Novel Photocatalytic Metal Oxides

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University of Nebraska at Omaha (UNO)
May 15, 2012

Project ID # **PD079**

Overview

Timeline

Start Date: Sept 1, 2010
End Date: Aug 31, 2012
Percent Complete: 85%

Barriers

Materials Efficiency: develop materials with appropriate band gap and band edge values for water splitting.

Budget

Total project funding
DOE share: $250,000
UNO share: $63,068
Funding received in FY2011: $ 0

Partners

Dr. Fereydoon Namavar, University of Nebraska Medical Center
Dr. Barry Cheung, University of Nebraska-Lincoln
Dr. Hsiang-Lin Liu, National Normal University, Taiwan

Relevance

- Principal Objective:
  - to develop improved solid-state photocatalysts for the decomposition of water into hydrogen gas using solar radiation.
- Near-term Objectives:
  - engineer band gap of cesium niobate ($Cs_2Nb_4O_{11}$) through computer modeling for optimum photocatalytic activity in the visible portion of the solar spectrum
  - fabricate and experimentally examine materials identified

Technical Approach

- Barrier:
  - Materials efficiency for photocatalytic production of hydrogen from water using sunlight
- Technical approach:
  - Design and modify band gaps and band edges of materials through state-of-the-art computer simulations to improve efficiencies of energy absorption
  - Examine doping of cesium niobate (CNO) with elements and compounds (specifically oxides) known to extend absorption spectra to harvest visible light energy

Milestones

Milestone	Progress Notes	Comments	% Complete
Bandgap Calculations	computer simulations have been completed	calculations agree with photoluminescence experiments	100%
Materials Synthesis	sol-gel synthetic route for CNO production perfected	band gap determined to be 3.5 eV by luminescence spectroscopy	100%
Computer Doping Study	set up initial calculations and tests	expect all calculations to be completed by May 2012	90%
Solid Solutions Synthesis	started in December 2011	dopants and levels to be determined from computer study	50%

Technical Accomplishments and Progress: Doping Model Calculations

Our calculations are carried out within the density functional theory (DFT) as implemented in VASP code using projector augmented-wave (PAW) method, and generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) parameterization. We adopt a uniform $3 \times 1 \times 2$ k-point grid for the Brillouin zone sampling and a plane-wave basis set with energy cut-off of 400 eV.

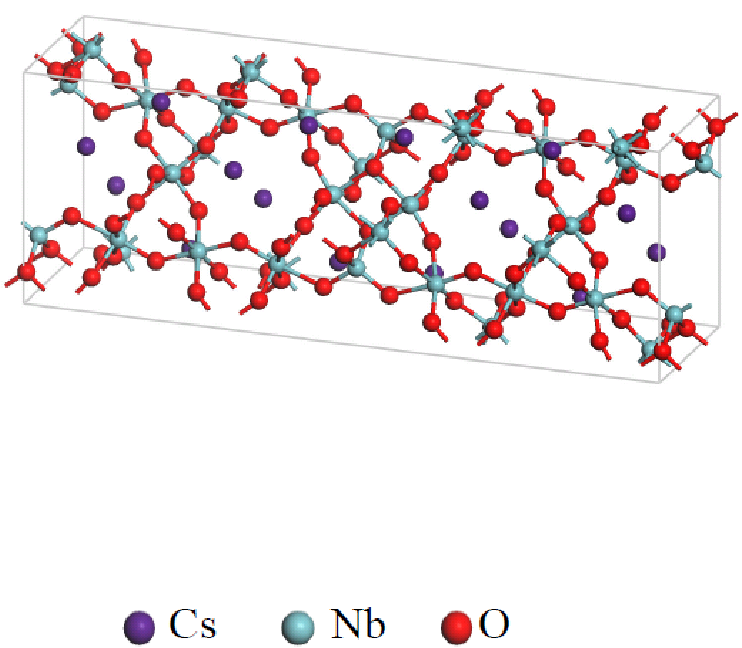
For low-temperature cesium niobate with *Pnna* symmetry, we construct a $7.47 \times 28.90 \times 10.49$ Å orthorhombic unit cell that contains 16 Cs, 32 Nb, and 88 O atoms. Then one, two, or forty O atoms are replaced by S or N, and one or sixteen Nb atoms are replaced by V or Ta.

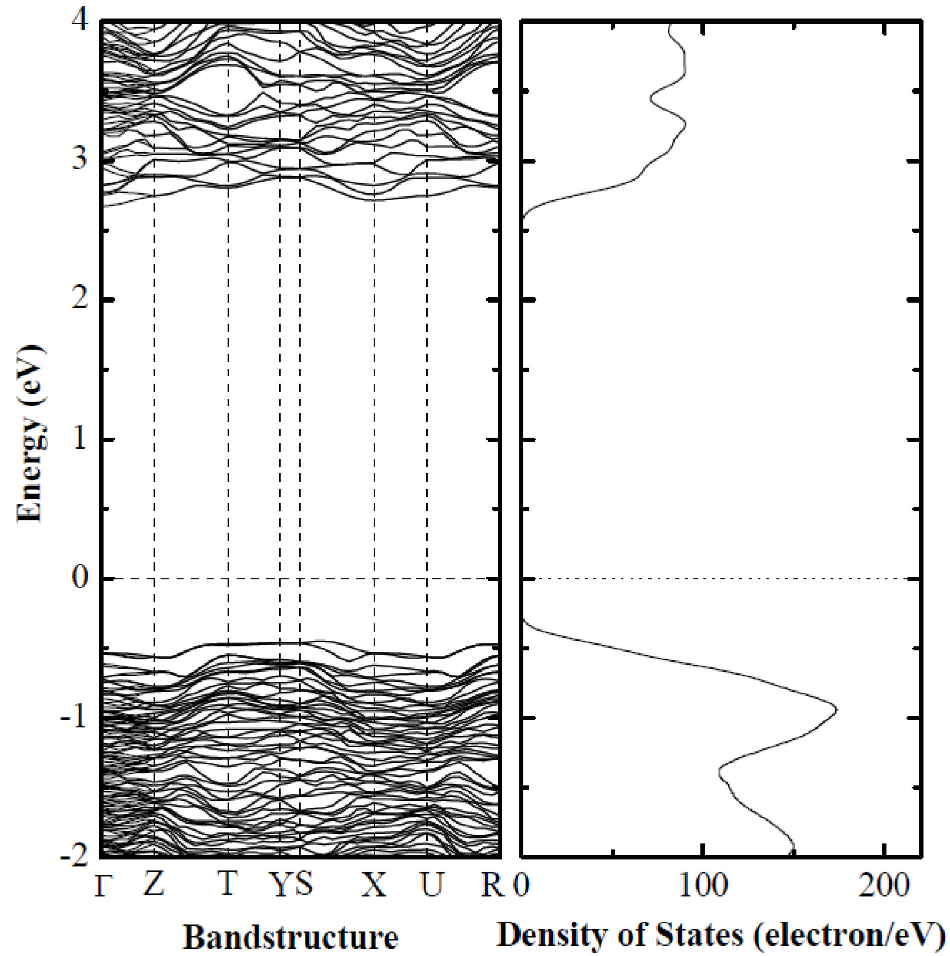
Calculated band gaps with various dopants

sample	calculated band gap (eV)
CNO	3.12
CNO with 1.14% S	2.92
CNO with 2.27% S	2.18
CNO with 3.13% V	2.47
CNO with 3.13% Ta	3.10

