

Let the True Colors Shine Through

This report features the work of Ru-Shi Liu and his co-workers published in *Chem. Mater.* **24**, 2220 (2012).

White light-emitting diodes (WLED), which are free of mercury, have the promising features of a small size and a long life, making them a potential replacement for both conventional incandescent and fluorescent lamps for general applications of lighting in the near future. The features of long life and freedom from mercury would contribute to solving environmental problems. The luminous efficacy (LE) of a white LED lamp now exceeds not only that of a conventional incandescent lamp but also that of a fluorescent lamp. With the luminous efficacy of white LED progressing steadily, their color-rendering properties, however, cannot fully meet the requirements for general lighting applications, and must be greatly improved.

There are basically at least two approaches for the production of white-light LED lamps. The first method (RGB- or trichromatic white LED) uses multiple LED additively mixed to generate white light; its advantage is that the intensity of each LED diode can be adjusted to match the requirement, but the major disadvantage is the high cost of production and the low color-rendering index (CRI) of RGB-LED. The second method, a phosphor-converted LED (p-LED) uses blue or sometimes ultraviolet LED in combination with a phosphor that absorbs a portion of the blue light and emits a broader spectrum of white light. The CRI value can achieve over 90. The low cost and adequate performance makes this the most widely used LED technology for general lighting today. The blue-light-emitting LED emit no light in the infrared or ultraviolet spectral region, which can avoid damage to an illuminated object. These lamps hence become suitable for the lighting of art objects, in shop-window displays, for in-house lighting and for medical applications, but require much higher color-rendering properties to improve the performance. To grasp the phosphor photoluminescent properties with various parameters is important for the control of the LE and the CRI of the device.

To understand the luminescent function and mechanism of phosphors, Prof. Liu and his co-workers applied X-ray diffraction (XRD), UV excited photoluminescence, and X-ray absorption near-edge structure (XANES), performed at NSRRC beamlines **BL01C2**, **BL03A1** and **BL17C1** to analyze a new Eu^{3+} -activated oxyfluoride phosphor $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{F}_2:\text{Eu}^{3+}$ ($\text{CAOF}:\text{Eu}^{3+}$) material.¹

To achieve the requirement of illumination, Prof. Liu's research team studied the crystal chemistry to reduce Eu ions from oxidation state 3+ to 2+ in the lattice. The replacement of $\text{Al}^{3+}-\text{F}^-$ by the dopant $\text{Si}^{4+}-\text{O}^{2-}$ was adopted to enlarge the activator site that enables Eu^{3+} to be reduced. They used powder XRD and a high-resolution transmission electron microscope (HRTEM) to examine the crystallization. The results of the photoluminescence indicated that the phosphors $\text{Ca}_{12}\text{Al}_{14-z}\text{Si}_z\text{O}_{32+z}\text{F}_{2-z}:\text{Eu}$ ($z = 0 - 0.5$) as synthesized display an intense blue emission with a maximum at 440 nm that is produced by the 4f-5d transition of Eu^{2+} , with the intrinsic emission of Eu^{3+} under UV excitation. To

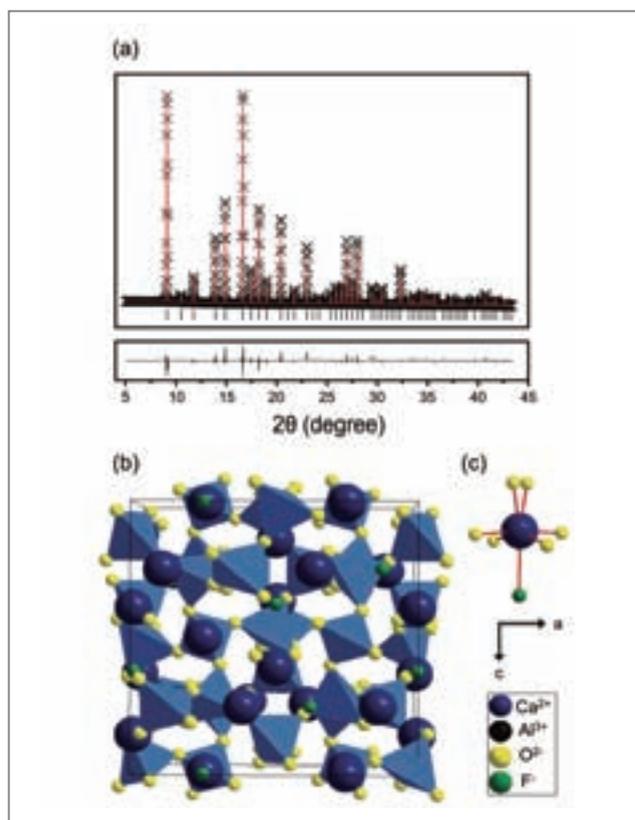


Fig. 1: (a) Observed (crosses) and calculated (solid line) XRD patterns of the Rietveld refinement of $\text{Ca}_{11.9}\text{Al}_{14}\text{O}_{32}\text{F}_2:\text{Eu}_{0.1}$, (b) crystal structure of the $\text{Ca}_{11.9}\text{Al}_{14}\text{O}_{32}\text{F}_2$ unit cell viewed in the b -direction, and (c) coordination geometry of Ca^{2+} site in $\text{Ca}_{11.9}\text{Al}_{14}\text{O}_{32}\text{F}_2$. (courtesy of Prof. Liu with the figure adapted from the reference)

