipped with energy dispersive X-ray spectroscopy (EDS), were operated at an accelerating voltage of 3 and 10 kV to obtain FE-SEM images and EDS mapping spectra, respectively. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was performed using an Optima 8000 PerkinElmer ICP-OES spectrometer. A Talos F200X Thermo Fisher Scientific field-emission transmission electron microscope (FE-TEM) was utilized to obtain a high-resolution transmission electron microscope (HRTEM) image and selected area diffraction (SAED) patterns. The UV–visible diffuse reflectance (DRS) spectra were recorded in the 200–800 nm

range using a Cary 60 Agilent UV-visible spectrophotometer, with BaSO<sub>4</sub> serving as the reference standard. The N<sub>2</sub> adsorption-desorption analysis was performed using a Micromeritics ASAP 2420 porosimeter with N<sub>2</sub> as the adsorbent. The specific surface areas were determined using the BET method. The samples were degassed at a temperature of 150 °C for a duration of 3 h before analysis. X-ray photoelectron spectroscopy (XPS) data were recorded on a JEOL JPS-9010MC with an Al K<sub>α</sub> source (12 kV, 25 mA) and under a high vacuum pressure (10<sup>-7</sup> Pa). All binding energy values were referenced to adventitious graphitic carbon at 284.80 eV, with all XPS spectra deconvoluted using a Shirley background subtraction.

Transient absorption spectroscopy was conducted in diffuse reflection mode. A Nd:YAG laser (Litron Lasers, Stable Resonator Nano S 120–20) was used as the excitation source, generating 355 nm UV light from the third harmonic (≈240 μJ.cm<sup>-2</sup> per pulse, repetition rate of 0.7 Hz, ≈4–7 ns pulse width). A 100 W Bentham IL1 quartz halogen lamp was used to generate probe light. Long pass filters (Comar Instruments) were placed between the lamp and the sample to minimize short wavelength irradiation of the sample. Transient changes in diffuse reflectance from the sample were collected using a 2" diameter, 2" focal length lens and directed to a monochromator (Oriel Cornerstone 130). These changes were measured at wavelengths from 600 to 1100 nm, in 100 nm intervals. Time-resolved changes in diffuse reflectance from the microsecond to second timescale were collected using a Si photodiode (Hamamatsu S3071). Data for times faster than 3.6 ms were recorded using an oscilloscope (Tektronics DPO3012) after passing through an amplifier box (Cotronics), and data for times slower than 3.6 ms were recorded on a National Instruments DAQ card (NI USB-6251). Acquisitions were triggered by a photodiode (Thorlabs DET10A) from scattered laser light. Data were acquired and processed using home-built software written in Labview. Each kinetic trace was obtained from the average of between 100 and 200 laser pulses and measurements. Measurements were carried out in air. In standard experiments, a few milligrams of each powder sample were pressed between two microscope slides (VWR microscope slides 631–1552), held together at both ends using masking tape (Comply lead free steam indicator tape, Type 1), to make a pressed powder sample. For chemical scavenger experiments, a few microlitres of a chemical scavenger were placed on the surface of one side of the powder sample before being closed between the two microscope slides, with measurements carried out on the side of the sample where the scavenger was placed. Two chemical scavengers were studied, glycerol (Sigma-Aldrich, ≥99.0%) and an aqueous silver nitrate solution (Acros Chemicals, 99.99%, 20 mM), with both studied for the single probe wavelength of 800 nm for all samples.

## 2.4. Computational Method

To investigate the electronic band structure and density of states (DOS) of Ag<sub>0.5</sub>Bi<sub>2.5</sub>Nb<sub>2</sub>O<sub>9</sub>, first-principles computational calculations were performed using the projector augmented wave (PAW) method<sup>[23]</sup> in the Vienna ab initio simulation package (VASP).<sup>[24]</sup> The exchange-correlation energy was calculated using the Perdew-Burke-Ernzerh (PBE) functional within the generalized gradient approximation (GGA).<sup>[25]</sup> A plane wave basis set with a cut-off energy of 520 eV was used to expand the electronic wave functions for optimizing the crystal structures. Brillouin zone integration for all structures was carried out using a Monkhorst-Pack<sup>[26]</sup> mesh with a 7 × 7 × 1 grid in primitive cells. Convergence criteria for energy and force relaxation were set to 0.001 eV/atom and 0.01 eV/Å, respectively.

## 2.5. Photocatalytic Test

Rhodamine B was used as a model organic dye to evaluate the photocatalytic properties of the synthesized photocatalysts. In the standard procedure, 50 mg of the photocatalyst was added to a photocatalytic reactor containing 50 mL of a 10 ppm solution of Rhodamine B solution. The mixture was stirred in the dark for 30 min to allow adsorption-desorption equilibrium to be reached. The visible light source used in the experiment was a 300 W PLS-SXE300D/300DUV PerfectLight xenon lamp coupled with a filter (≥400 nm). The suspension was then exposed to light while maintaining a temperature of 25 °C with a cooling system. The suspension was taken at specific intervals, and the photocatalyst was separated from the dye solution by centrifugation. The Rhodamine B concentration was determined by applying the Beer-Lambert Law to the absorbance maximum seen at λ<sub>max</sub> = 554 nm using an extinction coefficient of 1.00 L.M<sup>-1</sup>.cm<sup>-1</sup> from spectra collected using a V-630 Jasco UV-Vis spectrophotometer.

To identify the active species involved, trapping experiments were conducted following the same procedure, with the addition of 1 mM of ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), 1 mL of isopropyl alcohol (IPA) and 1 mM of benzoquinone (BQ) to scavenge holes (h<sup>+</sup>), hydroxyl radicals (•OH) and superoxide anion radicals (O<sub>2</sub><sup>-</sup>), respectively.<sup>[27,28]</sup>

## 3. Results and Discussion

### 3.1. Material Characterizations

#### 3.1.1. Crystal Structures

Figure 1a illustrates that the XRD patterns of all samples produced herein can be indexed to the host phase of Na<sub>0.5</sub>Bi<sub>2.5</sub>Nb<sub>2</sub>O<sub>9</sub>, based on the standard database (PDF42-0397). This Aurivillius-type compound possesses orthorhombic symmetry with a space group of A2<sub>1</sub>am. While the peak positions of the XRD pattern of the ABNO sample agree well with the literature for Na<sub>0.5</sub>Bi<sub>2.5</sub>Nb<sub>2</sub>O<sub>9</sub>, the patterns of the Ag-doped samples, including AGBNO IE, AGBNO MIE, and AGBNO AIE, show a slight shift in diffraction peaks toward smaller angles, indicating larger lattice parameters and enhanced cell volume expansion (%) (Table 1). This observation is strongly indicative of the successful incorporation of Ag into Na<sub>0.5</sub>Bi<sub>2.5</sub>Nb<sub>2</sub>O<sub>9</sub>, due to the expected substitution of larger Ag<sup>+</sup> ions (r<sub>i</sub> = 1.15 Å) for Na<sup>+</sup> ions (r<sub>i</sub> = 1.02 Å) in the lattice, which confirms the successful preparation of a series of Ag<sub>x</sub>Na<sub>0.5-x</sub>Bi<sub>2.5</sub>Nb<sub>2</sub>O<sub>9</sub> materials. By using Scherrer's equation, the ABNO crystal had an approximate crystallite size of 20.21 nm, while the AGBNO samples had slightly smaller crystallite sizes (Table 1). Furthermore, preferred growth was seen in the (200)/(020) crystal planes in these AGBNO samples, similar to that of ABNO.<sup>[8,22,29]</sup>

The high-resolution TEM images revealed the d-spacing of the (200) crystal plane in all samples. This suggests the {001} exposed surface crystal planes, consistent with the orthorhombic crystal system and the crystal evolution mechanism. As shown in Figure 1b–e, the d-spacings of 0.274, 0.277, 0.276, and 0.272 nm correspond to the (200) plane of ABNO, AGBNO IE, AGBNO MIE, and AGBNO AIE, respectively. A slight expansion of d<sub>200</sub> was observed in AGBNO IE and AGBNO MIE, suggesting

