Electronic Supplementary Material (ESI) for RSC Advances.
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Supplementary information for "Combined Experimental and DFT Approach to $BiNbO_4$ Polymorphs"

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EDX ANALYSIS

To perform chemical species identification of our samples Energy-dispersive X-ray spectroscopy (EDX) spectra of α-BNO and β-BNO samples have been obtained as shown in Fig. S1. The weight percent wt. (%) and atomic percent at. (%) of chemical species Bi, Nb and O are displayed in Table S1.

EDX Analysis			
Sample	Element	at. (%)	wt. (%)
α-BNO	Bi	16.47	51.65
	Nb	24.52	34.19
	O	59.01	14.16
β-BNO	Bi	15.74	51.66
	Nb	22.49	32.81
	O	61.78	15.52

TABLE S1. Chemical species identification and atomic percentage at. (%) and weight percentage wt. (%) concentration analysis using EDX of α-BNO and β-BNO respectively.

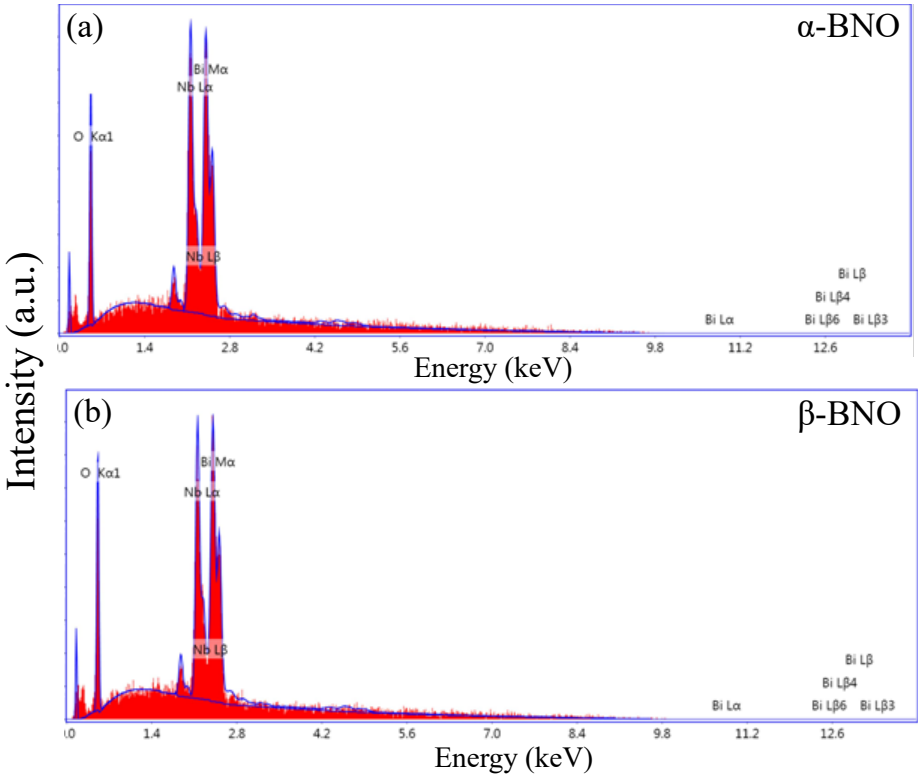

FIG. S1. EDX spectra of (a) α-BNO, (b) β-BNO

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The FTIR absorption spectra of α-BNO and β-BNO were characterized according to the relevant chemical bond vibrations in Table S2. The peaks in the GGA-PBE based phonon density of states were used to identify the FTIR peaks. The GGA-PBE provided good match for the FTIR absorption with the experimentally observed ones for both polymorphs.

FTIR Peak Analysis				
α-BNO		β-BNO		
Exp. (cm^{-1})	DFT (cm^{-1})	Exp. (cm^{-1})	DFT (cm^{-1})	Peak Assign.
400	395	-	-	Bi-O Stretching
-	-	454	448	Bi-O Stretching
480	480	-	-	Bi-O Stretching
540	538	542	546	NbO_6 Octahedral Stretching
-		598	601	NbO_6 Octahedral Stretching
-		846	841	Bi-O-Bi Stretching
888	840	-	-	Bi-O-Bi Stretching
1014	-	-	-	BiO_6 Octahedral Stretching
1036	-	-	-	BiO_6 Octahedral Stretching
1056	-	-	-	BiO_6 Octahedral Stretching
1250	-	-	-	Nb-O Stretching
1394	-	-	-	-OH Bending

TABLE S2. RT experimental (Exp.) and DFT based FTIR peaks of both α-BNO and β-BNO.

