$RE_{2+x}I_2M_{2+y}$ (RE = Ce, Gd, Y; M = Al, Ga): Reduced Rare Earth Halides with a Hexagonal Metal Atom Network

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The title compounds were synthesized from RE, REI_3 (RE = Ce, Gd, Y) and Al or Ga under an Ar atmosphere at 930 – 950 °C. The non-stoichiometric $Ce_{2+x}I_2Al_{2+y}$ and $Ce_{2+x}I_2Ga_{2+y}$ compounds crystallize in the space group $R\bar{3}m$ (No. 166) with lattice constants a = 4.3645(3), c = 35.914(2) Å for the Al and a = 4.3009(2), c = 35.680(4) Å for the Ga compound. Excess electron density found in the Wyckoff position 3*a* could be due to a fractional occupation by Ce or M (x = 0.06, y = 0 or x = 0, y = 0.11 in the case of the Ga compound). The stoichiometric $Gd_2I_2Ga_2$ and $Y_2I_2Ga_2$ compounds crystallize in the space group $P\bar{3}m1$ (No. 164) with lattice constants a = 4.1964(1) and 4.1786(7) Å, c = 11.4753(4) and 11.434(2) Å, respectively. Their structures feature M-centered (M = Al, Ga) RE trigonal prisms condensed *via* common rectangular faces. The electronic origin of the surplus of metal atoms in the octahedral voids between the I-layers of the Ce compounds was explored *via* extended Hückel-type calculations. Magnetic susceptibility, electrical resistivity and heat capacity measurements have also been carried out. These reveal a metal-insulator transition of $Gd_2I_2Ga_2$ at 40 K.

Key words: Cerium, Gadolinium, Yttrium, Aluminum, Gallium, Reduced Halide