Critical overviews about conventional ideas for white-LED (oxy)nitride phosphors: *covalency* and *stiffness*

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Research on white-LED (oxy)nitride phosphors doped with Eu^{2+}/Ce^{3+} ion has been extensively conducted in the last decade [1,2]. Why did they attract attentions so much? It seems that many researchers rely on some conventional ideas: (oxy)nitride phosphors can be excited by blue or near-ultraviolet (nUV) light and emit longer-wavelength visible photoluminescence (PL) owing to *high covalency*; optical transitions involving a 5d-orbital electron of the activator occur at wavelength longer than in most oxides as a result of *high covalency* inducing strong nephelauxetic effect. (Oxy)nitride phosphors may be expected to exhibit small thermal quenching of PL due to *rigid* Si-N framework (*stiffness*) that may induce small Stokes shift. Further, (oxy)nitrides appear chemically more stable than most oxides and sulfides.

Nonetheless, it has been gradually noticed that the above naïve expectations are somewhat optimistic. Not all of (oxy)nitrides can be utilized as host materials for white LED phosphor, partly because Ce^{3+}/Eu^{2+} dopants cannot have suitable emission and excitation spectra for blue or nUV LED – unexpectedly too short excitation/emission –, and partly because thermal quenching of luminescence is too severe for practical use in white LED package where phosphor temperature may rise up to 80 to 150°C.

Thus, we have reexamined vague ideas on *covalency* and *stiffness* for deeper understanding of optical properties of (oxy)nitride phosphors [3]. In this talk, computational chemical approaches for design and analysis of white-LED (oxy)nitride phosphors are overviewed. In particular, first-principles investigations on (oxy)nitride phosphor hosts are exemplified; in particular, dielectric constant/refractive index (as an indicator of nephelauxetic effect) and vibrational and elastic properties (maybe related to configurational coordinate diagram). Luminescent properties of Eu^{2+}/Ce^{3+} dopants are discussed qualitatively on the basis of these results. It is stressed that the notion on covalency and stiffness may not be always accurate.

Future perspectives of theoretical studies such as accurate computation of band gap of host materials (GW, hybrid functional) and 5d and 4f levels of Eu^{2+}/Ce^{3+} dopants are addressed, by taking some examples such as $Ba_3Si_6O_{12}N_2$:Eu^{2+} (530nm peak, Stokes shift: $2.8\times10^3 cm^{-1}$, with smaller thermal quenching of PL than $(Ba,Sr)_2SiO_4$:Eu^{2+}) and $Ba_3Si_6O_9N_4$:Eu^{2+} (480nm peak, Stokes shift: $3.2\times10^3 cm^{-1}$, with little PL at R.T.) (Table.1). Auto-ionization model will be discussed as a plausible thermal quenching model.

Table 1. Computed physical properties of $Ba_3Si_6O_{12}N_2$ and $Ba_3Si_6O_9N_4$: band gap(E_g in eV) [4], average bulk modulus(K in GPa), shear modulus(G in GPa), Young's modulus(E in GPa), and Debye temperature(Θ_D in K) [5].

	E_g	K	G	E	Θ_D
$Ba_3Si_6O_{12}N_2$	6.88	68	41	104	433
$Ba_3Si_6O_9N_4$	6.45	84	53	130	489

References:
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