ELECTRONIC PROPERTIES SIMULATION

The HSE06 spin-polarized total density of states (TDOS) and its projection onto the different constituent atomic orbitals as a function of energy E within a range of 14 eV window containing the Fermi level (E_F) in the middle for both α-BNO and β-BNO are shown in Fig. S2. Here Hartree-Fock exchange $\alpha_{HF} = 25\%$ and the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is 4 and 3.65 eV for α-BNO and β-BNO respectively. By changing the α_{HF}, we can tune the energy band gap of both polymorphs as can be shown from band structure simulation in Fig. S3. The indirect band gap E_g can be shrunk to 3.84 and 3.41 eV by reducing the α_{HF} to 15% and 10% from 25% in the case of the α-BNO, see Fig. S3(a)&(B). Similarly, the direct E_g can be reduced to 3.65 eV with the use of $\alpha_{HF} = 15\%$ as shown in Fig. S3(c).

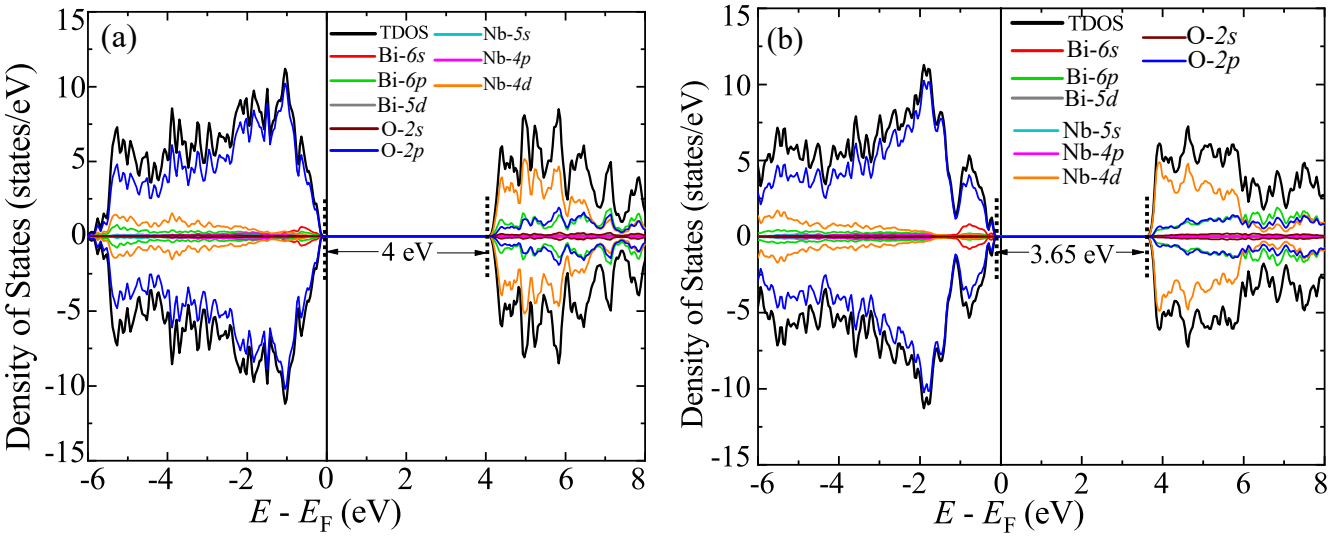

FIG. S2. Spin polarized total density of states (TDOS) and its projection onto different orbitals of Bi, Nb and O in (a) α-BNO and (b) β-BNO using HSE06 with $\alpha_{\mathrm{HF}} = 25\%$.