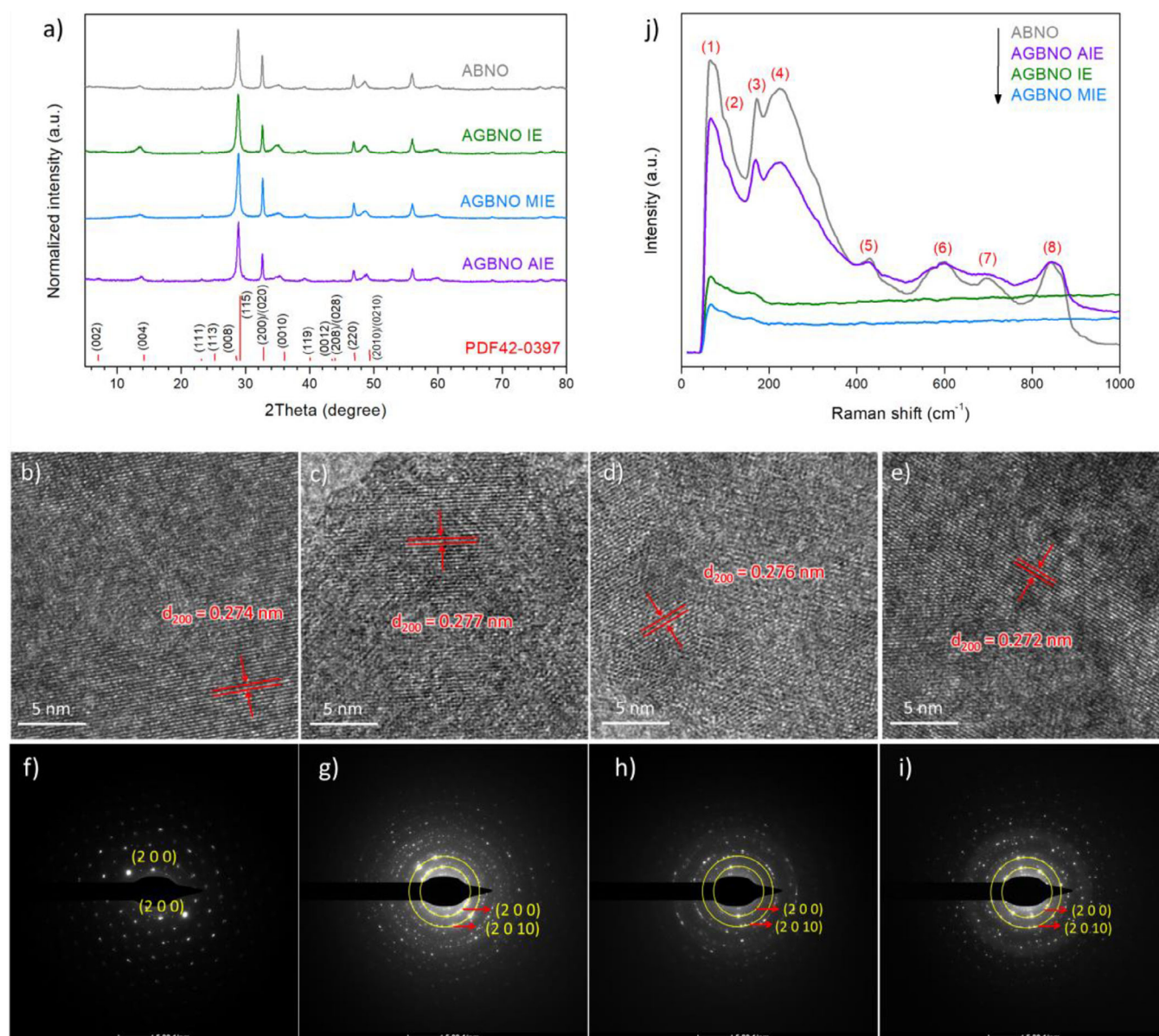


**Figure 1.** XRD patterns of all samples a). High resolution TEM images and selected area electron diffraction (SAED) patterns of ABNO b,f), AGBNO IE c,g), AGBNO MIE d,h) and AGBNO AIE e,i). Raman spectra of all samples j).

| Table 1. Unit cell parameters (including <i>a</i> , <i>b</i> , <i>c</i> and cell volumes), percent unit cell expansion relative to ABNO, crystallite size, surface area, and band gap energy of all samples produced herein. |                   |            |             |                                |              |                     |                                                          |              |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|------------|-------------|--------------------------------|--------------|---------------------|----------------------------------------------------------|--------------|
| Sample                                                                                                                                                                                                                       | Cell parameters/Å |            |             | Cell volume (V)/Å <sup>3</sup> | %V expansion | Crystallite size/nm | <i>S</i> <sub>BET</sub> /m <sup>2</sup> ·g <sup>−1</sup> | Band gap /eV |
|                                                                                                                                                                                                                              | <i>a</i>          | <i>b</i>   | <i>c</i>    |                                |              |                     |                                                          |              |
| ABNO                                                                                                                                                                                                                         | 5.4683(7)         | 5.4716(11) | 25.4773(25) | 762.29(14)                     | –            | 20.21               | 18.36                                                    | 3.1          |
| AGBNO IE                                                                                                                                                                                                                     | 5.4785(7)         | 5.4874(11) | 25.5876(25) | 769.60(14)                     | 0.91         | 19.23               | 11.43                                                    | 3.0          |
| AGBNO MIE                                                                                                                                                                                                                    | 5.4815(7)         | 5.4845(11) | 25.5331(25) | 767.62(14)                     | 0.70         | 19.79               | 22.56                                                    | 3.1          |
| AGBNO AIE                                                                                                                                                                                                                    | 5.4782(7)         | 5.4911(11) | 25.4727(25) | 766.68(14)                     | 0.58         | 18.83               | 24.68                                                    | 3.2          |

a significant amount of  $\text{Ag}^+$  was incorporated into the lattice of  $\text{Ag}_x\text{Na}_{0.5-x}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ . Their selected area electron diffraction (SAED) patterns (Figure 1f–i) further confirmed the crystalline nature of the samples, where ABNO formed single crystals and AGBNO (i.e., AGBNO IE, AGBNO MIE, AGBNO AIE) formed polycrystals.

Raman spectra (Figure 1j) further revealed details on the lattice structures. While ABNO exhibits all Raman bands consistent with the vibrational modes of  $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ ,<sup>[30,31]</sup> the introduction of  $\text{Ag}^+$  altered the lattice. No enhanced intensities were observed, confirming the successful incorporation of  $\text{Ag}^+$  rather than Ag metal, which typically induces surface plasmon resonance and leads to surface-enhanced Raman scattering.<sup>[32]</sup> The Raman spectrum of AGBNO AIE was similar to that of ABNO, but a substantial reduction in peak intensities across all bands was observed in AGBNO IE and AGBNO MIE. The bands (1), (2) and (4), associated with  $\text{Bi}^{3+}$  vibrations in the  $(\text{Bi}_2\text{O}_2)^{2+}$  layer, showed reduced intensities in AGBNO AIE and were dramatically suppressed in AGBNO IE and AGBNO MIE. Band (5), related to  $\text{Bi}^{3+}$ –O vibrations at the A-site, remained, while  $\text{Nb}^{5+}$ –O stretching bands (3), (6) and (8) exhibited variations in AGBNO AIE. Additionally, band (7) was attributed to lattice distortion or stress. The bands (3), (5), (6) and (7) disappeared entirely in AGBNO IE and AGBNO MIE. These observations suggest that the presence of  $\text{Ag}^+$  and its contents in the structure suppresses certain vibration modes.

