Transition Metal-Indium Substitution in Y_3Rh_2-type Compounds

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New rare earth metal-rich indium compounds $RE_3T_{2-x}In_x$ (*RE* = Gd, Tb, Dy, Ho, Er, Tm; *T* = Rh, Pd, Ir) were synthesized from the elements *via* high-frequency melting and subsequent annealing in sealed silica ampoules. These intermetallics crystallize with substitution variants of the tetragonal Y_3Rh_2-type structure, space group *I*4/*mcm*, *Z* = 28. All samples were studied by powder and single crystal X-ray diffraction: a = 1164.2(2), c = 2486.5(5) pm, for $Tb_3Rh_{1.25}In_{0.71}$, a = 1139.4(2), c = 2480.8(5) pm for $Er_3Rh_{1.48}In_{0.52}$, a = 1153.7(2), c = 2465.4(5) pm for $Tm_3Rh_{1.25}In_{0.71}$, a = 1146.4(2), c = 2498.4(5) pm for $Tb_3Ir_{1.62}In_{0.33}$, a = 1154.9(2), c = 2500.1(5) pm for $Tb_3Ir_{1.52}In_{0.44}$, a = 1187.8(2), c = 2559.2(5) pm for $Gd_3Pd_{1.27}In_{0.71}$, and a = 1169.1(2), c = 2530.3(5) pm for $Ho_3Pd_{1.27}In_{0.71}$. The indium atoms show different site occupancies on the transition metal positions, and for most crystals small defects occur for one transition metal site. $Gd_3Rh_{1.30}In_{0.64}$ (a = 1166.3(2), c = 2512.0(5) pm) and $Dy_3Rh_{1.31}In_{0.64}$ reveal complete rhodium–indium ordering. These two indides crystallize with the *translationengleiche* subgroup *I*4/*m*. The rare earth atoms in these $RE_3T_{2-x}In_x$ indides have coordination numbers between 13 and 15. A striking structural motif is the tetrahedral indium coordination in the first coordination sphere of the *RE*5 position (305 pm Gd–In in $Gd_3Rh_{1.30}In_{0.64}$). The transition metal atoms show trigonal prismatic or square anti-prismatic rare earth coordination. In all compounds investigated, the indium atoms substitute these metals only at the square prismatic sites and at one site of coordination number 10. The crystal chemical consequences of the different ordered and statistical transition metal–indium substitutions are discussed.

Key words: Indium, Intermetallics, Crystal Chemistry