FIRST-PRINCIPLE AND EXPERIMENTAL CHARACTERIZATION OF THE ELECTRONIC PROPERTIES OF $CaGaSiN_3$ AND $CaAlSiN_3$: IMPACT OF CHEMICAL DISORDER

Ján Minár[1], Robin Niklaus[2], Jonas Häusler[2] and Wolfgang Schnick[2]

[1] New Technologies Research Center, University of West Bohemia, Pilsen, Czech Rep.,
[2]Department of Chemistry, University of Munich, Munich, Germany

E-mail: jminar@ntc.zcu.cz

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Abstract

White light emitting diods (LEDs) are regarded as a promising energy-efficient and ecological light source, because they have much less energy losses than incandescent bulbs and present much less toxical hazard than luminescent lamps. There are two ways to produce white light in LEDs. One way is to have a combination of three LEDs each of which emitting a primary colour so that an impression of white light is created. These are called RGB system white LEDs. Another -- technologically more attractive -- way to get white light is to have a blue light diode (usually an InGaN chip) covered with luminescent materials which subsequently convert the monochromatic exciting light into broad-spectrum light. The converting luminescent materials are called ``phosphors'', therefore this second type of white LEDs is called phosphor-converted LEDs or simply pc-LEDs [1,2].

White light in pc-LEDs is thus formed by combining that part of the exciting blue light which passes through the phosphors unaltered with light which originates from the converting phosphors; this light undergoes a wavelength conversion owing to non-radiative energy losses (Stokes shift). One can use just a single yellow phosphor or one can use a combination of red and green phosphors (multi-phosphor approach). Most commercially available white-light pc-LEDs contains only one broadband yellow emitting phosphor --- typically a Ce-doped garnet. This material is very useful in many aspects, however, it suffers from inadequate ability to reproduce colours of objects because of its limited power distribution in the red light spectral range. Therefore an intensive effort is under way to develop new phosphors that could be used to design better pc-LEDs via the multi-phosphor approach [1,3,4,5,6,7,8,9]. Basic requirements laid on an optimal pc-LED are (i) a high luminescence efficiency and (ii) spectral power distribution such that illuminated objects appear in the same colours as in the daylight. Meeting these two requirements often goes against each other, so one of the challenges of current research on pc-LEDs is striking the right balance [8]. The luminescence process in pc-LEDs includes absorption of the exciting blue-LED radiation, non-radiative energy decrease (typically due to emission of phonons) and radiative recombination leading to the desired emission. Properties of phosphors thus depends on many factors. Theoretical understanding of them would promote design of better white-light pc-LED sources. This is a complicated task that has to be approached on a step-by-step basis. One of these steps is detailed understanding of the electronic structure of phosphors. It is the electronic structure that mostly determines optical properties, such as absorption and emission spectrum. Though knowing the electronic structure alone is not sufficient to describe luminescence properties, its quantitative knowledge will help to understand the basic ground state and excited state properties of phosphors. In particular ab-initio calculations of electronic structure can provide valuable information on the trends how certain properties depend on the dopant and ligands chemical type and/or concentration.

We report a depleting investigation of the electronic, mechanical and optical properties of the recently discovered nitridogallosilicate $CaGaSiN_3$ which has potential as a LED-phosphor host material [10]. We focus on chemical disorder effects, originating of the Ga/Si site, comparing them to isostructural $CaAlSiN_3$ as it is demonstrated on Fig .1. We calculate the elastic moduli and the Debye temperature in terms of the quasi harmonical approximation. Spectral properties like the joint density of states (JDOS) are evaluated and the absorption, reflectance and energy loss function are obtained from the dielectric function. The optical band gap of $CaGaSiN_3$ from experiment is compared to the electronic band gap in terms of electronic DOS and band structure calculations. All properties are evaluated for different ordering models of Ga/Si while the experimentally observed substitutional disorder is accounted for by utilizing the Coherent Potential Approximation (CPA). We conclude a shrinking of the band gap for both $CaGaSiN_3$ and $CaAlSiN_3$ due to atomic disorder, which is unfavorable for potential phosphor applications. This conclusion can be summarised in so called Bloch spectral fucntion, which represents band structure of disordered material and is shown in Fig. 2. This study contributes to materials design considerations, and provides a close look on the electronic impact of substitutional disorder. Moreover, we open the scope to future investigations on solid solutions and phosphor host materials with low doping concentrations [10].

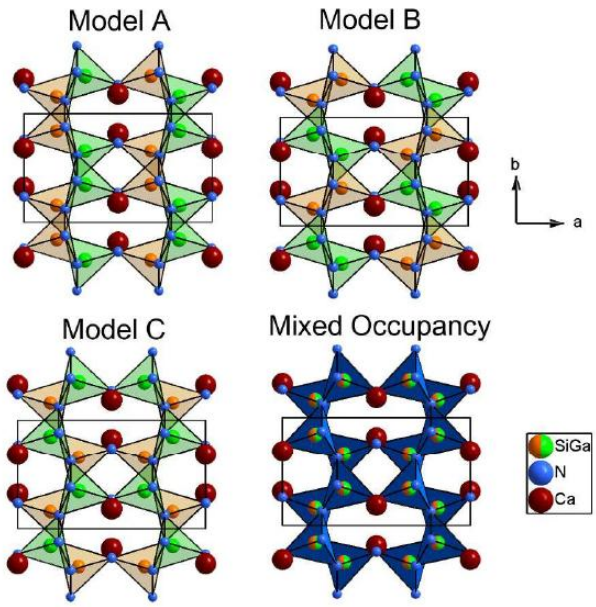

Fig.1: *Different Si/Ga ordering variants (A–C) for orthorhombic $CaGaSiN_3$. Model for mixed Si/Ga occupation from experimental data. Structures illustrated by $(Si/Ga)N_4$ tetrahedra in corresponding color. Reproduced from [10].*

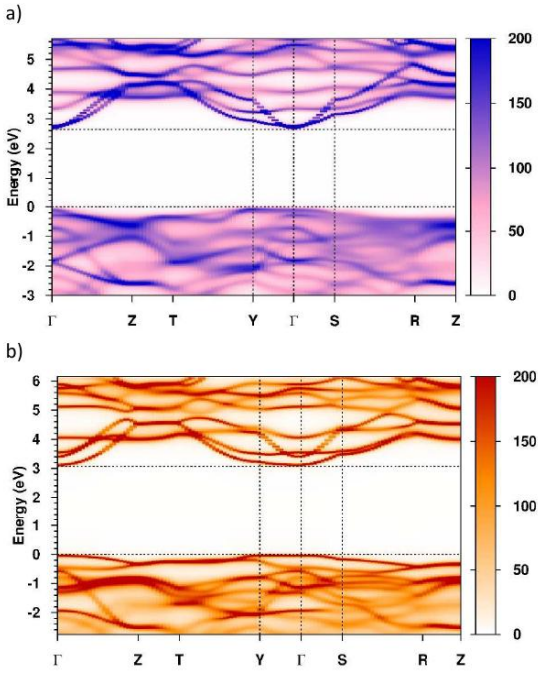

Fig. 2: *Bloch spectral function along high symmetry directions in the first Brillouin zone for the fully disordered structure of CaGaSiN3 (a) and CaAlSiN3 (b) obtained as symmetrized average of the relaxed ordering models and calculated within the KKR approach based on the CPA. Reproduced from [10].*

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