### 3.1.2. Chemical Composition

The elemental composition of all samples was determined by XPS and EDS. XPS survey spectra showed that all expected elements were present, with no indication of any impurities (Figure S1). The oxidation states of the constituent elements were investigated through high-resolution XPS spectra of core-level orbitals, as shown in Figure 2, with the binding energies reported in Table S1. The deconvoluted peaks obtained from the Bi 4f XPS spectra (Figure 2a) of ABNO were 163.85 and 158.55 eV for Bi 4f<sub>5/2</sub> and Bi 4f<sub>7/2</sub>, respectively, corresponding to  $\text{Bi}^{3+}$  species.<sup>[8,33]</sup> When  $\text{Ag}^+$  was incorporated into the structure, these fitted peaks of AGBNO IE, AGBNO MIE, and AGBNO AIE slightly shifted to higher binding energies. This effect was also observed in the Nb 3d region (Figure 2b), with the oxidation state assigned to  $\text{Nb}^{5+}$ .<sup>[8,22]</sup> The oxidation states of  $\text{Ag}^+$  and  $\text{Na}^+$  were confirmed by the Ag 3d and Na 1s core-level XPS spectra, respectively (Figure 2c).<sup>[8,22,34]</sup>  $\text{Ag}^+$  was detected in AGBNO IE and AGBNO MIE; however, a very weak signal was found in AGBNO AIE. Further ICP-OES analysis of this sample revealed low levels of Ag, corresponding to the molar ratio of  $\text{Ag}:\text{Na}:\text{Bi}:\text{Nb}$  for 0.03:0.10:1.36:2. Details of O bonding in the crystal structure were clarified through O 1s XPS spectra (Figure 2d). In all samples, three types of O bonding associated with different chemical species were detected:  $\text{O}_\text{l}$  represents lattice oxygen,  $\text{O}_\text{II}$  corresponds to oxygen bonded to carbon and  $\text{O}_\text{III}$  indicates organic oxygens.<sup>[35]</sup> The binding energies of  $\text{O}_\text{II}$  and  $\text{O}_\text{III}$  were similar in all samples, however, the  $\text{O}_\text{l}$  peaks, as well as Bi 4f and Nb 3d peaks in AGBNO samples, were significantly higher in energy than those seen in ABNO and attributed to the effect

of higher electron densities in  $\text{Ag}^+$ , i.e., Fermi level shifts toward the conduction band.

The elemental constituents were further verified through the EDS technique. Figure 3a–d illustrates EDS mappings of all elemental compositions. The results showed that all samples contained Na, Bi, Nb, and O, while the AGBNO samples additionally included Ag. Elemental mapping shows that all elements are consistently distributed across all samples, indicating the formation of homogeneous compounds. The chemical composition of all samples can be described using the molar ratios of  $\text{Na}:\text{Bi}:\text{Nb}$  as 1.23:3.16:2 for ABNO and  $\text{Ag}:\text{Na}:\text{Bi}:\text{Nb}$  as 0.33:0.18:3.20:2, 0.38:0.18:3.19:2, and 0.07:0.16:2.76:2 for AGBNO IE, AGBNO MIE and AGBNO AIE, respectively. These ratios correspond to the general formula of the synthesized compounds.

### 3.1.3. Physical Properties

The morphologies of all synthesized samples are illustrated in SEM images (Figure 4). Under hydrothermal conditions, this layered compound preferentially grows with a sheet-like morphology.<sup>[8,22,36]</sup> Accordingly, ABNO particles formed nanosheets, as shown in Figure 4a. After  $\text{Ag}^+$  ion exchange, the nanosheet structures were preserved in AGBNO IE (Figure 4b). However, with the use of microwave irradiation (AGBNO MIE), the nanosheet structures broke into smaller nanosheets and agglomerated to form larger particles (Figure 4c). Similarly, the use of a weak acid solution (AGBNO AIE) resulted in thinner nanoplates with very small pores distributed across the particles (Figure 4d). All synthesized samples were characterized as non-porous or mesoporous materials with weak interactions between the adsorbent and adsorbate, as determined by  $\text{N}_2$  adsorption-desorption isotherms (Figure S2). The BET specific surface areas of all samples are reported in Table 1. Under various ion exchange conditions, the resulting BET surface area differed from the original compound, ABNO ( $18.36 \text{ m}^2 \text{ g}^{-1}$ ). A conventional ion exchange method produced a lower BET surface area of  $11.43 \text{ m}^2 \text{ g}^{-1}$  (AGBNO IE). In contrast, modified ion exchange conditions increased the specific surface area by 1.2 times ( $22.56 \text{ m}^2 \text{ g}^{-1}$ ) and 1.3 times ( $24.68 \text{ m}^2 \text{ g}^{-1}$ ) for AGBNO MIE and AGBNO AIE, respectively. This enhancement in surface area can be attributed to an increase in the fraction of larger pores (see the insets in Figure S2).

### 3.1.4. Optical Properties and Electronic Band Structure

Optical band gap energies were determined using the Kubelka-Munk (K-M) function, described by the equation:  $F(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$ , where  $R$  is the percent reflectance obtained from diffused reflectance spectroscopy (DRS) and  $R_\infty$  represents  $R_{\text{sample}}/R_{\text{standard}}$ . The Tauc plot, derived from the K-M function, is expressed as  $[F(R_\infty)h\nu]^n = \alpha(h\nu - E_g)$ , where  $\alpha$  is the absorption coefficient,  $h$  is Planck's constant,  $\nu$  is the photon frequency,  $E_g$  is the band gap energy and  $n$  is a coefficient indicating the type of electronic transition ( $n = 1/2$  for indirect transitions and  $n = 2$  for direct transitions). Figure 5a shows the Tauc plots of all samples, obtained from DRS spectra (Figure 5b), along with their corresponding band gap energies (inset). The

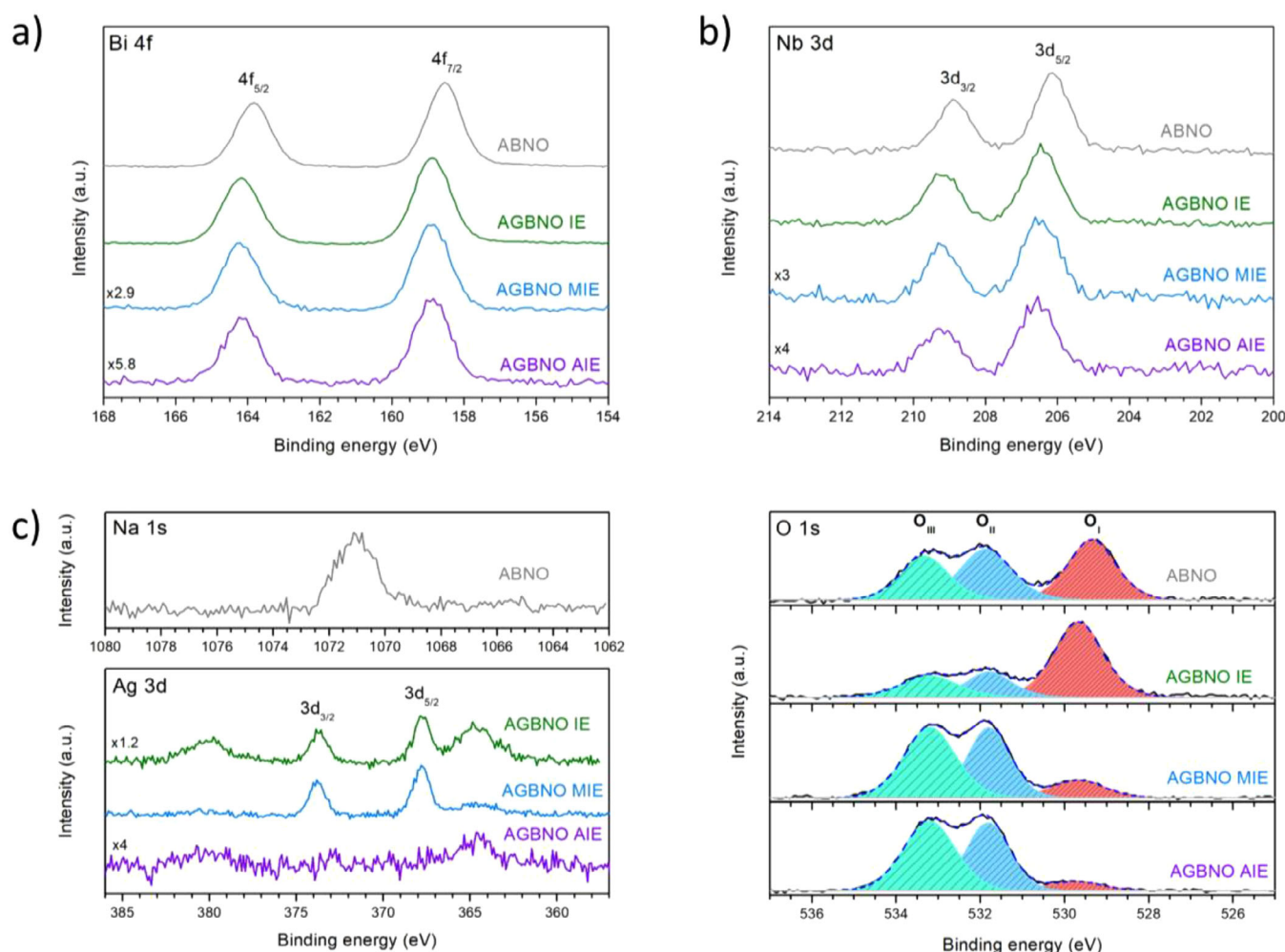


**Figure 2.** XPS core-level spectra of all samples, including Bi 4f a), Nb 3d b), Na 1 s/Ag 3d c) and O 1 s d).

band gap of ABNO was consistent with previous reports.<sup>[8,22]</sup> The band gaps of the Ag-containing compounds produced herein were similar to that of ABNO, despite their different colors, as shown in the inset figure. The dark grey color observed in AGBNO IE and AGBNO MIE could be attributed to the presence of a hump feature observed at lower photon energies before the main absorption edge, indicating sub-level or defect states caused by the contribution of Ag orbitals.

