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Designing novel phosphor materials for efficient LED

a. Introduction Light-emitting diode (LED) is on its way to becoming the major lighting source due to its high energy-efficiency and materials endurance. The major challenge in this field is the lack of green LED light source, an important component to synthesize white light (Fig. 1a). One simple and efficient technique to overcome this problem is to downconvert the blue light generated from GaN-based LED to green and red lights (Fig. 1b and 1c). In the past decades, phosphor materials have partnered GaN LED to produce white light.¹⁻⁴ However, despite the rich choice of materials, current phosphors are not efficient enough, which is one of the major bottlenecks for reaching solid-state lighting efficiency goals.

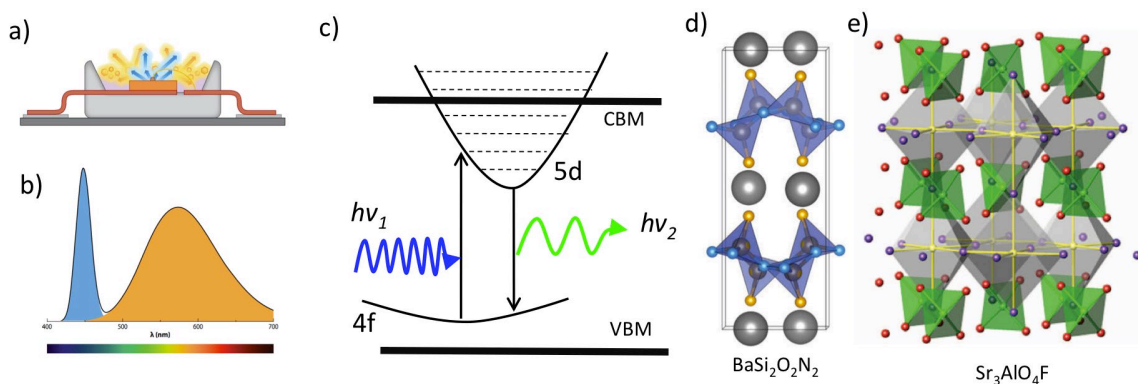


Figure 1. a) LED device; b) spectrum using phosphor down-converting; c) down-converting mechanism; d) an oxynitride phosphor; e) an oxyfluoride phosphor.

Many promising phosphors are known to have low quantum yield, especially at the operating temperature, wasting a large amount of energy while down-converting blue or UV lights. A major approach to improve phosphor efficiency and to tune the spectra is through the variation of compositions. The traditional approach is mixing the metal ions with different size. This method can only fine-tune the structure to affect the absorption and emission of the light, and therefore its results are quite limited.⁵⁻⁸ On the other hand, very few studies have been conducted to the alternation of anions, for example replacing the O atoms by F (or N) atoms partially or completely.⁹⁻¹⁴ Blending F into the structure may greatly enhance the stability since the fluorides are generally more stable than oxides, therefore has an indispensable advantage. Moreover, the combining of different anions usually has very strong effect while tuning the electronic structures and properties of materials. In recent years, a number of experimental and computational studies have been conducted for oxyfluorides.¹⁵⁻³² These studies showed promising applications of these mixed anion materials in many areas, including photocatalysis,³³⁻³⁵ Li-ion battery, phosphorous for solid-state lighting,^{31,36} supercapacitors,³² etc. However, it is a very challenging task to combine different anions such as O and F in compounds. That is why there are very few studies along this direction compared with the numerous works of tuning properties by combining different cations. Generally speaking, the synthesis involving fluorides require higher temperature and longer reaction time because of the stronger metal fluorine bonds. Therefore, it will be greatly helpful if we can know in advance the stability and the properties of the target compounds.

b. Purpose of the project. Our objective is to systematically search and design new

phosphor materials with atypical compositions, using quantum mechanics based computer simulations. Different to previous attempts, we will focus on mixing the anions, and will investigate the composition-structure and structure-property relations. After upgrading the structure search algorithm to adapt to complex materials, we will employ it to search possible structures of compounds with designed chemical compositions. With the identified structure of stable compositions, we will calculate its related properties including the band gaps, the band edge states, and the elastic moduli. Only those with a large gap, proper edge position, and large bulk modulus will be selected as candidate materials.