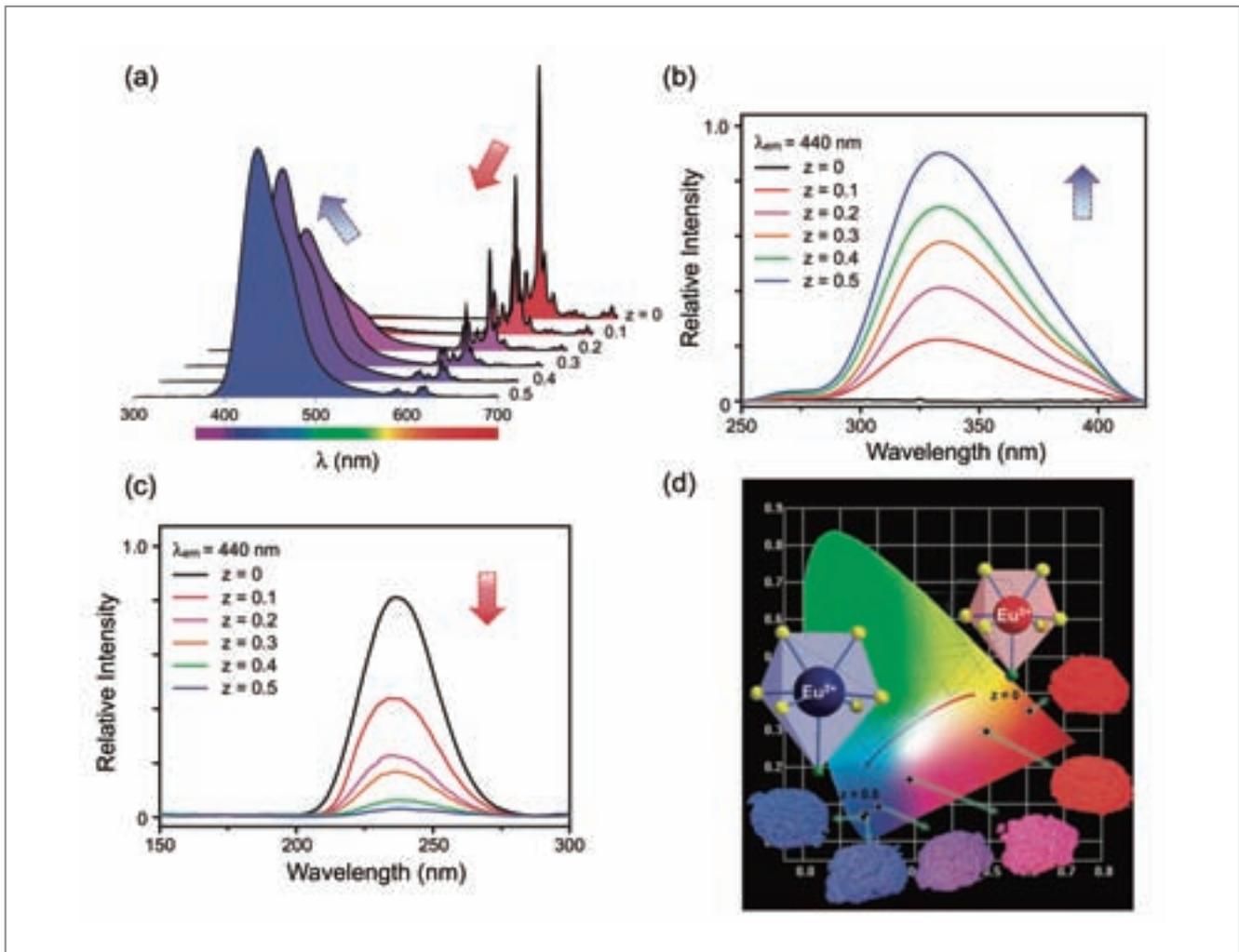


Fig. 2: (a) VUV emission spectra ($\lambda_{ex} = 254$ nm), (b) PL excitation spectra ($\lambda_{em} = 440$ nm), (c) VUV excitation spectra ($\lambda_{em} = 613$ nm) of $\text{Ca}_{11.9}\text{Al}_{14-z}\text{O}_{32+z}\text{F}_{2-z}\text{Eu}_{0.1}$ ($z = 0 - 0.5$), and (d) dependence of the CIE chromaticity coordinates on the value of z in $\text{Ca}_{11.9}\text{Al}_{14-z}\text{O}_{32+z}\text{F}_{2-z}\text{Eu}_{0.1}$ ($z = 0 - 0.5$) upon excitation at 254 nm. The inset shows the schematic variation of the activator site driven by incorporation of $\text{Si}^{4+}\text{-O}^{2-}$ and the irradiated phosphor images of each composition under a UV lamp emitting at 254 nm. (courtesy of Prof. Liu with the figure adapted from the reference)

understand the substitution effect of $\text{Si}^{4+}\text{-O}^{2-}$ in the coordination environment of the activator site, they also utilized Rietveld refinements to investigate the crystal structure and its character.

Furthermore, the valence states of Eu in the samples were analyzed with XANES. The quantity of substituted $\text{Si}^{4+}\text{-O}^{2-}$ tuned the chromaticity coordinates of $\text{Ca}_{12}\text{Al}_{14-z}\text{Si}_z\text{O}_{32+z}\text{F}_{2-z}\text{Eu}$ phosphors from (0.6101, 0.3513) for $z = 0$ to (0.1629, 0.0649) for $z = 0.5$, indicating the potential for developing phosphors for WLED.

Prof. Liu and his co-workers concluded that, using an activator of which the valence is tunable on controlling the size of the activator site, represents a hitherto unreported structural motif for the design of phosphors in phosphor-converted light-emitting diodes (pc-LED).

Reference

1. K.-W. Huang, W.-T. Chen, C.-I. Chu, S.-F. Hu, H.-S. Sheu, B.-M. Cheng, J.-M. Chen, and R.-S. Liu, *Chem. Mater.* **24**, 2220 (2012).