

II.G.10 Novel Photocatalytic Metal Oxides*

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*Congressionally directed project

- 8% plant-to-hydrogen solar efficiency
- Projected durability of 1,000 hours

FY 2011 Accomplishments

- Calculated the band structure and bandgap for cesium niobate.
- Developed a sol-gel synthesis route to fabricate cesium niobate.
- Commenced computer doping study.



Introduction

This work seeks to develop new solid-state photocatalysts for the decomposition of water into hydrogen and oxygen gas. The catalyst should have band edges appropriate for the oxidation and reduction reactions that occur during the decomposition process. Appropriate band edges would result in a bandgap of about 2.3 eV, in accordance with DOE technical targets. This bandgap would place the catalyst's absorption edge into the visible portion of the spectrum and render the catalyst more efficient than current catalyst at utilizing the available solar spectrum. Cesium niobate is a newly discovered photocatalyst but has band edges that are not optimized for the oxidation and reduction reactions that occur during water decomposition. We are seeking to optimize the band edges by examining various solid solutions through computer modeling.

Approach

We are examining cesium niobate and solid solutions thereof through computer simulations to determine the composition with an electronic structure most conducive for the photocatalytic decomposition of water into hydrogen and oxygen gas. We conduct our calculations through the density functional theory (DFT) method, which is a commonly adopted approach utilized by the condensed matter community. The method treats many-particle systems, such as ionic solids, by approximating their wave functions from spatially dependent electron density. The method is effective in deducing electronic, optical, and mechanical properties of materials and facilitates explanation to and comparison with experimental results. In this project, we combine DFT with different boundary conditions and generate very large unit-cell structures, which is both laborious and time-consuming but essential for accurate prediction of materials properties.

We examine compositions with cesium niobate as the base but with judicious substitutions of other metals and

Fiscal Year (FY) 2011 Objectives

- Develop improved solid-state photocatalysts.
- Model candidate metal oxides through computer simulations.
- Synthesize and characterize materials identified by models.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability

Technical Targets

Development of Semiconductor Materials for Photoelectrochemical Production of Hydrogen: This project is conducting theoretical studies of cesium niobate ($\text{Cs}_2\text{Nb}_4\text{O}_{11}$) and its solid solution modifications to discover new, more efficient oxide catalysts for photoelectrochemical production of hydrogen from water. Compositions identified by computer modeling will then be fabricated and characterized. The materials should meet the following DOE targets:

- 2.3-eV useable bandgap

nonmetals in order to adjust the electronic band edges to the desired values. Compositions with the desired properties are then synthesized in the laboratory and characterized for structure, optical absorption, and catalytic activity.

Results

We have completed the band structure calculations of both the high and low-temperature phases of cesium niobate (CNO). Figure 1 shows the results for the low-temperature phase, which is the one that occurs at room temperature; the phase transition occurs at 165°C. The calculated bandgap is about 3.1 eV. Understanding of the band structure allows us to calculate the optical absorption of CNO so as to monitor and modify the band edges as we engineer the CNO material to facilitate photocatalytic decomposition of water into its constituent gases.

The optical absorption spectra of CNO with polarized and unpolarized light are shown in Figures 2 and 3, respectively. In the range of 0-10 eV, two absorption peaks dominate all spectra: one around 4.8 eV and a second, higher one around 6.0 eV. The absorption intensity order is $[100] > [001] > [010]$ for polarized light and $[010] > [001] > [100]$ for unpolarized light, that is, in the opposite order. This is because, for unpolarized light, the spectrum of one incident direction (i.e., $[100]$) equals the spectrum average of polarized light in the vertical plane (i.e., $[100]$).

We have developed a sol-gel synthesis route to fabricate CNO at relatively short reaction times. In this procedure,

niobium(V) chloride, cesium carbonate, anhydrous citric acid, and deionized water are used as starting materials. At room temperature, the niobium chloride is dissolved in methanol with constant stirring to get a clear, colorless solution. Citric acid is then added to the solution. Separately, stoichiometric cesium carbonate and additional citric acid are dissolved in deionized water and added to the niobium chloride methanolic solution. The final solution is heated with constant stirring at 80-110°C to evaporate the methanol and water and produce a clear gel. The gel is then heated at 400°C for one hour to produce a black amorphous material. Heating this material at 700°C for two hours or at 900°C for as little as 0.5 hours produces single-phase CNO. In contrast, fabrication through standard solid-state reaction from the metal oxides requires several days of heating at