$Cs_2Nb_4O_{11}$

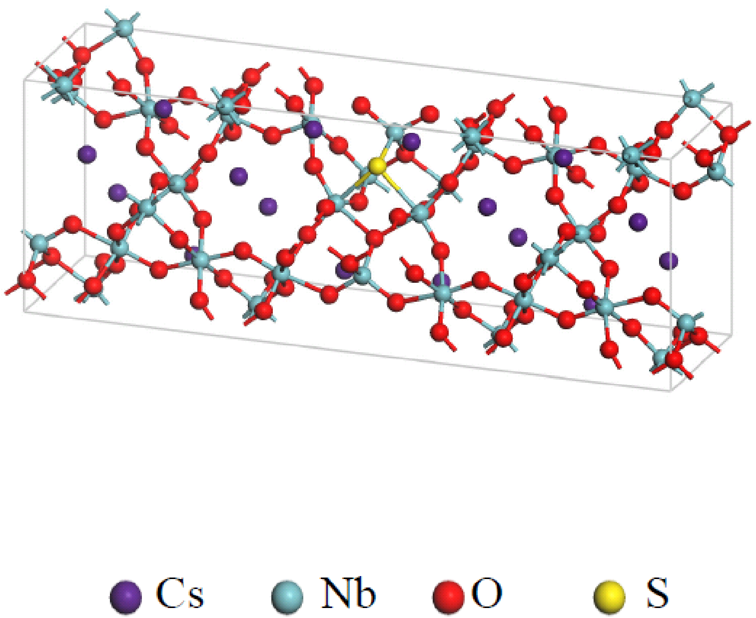
Band gap: 3.12 eV

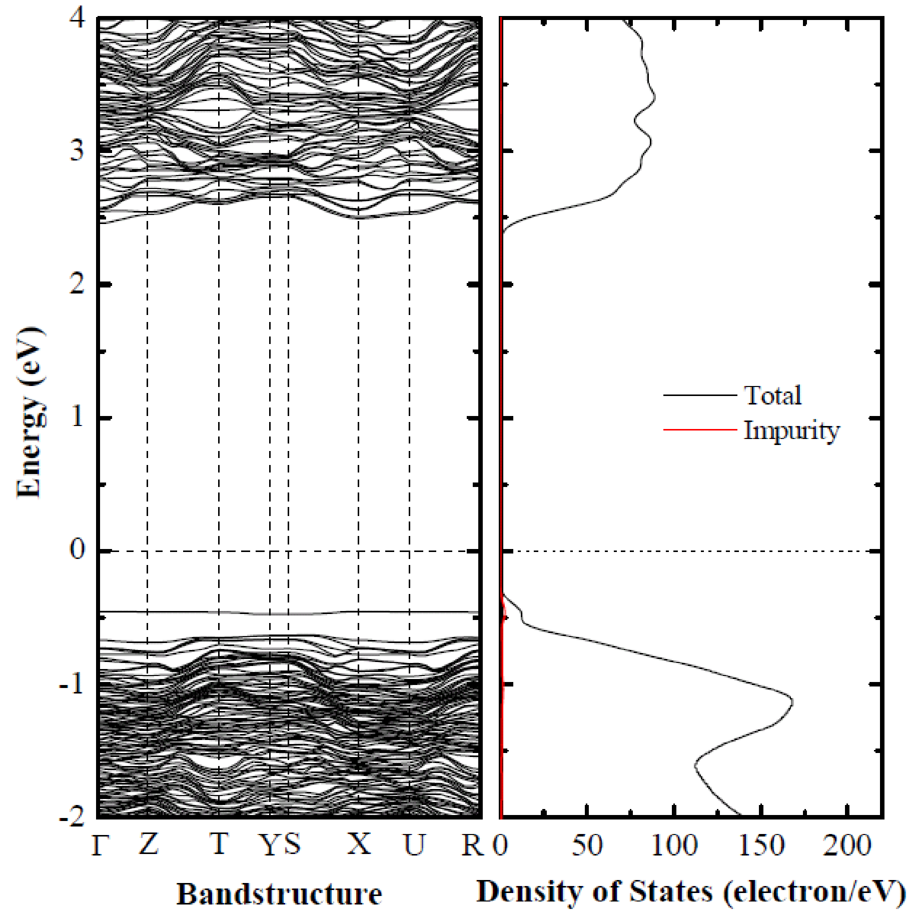




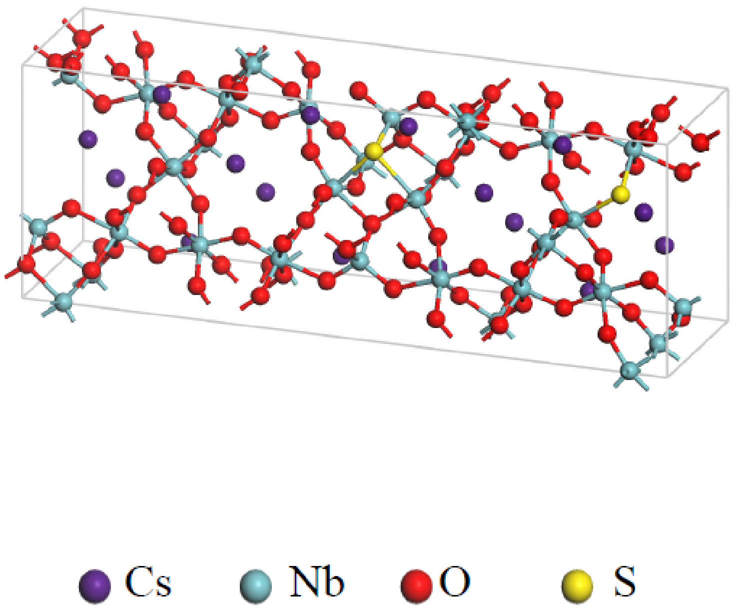
$Cs_2Nb_4O_{10.875}S_{0.125}$ (1.14% S)

