Developing Novel Chemistry for Solid-State Lighting Phosphors and Other Applications

Challenge:

Solid-state lighting, that is, the use of light-emitting diodes (LEDs), has the potential to cut global electricity usage, and, therefore, reduce overall global energy consumption by significant amounts. But one of the challenges still facing LED engineering is the production of high-efficiency white lighting LEDs. "High-efficiency" in this usage indicates the efficiency of transformation of electrical energy (electrons) input to light (photons or lumens) output. Overall, this is expressed as a high luminous efficiency of radiation (LER). To achieve white lighting requires combinations of colored LED output, where each color is rendered with a high LER. In current white LEDs, red phosphors are employed to improve the color-rendering index to a more realistic white light, and currently employed red phosphors do not have a particularly high LER. This research is employing ingenious chemistry to develop red phosphors with a high LER, which absorb blue light and emit red. Hence the chemistry must develop compounds with both efficient blue-light absorption and efficient red radiation — this is referred to as "down-conversion" because a higher-frequency (higher-energy) light (blue) is converted to a lower-frequency (lower-energy) light (red). This absorption-to-emission efficiency is expressed as a high quantum yield (QY). (The maximum QY is 1, meaning that every (blue) photon absorbed results in a (red) photon emitted.) Development of such compounds, in turn, points to applications beyond SSL.

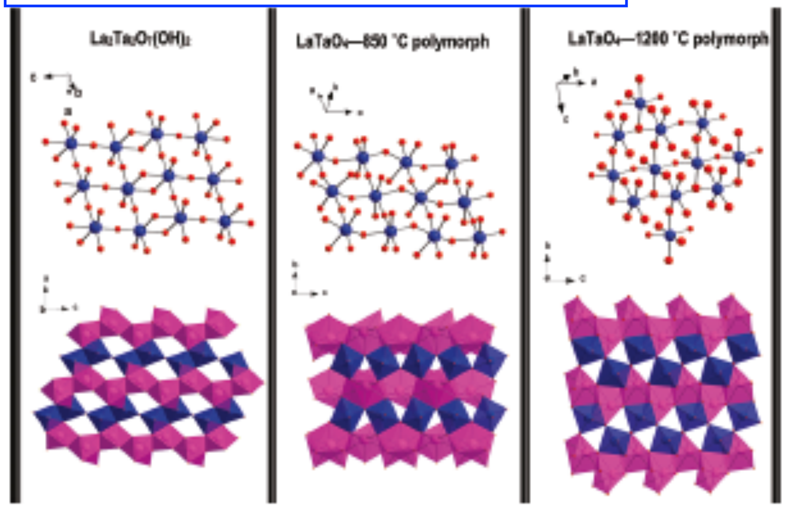
Research:

Appropriating Tantalate Chemistry

One focus of these studies is the chemical manipulation of rare-earth tantalates, that is a combination of rare-earth cation with the tantalate anions, (TaO_3) , (TaO_4) or other tantalum-oxygen combinations such as (Ta_2O_7). Tantalates are chemically and electrochemically stable, and they illustrate the importance of form-function relationships at the atomic scale (arrangement of atoms in space) and on the nanoscale (nanoparticle size and other features).

The basis of this research involves the synthesis of new tantalate polymorphs (structural forms defined by the exact spatial arrangement of the atoms in the tantalate crystal). Where, previously, three polymorphs were known, this research—through novel synthesis methods beyond the scope of this article (for complete technical details, see http://pubs.acs.org/doi/pdf/10.1021/cm9020645)—has discovered a fourth polymorph with distinctive properties, including its potential use as a red phosphor in LEDs, when combined with the cation of a rare earth element.

Illustration of different tantalate polymorphs (tantalum atoms, blue, oxygen atoms, red). While the stoichiometry (ratio of tantalum to oxygen) is identical, the arrangement of atoms in space is quite different.

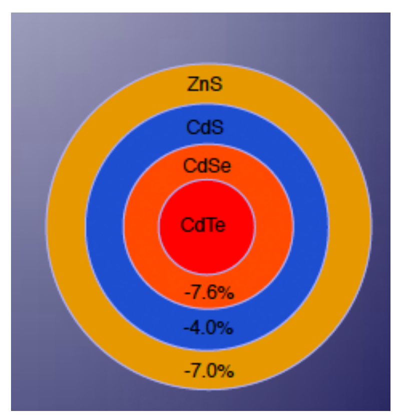


This research focused on Europium (Eu^{3+}) tantalates and their properties that included a high quantum yield of narrowband, ~610-nm red emission, ideal for inclusion in white-light LEDs. Sandia researchers discovered that the new tantalate polymorph had a higher rare-earth site distortion in the crystal structure, which correlated with its higher quantum yield.

Although the blue absorbance driving this blue-to-red down-conversion was superior to that of other Eu^{3+} phosphors, it was still lower than desirable for optimal efficiency. Hence, the researchers on this project have attempted a variety of Eu substitutions by other rare earths like samarium (Sm) and gadolinium (Gd), even going so far as to try a transition metal such as manganese (Mn). In each case, the performance was not as desirable as that of the Eu compound. The research is ongoing, with one possible route to make the Eu^{3+}tantalates into transparent monoliths (transparent blocks or plates) to compensate for their low blue absorbance. This accomplishment would give the blue light an increased optical path length within the (Eu^{3+}) tantalate crystal, and hence a greater probability of absorption as more molecules would be exposed and have the chance at absorbing the blue light. Such optical engineering has been successful with other phosphors, and so there is reason to believe in its potential value.

Nanoparticles

In a parallel research effort, this Sandia chemical engineering team is pursuing core-shell layered nanoparticles with a cadmium-tellurium (CdTe) core and surrounding shells of cadmium-selenium (CdSe), and cadmium sulfide (CdS) — a heterostructured nanoparticle. In this ingenious bit of chemistry, the crystal structures of the outer layers gradually place a strain on the CdTe core's crystal structure, leading to its ability to absorb blue light and emit red. CdTe nanoparticles have a high efficiency of blue absorption across a band of blue wavelengths and exhibit QYs of over 0.95 (over 95% of absorbed blue light emitted as red). Furthermore, the nanoparticles can be tuned by this technique to emit wavelengths other than red, providing the option for a variety of LED products.



Schematic drawing of core-shell nanoparticle with CdTe core and shells of CdSe and CdS

Red phosphors produced by the core-shell nanoparticle method

As this work proceeds, researchers will be investigating whether this high QY can be maintained at elevated temperatures (approximately 150 °C), and also whether it will be possible to control the lattice mismatch strain that is at the heart of this work, but which can also lead to undesirable core defects such as nonradiative recombination centers that can decrease quantum yield.

Significance:

Beyond SSL, rare-earth tantalates have potential applications in photocatalysis such as the light-driven production of hydrogen (H_2) or photodecomposition of contaminants in the environments. These are important applications, but the SSL applications are incredibly important because in enabling high-efficiency white-light LEDs, the energy savings are potentially enormous. With fluorescents providing 25% efficiency, LEDs can yield efficiencies of from 50% to even as high as 80%, thus cutting electricity usage for lighting at least in half, possibly even more. Estimates are that this could ultimately cut global electricity consumption by at least 10%.

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