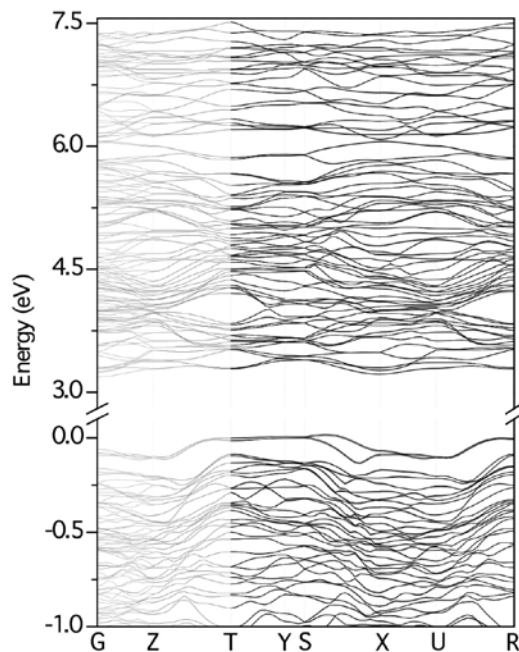


FIGURE 1. Band Structure for Low-Temperature CNO: G = (0,0,0), Z = (0,0,0.5), T = (-0.5,0,0.5), Y = (-0.5,0,0), S = (-0.5,0.5,0), X = (0,0.5,0), U = (0,0.5,0.5), and R = (-0.5,0.5,0.5).

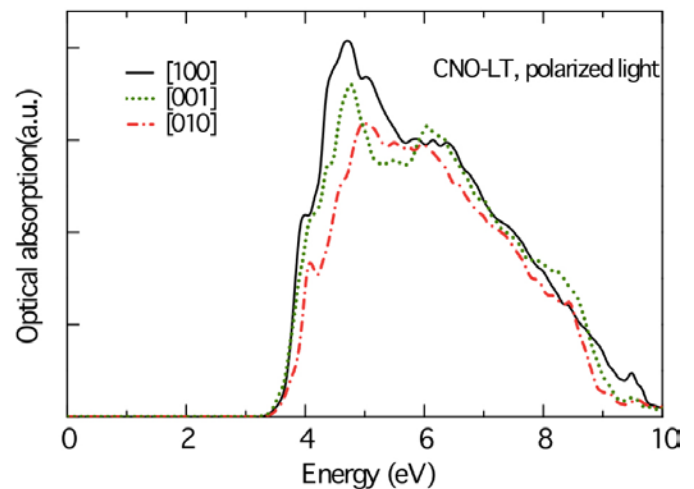


FIGURE 2. Optical Absorption Spectra of Low-Temperature (LT) CNO with Light Polarized along $[100]$, $[010]$, and $[001]$

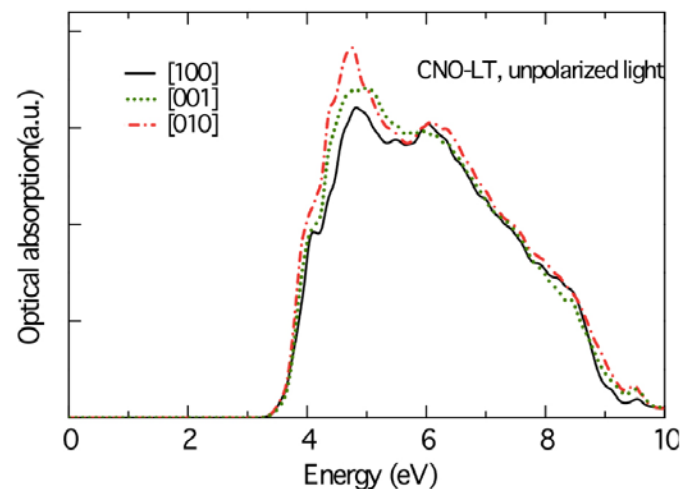


FIGURE 3. Optical Absorption Spectra of Low-Temperature CNO with Unpolarized Light along $[100]$, $[010]$, and $[001]$

high temperature and with several intermediate grinding. Figure 4 shows X-ray diffraction patterns of sol-gel samples heated for two hours at various temperatures.

Conclusions and Future Directions

The bandgap of CNO is approximately 3.1 eV and must be modified to a smaller value so that it absorbs into the visible portion of the solar spectrum. We have commenced a computer study to engineer a smaller bandgap material through elemental substitution in the CNO structure. We will fabricate and characterize any material deemed suitable that the computer study identifies.

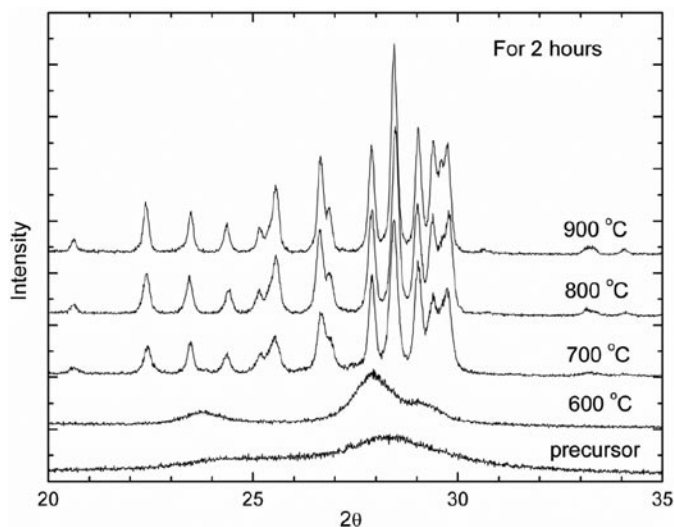


FIGURE 4. X-Ray Diffraction Patterns after Heat Treatment of the Precursor for Two Hours at Different Temperatures