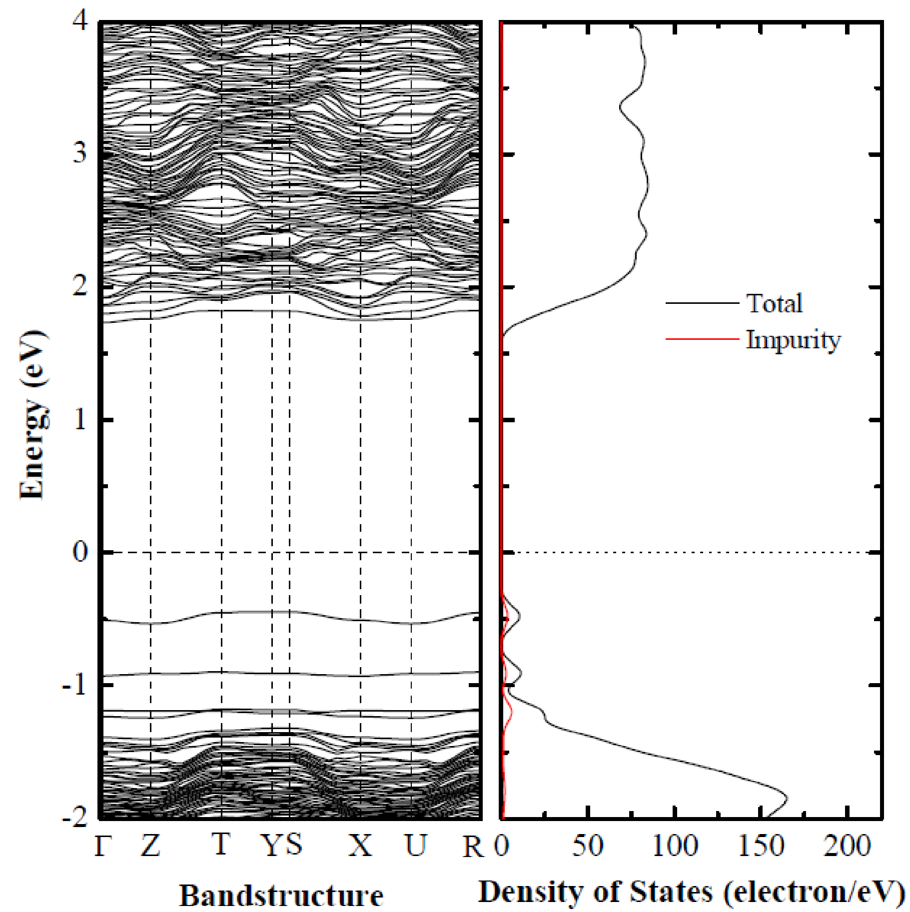
Band gap: 2.92 eV





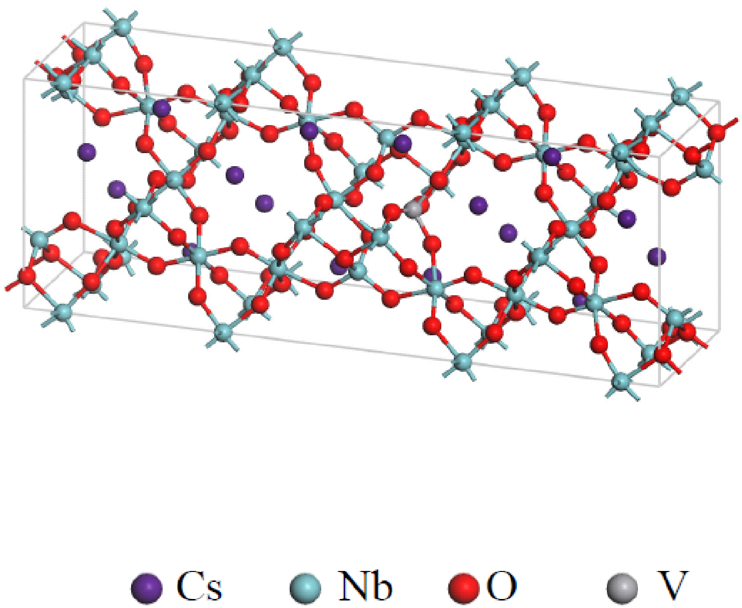
$Cs_2Nb_4O_{10.75}S_{0.25}$ (2.27% S) Band gap: 2.18 eV

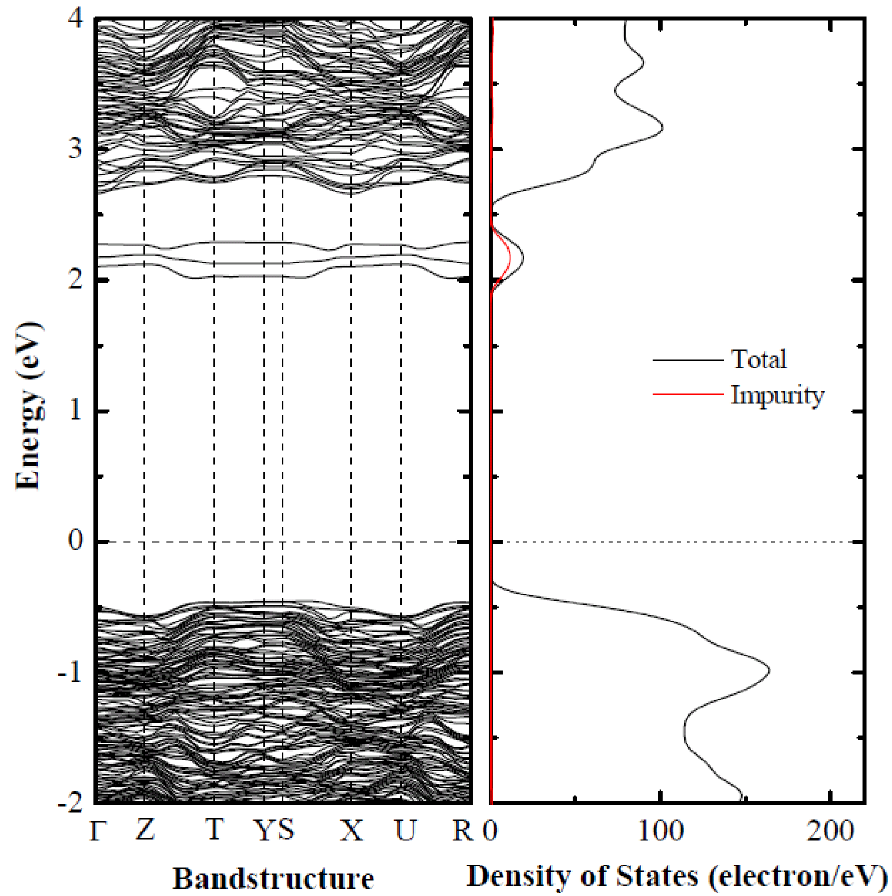




$Cs_2Nb_{3.875}V_{0.125}O_{11}$ (3.13% V)