c. Methodology The study will be conducted by use of computer simulations that are based on quantum mechanics descriptions of the electron states^{37,38} and the automatic generation and search of the crystal structures.³⁹⁻⁴¹ In this so-called first principles approach, all properties are determined by the quantum mechanics and fundamental particle parameters such as electron charge and mass, without any further experimental input of the structures and properties of materials.

Task 1. Exploring structure features and stabilities with varying anion

compositions: We plan to conduct a systematic search of stable structures for oxyfluorides and nitroxides throughout the compositions with varying anion ratio. While anion composition varies, the major feature in the crystal structure may change dramatically, including the symmetry, the coordination, and the connectivity etc. Through the systematic study of the structures, we expect to identify the ideal composition that can produce stable and promising phosphors with high yield and high thermal quenching temperature.

Task 2. Structure-property relation and rare earth doping of phosphors: Once stable compounds and their structures are identified through our structure search, we will proceed to calculate their properties that are related to light down-conversion. This includes the bulk band structure, the elastic modulus, the band edge states (ionization energy and electron affinity) and the formation energies and transition levels of the rare earth dopants.

d. Timeline

- Crystal structure search with varying O/F and O/N ratios for selected compounds, about 12 weeks.
- Stability study based on the above-searched structures, about 10 weeks.
- Electronic structure and bonding feature for the identified stable compounds, about 15 weeks.
- Write manuscripts and a report, about 15 weeks.

e. Significance

Impact on my research group: I have been very active in the research field of materials design using quantum mechanics based crystal structure search. In the past 5 years, I have published many papers in top journals in this area, including 1 in Nature Chemistry, 3 in Nature Communications, 5 in top chemistry journals (JACS and Angewandte Chemie).

My next major goal is to secure a large external grant from a major funding agent such as NSF, DOE or DOD. Designing novel phosphor materials is one promising direction.

However, I need more preliminary results in order to convince the funding manager and the reviewers. Starting from 2018 Fall, I will need to teach 12 units per semester. An award from the Probationary Faculty Support will provide the necessary release time in

order to keep the momentum of our research in materials design and to secure a major external funding.

Impact on the research community 1. Gain a comprehensive understanding of the structural evolution with varying O/F ratios in metal oxyfluoride compounds and its effect on the electronic structure and properties. 2. Investigate the effect of replacing O with F on the electronic structure and mechanical properties of the phosphors.

f. Impact on instruction: My research topics and techniques, such as reaction enthalpies, electron states of atoms and solids, quantum chemistry methods are directly related to courses such as Chem102 and Chem352. Since joining CSUN, I have been exploring the possibility to exploit the pedagogic value of computer simulations and offer CSUN students direct illustrations of chemistry on computer screens. Furthermore, I have advised more than 10 CSUN undergraduate students doing research in my lab. They have co-authored 4 journal articles so far including one in Nature Communications. In the next year, the PI plans to advise 3-5 undergraduate and 1 graduate student. The undergraduate students will be involved in implementing specific features in computation programs, constructing initial files for oxyfluoride and related materials, and researching literature. The graduate student (3-year M.S. candidate) will be trained to perform calculations and analyze electronic structures. He/she will also work together with the PI to extend the research scope by exploring the calculation of the rare-earth metal doping of the identified new phosphor materials. Their experience in our lab will make them much better prepared for the job market and the graduate programs at R1 universities.

g. Dissemination 1) My top goal is to secure a large research fund from a major funding agent (NSF, DOE, DOD etc.) by the end of the supported period. 2) 1-2 publications in

prestigious journals: one on stability, structure evolution and properties of oxyfluoride phosphors; and the other on structure and stability of oxynitride phosphors. 3) The work will also be reported in international conferences such as the American Physical Society (APS) March meeting.

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