To understand the role of  $\text{Ag}^+$  incorporation into  $\text{Ag}_x\text{Na}_{2.5-x}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  on the electronic properties, the calculated electronic band structure of  $\text{Ag}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  was investigated. The structural model of  $\text{Ag}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  (Figure 5c) was obtained with the fully relaxed lattice parameters:  $a = 5.657 \text{ \AA}$ ,  $b = 5.577 \text{ \AA}$ ,  $c = 25.380 \text{ \AA}$ , and  $V = 800.701 \text{ \AA}^3$ . The calculated band structure and density of states (DOS) of  $\text{Ag}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  are shown in Figure 5d. The valence band maximum (VBM) was primarily derived from the combination of O  $p$ -orbitals and Ag  $d$ -orbitals, spanning from 0 to  $-1 \text{ eV}$ . The conduction band minimum (CBM) mainly consists of O  $p$ -orbitals and Nb  $d$ -orbitals. The overall valence band is dominated by O  $p$ -orbitals, spanning the energy range from 0 to  $-6 \text{ eV}$ , while the conduction band is dominated by Nb  $d$ -orbitals,

spanning from 2 to 6 eV. The obtained indirect band gap of 2.017 eV indicated semiconductor behavior. In comparison, the analogous parent compound of  $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  showed an indirect band gap of 2.497 eV,<sup>[22]</sup> where the smaller band gap seen in  $\text{Ag}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ , where all of  $\text{Na}^+$  was replaced by  $\text{Ag}^+$ , was a result of the hybridization of Ag  $d$ -orbitals with O  $p$ -orbitals in the VBM.<sup>[35]</sup> In the case of partial  $\text{Ag}^+$  substitution, sub-bandgap states associated with Ag orbitals might introduce localized energy levels, leading to additional absorption features.

### 3.2. Charge Carrier Dynamics

TAS was used to investigate the charge carrier behavior in all samples, as it is a powerful technique for monitoring non-radiative recombination, which is more dominant in oxide perovskites.<sup>[37,38]</sup> A photograph of our purpose-built transient absorption spectroscopy setup is shown in Figure S3. First, experiments conducted in air and in the absence of any chemical scavengers will be discussed to analyze the intrinsic lifetime of photogenerated charge carriers in these materials. And secondly,

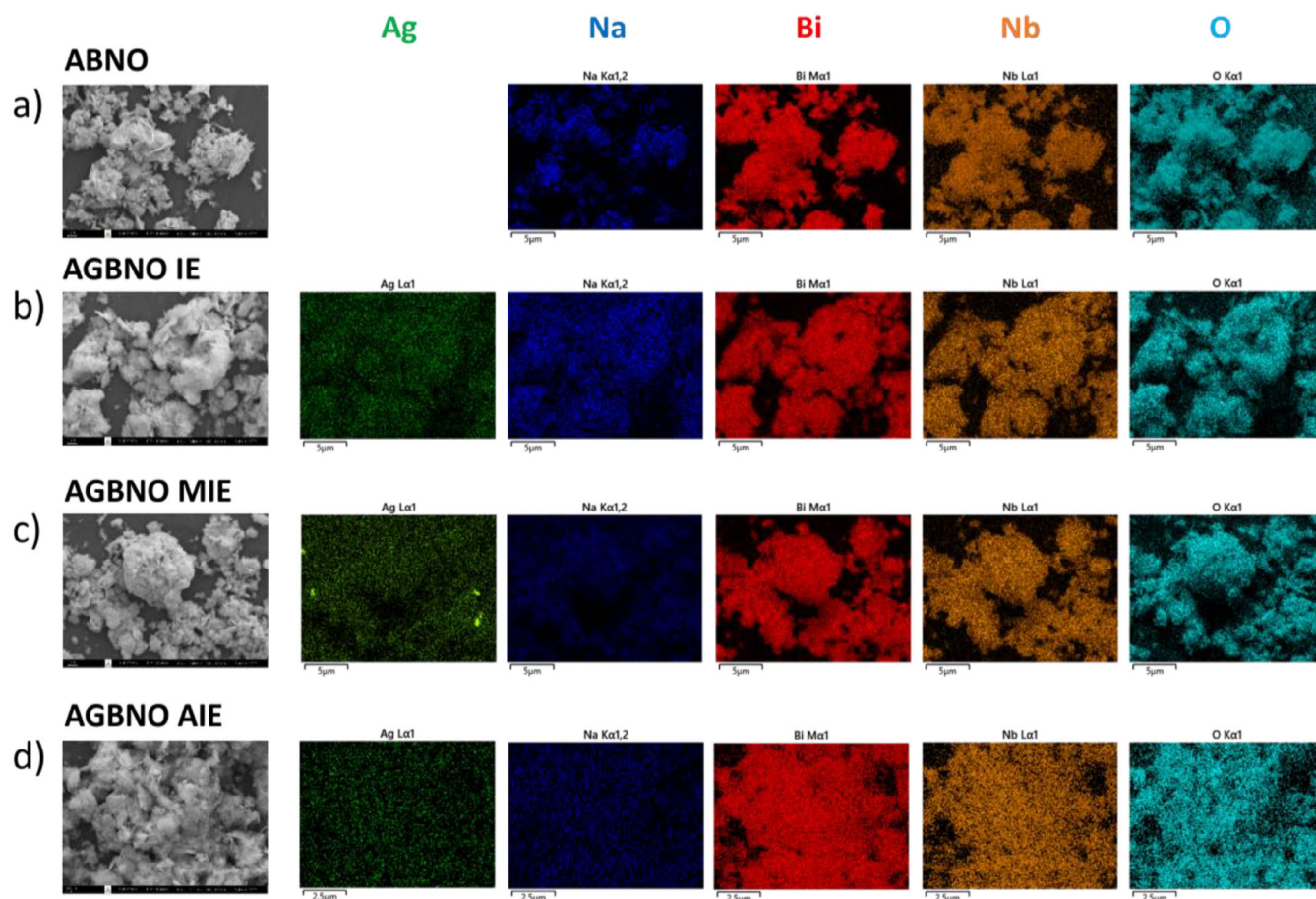


Figure 3. Energy dispersive X-ray Spectroscopy (EDS) elemental maps of ABNO a), AGBNO IE b), AGBNO MIE c) and AGBNO AIE d).