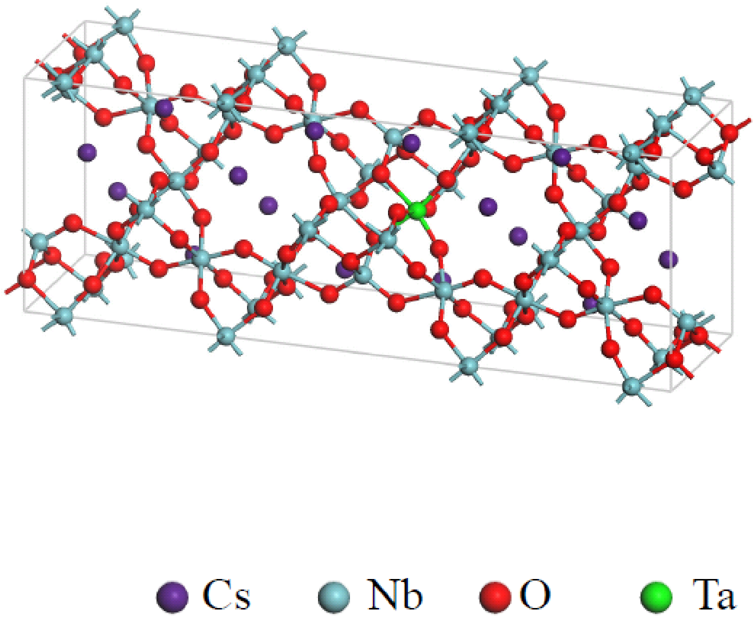
Band gap: 2.47 eV

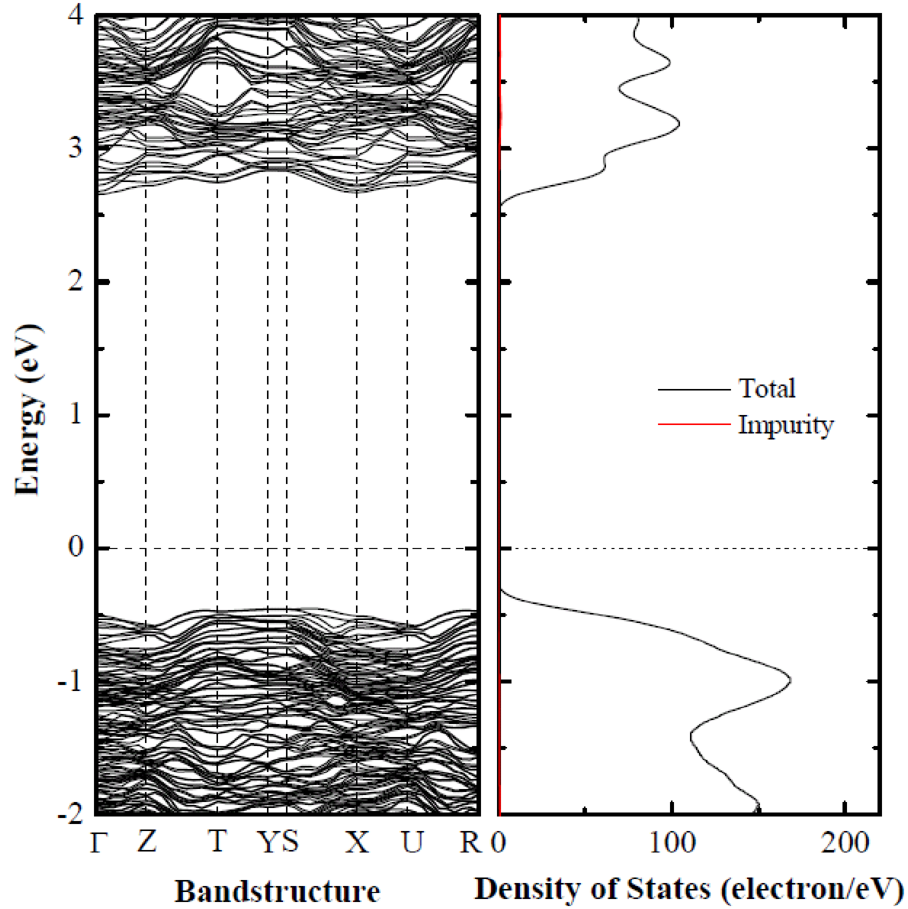




$Cs_2Nb_{3.875}Ta_{0.125}O_{11}$ (3.13% Ta)

Band gap: 3.10 eV





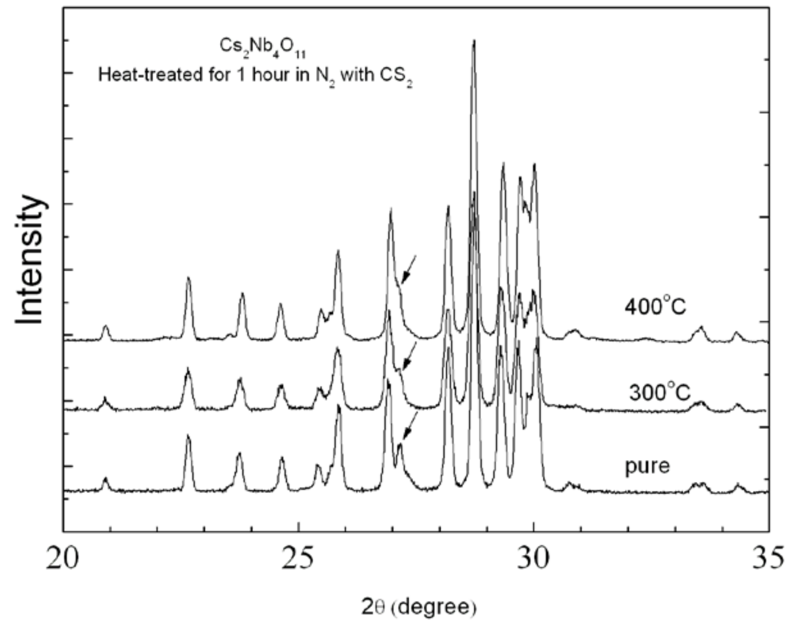
Technical Accomplishments and Progress: Sol-gel Synthesis

CNO has been synthesized by a sol-gel method using cesium carbonate, niobium chloride, anhydrous citric acid, methanol, and deionized water as starting materials. The sol-gel precursor formed by a room-temperature preparation and low-temperature heating. It is then fired at high temperatures and after only two hours of reaction time produces a single-phase product.

Technical Accomplishments and Progress: Solid-Solution Synthesis

Sulfur-doped CNO has been synthesized by passing gaseous carbon disulfide over CNO at elevated temperatures for a set amount of time. Chemical analysis in progress to determine dopant amounts as a function of experimental conditions.

XRD data for CNO treated with CS_2 for one hour at different temperatures.



Collaborations

- Partners
  - Dr. Fereydoon Navamar, University of Nebraska Medical Center
  - Dr. Barry Cheung, University of Nebraska–Lincoln

  These partners assist in sample characterization.
  - Dr. Hsiang-Lin Liu, National Normal University, Taiwan

  This partner assists in optical measurements.

Proposed Future Work

- Calculate the effects of doping CNO with metals by evaluating the bandgaps and band edges of the various composites.
- Perfect synthesis conditions for the sulfur-doped CNO.
- Characterize the properties of composites by experimental analysis.

Summary

- Relevance: Engineer improved band gaps and band edges in photocatalysts for production of hydrogen from water.
- Approach: Use computer simulations of CNO and doped solid solutions to identify candidate systems. We noticed that S and V are most effective in reducing the band gaps.
- Technical Accomplishments and Progress: Developed sol-gel synthesis of CNO; calculated band gap and band structure.
- Proposed Future Research: Examine CNO solid solutions with various dopants through computer simulations and synthesize systems that are most promising for photocatalysis.