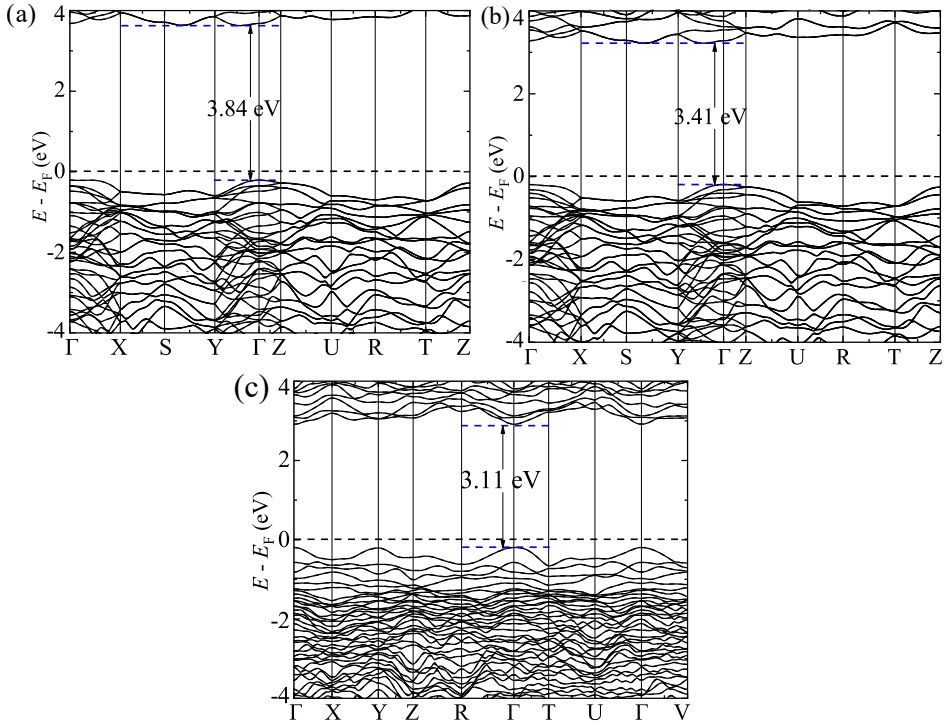

FIG. S3. Electronic band structure along high symmetry k-points Γ, Y, Z, S, X, Z, U, R, T and V for (a) α-BNO with $\alpha_{\mathrm{HF}} = 15\%$, (b) α-BNO with $\alpha_{\mathrm{HF}} = 10\%$ and (c) β-BNO with $\alpha_{\mathrm{HF}} = 10\%$ using HSE06 functional.

OPTICAL PROPERTIES SIMULATION

The optical Loss Function L, Extinction Coefficient K, Reflectance R and Optical Conductivity σ are simulated using GGA-PBE and HSE06 functional for both α-BNO and β-BNO as can be seen from Fig. S4.

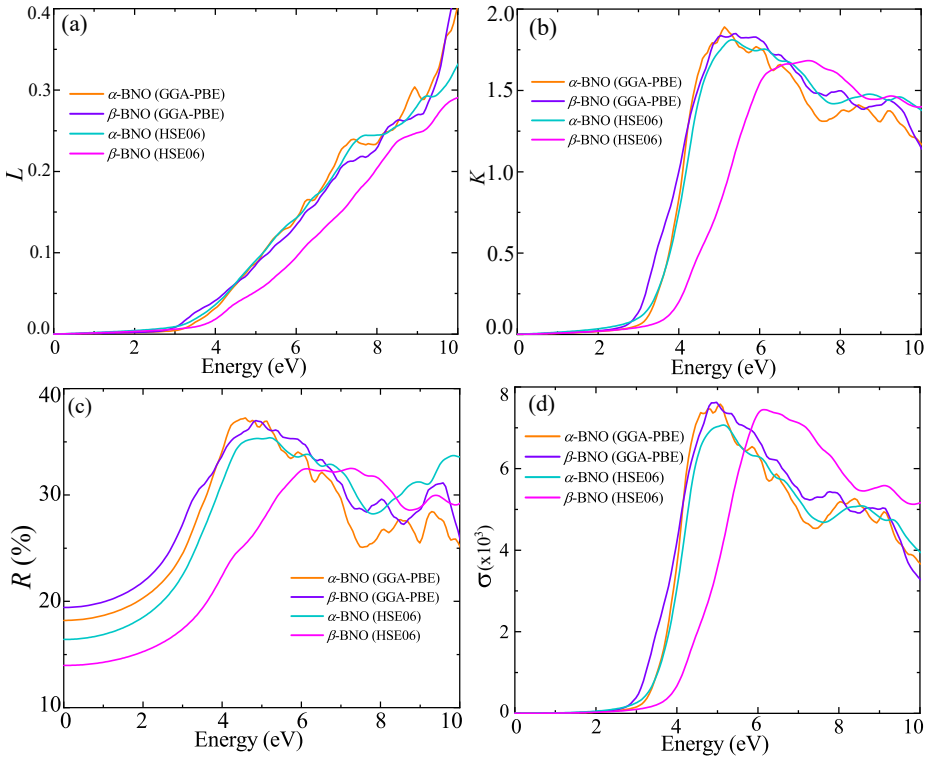

FIG. S4. Optical properties (a) Loss Function L, (b) Extinction Coefficient K, (c) Reflectance R, (d) Optical Conductivity σ as a function photon energy E calculated from GGA-PBE and HSE06 functional averaged over three different polarization E_x, E_y and E_z in case of α-BNO ($\alpha_{HF} = 2\%$) and β-BNO ($\alpha_{HF} = 20\%$).

