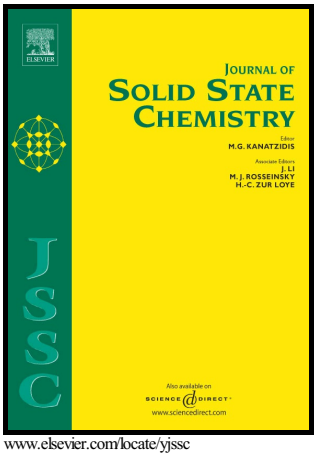

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Photoluminescence of A- and B-site Eu^{3+} -substituted $(Sr_xBa_{1-x})_2CaW_yMo_{1-y}O_6$ phosphors

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Abstract

The photoluminescence of two series of A- and B-site Eu^{3+} substituted $(Sr_xBa_{1-x})_2CaW_yMo_{1-y}O_6$ double perovskite phosphor materials, $(Sr_xBa_{1-x})_{1.96}Eu_{0.02}K_{0.02}CaW_yMo_{1-y}O_6$ and $(Sr_xBa_{1-x})_2Ca_{0.96}Eu_{0.02}Li_{0.02}W_yMo_{1-y}O_6$ (x and y = 0, 0.25, 0.50, 0.75, 1), were studied systematically as a function of stoichiometry and crystal structure. The Eu^{3+} lattice sites controlled by co-doping with either K or Li were confirmed by Raman spectroscopy. The variation in integrated emission intensity and emission colour over the experimental matrix was examined using statistical tools, and the observed trends were rationalized based on the physical and electronic structure of the phosphors. Phosphors with Eu on B-site with maximum Sr content had remarkably higher emission intensities than all other materials, but the emission was more orange than red due to domination of the $^5D_0$ - $^7F_1$ (595 nm) transition of Eu^{3+}. The relative intensities of the $^5D_0$ - $^7F_2$ (615 nm) and $^5D_0$ - $^7F_1$ transitions of Eu^{3+}, and thus the red-shift of the emission, decreased linearly with increasing Sr content in the A-site Eu-substituted phosphors, and reached a maximum for $Sr_{1.96}Eu_{0.02}K_{0.02}CaW_{0.25}Mo_{0.75}O_6$. A maximum external quantum efficiency of 17 % was obtained for the phosphor $Sr_2Ca_{0.7}Eu_{0.15}Li_{0.15}W_{0.5}Mo_{0.5}O_6$ with Eu on B-site.

Keywords

Phosphor, red, WLED, photoluminescence, quantum efficiency, double perovskite

Introduction

White light emitting diodes (WLEDs) are increasingly replacing incandescent, xenon, halogen and fluorescent light sources for general illumination because they offer higher efficiency, longer lifetimes and an absence of toxic elements. The most widely available commercial solution today is the combination of a blue LED and yellow phosphor. However, these devices exhibit a high colour temperature and a low colour rendering (index) CRI due to the lack of a red component in the spectrum. Another option, which can provide improved colour rendering, is the application of an LED which emits in the near ultra violet (NUV) in combination with red, blue and green (RGB) phosphors. As long as the electrical to optical power conversion is more efficient in the NUV than in the blue LEDs, NUV LED + RGB phosphors may yield an overall more efficient design [1]. Efficient phosphors for conversion from NUV to blue and green already exist, but the technology is limited by a lack of stable and efficient red phosphors.

Smet et al. [1] have shown by computer simulation that a WLED with very high luminous efficiency and acceptable colour rendering can be achieved by combining line emission at 460, 540 and 610 nm. The red component fits very well with the emission of the $^5D_0$-$^7F_2$ transition of Eu^{3+} at 615 nm. The usefulness of Eu^{3+} is however limited by low intensity in NUV excitation due to spin- and parity-forbidden transitions. Increased excitation can be obtained by charge transfer from the surrounding matrix to Eu^{3+} and/or by doping the Eu^{3+} to non-centrosymmetric lattice sites. Furthermore, the symmetry around the Eu^{3+} ion is highly important for the emission colour, since the $^5D_0$-$^7F_2$ electric dipole transition is hypersensitive to inversion symmetry. The $^5D_0$-$^7F_1$ magnetic dipole transition at 595 nm will dominate if Eu^{3+} is in a centrosymmetric lattice site, whereas the 615 nm emission line will become substantial only when Eu^{3+} is situated in a non-centrosymmetric lattice site.

Since Sivakumar and Varadaraju in 2006 observed efficient energy transfer from the MoO_6-group of the host material to Eu^{3+} in doped Sr_2CaMoO_6 and Ba_2CaMoO_6 under NUV excitation [2], Mo-containing double perovskites of general formula $A_2BB'O_6$ have become interesting host materials for red phosphors in WLEDs. One of the most promising systems is $(Sr_xBa_{1-x})_2CaW_yMo_{1-y}O_6$ [2-9] . While the Sr/Ba ratio mainly influences the emission via changes in the crystal structure, the W/Mo ratio changes the nature of the absorbing group. Although WO_6–groups do not absorb well in the NUV, it has been shown that inclusion of W can reduce cross-relaxation losses by blocking energy transfer between MoO_6-groups [4]. The crystal structure