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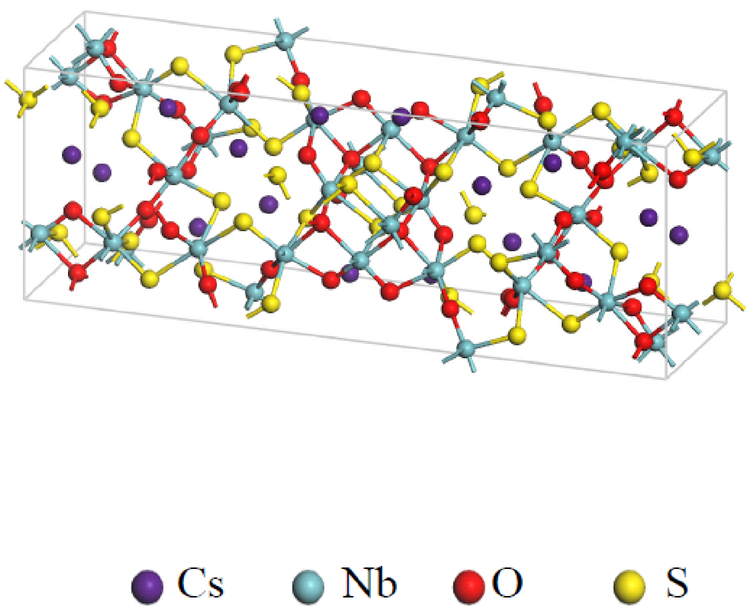
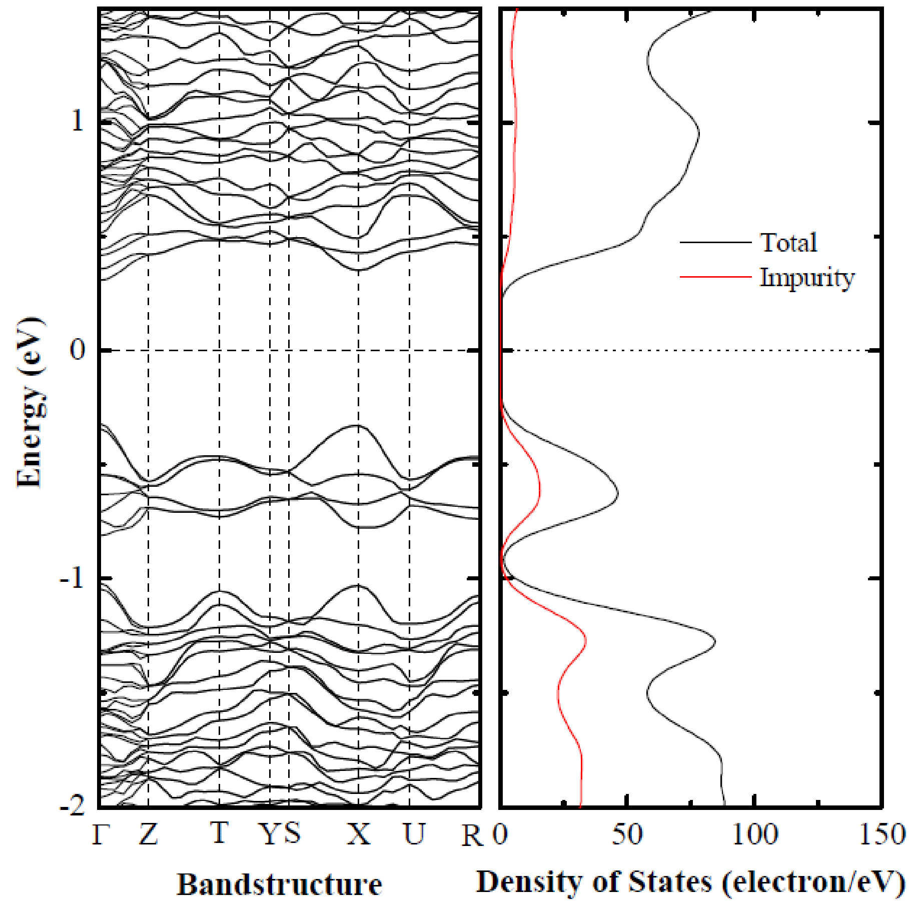
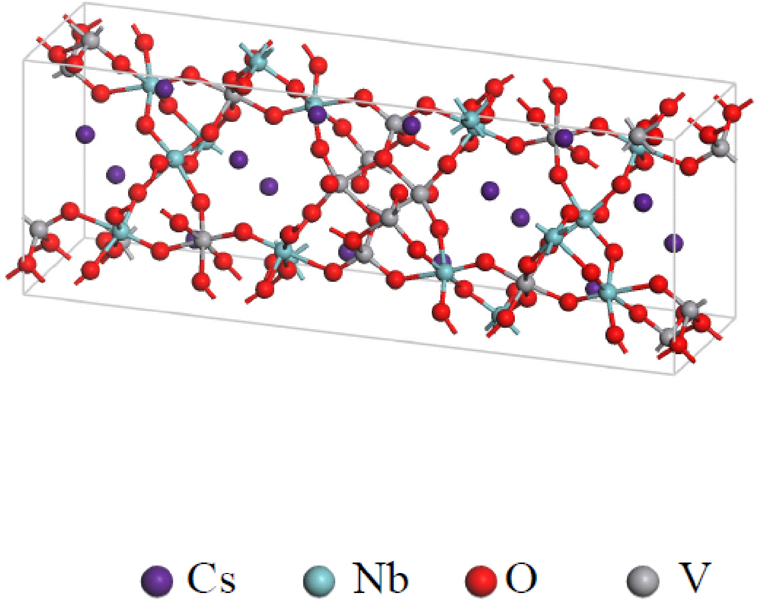
Technical Back-Up Slides

