Rapid identification of advanced phosphors for solid-state white LEDs

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The Debye temperature is an ideal proxy for efficient photoluminescence.

Replacing incandescent light bulbs with LED-based solid-state white lighting devices provides a good opportunity to reduce energy usage. White LEDs are more efficient, have longer lifetimes, better color stability, are free of mercury, and are more physically robust compared with traditional lighting sources. However, it is difficult to control the color quality and lifetime of the three independent LEDs (red, green, and blue) that are required for the production of white light, and therefore most white LEDs rely on the conversion of LED light via inorganic phosphors (luminescent materials). As such, advanced phosphors, with improved quantum yields and enhanced thermal stability, are required to develop the next generation of highly efficient, solid-state white lights.

There are three primary methods for producing white light from LEDs. The first approach combines multiple LEDs (emitting light at different wavelengths) into a single device so that the blended light appears white. A second method uses a blue LED to excite a yellow-emitting phosphor. The combined blue and yellow light appears white. The third technique uses a near-UV or UV LED and multiple phosphors that emit light across the entire visible spectrum. Design rules, which chemists use to synthesize new materials, do not yet exist for the development of complex inorganic phosphors. Most new luminescent materials are instead discovered through chemical substitution within known compounds or with high-throughput combinatorial searches. Neither of these two approaches, however, are specifically targeted toward the discovery of novel phosphors that have a high probability of photoluminescence.

We have recently developed proxies that can be used instead of strict design rules to target the discovery of phosphors with high photoluminescent quantum yields (Φ). We have found that structural rigidity is the best proxy for host compounds with high Φ. Although this phenomenon in relation to molecules (e.g., the organic dye phenolphthalein compared to fluorescein) is well known, until now it has been difficult to identify the structural rigidity of solid-state compounds by simply comparing their crystal structures.

We have found that the most tractable proxy for the structural rigidity of inorganic phosphor hosts is a material’s Debye temperature — ΘD — the temperature required to activate the

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highest energy vibrations in a solid. A high value of \( \Theta_D \) indicates that a host has a high degree of structural connectivity and is vibrationally rigid. High \( \Theta_D \) values should limit vibrational relaxation, and make it a good predictor of high \( \Phi \). Experimental measurements of Debye temperatures involve low-temperature (often <4K) heat capacity measurements or atomic displacement parameters determined through neutron diffraction. These time-intensive measurements are unsuitable for our goal of rapidly screening large numbers of potential host compounds. We therefore approximate \( \Theta_D \) using elastic constants that are calculated from ab-initio density functional theory (DFT).

Using a quasi-harmonic Debye model, which depends solely on bulk modulus and Poisson’s ratio (obtained from DFT), we can accurately calculate \( \Theta_D \). We have confirmed that there is a positive correlation between \( \Theta_D \) and the \( \Phi \) of a material when it includes cerium (Ce\(^{3+}\)), for a number of known phosphors that encompass a variety of coordination environments and compositions (see Figure 1). A material has a higher tendency for photoluminescence when it has a high value of \( \Theta_D \). It is therefore advantageous to search for high-\( \Theta_D \) materials as potential new phosphor hosts. The host, however, must also be able to accommodate electronic transitions from the active luminescent center. Band dispersion theory predicts that highly connected structures, which are required for high \( \Theta_D \) values, often result in the material having a small bandgap (\( E_g \)). We use a hybrid functional calculation to determine the bandgap of our new materials.

Ultimately, new phosphor hosts must exhibit a specific balance between their band dispersion and Debye temperature. We use these two parameters to create a sorting diagram that allows convenient computational screening of many potential phosphor hosts (see Figure 2). Our most notable observation is that materials with the highest quantum yields plot in the top-right corner (i.e., with high \( \Theta_D \) and \( E_g \) values) of this figure. By focusing our screening on this region of the plot we are therefore most likely to discover additional compounds that have a high probability of efficient photoluminescence.

We have developed a method to rapidly screen vast databases of known inorganic structures to find materials with a high probability of displaying efficient photoluminescence. This will improve the rate of discovery of novel phosphor materials and help develop new solid-state white lights. We are now investigating materials that have a non-Ce\(^{3+}\) luminescent center as we strive to understand the performance of other rare-earth–substituted phosphors.

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**References**