

Strong Absorption and Ultrafast Localisation in NaBiS₂ Nanocrystals with Slow Charge-Carrier Recombination

- Main text

Figs. 1a,b:

Crystal structure and stability of NaBiS₂ NC films

NC films prepared, X-ray Powder Diffraction (XRD) measurements and photographs taken by Yi-Teng Huang. The crystal structure in the inset of Fig. 1a drawn by Seán R. Kavanagh. Experimental raw data provided in the “NaBiS₂ - Experimental Raw data” folder.

Figs. 1c,d:

Absorption coefficient spectrum and ultra-thin SLME of NaBiS₂

NC films prepared by Yi-Teng Huang. Absorption coefficient spectrum acquired from the ultraviolet-visible spectrophotometry (UV-Vis), cross-sectional profile (by using atomic force microscopy) taken by Yi-Teng Huang, along with the normalised photothermal deflection spectroscopy (PDS) absorption spectrum taken by Alexander J. Sneyd. The absorption coefficient spectrum of other absorbers were extracted from the references as listed in the caption of Fig. 1. The SLME values calculated by Yi-Teng Huang using code written by Robert Hoye. Experimental raw data and extracted data provided in the “NaBiS₂ - Experimental Raw data” folder.

Figs. 1e,f:

Structural and optical properties of NaBiS₂ NC films

Data calculated and analysed by Seán R. Kavanagh, in the folder “DOSs”. Experimental PYS spectrum provided by Dr. Marin Rusu, and included in the “NaBiS₂ - Experimental Raw Data” folder.

Fig. 2:

Electronic structure and localised states in NaBiS₂

Data calculated and analysed by Seán R. Kavanagh, in the “Computational Raw Data Main Files”, “Polarons” and “PyVASPWfc” folders.

Figs. 3a,b,c,d:

Short-time and long-time TA spectrum of NaBiS₂ NC films

NC films prepared by Yi-Teng Huang. TA spectrum taken and analysed by Yi-Teng Huang. Experimental raw data and fitted data provided in the “NaBiS₂ - Experimental Raw data” folder.

Figs. 3e,f:

Optical-pump-terahertz-probe (OPTP) kinetics of NaBiS₂ NC films

NC films prepared by Yi-Teng Huang. OPTP measurements taken and analysed by Dr. Marcello Righetto. Experimental raw data and fitted data provided in the “NaBiS₂ - Experimental Raw data” folder.

Figs. 4a,b:

Singular-value decomposition (SVD) analysis of the short-time TA spectrum

SVD spectrum and kinetics analysed by Yi-Teng Huang. Extracted data provided in the “NaBiS₂ - Experimental Raw data” folder.

Fig. 4c:

Physical mechanism behind the unusual charge-carrier kinetics in NaBiS₂.

Data calculated and analysed by Seán R. Kavanagh, in the “Polarons” folder.

Fig. 4d,e,f:

Defect impact on NaBiS₂ NC films

Pristine and annealed NC films prepared by Yi-Teng Huang. Normalised PDS absorption spectra measured by Alexander J. Sneyd. OPTP measurements taken and analysed by Dr. Marcello Righetto. Long-time TA measurements taken and analysed by Yi-Teng Huang. Experimental raw data and fitted data provided in the “NaBiS₂ - Experimental Raw data” folder.

- Supplementary Information

Supplementary Fig. 1:

Transmission electron microscopy (TEM) images of NaBiS₂ NCs with different sizes.

NCs with different sizes synthesised by Yi-Teng Huang. TEM images taken by Kaiwen Zhang and Dr. Linjie Dai. Size distribution of NCs analysed by Yi-Teng Huang. Size distribution data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 2:

Phase stability of NaBiS₂ NC films.

NC films prepared by Yi-Teng Huang. XRD measurements and photographs taken by Yi-Teng Huang. Experimental raw data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 3:

Cross-sectional profile of the NaBiS₂ NC film.

NC films prepared by Yi-Teng Huang. AFM measurements taken and analysed by Yi-Teng Huang.

Supplementary Fig. 4:

Tauc plot of the NaBiS₂ NC film.

NC films prepared by Yi-Teng Huang. Normalised PDS spectrum and UV-Vis spectrum measured by Alexander J. Sneyd and Yi-Teng Huang, respectively. Tauc plot drawn and analysed by Yi-Teng Huang. Experimental raw data and fitted data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 5:

Schematic Molecular Orbital (MO) diagram of the upper valence band (VB) electronic structure in NaBiS₂ and AgBiS₂.

Diagram generated by Seán R. Kavanagh based on analyses of the electronic structure of both NaBiS₂ and AgBiS₂ detailed in the “Computational Raw Data Main Files” folder.

Supplementary Fig. 6:

First Brillouin Zone (BZ) of an F-centred cubic lattice, to which the disordered NaBiS₂ crystal space group ($Fm\bar{3}m$) belongs.

Diagram generated by Seán R. Kavanagh from symmetry analysis of the NaBiS₂ crystal structure

Supplementary Fig. 7:

Calculated absorption coefficient spectrum of disordered $Fm\bar{3}m$ NaBiS₂.