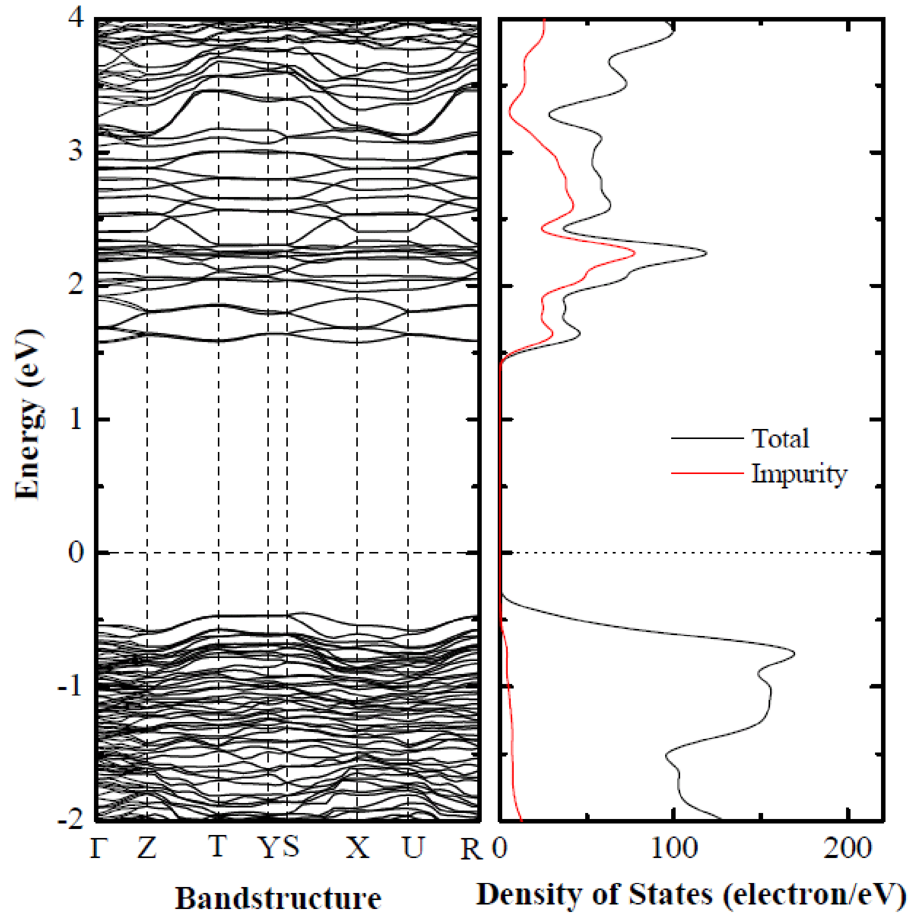
$Cs_2Nb_4O_6S_5$ (45.45% S) Band gap: 0.62 eV





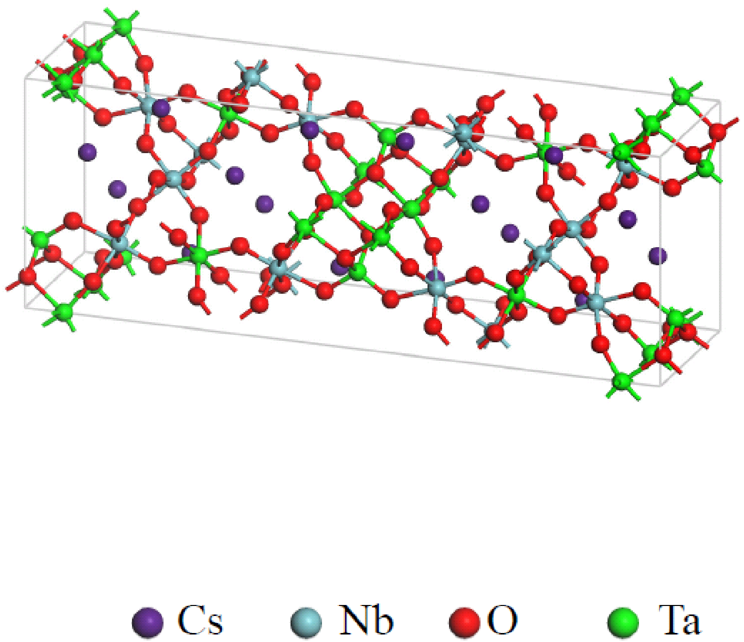
$Cs_2Nb_2V_2O_{11}$ (50% V) Band gap: 2.02 eV

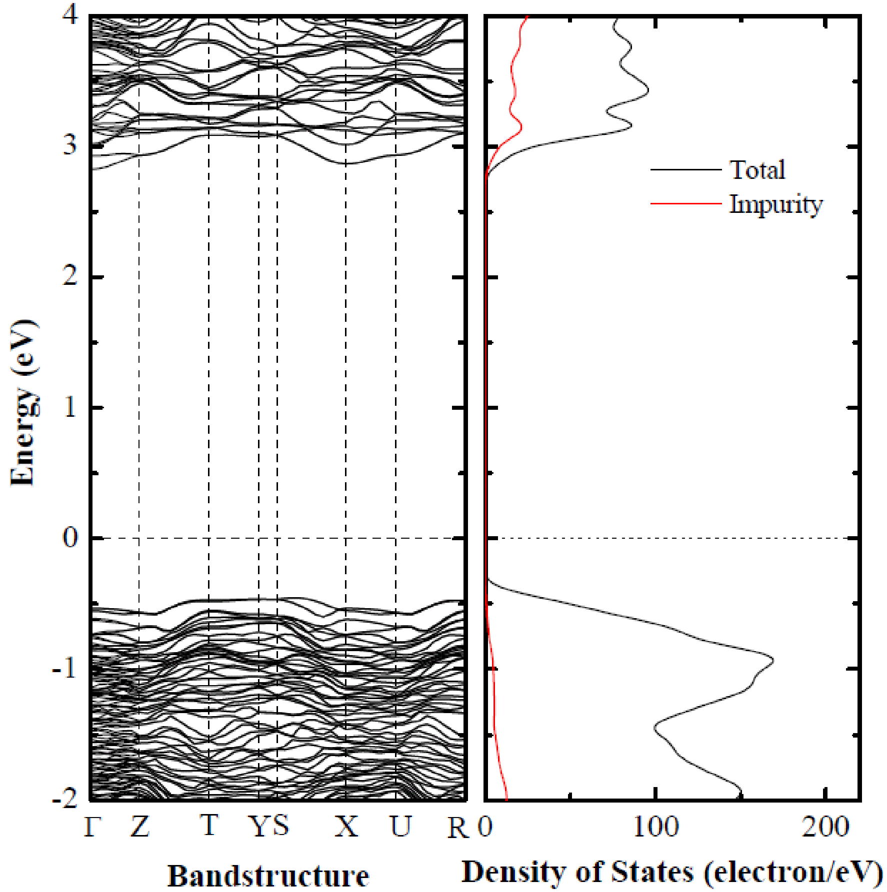




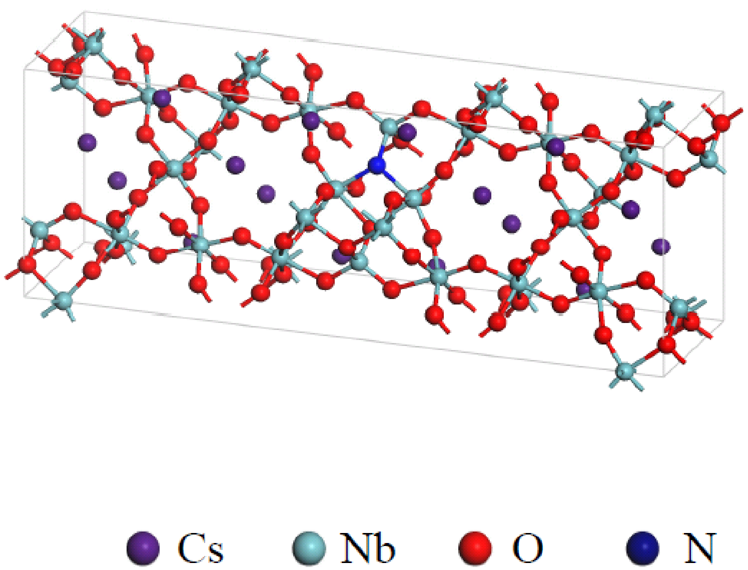
$Cs_2Nb_2Ta_2O_{11}$ (50% Ta)

