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 Eu\(^{3+}\) ions in many hosts emit in red, but the UV excitation efficiency is very low due to the nature of 4f-4f transitions. Eu\(^{3+}\) 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, Pr\(^{3+}\) doped CaTiO\(_3\) is investigated. Strong red emission at 612nm from \(1^D_2\) to \(3^H_4\) transition of Pr\(^{3+}\) was observed. Blue emission of \(3^P_0\) to \(3^H_4\) is thermally quenched at room temperature. Excitation spectrum showed that the 4f-5d absorption transition of Pr\(^{3+}\) 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 Ca\(^{2+}\) partially by Sr\(^{2+}\) did not change the excitation spectrum much, therefore did not improve the UV excitation efficiency. Oppositely, the Pr\(^{3+}\) red emission decreased with increasing the content of Sr. The red emission was ten times weaker in SrTiO\(_3\) than in CaTiO\(_3\). In addition, the system Ca\(_{n}\)Sr\(_{1-n}\)TiO\(_3\) 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 \(3^P_0\) became predominant even at room temperature.

In the case of Pr\(^{3+}\)-CaTiO\(_3\) codoped with Bi\(^{3+}\), it was found that the UV excitation was enhanced. The shoulder in the spectral range from 360 to 380nm in the excitation spectrum of Pr\(^{3+}\)-CaTiO\(_3\) 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 Bi\(^{3+}\) ions in the sample is not quite clear. Bi\(^{3+}\) has strong absorption transition from the ground state \(5\mathrm{S}_4\) to the excited states \(3^P_1\) and \(3^P_3\) in UV. It may then serve as a sensitizer.

In addition, detailed energy level structure of Pr\(^{3+}\) in CaTiO\(_3\) was studied. Temperature dependence of luminescence was measured. Thermal quenching, concentration quenching and effects of phase transitions on luminescence are discussed.

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Reference