Data calculated and analysed by Seán R. Kavanagh, in the “Absorption” data folder.

Supplementary Fig. 8:

Fraction of Na, Bi and S elements in NaBiS₂ NC films annealed at 100 °C for different times.

NC films prepared and annealed by Yi-Teng Huang. Time-of-Flight Elastic Recoil Detector Analysis (ToF-ERDA) measured by Jaakko Julin and Mikko Laitinen. Data analysed by Mari P. Napari. Experimental raw data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 9:

Normalised signal kinetics extracted from the two ground state bleach (GSB) peaks in long-time TA spectrum of NaBiS₂ NC films.

NC films prepared by Yi-Teng Huang. TA measurements taken and analysed by Yi-Teng Huang. Experimental raw data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 10:

Effect of post-annealing treatment on NaBiS₂ NC films.

NC films prepared and annealed by Yi-Teng Huang. X-ray photoelectron spectroscopy (XPS) measurements taken by Dr. Andrew J. Britton. XRD measurements taken by Yi-Teng Huang. All the data analysed by Yi-Teng Huang. PDS measurements taken by Dr. Szymon J. Zelewski. Experimental raw data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 11:

Average calculated a Na-S and b Bi-S bond lengths for disordered (Fm3m) NaBiS₂ in a representative 400-atom SQS supercell

Data calculated and analysed by Seán R. Kavanagh, in the “Computational Raw Data Main Files” and “Na Vacancies” data folder.

Supplementary Fig. 12:

XRD patterns of NaBiS₂ NC films post-annealed at different temperatures

NC films prepared and annealed by Yi-Teng Huang. XRD measurements taken and analysed by Yi-Teng Huang. Experimental raw data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 13:

Absorbance spectrum of NaBiS₂ NC films composed of different sizes.

NC films prepared by Yi-Teng Huang. PDS measurements taken by Dr. Szymon J. Zelewski. Experimental raw data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 14:

Scanning electron microscopy (SEM) images of pristine and annealed NaBiS₂ NC films.

NC films prepared and annealed by Yi-Teng Huang. SEM images taken by Yi-Teng Huang. Experimental raw data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 15:

Normalised photo-induced absorption (PIA) kinetics extracted from short-time TA measurements of pristine and annealed NaBiS₂ NC films

NC films prepared and annealed by Yi-Teng Huang. Data analysed by Yi-Teng Huang. Experimental raw data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 16:

Elliott fit to the absorption coefficient spectrum onset of NaBiS₂ NC thin film

Used the absorption coefficient spectrum from Fig. 1c. Fitting performed by Dr. Marcello Righetto. Experimental raw data and fitted data provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 17:

A 2D short-time TA spectrum including both wavelength and kinetics information

NC films prepared by Yi-Teng Huang. TA measurements taken and analysed by Yi-Teng Huang. 2D spectrum for SVD analysis provided in the “NaBiS₂ - Experimental Raw data - SI” folder.

Supplementary Fig. 18:

Schematic of the two-level mobility model used to fit the OPTP data

Illustration made by Dr. Marcello Righetto

Supplementary Fig. 19:

Computed phase stability map of NaBiS₂ with HSE06+SOC

Data calculated and analysed by Seán R. Kavanagh, in the “Computational Raw Data Main Files”, “PhaseDiagram” and “Na Vacancies” folders.

Supplementary Fig. 20:

Defect formation energy diagram for Na vacancies in ordered $R\bar{3}m$ NaBiS₂

Data calculated and analysed by Seán R. Kavanagh, in the “Computational Raw Data Main Files”, “PhaseDiagram” and “Na Vacancies” folders.

Supplementary Fig. 21:

Formation energies of neutral (V_{Na}^0) and negatively charged (V_{Na}^{-1}) Na vacancies in disordered (SQS) NaBiS₂

Data calculated and analysed by Seán R. Kavanagh, in the “Computational Raw Data Main Files”, “PhaseDiagram” and “Na Vacancies” folders.

Supplementary Fig. 22:

Formation energies of a V_{Na}^0 and b V_{Na}^{-1} in disordered (SQS) NaBiS₂ as a function of vacancy site distance from the localised Sp state

Data calculated and analysed by Seán R. Kavanagh, in the “Computational Raw Data Main Files”, “PhaseDiagram” and “Na Vacancies” folders.

Supplementary Fig. 23:

Defect formation energy diagram for Na vacancies in disordered (SQS) NaBiS₂, calculated using HSE06+SOC

Data calculated and analysed by Seán R. Kavanagh, in the “Computational Raw Data Main Files”, “PhaseDiagram” and “Na Vacancies” folders.

Supplementary Fig. 24:

Electronic density of states (DOS) for V_{Na-1} in disordered (SQS) NaBiS₂, calculated using HSE06+SOC

Data calculated and analysed by Seán R. Kavanagh, in the “Computational Raw Data Main Files”, “PhaseDiagram” and “Na Vacancies” folders.