MS23-2-1 Architecture of rare earth-rich complex intermetallics based on polyicosahedral clusters #MS23-2-1

P. Solokha [1], S. De Negri [1], R. Freccero [1]
[1]Università di Genova - Genova (Italy)

Abstract
The rare earth (*RE*)–transition metal (*T*)–Mg ternary systems are characterized by numerous intermetallic compounds, spread all over the concentration range. Particularly, the rare-earth rich ones make up a large family of compounds, distributed among some characteristic stoichiometries, such as 4:1:1 (*cF*96-Gd_4RhIn), 23:7:4 (*hP*68-$Pr_{23}Ir_7Mg_4$, *hP*68-$Yb_{23}Cu_7Mg_4$), 15:5:2 (*hR*132-$La_{15}Rh_5Cd_2$) and 9:1:4 (*hP*28-Hf_9BMo_4) [1-3] (see figure 1). These complex intermetallics possess common structural features: 1) *T*-centred trigonal prisms with *RE*s at vertices; 2) absence of Mg-*T* interactions; 3) binary core-shell polyicosahedral clusters (PCs), consisting by a core of Mg (formed by one to few atoms) icosahedrally coordinated by *RE*s (see figure 1).In this work, some new members of this family are presented:The RE_4CuMg (*RE* = Yb, Ca) compounds show the very common 4:1:1 stoichiometry but crystallize in a new structure type (*hR*144-Ca_4CuMg, space group *R*-3*m*, *a*=10.376(2) Å, *c*=51.2790(6) Å). Binary core-shell PCs are indeed present, with Mg7@*RE*32 composition, found in this structure for the first time.The $Y_{37}Ni_{13}Mg_4$ compound is the first representative of a *hP*108 structure (space group $P6_3/mmc$, *a*=9.688(2) Å, *c*=34.423(7) Å), corresponding to a stoichiometry never reported before. Binary core-shell PCs of Mg3@*RE*20 and Mg@*RE*12 compositions highlight a similarity with 23:7:4 compounds of $Yb_{23}Cu_7Mg_4$ type.Data on these new compounds, together with those in the literature, evidence that, with the same stoichiometry, some structures, the cubic 4:1:1 and the hexagonal 23:7:4 ($Pr_{23}Ir_7Mg_4$ type), are preferred by typical trivalent *RE*s, instead, the rhombohedral 4:1:1 and the hexagonal 23:7:4 ($Yb_{23}Cu_7Mg_4$ type) are formed by the divalent ones. These structural differences are reflected in the Mg-centred PCs (Mg4 tetrahedral cores for trivalent *RE*s, Mg isolated atoms + Mg3 triangular cores for divalent *RE*s). On the other hand, known Y-rich phases show similarities with both groups, depending on composition.All compounds under consideration stay on the compositional line indicated in pink in figure 1: in fact, their compositions can be described as simple linear combinations of RE_7T_3 and RE_9TMg_4 parent types, as follows:$RE_{37}T_{13}Mg_4$ = RE_9TMg_4 + $4RE_7T_3$2$RE_{15}T_5Mg_2$ = RE_9TMg_4 + $3RE_7T_3RE_{23}T_7Mg_4$ = RE_9TMg_4 + $2RE_7T_3$4RE_4TMg = RE_9TMg_4 + RE_7T_3This fact allows to rationalize the apparently weird and random observed stoichiometries.A deeper crystal structure analysis will be presented leading to a unified description of the architecture of these *RE*-rich intermetallics according to an elegant structural principle. This generalization is useful to guide discovery of new representatives as well as revision of inconsistent data.

References
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Binary core shell PCs in RE-T-Mg compounds