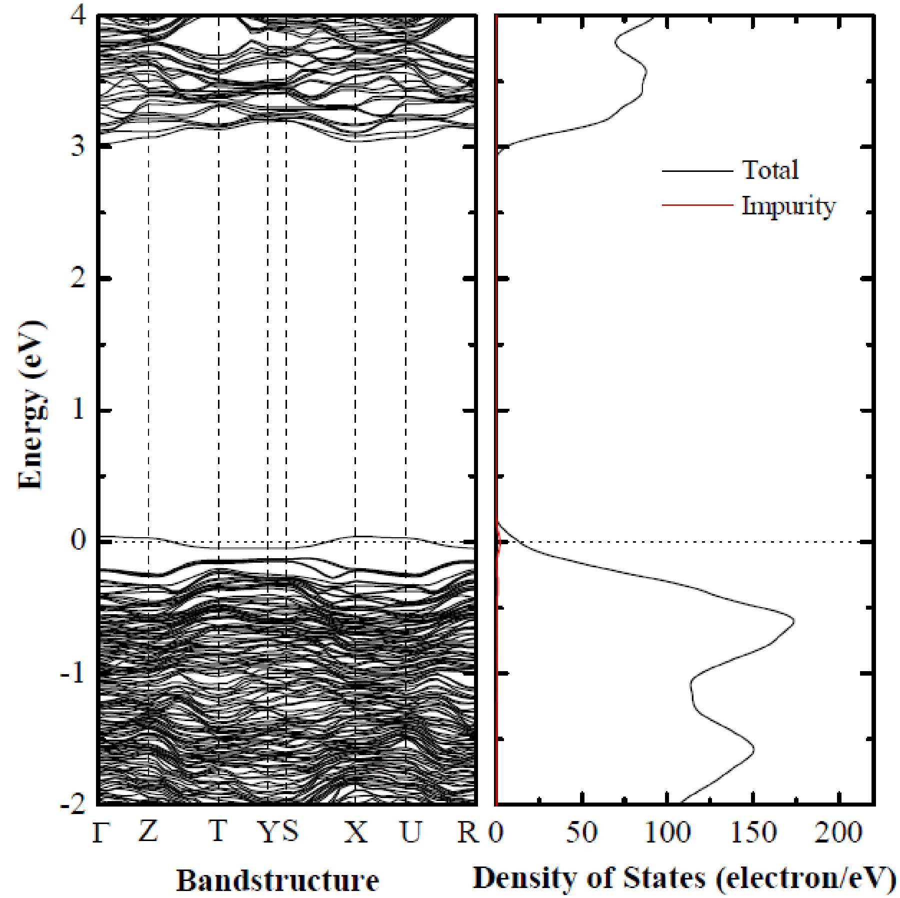
Band gap: 3.28 eV





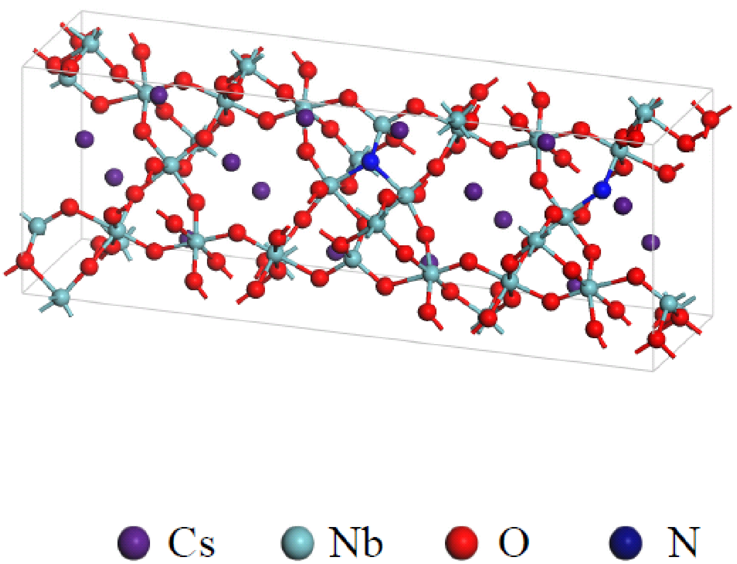
$Cs_2Nb_4O_{10.875}N_{0.125}$ (1.14% N) Band gap ≈ 2.98 eV

