

Exploring New Generation of Europium and Terbium Activated Phosphors via experiments and first-principles calculations

Objectives

1. To better understand the new generation of phosphors (luminescent materials) activated by Europium and Terbium via experiment investigations.
2. To gain physical insight into the mechanism of luminescence and to study the interplay between the atomistic and electronic properties of Europium and Terbium activated phosphors at atomistic level through first-principles calculations.
3. To optimise the quality of luminescence in the Europium and Terbium activated phosphors via the theoretical insight gained from first-principles calculations.
4. To initiate a highly prospective research area, i.e., computational-intensive first-principles calculations (also known as ab initio calculations or DFT calculations) to complement our local solid-state experimental researches.
5. To develop our local human capital in computational condensed physics / computational materials science researches.

Background

A phosphor is a material that is able to emit light upon absorbing energy, or shows luminescence properties. It can emit light for a time scale from seconds up to many hours after it was briefly excited. Most commonly, phosphor materials involves transition metals or rare earth ions from lanthanides. Host structures such as CaWO_4 , YTbO_4 , SrAl_2O_4 doped with transition metals or rare earth ions impurities (known as activators in the literature) are widely used luminescence material nowadays. Two specific types of host lattices, namely Yttrium Tantalite (YTbO_4) and Yttrium Niobate (YNbO_4) are efficient phosphors that have seen widespread commercial use such as in X-ray medical imaging, electronic detector system, films/screen cassettes and etc. The latest development in the frontier of Yttrium and Tantalum-activated phosphors are well summarised in the textbook authored by Prof. Nazarov [Nazarov, 2011], who is also one of the team members for this research grant application. Prof. Nazarov, who is currently with the School of Materials and Mineral Resources Engineering, USM Engineering campus in Nibong Tebal, is an internationally renowned expert in the area of luminescence. His authority in the research field is self-evident when one reads the text book he has authored [Nazarov, 2011]. Basically, the luminescence of the phosphor is not only related to the host structure. Phosphor with niobate group NbO_4^{3-} and tantalate group TaO_4^{3-} give blue light upon excitation. With the addition of activator such as Europium Eu^{3+} and Terbium Tb^{3+} , for example in the structure $\text{YNbO}_4:\text{Eu}^{3+}$, the emission can be

shifted to longer wavelength. The activator absorbs the excitation energy directly and thus takes the electron into the excited states. In these phosphors activated by rare earth materials, both of the emission centers from host lattice and rare earth contribute to the overall luminescence. Europium and Terbium activated phosphors nowadays find their applications in emissive display and fluorescent light.

Recently, there is an increased interest on the enhancement of emission intensity under UV excitation by substitution of cations in the host lattice by rare Earth elements. Specifically, researchers in this field are exploring the possible improvement of emission by incorporate secondary ions into the existing systems, e.g. $(Y,M)NbO_4:Eu^{3+}$, where M stands for Al, Ga atoms. This idea is seen as a promising way leading to a much improved, novel next-generation phosphor. Nevertheless, for the time being, there are very few publications in the literature on this frontier. The absence of sufficient research work on this area provides a highly promising avenue to pursue not only for academic interest but also for promising practical applications. The textbook by Prof. Nazarov provides a very comprehensive review and summary for the technical issues related to the matter [Nazarov 2012].

In the theoretical front, phosphors are mostly crystalline, periodic systems. Periodic systems in the weak interactions limit are well understood in the framework of energy band theory, where the famous Bloch theorem plays a fundamental role [Ashcroft and Mermin, 1987; Kittel 2004]. At the first-principles level, these periodic systems are governed by many-body quantum theory. In principle one can extract all physically-interested characteristics, e.g., optical spectrum, and energy bandgaps measured experimentally, by solving the many-body quantum-mechanical equations. But such a task was forbiddingly difficult except for extremely simplistic systems. Density Functional Theory (DFT) was first proposed in the 1960's as a practically viable method to achieve this otherwise impossible mission. For his accomplishment, the inventor of DFT, Kohn, was granted as one of the [recipients](#) of the 1998 Nobel Chemistry prize [Kohn 2012]. DFT has since been continuously improved in terms of its implementation, methodology and accuracy. The advancement in DFT has been particularly astonishing in recent years due to the great leap in both computing technology and improvement in novel numerical methods. For a very comprehensive text book on DFT computation in condensed matter physics, see for example [Martin 2004]. The essential physical properties of a given periodic system can be calculated using the DFT codes which take care of all the relevant quantum interactions. DFT calculations are known as first-principles or ab initio calculations because they can be calculated without the need of empirical parameters measured from experiments. The powerfulness and success of DFT in predicting physical properties of periodic systems in many major types of materials systems make it a perfect tool for computational materials science research, especially to probe the electronic structures. It is now a routine practice to use software packages of DFT to perform first-principle calculations as an effective and reliable tool to gain insight into crystalline systems for their electronic and other physical properties in the absence of empirical data.

