Incommensurate modulated structures and luminescence in scheelites

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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. 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 CaGd\(_2\)(1-x)Eu\(_2x\)(MoO\(_4\))\(_4\)(1-y)(WO\(_4\))\(_4y\) \((0\leq x\leq 1, 0\leq y\leq 1)\) solid solutions. Within this series all complex molybdenum oxides have \((3+2)\)D incommensurately modulated structures with superspace group I\(_4\)1/a(α,β,0)00(−β,α,0)00, while the structures of all tungstates are \((3+1)\)D incommensurately modulated with superspace group I\(_2\)/b(αβ0)00. In both cases the modulation arises due to cation-vacancy ordering at the A site. The replacement of the smaller Gd\(_3+\) by the larger Eu\(_3+\) at the A-sublattice does not affect the nature of the incommensurate modulation, but an increasing replacement of Mo\(_6+\) by W\(_6+\) switches the modulation from \((3+2)\)D to \((3+1)\)D regime. Acknowledgement. This research was supported by FWO (project G039211N, Flanders Research Foundation) and Russian Foundation for Basic Research (Grants 11-03-01164, and 12-03-00124).

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