NEW RHENIUM-BASED INTERMETALLIC COMPOUNDS: CRYSTAL STRUCTURE, BONDING, AND PROPERTIES

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We report 5 new intermetallic compounds of rhenium found in the Re–Ga–Zn and Re–Ga–Ge ternary systems. These display an unexpected variety of crystal structures, unusual bonding patterns, and transport properties. $ReGa_3Zn$ crystallizes in the cubic unit cell (Im–3m, a = 5.7611(6) Å) and is the 5th representative of the rare $PtHg_4$ structure type. With decreasing the Ga:Zn ratio another compound, $Re_8Ga_{20}Zn_{21}$, forms with the hexagonal V_8Ga_{41} structure type (R–3, a = 13.8723(9), c = 14.7887(10) Å). Replacement of Zn with Ge leads to three other intermetallic compounds. $ReGa_2Ge$ belongs to the well-known $FeGa_3$ structure type ($P4_2/mnm$, a = 6.5734(3), c = 6.7450(8) Å), $ReGaGe_2$ has its own structure type (*Cmcm*, a = 3.26861(4) Å, b = 9.1746(1) Å, c = 8.5320(1) Å) and demonstrates packing of the $Re(Ga,Ge)_9$ polyhedra, whereas $Re_5Ga_2Ge_3$ is an intergrowth structure featuring an alteration of α-Po and bcc fragments along the c axis of the tetragonal unit cell (I4/mmm, a = 2.89222(3), c = 15.1663(3) Å).

Surprisingly, all 5 new intermetallic compounds demonstrate very narrow homogeneity ranges. With the exception of $Re_5Ga_2Ge_3$ these ranges could not be detected by a combination of powder X-ray diffraction and metallographic analysis. We believe that such narrow compositional ranges are associated with the peculiar bonding patterns. Although they are different for all compounds, the common feature of the bonding patterns is unusually strong localization of directional bonds, alien for intermetallic compounds. It is worth noting that three of these compounds, namely $ReGa_3Zn$, $ReGa_2Ge$, and $ReGaGe_2$ display a semiconducting type of conductivity. Despite dissimilarity of their electronic structures, the common feature for these three compounds is strong hybridization of rhenium *d*-states with *s*- and *p*-states of Zn/Ga/Ge that leads to a gap opening, and for a certain concentration of valence electrons the Fermi level falls into the gap ensuring non-metallic properties of intermetallic compounds. Details of crystal structures, bonding patterns, and transport properties will be discussed in this paper.

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