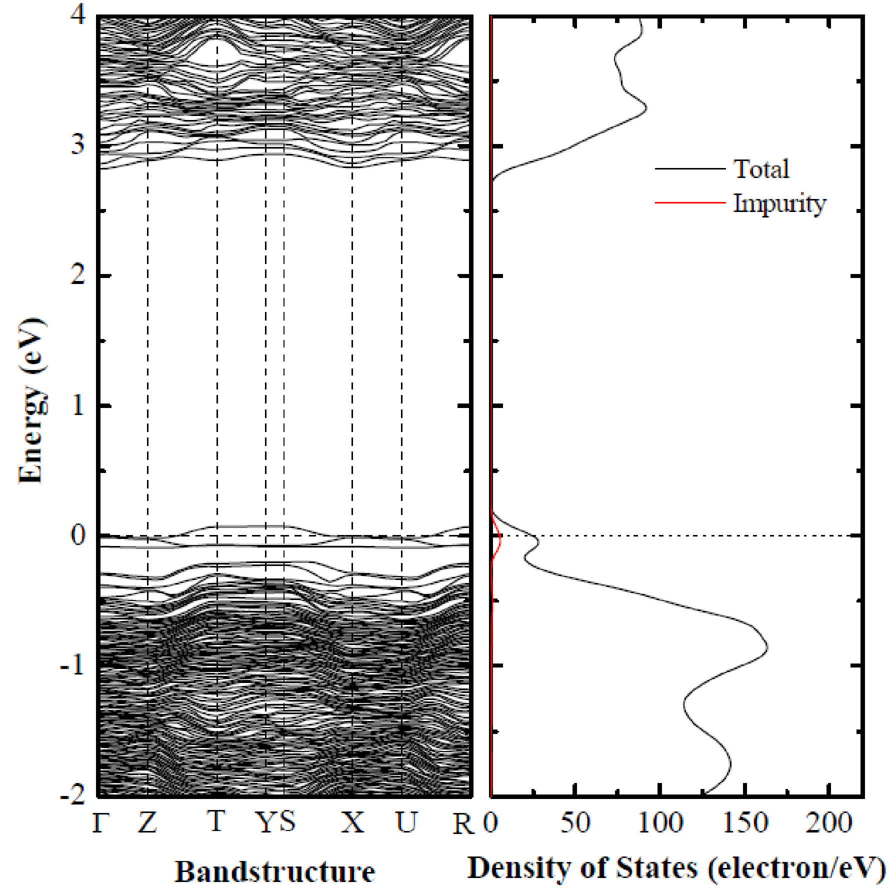


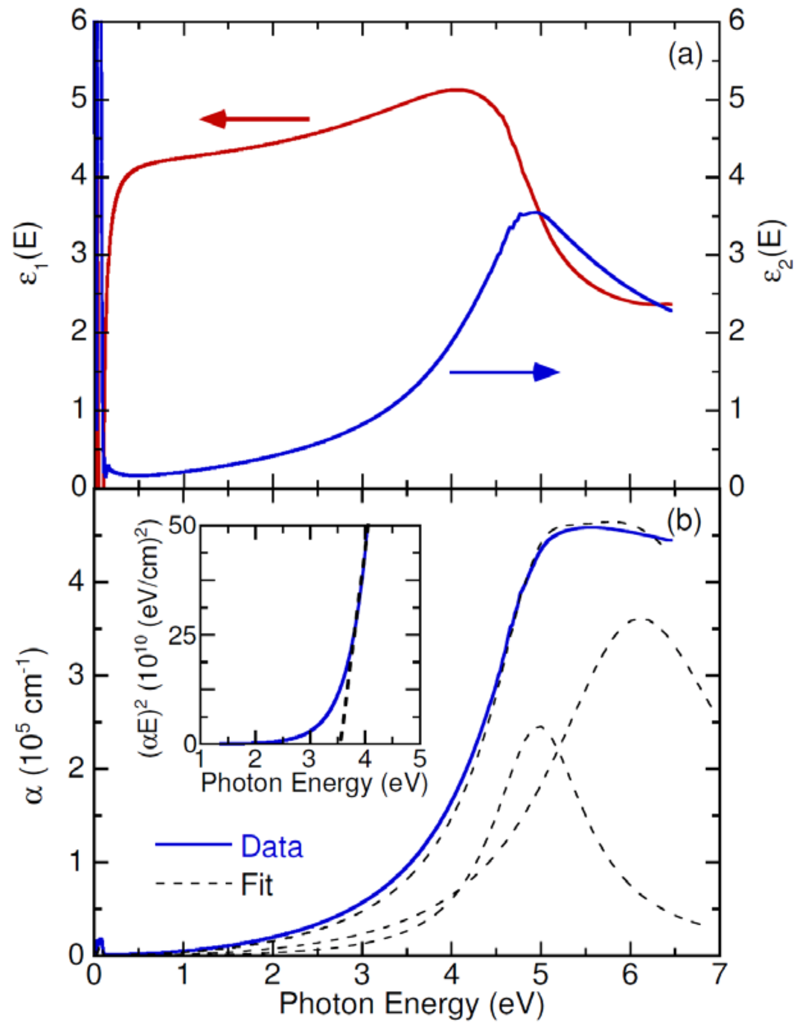


$Cs_2Nb_4O_{10.75}N_{0.25}$ (2.27% N)

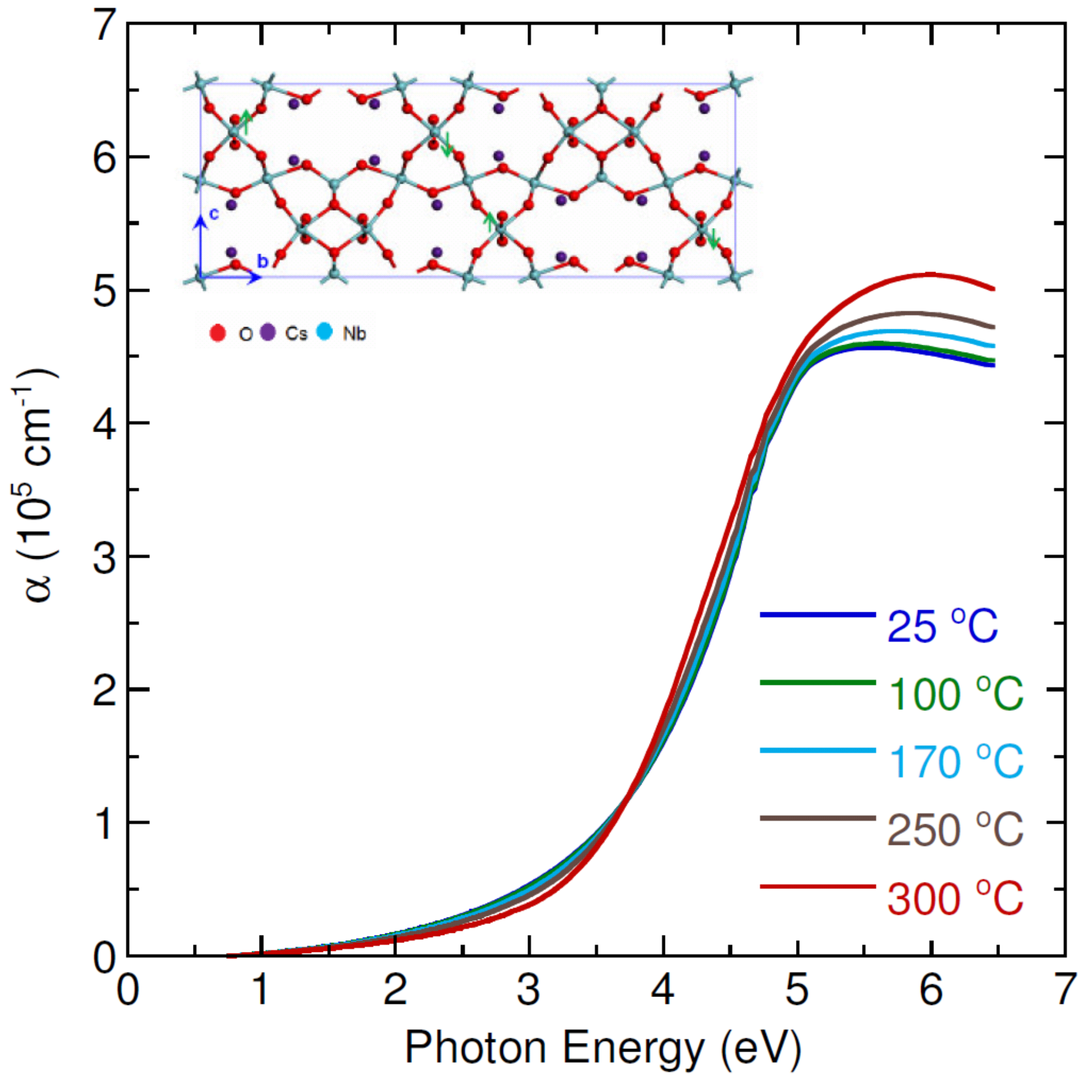
Band gap ≈ 2.76 eV







(a) Real (red) and imaginary (blue) part of room-temperature dielectric functions for CNO. (b) Optical absorption coefficient for CNO.



Temperature dependence of optical absorption coefficient for CNO.