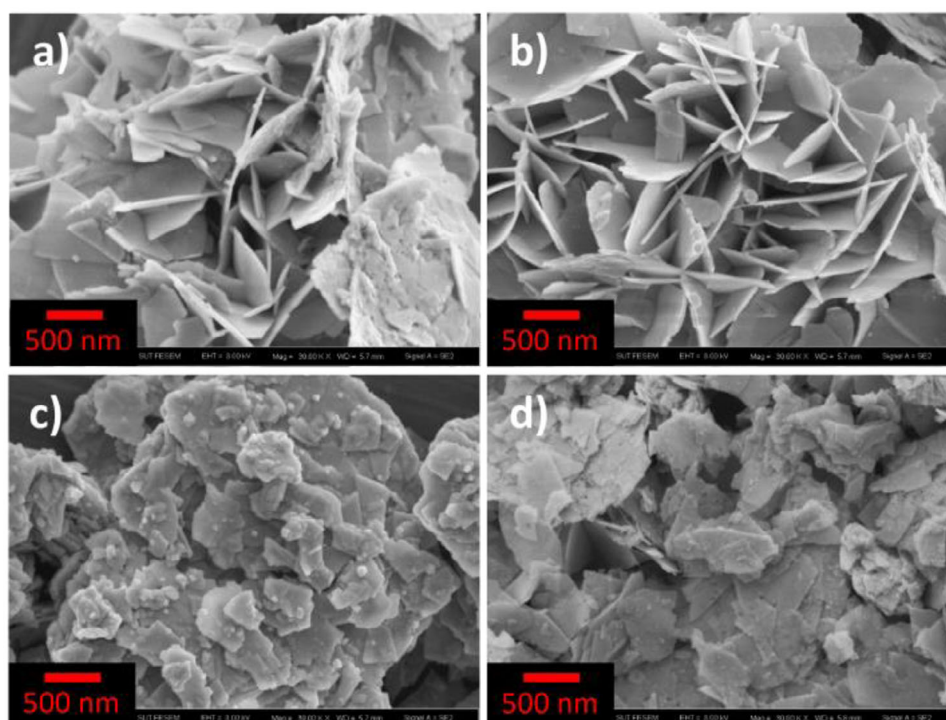


Figure 4. Scanning electron microscopy (SEM) images of ABNO a), AGBNO IE b), AGBNO MIE c) and AGBNO AIE d).

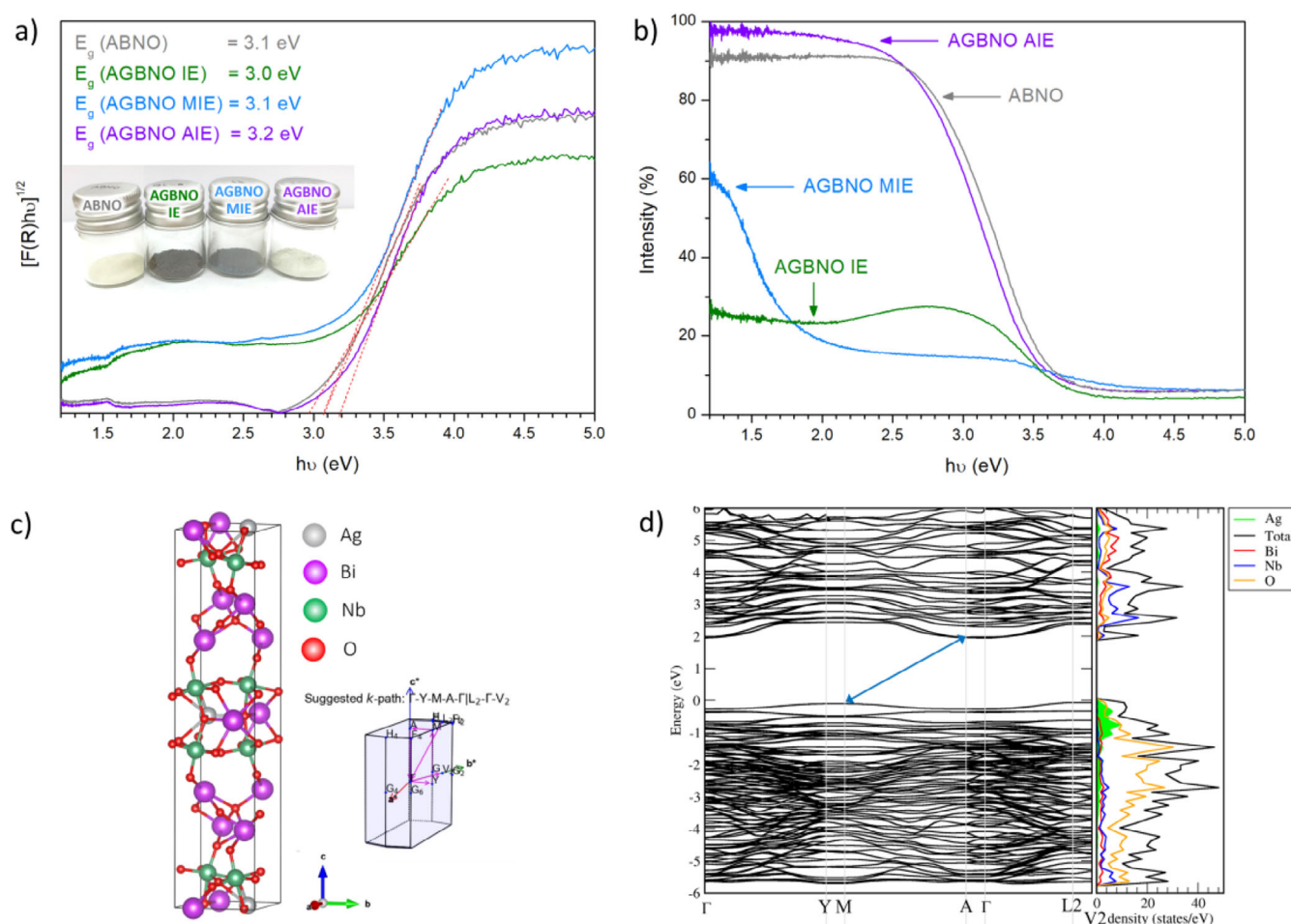


**Figure 5.** Tauc plots derived from the Kubelka-Munk function (a) and the corresponding band gap energies with photographs of all samples (inset). The structural model and reciprocal lattice of  $\text{Ag}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  (b) and the corresponding calculated DFT electronic band structure and density of states (DOS) (c).

from experiments conducted in air in the presence of either an electron (aqueous silver nitrate solution) or hole (glycerol) scavenger will be discussed to examine the reactivity of the charges formed.

### 3.2.1. Intrinsic Transient Absorption Spectra

The transient absorption spectra for each of the samples are shown in Figure S4. The transient absorption spectra for all samples are compared in Figure 6. At 10 ms after the laser pulse, shown in Figure 6a, broad photoinduced absorption spectra across the visible range are seen for the ABNO and AGBNO AIE samples. The strongest photoinduced absorption was seen in the ABNO sample, followed by AGBNO AIE. The AGBNO IE and AGBNO MIE samples showed different behavior, with both showing a strong ground state bleach signal seen at 600 nm at early timescales (up to  $\approx 100$   $\mu\text{s}$ ), and much weaker photoinduced absorption from 700 to 1100 nm. This difference was attributed to their significantly different optoelectronic properties, with both AGBNO IE and AGBNO MIE samples appearing grey in color and showing broad absorption across the visible spectrum, whereas

the AGBNO AIE and ABNO samples were distinctly white in color and did not possess such broadband absorption. However, by the 1 ms timescale, the ground state bleach signals seen at 600 nm in both AGBNO IE and AGBNO MIE samples had decayed, and broad photoinduced absorption was seen across the visible, as shown in Figure 6b. The photoinduced absorption and thus the population of charge carriers in these AGBNO IE and AGBNO MIE samples were comparatively lower than ABNO and AGBNO AIE samples. Of the series of samples, AGBNO MIE appeared to show the most distinctly different transient absorption behavior, with a normalised plot of the transient absorption spectrum at 1 ms being more broadband than the other samples, as shown in Figure 6c. With regards to ABNO, changes in the transient absorption spectrum with time indicated that the population and energy of charge carriers change with time. Increased absorption in the higher energy (i.e., blue region) at later times may represent an increase in the population of more deeply trapped charge carriers. This indicates that charge carriers likely recombine through a trapping-detrapping hopping mechanism<sup>[39]</sup> in ABNO, with similar behavior seen in AGBNO AIE.

