

ENHANCEMENT OF UV EXCITATION OF THE RED PHOSPHOR Pr³⁺ DOPED CaTiO₃

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LEDs to emit efficiently white light are ideal solid-state light sources, in which lightening industries are interested. To produce white light, one of most important approach is to combine UV or blue LEDs with phosphors, which down-convert LED emission to longer wavelength light. In order to have good color rendering, tricolor (450/520/610nm) phosphors are suggested to use for such phosphor-LEDs^[1]. In this design, the emission wavelengths of LEDs can be selected in the range from 370 to 400nm. In other word, the semiconductor alloy GaInN for the LEDs will contain less In. Such LEDs might be relatively easier to be manufactured. On other hand, phosphors efficiently pumped in this wavelength range are relatively easier to be found than those pumped in longer wavelength.

Unfortunately, not many tricolor phosphors currently available have efficient excitation in the above wavelength range. This is especially true for red phosphors. Although Eu³⁺ ions in many hosts emit in red, but the UV excitation efficiency is very low due to the nature of 4f-4f transitions. Eu²⁺ in CaS has shown red emission band at 650nm with efficient excitation in the above wavelength range, but the phosphor is chemically unstable.

In this work, Pr³⁺ doped CaTiO₃ is investigated. Strong red emission at 612nm from ¹D₂ to ³H₄ transition of Pr³⁺ was observed. Blue emission of ³P₀ to ³H₄ is thermally quenched at room temperature. Excitation spectrum showed that the 4f-5d absorption transition of Pr³⁺ was very strong and fell in the UV range from 250 to 390nm. However, the absorption in the spectral range 370-400nm is not as strong as the peak at 340nm. Efforts have then made to shift the peak position of absorption to the longer wavelength through molecule engineering.

Substituting Ca²⁺ partially by Sr²⁺ did not change the excitation spectrum much, therefore did not improve the UV excitation efficiency. Oppositely, the Pr³⁺ red emission decreased with increasing the content of Sr. The red emission was ten times weaker in SrTiO₃ than in CaTiO₃. In addition, the system Ca_{1-x}Sr_xTiO₃ underwent three compositional phase transitions at room temperature with changes of content of Sr. In the tetrahedral phase (0.95 < x < 0.7), the blue emission of ³P₀ became predominant even at room temperature.

In the case of Pr³⁺:CaTiO₃ codoped with Bi³⁺, it was found that the UV excitation was enhanced. The shoulder in the spectral range from 360 to 380nm in the excitation spectrum of Pr³⁺:CaTiO₃ was developed to a strong peak. The UV excitation efficiency in the spectral range 370-390nm is enhanced by about three times. The

physical role of Bi³⁺ ions in the sample is not quite clear. Bi³⁺ has strong absorption transition from the ground state ¹S₀ to the excited states ¹P₁ and ³P_J in UV. It may then serve as a sensitizer.

In addition, detailed energy level structure of Pr³⁺ in CaTiO₃ was studied. Temperature dependence of luminescence was measured. Thermal quenching, concentration quenching and effects of phase transitions on luminescence are discussed.

The work is supported by NASA.

Reference

1. Arturas Zukauskas, Michael S. Shur, and Remis Gaska, MRS Bulletin, 26 (2001) 764.