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SCHEELITE RELATED COMPOUNDS AS EFFICIENT PHOSPHOR FOR PC-WLEDS AND THERMOGRAPHIC APPLICATION

Morozov V. A., Deyneko D.V., Lazoryak B.I.

Lomonosov Moscow State University, GSP-1, Leninskie Gory 1, Moscow, 119991, Russia, e-mail:morozov111vla@mail.ru

Scheelite ($CaWO_4$) related compounds $(A',A'')_n[(B',B'')O_4]_m$ with B', B''=W and/or Mo are promising new materials for red phosphors in pc-WLEDs (phosphor-converted white-light-emitting-diode) and solid-state lasers. Scheelites can be prepared with a large concentration of vacancies in the A sublattice, giving compositions characterized by a (A'+A''):($B'O_4$+$B''O_4$) ratio different from 1:1. The creation of cation vacancies in the scheelite-type framework and the ordering of A cations and vacancies are a new factor in controlling the scheelite-type structure and properties. The creation and ordering of A-cation vacancies and the effect of cation substitutions in the scheelite-type framework are investigated as a factor controlling the scheelite-type structure and luminescent properties of $Ag_xR^{3+}_{(2-x)/3}\square_{(1-2x)/3}WO_4$ (R = Eu, Sm) and $Ag_xGd_{(2-x)/3-0.3}Eu_{0.3}\square_{(1-2x)/3}WO_4$ scheelite-type phases. Transmission electron microscopy also confirmed the (3+1)D incommensurately modulated character of $Ag_xR^{3+}_{(2-x)/3}\square_{(1-2x)/3}WO_4$ (R = Eu, Sm; x = 0.286, 0.2) phases.

The luminescent properties of all phases under near-ultraviolet (n-UV) light have been investigated were related to the structural properties of the materials. Eu-based phosphors emit intense red light dominated by the $^5D_0 - {}^7F_2$ transition at 613 nm, along with other transitions from the $^5D_0$ excited states. The excitation spectra of $Ag_xEu^{3+}_{(2-x)/3}WO_4$ (x = 0.5, 0.286, 0.2) phosphors show the strongest absorption at 395 nm, which matches well with the commercially available n-UV-emitting GaN-based LED chip. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition on the $Ag_xEu^{3+}_{(2-x)/3}WO_4$ emission spectra is reduced almost 7 times with decreasing x from 0.5 to 0 but it does not change practically in the range from x = 0.286 to x = 0.200. The emission spectra of Gd-containing samples show a completely different trend as compared to only Eu-containing samples. The Eu^{3+} emission under excitation of Eu^{3+} ($^5L_6$) level (λ_{ex} =395 nm) increases more than 2.5 times T with the increasing Gd^{3+} content from 0.2 (x = 0.5) to 0.3 (x = 0.2) in the $Ag_xGd_{(2-x)/3)-0.3}Eu^{3+}_{0.3}WO_4$. Sm-based phosphors under n-UV light show the characteristic emission lines in the range of 550–720 nm, corresponding to $^4G_{5/2} \rightarrow {}^6HJ$ (J = 5/2, 7/2, 9/2 and 11/2) transitions of Sm^{3+} ions, with the J = 9/2 transition at the ~648 nm region being dominant for all PL spectra. Different temperature dependencies were found for the intensity of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ and $^4G_{5/2} \rightarrow {}^6H_{7/2}$ bands. The emission intensity ratios (R) for these bands vary reproducibly with temperature, allowing the use of these materials as thermographic phosphors.

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