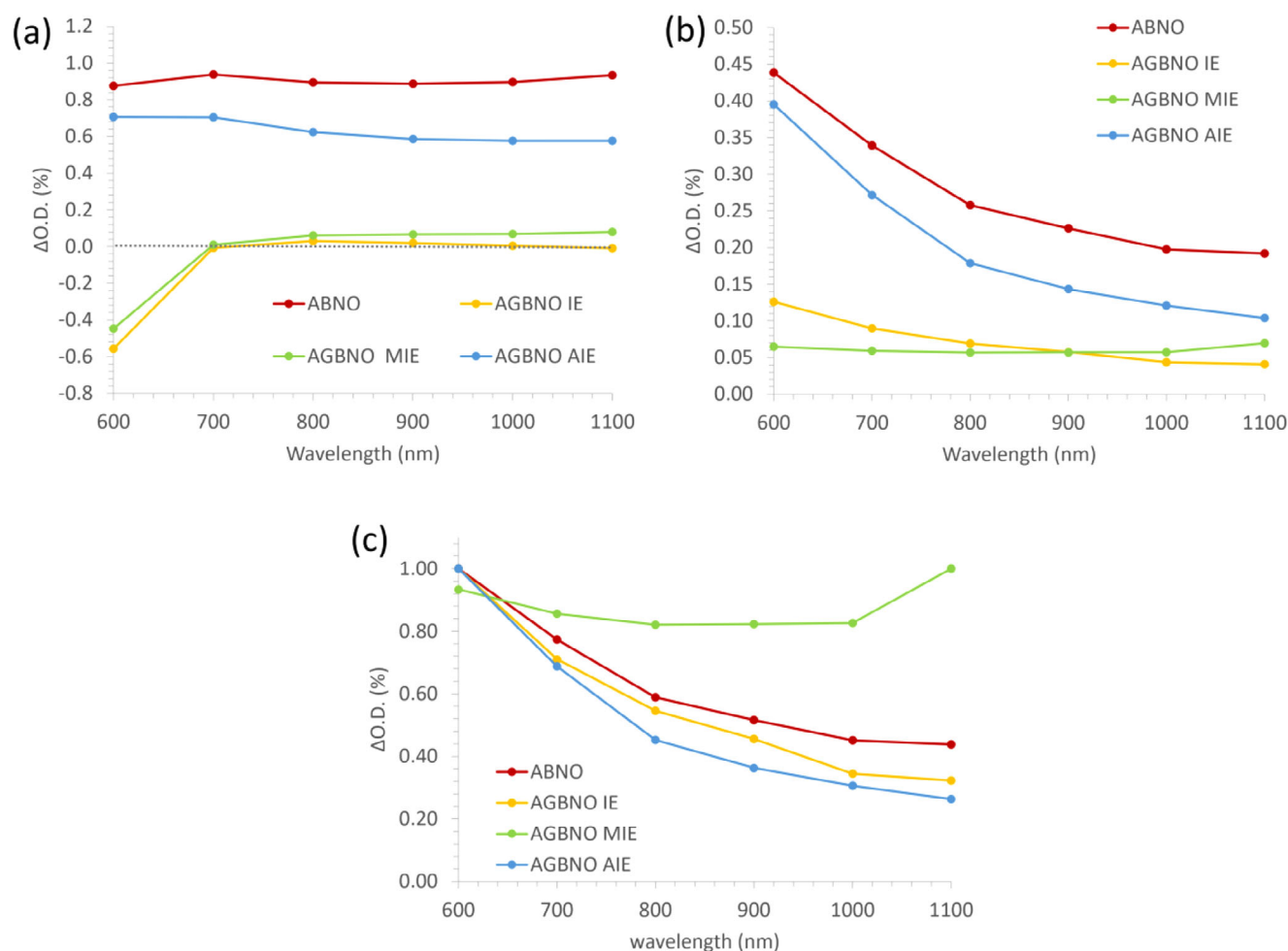


**Figure 6.** Comparisons of the transient absorption spectra in air of all samples at 10  $\mu$ s (non-normalised) a), 1 ms (non-normalised) b), and 1 ms (normalised) after the laser pulse c). Samples were measured at probe wavelengths of 600 to 1100 nm in 100 nm intervals using a 355 nm laser pulse excitation (6 ns pulse width, 0.67 Hz,  $\approx 240 \mu\text{J}\cdot\text{cm}^{-2}$  per pulse).

### 3.2.2. Intrinsic Charge Carrier Kinetics

The transient absorption kinetics of ABNO and the series of AGBNO samples are shown in Figure S5. The intrinsic charge carrier kinetics of these samples at the probe wavelength of 800 nm are shown in Figure 7. Non-normalised data shown in Figure 7a shows that ABNO possessed the highest degree of transient absorption at 10  $\mu$ s after the laser pulse ( $\approx 0.89 \Delta\text{O.D.}\%$ ), and therefore, likely possesses the largest population of charge carriers at this timescale. This was followed by AGBNO AIE (22480.62  $\Delta\text{O.D.}\%$ ), AGBNO MIE ( $\approx 0.06 \Delta\text{O.D.}\%$ ), and then AGBNO IE ( $\approx 0.03 \Delta\text{O.D.}\%$ ). A normalised plot of this data from 10  $\mu$ s after the laser pulse, shown in Figure 7b revealed distinctly differing charge carrier dynamics across the sample series. In the ABNO and AGBNO AIE samples, the dynamics could be described using a power-law model, where ideal bimolecular electron-hole recombination is disrupted by a multiple trapping process, in which a carrier is repeatedly thermally excited to the band edge to move and ultimately recombine.<sup>[40]</sup> However, in the AGBNO IE and AGBNO MIE samples, a slow rise in population was seen until

the  $\approx 100 \mu$ s timescale, which then subsequently decayed with behavior that could be described using a stretched exponential model.<sup>[41]</sup> The time taken for half the population of charges to decay from the start of the measurement at 10  $\mu$ s is termed  $t_{50\%}$ . The  $t_{50\%}$  was shortest in the AGBNO AIE sample ( $\approx 150 \mu$ s), followed by ABNO ( $\approx 180 \mu$ s), AGBNO MIE ( $\approx 0.1$  s) and AGBNO IE ( $> 1$  s).

### 3.2.3. The Effect of Chemical Scavengers on Charge Carrier Dynamics

The effect of commonly used hole (alcohol, i.e., glycerol) and electron (aqueous silver nitrate solution) scavengers on the charge carrier dynamics of ABNO and the series of Ag-doped samples was investigated at the probe wavelength of 800 nm (Figure 7c,d). All samples showed some degree of change in the presence of both glycerol hole and silver nitrate electron scavengers, with the changes most pronounced at longer timescales from 22481 ms (Figure S6). The time of 1 ms was chosen as this is the timescale at which charge carriers