PHOTOCATALYTIC MEASUREMENTS

The MB dye degradation fraction C/C_0 is plotted for both α-BNO and β-BNO in Fig. S5(a), where C_0 marks the initial MB dye concentration and C represents the same at some specific irradiation exposure time t. The photocatalytic degradation efficiency (%) of the MB is defined as $(C_0 - C)/C_0 \times 100$. By assuming linear reaction kinematics, the MB

dye degradation reaction can be modeled as $\ln(C/C_0) = kt$, where k defines the reaction rate. By linear fitting the $\ln(C/C_0)$ vs. t, as shown in Fig. S5(b), one can estimate the value of k. The estimated values of k for both α-BNO and β-BNO are presented in Fig. S5(c).

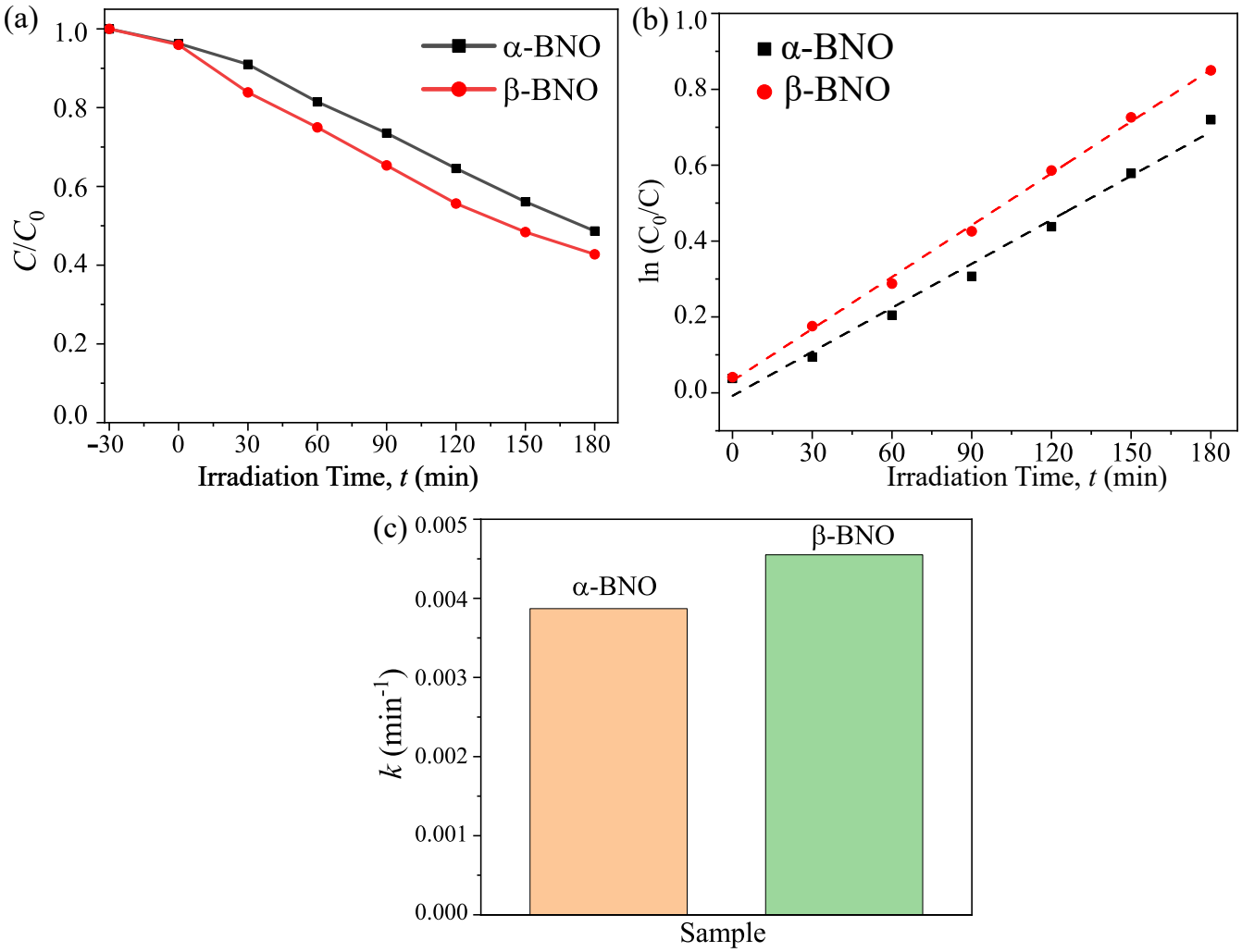

FIG. S5. (a) Time-dependent photocatalytic degradation fraction C/C_0, (b) Linear fitted time-dependent photocatalytic degradation fraction of MB and (c) Comparison among reaction rate constant k of both α-BNO and β-BNO.

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