\( RE_{2+x}I_2M_{2+y} (RE = Ce, Gd, Y; M = Al, Ga) \): 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 3a 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