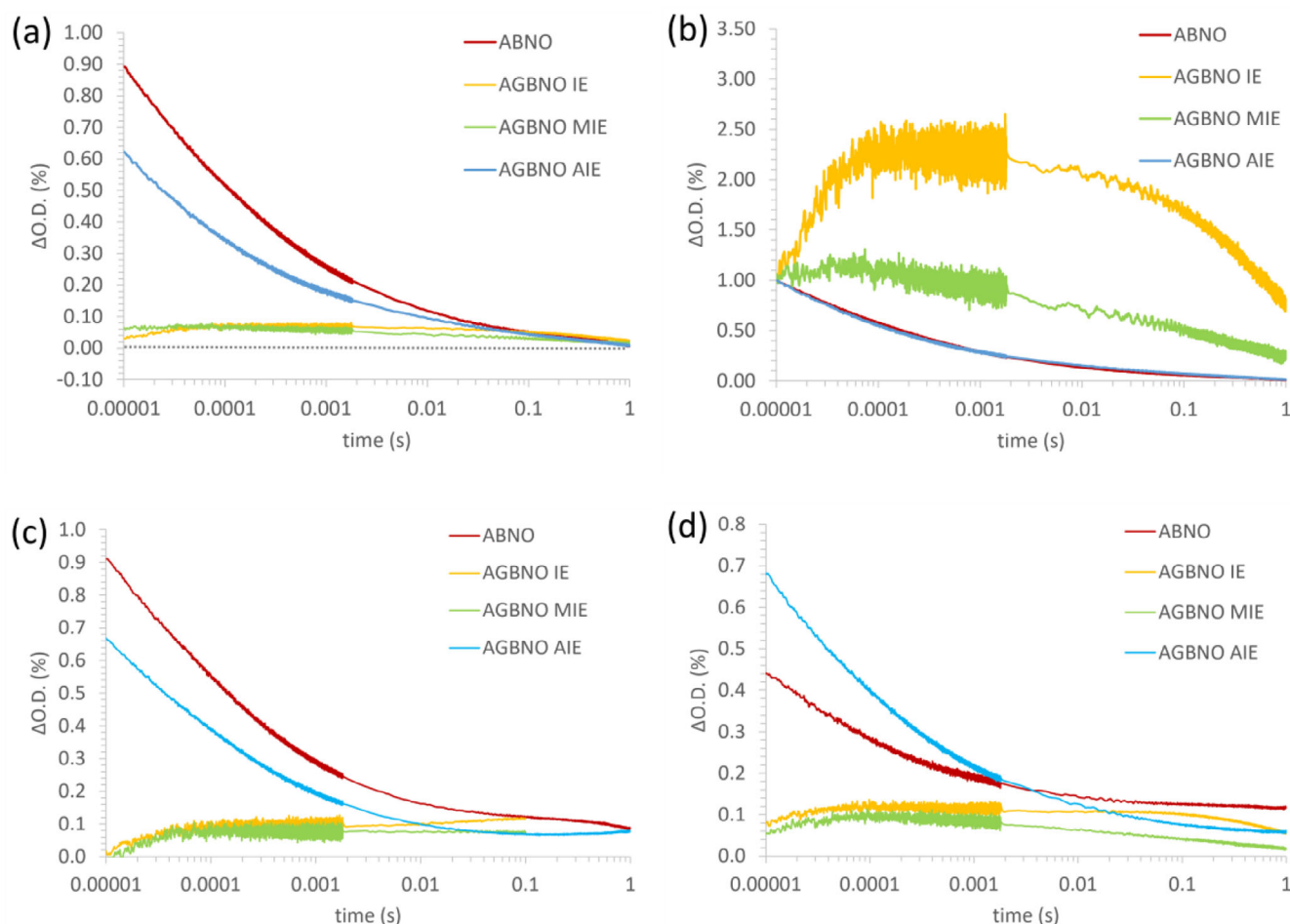


**Figure 7.** Transient absorption decay kinetics of all samples, for non-normalised data a) and data normalised to 1 at 10  $\mu$ s after the laser pulse b), in the presence of a glycerol hole scavenger c) and in the presence of a silver nitrate electron scavenger d). All measurements were carried out at a probe wavelength of 800 nm from the time of 10  $\mu$ s to 1 s after a 355 nm laser pulse pump excitation ( $2248725 \mu\text{J}\cdot\text{cm}^{-2}$  per pulse, repetition rate of 0.7 Hz, 22484–7 ns pulse width).

are typically drive to photocatalytic processes, such as water splitting and radical formation reactions (e.g., superoxide and hydroxyl radicals). Nevertheless, the samples that showed the highest overall degree of transient absorption in air and long-lived charges in both electron and hole scavengers were the ABNO and AGBNO AIE samples.

### 3.3. Photocatalytic Properties

To evaluate the catalytic efficiency of the synthesized materials, Rhodamine B was used as a model pollutant. Figure 8a shows the changes of Rhodamine B concentration ( $C$ ) over time, normalized to its initial concentration ( $C_0$ ), represented as  $C/C_0$ , under both dark absorption and light exposure. The  $C/C_0$  of the blank solution remained unchanged under visible light for 2 h. By using the synthesized materials alone, ABNO can degrade  $\approx 10\%$  of Rhodamine B. Notably, the ABNO prepared in this work was obtained via a different preparation method compared to the previously reported sample.<sup>[8]</sup>

The photocatalytic degradation of ABNO improved with the introduction of  $\text{Ag}^+$  into the structure. Among the samples, AGBNO AIE achieved the highest efficiency, with 96% degradation of Rhodamine B over the 120-min period. AGBNO IE and AGBNO MIE exhibited similar photocatalytic properties, with degradation rates of 39% and 30%, respectively. A pseudo first-order kinetic model was applied to determine reaction kinetics using the equation:  $\ln(C/C_0) = -k_{\text{app}}t$ . The reaction kinetic plots are shown in Figure S7. The apparent kinetic constants ( $k_{\text{app}}$ ) of all catalysts (Figure 8b) followed the same trend as their percentage degradations, with AGBNO AIE showing the highest  $k_{\text{app}}$  value of  $4.01 \times 10^{-2} \text{ min}^{-1}$ , confirming its superior catalytic activity. This demonstrates that our catalyst exhibited superior performance compared to other Aurivillius-phase perovskites that degrade Rhodamine B, including  $\text{PbBi}_2\text{Nb}_2\text{O}_9$  ( $0.0118$ ,<sup>[42]</sup>  $0.000913$  and  $0.0097 \text{ min}^{-1}$ ),<sup>[43]</sup>  $\text{Na}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  ( $0.0248 \text{ min}^{-1}$ ),<sup>[9]</sup>  $\text{Li}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  ( $0.0025 \text{ min}^{-1}$ )<sup>[9]</sup> and  $\text{K}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  ( $0.0052 \text{ min}^{-1}$ ).<sup>[9]</sup> The best photocatalyst, AGBNO AIE, demonstrated excellent stability over four cycles of photocatalytic testing (Figure 8c), which was further confirmed by additional physical characterizations

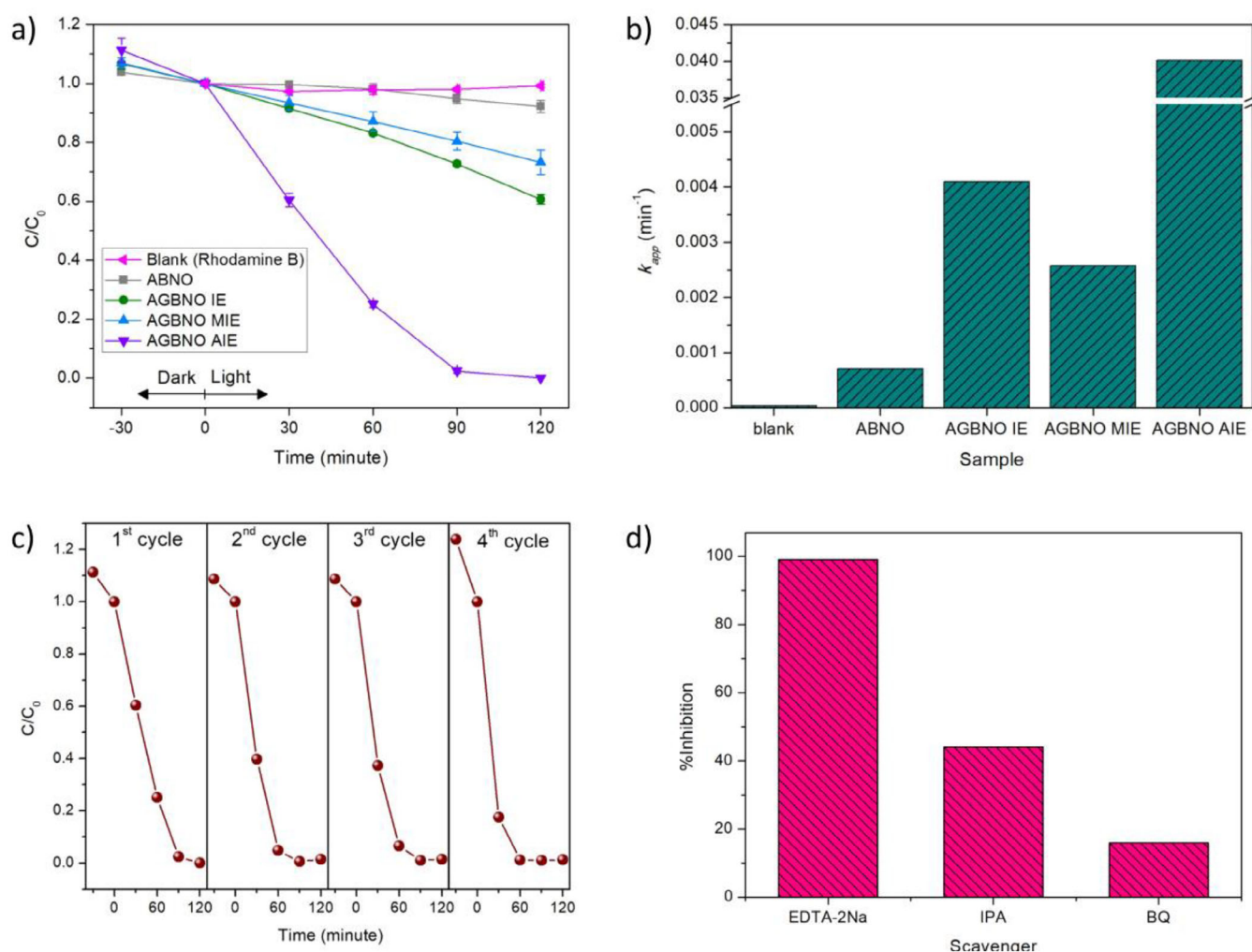


**Figure 8.** Photocatalytic degradation efficiency of Rhodamine B under visible light irradiation for all samples and the blank (Rhodamine B solution) a), apparent kinetic constants b), recycling test c) and trapping experiments d) for AGBNO AIE.

