Recently, rare earth doped vanadate phosphors have paid considerable attention owing to their long-wavelength excitation properties, which enable their use in LEDs, fluorescent lamps, and flat panel displays. The luminescence performance of a material can be enhanced significantly by the suitable selection of host material. Since the white light-emitting diodes (WLEDs) gaining much more attention. Generation of the white light by combining an ultraviolet (UV) LED and appropriate phosphors is most desirable. Hence, it is essential to develop efficient phosphors to convert the near-UV pump light with a range of 300-400 nm into the visible wavelength. In order to fabricate excellent WLEDs, the excitation wavelength of the red phosphors should match the emission of the near UV-LEDs (350-410 nm) or blue LEDs (440-470 nm). Therefore, the phosphor materials play an important role in WLEDs. Most vanadates exhibit intense broadband emission from 400 nm to 700 nm under UV excitation because of tetrahedral VO$_4$ with Td symmetry. The broadband emission spectra of vanadate phosphors are due to the charge transfer (CT) of an electron from the oxygen 2p orbital to the vacant 3d orbital of V$^{5+}$ in tetrahedral VO$_4$ with Td symmetry. The luminescence is attributed to the $^3$T$_2$→$^1$A$_1$ and $^3$T$_1$→$^1$A$_1$ transitions. Nanocrystalline high-quality Ca$_{3-3x/2}$(VO$_4$)$_2$:xEu (0.01≤x≤0.09) phosphors are successfully synthesized by the solution combustion method. The crystal structure, particle size, and photoluminescence (PL) properties of the annealed Ca$_{3-3x/2}$(VO$_4$)$_2$:xEu phosphors are studied. The impact of concentration and temperature on the luminescence properties of the Eu$^{3+}$ activated Ca$_{3-3x/2}$(VO$_4$)$_2$:xEu phosphors are studied. The characteristic PL peaks caused by the $^5$D$_{0}→^7$F$_{1}$, $^5$D$_{0}→^7$F$_{2}$, $^5$D$_{0}→^7$F$_{3}$, $^5$D$_{0}→^7$F$_{4}$, $^5$D$_{1}→^7$F$_{2}$, $^5$D$_{1}→^7$F$_{3}$, $^5$D$_{1}→^7$F$_{4}$, and $^5$D$_{2}→^7$F$_{3}$ transitions of Eu$^{3+}$ are observed at 537, 556, 592, 613, 654, and 701 nm, respectively. The Ca$_{3-3x/2}$(VO$_4$)$_2$:xEu phosphors show the strongest red emission at 613 nm under ultraviolet (UV) excitation because of the charge transfer state of VO$_4^{3-}$ and f-f transitions of Eu$^{3+}$ ions. In this study, the Ca$_{3-3x/2}$(VO$_4$)$_2$:xEu phosphors can be used as red phosphors for white light-emitting diodes (LEDs).