10-5-2020

Discovery Research for New Optical Materials

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Abstract

This project utilizes the MGI approach in order to discover new compounds at an accelerated rate. Novel materials for optical applications, such as luminescent scintillators, are desired for improvement of properties. Using density functional theory (DFT) calculations, new single-crystal scintillating materials can be optimized leading to more efficient scintillation. (5) Two existing compounds in the quaternary system Na-O-Si-Y were chosen and further modified using substitutions into proposed structures that can be investigated. The two original compounds, NaO_4SiY and $NaO_{26}Si_6Y_9$, were chosen and modified because of their already high density by substituting yttrium for lanthanum, sodium for potassium and yttrium for lanthanum, and lastly yttrium for zirconium and sodium for potassium. The potassium substitution allows the structure to slightly expand in order to yield more realistic bond distances. This yields a total of 8 structures, with 6 being proposed structures for study. Figure 1 shows the band gap for the NaO_4SiY.

Introduction

Previous modeling work has focused on aqueous speciation (9), where reactant amounts were chosen at the edge of stability regions for stable oxides or hydroxides. Based on previous work for discovery of $Zn_2EDTA.2H_2O$ single crystals (1), yield diagrams for our current systems similarly shows optimum stoichiometries for potential discovery of new compounds. It was found that hydrothermal conditions for this compound were just outside of the stability region for ZnO. For K-La-Zr-O and similar systems, OLI Analyzer speciation software has been used to guide the best synthetic conditions for discovery of new optically active materials.

By altering the composition of the starting materials, it is possible to generate trace amounts of crystals that have either never before been synthesized or have only been hydrothermally synthesized at much higher temperatures. (4, 7, 8, 10) Utilizing substitutions for heavier materials increases the density of the crystal which has been shown to increase the scintillation properties. Density functional theory is a computational method used for modeling structures to investigate electronic structure. DFT can be used to look at the functionals of spatially dependent electron density. (5) This allows for specific properties of scintillators to be explored.

Procedures

- Mercury crystal imaging software was used to determine best base structures—starting stoichiometries—in the Na-Si-Y-O system for substitution of heavier metals to increase density.
- Metal-oxygen bond distances were carefully examined to see which metal subsitutions are more feasible.
- NaO_4SiY and $NaO_{26}Si_6Y_9$ were chosen as base structures, based on highest density.
- Y-La substitution was carried out using enCIFer software to edit crystallographic information file (cif), replacing all Y atoms with La atoms. This step was done to each base structure with Na-K and Y-Zr substitutions.
- Full substitutions and 50 atomic % compositions are being explored, shown in the table below.
- DFT calculations are in progress.

Proposed Structures

Original Compounds:	NaO_4SiY	$NaO_{26}Si_6Y_9$
Y-La Substitution:	$NaO_4SiLa_{0.5}Y_{0.5}$	$NaO_{26}Si_6La_{4.5}Y_{4.5}$
	NaO_4SiLa	$NaO_{26}Si_6Y_9$
Na-K, Y-La Substitution:	$K_{0.5}Na_{0.5}O_4SiLa_{0.5}Y_{0.5}$	$K_{0.5}Na_{0.5}O_{26}Si_6La_{4.5}Y_{4.5}$
	$KO_4SiLa_{0.5}Y_{0.5}$	$KO_{26}Si_6La_{4.5}Y_{4.5}$
	$K_{0.5}Na_{0.5}O_4SiLa$	$K_{0.5}Na_{0.5}O_{26}Si_6Y_9$
	KO_4SiLa	$KO_{26}Si_6Y_9$
Y-Zr, Na-K Substitution:	$K_{0.5}Na_{0.5}O_4SiZr_{0.5}Y_{0.5}$	$K_{0.5}Na_{0.5}O_{26}Si_6Zr_{4.5}Y_{4.5}$
	$KO_4SiZr_{0.5}Y_{0.5}$	$KO_{26}Si_6Zr_{4.5}Y_{4.5}$
	$K_{0.5}Na_{0.5}O_4SiZr$	$K_{0.5}Na_{0.5}O_{26}Si_6Zr_9$
	KO_4SiZr	$KO_{26}Si_6Zr_9$

DFT Results

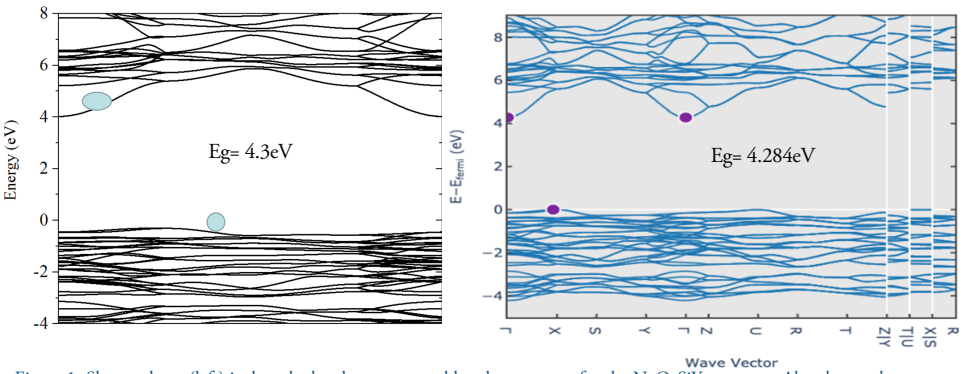

Figure 1: Shown above (left) is the calculated structure and band gap energy for the NaO_4SiY structure. Also shown above (right) is a reference band structure taken from Materials Projects. Both band gap energies are very similar at ~4.3 eV.

Future Work

- Continued DFT calculations
- Identification of previously unidentified phases
- Growth of larger crystals
- Continuation of this and related systems with different compositions of starting materials

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Acknowledgments

Dr. Ming Hu, Mechanical Engineering, U of SC
MADE in SC, SC EPSCoR, NSF #1655740
SC EPSCoR GEAR-CRP, U of SC Subward 20-4041
SURE Program, Winthrop University
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