(Figure S8). The crystal structure was maintained, as indicated by the consistent XRD pattern (Figure S8a). Although the nanosheet-like particles agglomerated (SEM image, Figure S8b), the chemical composition remained uniformly distributed across the sample (EDS maps, Figure S8c), corresponding to the fresh sample with a composition of  $Ag_{0.03}Na_{0.10}Bi_{1.36}Nb_2$  (EDS spectra, Figure S8d). To evaluate their broader potential for wastewater treatment, we also tested their photocatalytic performance on other pollutants, including methyl orange (an anionic dye) and tetracycline (an antibiotic). Our photocatalyst was unable to degrade methyl orange and did not enhance tetracycline degradation compared to ABNO. It achieved 49% degradation of 40 ppm tetracycline in 30 min, whereas ABNO achieved 60% degradation under the same conditions. As shown by the percentage of inhibition in Figure 8d, the main active species was the hole carrier, as the addition of the hole scavenger, EDTA-2Na, effectively inhibited Rhodamine B degradation. Hydroxyl radicals and superoxide anion radicals were minor active species produced in the photocatalytic reaction, as indicated by the

lower percentage of inhibition in the presence of isopropanol (IPA) and benzoquinone (BQ).

The superior photocatalytic performance in AGBNO samples could be explained by the effect of  $Ag^+$ . When it is substituted at the  $Na^+$  site, the local electronic environment at the A-site is altered due to its higher electronegativity compared to  $Na^+$ . As a result, this may lead to a redistribution of electron density within the lattice. Moreover,  $Ag^+$ , with a larger ionic size and more loosely bound d-electrons compared to  $Na^+$ , could induce greater polarization of the surrounding lattice. This might help generate a significantly stronger internal electric field, leading to enhanced charge separation.<sup>[44–46]</sup> Comparing ABNO and AGBNO IE, although ABNO indeed has a higher BET surface area, it has much less persistent charge carriers than AGBNO IE, which overall results in lower photocatalytic activity in ABNO compared with AGBNO, i.e., the surface area of a catalyst and the charge carrier dynamics are two distinct properties.<sup>[47]</sup> For a photocatalytic reaction to be promoted, a higher surface area can be an enabler, generally increasing the number of active

sites and increasing the probability that charge carriers can reach them. However, that is equally important is the population of charge carriers formed that persist until the photocatalytic reaction can occur.<sup>[48]</sup>

Differences among the Ag-doped samples prepared using different procedures can be attributed to their different physical properties. AGBNO AIE, with its thin and porous nanosheet morphology, yielded the highest photocatalytic performance because these characteristics provided a shorter distance for charge carrier migration to the surface where photocatalysis can occur. Thicker and nonporous nanosheets observed in AGBNO IE make charge carrier migration to an active site more difficult, resulting in lower photocatalytic activity. Where the sheets were thickest and most agglomerated, as seen in AGBNO MIE, the worst photocatalytic activity was exhibited. The BET surface area is a proxy for the number of active sites on the catalyst's surface. Despite AGBNO MIE having a relatively high surface area, its photocatalytic activity was the lowest among the three samples, which is likely due to unsuitable particle morphology and the weakest charge carrier dynamics. Notably, the  $S_{\text{BET}}$  value is highest for AGBNO AIE, aligning with its superior photocatalytic activity.

The TAS results highlight three key factors influencing the photocatalytic activity trend (AGBNO AIE > AGBNO IE > AGBNO MIE): (i) charge carrier population and lifetime, (ii) recombination mechanism, and (iii) interaction with scavengers. First, with regard to charge carrier population and lifetime: AGBNO AIE maintains the optimal balance, with a high charge carrier population ( $\Delta\text{O.D.}\%$  at 10  $\mu\text{s}$ ) and an optimal  $t_{50\%}$  (2248150  $\mu\text{s}$ ) — long enough for charge transfer but short enough to minimize recombination. In contrast, AGBNO IE has the lowest charge carrier population ( $\Delta\text{O.D.}\%$  at 10  $\mu\text{s}$ ) but the longest lifetime (>1 s), suggesting that carriers are more deeply trapped, limiting mobility. Second, is the recombination mechanism: the mode of charge carrier movement in AGBNO AIE is more favorable for photocatalysis than that in AGBNO IE and AGBNO MIE. It follows a trapping-detrappping hopping mechanism, allowing thermal excitation of photogenerated electrons back into the band-edge for their migration and participation in photocatalytic reactions at the surface. In contrast, AGBNO IE and AGBNO MIE follow a stretched exponential recombination model, where charge carriers are likely more deeply trapped, reducing their mobility and potential energy to drive photocatalytic reactions. Third, is the interaction with scavengers: AGBNO AIE has the most readily available charge carriers for photocatalytic reactions. It shows the strongest response to electron ( $\text{AgNO}_3$ ) and hole (glycerol) scavengers, indicating high charge transfer efficiency. AGBNO IE and AGBNO MIE exhibit weaker scavenger responses, suggesting that their charge carriers are more localized in states that hinder efficient transfer to the catalyst surface. Overall, these three aspects in regard to the charge carrier dynamics can be used to collectively explain why AGBNO AIE outperforms AGBNO IE and AGBNO MIE in our photocatalytic reaction.

Based on these physical properties, the findings suggest that morphology and charge carrier dynamics are the major factors influencing the photocatalytic activity of  $\text{Ag}^+$ -doped samples prepared using different procedures.

## 4. Conclusion

A series of new Aurivillius-phase  $\text{Ag}_x\text{Na}_{0.5-x}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  compounds was successfully synthesized using a hydrothermal method followed by ion exchange procedures. XRD patterns confirmed the formation of a single phase Aurivillius-phase in all samples, similar to the parent  $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  structure. The incorporation of  $\text{Ag}^+$  into the crystal structure was validated by Le Bail refinement, revealing expanded lattice parameters due to substitution of  $\text{Na}^+$  by larger  $\text{Ag}^+$  ions. Raman results further confirmed the incorporation of  $\text{Ag}^+$  into the lattice with doping levels inferred from the reduction in peak intensities. The presence of  $\text{Ag}^+$  along with Na, Bi, Nb, and O, was confirmed by TEM, EDS, XPS, and ICP-OES analyses. Oxidation states were identified by deconvolution of core-level XPS spectra, indicating the presence of  $\text{Ag}^+$ ,  $\text{Na}^+$ ,  $\text{Bi}^{5+}$  and  $\text{Nb}^{5+}$  states. DFT electronic band structure calculations showed significant contributions of Ag *d* states to the VBM. However, the bandgap energies of all  $\text{Ag}^+$ -doped samples remained comparable to that of  $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ .

The improved photocatalytic activity for the degradation of Rhodamine B was evident upon  $\text{Ag}^+$  doping. Depending on the ion exchange procedures, photocatalytic performance varied based on the ion exchange method, attributed to differences in morphology, surface area, and charge carrier dynamics. Among the samples, the one prepared using an acid-assisted ion exchange method demonstrated the highest photocatalytic performance. This was attributed to its porous nanosheet morphology, highest BET surface area and excellent charge carrier dynamics, including a high initial population of charge carriers formed with optimal lifetime, a trapping-detrappping hopping mechanism that facilitates charge carrier retention, high charge carrier mobility and efficient charge transfer to reaction sites. Furthermore, the most active catalyst showed excellent stability over several cycles of the photocatalytic test, highlighting its promise for wastewater treatment and environmental remediation.

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## Conflict of Interests

The authors declare no conflict of interest

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Aurivillius phase • Charge carrier dynamics • Layered perovskite • Noble metal cation • Photocatalysis

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