Hypothesis

Through computation modeling, specifically, first-principles calculations, one can improve experiments by providing insight to physical process happening at the atomistic level. Despite the fact that niobate group NbO_4^{3-} and tantalate group TaO_4^{3-} have seen much potential commercial values as persistent phosphors (i.e., phosphors that last for long hours), there is little calculation work done on the host materials, not to mention the activator-doped lattices as a whole. Two main issues pertaining to atomistic calculation of these phosphors are the emission spectrum of the host lattice and charge transfer transitions [Nazarov 2012]. To the best of our knowledge, there is almost no offer of explanation in the literature to the apparent discrepancy between the experimental spectra and the results calculated from other first-principles calculations for the niobate and tantalate host lattices [Lim 2012]. This provides the ground for us to believe that previous reports might have overlooked the contribution of certain quantum mechanical interactions, specifically those from the d- or f- electrons among the atoms in the host lattice. We hypothesis that the best approach to apprehend the discrepancies between experimental and simulation is through an improved variant of DFT calculations, known as LDA+ U and GGA+ U approach, which could account for the overlooked quantum mechanical interactions in the d- or f- electrons.

On the experiment side, this research will attempt to test the hypothesis that incorporating secondary rare-Earth ions such as Eu^{3+} or Tb^{3+} into niobate group or tantalate group will improve the quality of luminescence of a phosphor. We then use first-principles calculations to compliment as well as to improve the experimental output. The ab initio calculation shall also provide a tool to provide theoretical insight into the atomistic origin responsible to the luminescence.

Theoretical Framework

This study is based on the framework of first-principles calculations, specifically, via density functional theory, DFT. DFT was put on a firm footing by the Hohenberg-Kohn theorems, and Walter Kohn was awarded with Nobel Prize in Chemistry in 1998 for his contribution of Kohn-Sham density functional theory [Kohn 2012]. It is a quantum mechanical modeling method used to solve the electronic structure of a many-body system. The theory maps a multiple-atoms system into single electron problem to calculate the ground state energy. But when it comes to system with highly correlated electrons such as those possesses d- or f-electron and magnetic properties of certain system, DFT computation reveals its insufficiencies. An improvement based on DFT, known as the 'LDA+ U ' and 'GGA + U ', provides a viable way to account for the quantum interactions due to the highly correlated d- or f-electrons by including an effective on-site interaction to the existing Hamiltonian, taking into account the orbital dependence of the Coulomb and exchange interactions. We refer to Martin [Martin 2004] for a comprehensive discussion on technical and practical details of the DFT-related computation in general.

Methodology

The project shall have both experimental and theoretical components.

Experimental component:

Samples of the luminescence materials (e.g., niobates, tantalates doped with rare-Earth elements) will be prepared by chemical procedures in the School of Materials and Resource Engineering, USM, Nibong Tebal. Professor Nazarov will take charge of the experimental aspect of this research project. We shall use the facilities already in existence (in the School of Materials and Resource Engineering, USM, Nibong Tebal and the School of Physics, USM, Penang) to characterise and examine the photoluminescence and physical properties of the samples through standard experiment methodology for material characterisation, such as XRD, infrared spectroscopy, reflectance and Raman scatterings. Experimental work shall also be carried out by our overseas collaborators in South Korea and Moldova. We plan to involve our overseas collaborators so that they could help us to tap the resource at the Synchrotron radiation at Pohang Accelerator Laboratory, Korea to provide e.g., synchrotron X-ray diffraction patterns for our samples.

Computational component:

The electronic properties of the samples, which determine the experimentally measured properties of these samples, will be calculated using density functional theory software packages. These packages include ABINIT, WIEN2k, VASP, Crystals. These software packages are either free or have been already purchased by USM (but some may need to be upgraded to new versions). These are computationally demanding software packages especially if they are to be used to perform calculations mimicking realistic atomistic systems. In particular, they demand high performance computing (HPC) facility such as parallel computing capability and cluster computer systems. We are going to run these first-principles calculations using these software packages in the already-in-existence cluster computer systems in the School of Physics, USM (namely, the anicca and comsics computer clusters, both can be accessed at www.anicca.usm.my and www.comsics.usm.my). These are HPC facilities that have been set up single-handedly myself (YTL) in the last few years with the aid of other research grants.

It has been a norm in the materials research frontiers to adopt the computationally intensive first-principles calculations to do the otherwise impossible task of 'materials design'. In this approach, we build up semi-realistic models of desired materials atom-by-atom, and then calculate their electronic, optical, mechanical and thermal properties by computationally solving the

many-body quantum mechanical equations using the Nobel-prize winning DFT theory. To be technically specific, supercells mimicking the configurations of the host crystals with or without dopants (i.e. Tb^{3+} or Eu^{3+} ions) are built. By cleverly manipulating the DFT codes via non-trivial technical maneuvering of the computer software and hardware, we first calculate the ground state energy of these supercell systems with optimised geometry. Following that, the physical properties of these systems are derived from the optimised ground states. We are in particular interested in the density of states (DOS), band structures and phonons modes of these systems, which are directly relevant to the luminescence spectrum measured experimentally. In practice the DFT software packages provide highly reliable functionality to do most of these calculations semi automatically, but manual discretion based on physical insights are indispensable in the process of calculation. The preprint attachment we have submitted for publication in the journal Computational Materials Science [Lim et al. 2012] is a concrete proof of our ability to run these DFT software for the purpose of this researches.

