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Aperidic structures and luminescent properties in the scheelite family

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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. Recently a new application field has emerged for these materials due to their ability to visualize temperature gradients with high accuracy and spatial resolution, making them excellent thermographic phosphors. 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. Very often the substitution of Ca^{2+} by M^{+} and R^{3+} (R^{3+} = rare earth elements) in the scheelite-type structure leads to switching the structure from 3D to (3+*n*)D (*n* = 1,2) regime. 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 $Ag_xEu_{(2-x)/3}WO_4$ and $Ag_xGd_{(2-x)/3-0.3}Eu_{0.3}WO_4$ scheelite-type phases with the variable composition [1]. Transmission electron microscopy also confirmed the (3+1)D incommensurately modulated character of $Ag_xEu^{3+}_{(2-x)/3}WO_4$ (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. $Ag_xEu_{(2-x)/3}WO_4$ and $Ag_xGd_{(2-x)/3-0.3}Eu_{0.3}WO_4$ 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. Concentration dependence of the $^5D_0$-$^7F_2$ emission for $Ag_xEu_{(2-x)/3}WO_4$ samples differs from the same dependence for the early studied $Na_xEu^{3+}_{(2-x)/3}MoO_4$ ($0<x<0.5$) phases [2, 3]. The intensity of the $^5D_0$-$^7F_2$ emission 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 with the increasing Gd^{3+} concentration from 0.2 (x = 0.5) to 0.3 (x = 0.2) in the $Ag_xGd_{((2-x)/3)-0.3}Eu^{3+}_{0.3}WO_4$, after which it remains almost constant for higher Gd^{3+} concentrations.

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References:

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