Publication which is related to the project

1. First-principles LDA+*U* calculations and luminescence study of YTaO₄, Thong Leng Lim, Mihail Nazarov, Tiem Leong Yoon, Lay Chen Low, M. N. Ahmad Fauzi, submitted to Computational Materials Science on 8 Nov 2012 (pending).
2. M. Nazarov, D. Y. Noh, New Generation of Europium and Terbium activated Phosphors, Pan Stanford Publishing, 2011. (Text book by Prof. Nazarov).
3. M. Nazarov, A. Nor Nazida, M.N. Ahmad-Fauzi, A new direction in study of persistent materials, Enjinier 14 (Jun, 2012) 12. (Bulletin for the School of Materials and Mineral Resources Engineering, USM).
4. Wen Fong Goh, Tiem Leong Yoon, Sohail Aziz Khan, Molecular dynamics simulation of thermodynamic and thermal transport properties of strontium titanate with improved potential parameters, Computational Materials Science 60 (2012) 123-129.

The importance and the benefits of the research

- (1) The new generation luminescence materials of Europium and Terbium activated phosphors is a frontier research field not being widely explored in the global research community. We are proposing here to venture into this research field as world pioneers. The significance and benefit of being pioneers in a new research area is self-evident.
- (2) Three-in-one (experimental, theoretical, computational) research practice, like the one we propose in the project, is rare in Malaysia. But such a holistic approach is arguably the most effective and powerful way to advance in any serious research endeavour. In many solid state researches throughout the world, DFT is an integral part in their research programs as DFT can reliably compute, predict and simulate material

characteristics from first-principles. However, such model to conduct scientific research in materials science or solid state physics (first-principles plus theoretical plus experimental) is indeed extremely rare, if not non-existence, in Malaysia. Considering the fact that DFT is such an important tool for solid state physics research, developing our local DFT expertise is a most reasonable thing to do. On the other hand, we have only very few experts in Malaysia despite its obvious importance. The DFT research as proposed here is likely to initiate a synergic incorporation of a stronger theoretical component into the experimental research effort in our local research labs. Such a theoretical-experimental collaboration model is a win-win scenario to the experimentalists, the theorists, and the local solid state research as a whole.

In short, this research proposal is one which incorporates three disparately different approaches to perform investigation of luminescence materials. We are going to use experiment and chemical techniques to synthesis and characterise the new generation luminescence materials. We will apply hard-core theoretical knowledge of solid state physics for quantum systems to provide insight into the electronic structure of the systems under investigation. And we are going to deploy high-performing computing facility to run the DFT software packages to predict and describe from first-principles the realistic systems we are going to investigate, in this case, new generation luminescence materials. The most significant implications as what the benefit of this research are not only the new findings in new generation luminescence materials of Europium and Terbium activated phosphors. The research proposal's more valuable significance lies in the initiation to conduct an integrated approach to conduct solid-state physics researches.

Equipment and materials available in the university that are to be used for this research

High performance computing facility (HPC) in the School of Physics, USM. This includes:

- (i) Chakra, a 4-node, 32-cores cluster computer
- (ii) Anicca, a 20-node, 80 cores cluster computer
- (iii) Comiscs, a 20-node, 80 cores cluster computer
- (iv) DFT software packages: VASP, ABINIT, WIEK2k, Crystals.

Researcher(s) that involved in this research:

	<i>Name</i>	<i>School/ Department/ Unit</i>	<i>(role/contribution)</i>
1	YOON TIEM LEONG	PUSAT PENGAJIAN SAINS FIZIK	Researcher
2	MIHAIL NAZAROV	PUSAT PENGAJIAN KEJURUTERAAN BAHAN DAN SUMBER MINERAL	Experts responsible to conduct experiment and mentor to the the overall re-search progress.
3	LIM THONG LENG	Faculty of Engineering and Technology, Multimedia University, Jalan Ayer Keroh	Co-researcher. Expert in DFT calculations, from Multimedia University, Melaka.

References

Neil W. Ashcroft and N. David Mermin, Solid State Physics, Thomson Press (India) Ltd (1987).

Charles Kittel, Introduction to Solid State Physics, Wiley 8 edition (2004)

Walter Kohn - Autobiography. Nobelprize.org. 10 Oct 2012,
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1998/kohn-autobio.html

Richard M. Martin, Electronic Structure: Basic Theory and Practical Methods, Cambridge University Press (2004).

M. Nazarov, D. Y. Noh, New Generation of Europium and Terbium activated Phosphors, Pan Stanford Publishing (2011).

Thong Leng Lim, Mihail Nazarov, Tiem Leong Yoon, Lay Chen Low, M. N. Ahmad Fauzi, First-principles LDA+ U calculations and luminescence study of YTaO₄, paper submitted to Computational Materials Science, October 5, 2012 (pending)