Disentangling structural patterns in quaternary germanides with materials informatics and exploratory synthesis: $RE_4IrInGe_4$ (RE = Y, Ce–Nd, Sm, Gd, Ho–Er)

Authors: Anna Ponomarev,[1,2] Emil I. Jaffal,[1] Balaranjan Selvaratnam,[1] Danila Shiryaev,[1] Anton Oliynyk[1]

[1]*Department of Chemistry, Hunter College, City University of New York, New York 10065, NY, USA*

[2]*Honors College, McNulty Scholars, McNair Scholars*

HUNTER
The City University of New York

TRiO
RONALD E. McNAIR POST-BACCALAUREATE ACHIEVEMENT PROGRAM

Background

- Rare-earth (*RE*)–transition metal (*M*) germanides exhibit complex transport behaviors and serve as functional materials with recurring impurity phase patterns.
- In-lab software was used to investigate chemistry and site preferences of $Ho_4Ni_2InGe_4$- and $Tb_4RhInGe_4$-type compounds, revealing trends in atomic environments.
- Structural evolution of quaternary germanides was examined through prism-based environments, showing how covalent M–Ge/Ge–Ge interactions form rigid M_2Ge_2 layers weakly bonded to In and ionically with *RE*s.
- $Tb_4RhInGe_4$-type is less explored and often mutually exclusive with the $Ho_4Ni_2InGe_4$-type in *RE*–*M*–In–Ge systems. This work investigates underlying chemical factors governing which structure type stabilizes.
- Partial Least Squares–Discriminant Analysis (PLS-DA) was applied to classify crystallographic sites and visualize elemental trends. Our results highlight size and electronegativity as dominant factors for *RE*/Ge sites and *d*-electron configuration for *M* sites, offering insight into phase stability and site segregation.

Objective/Hypothesis

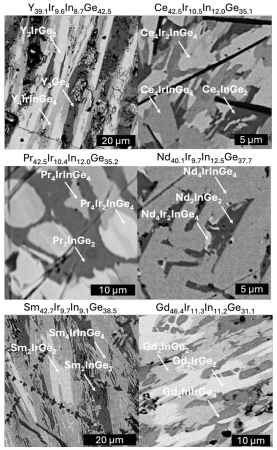
Our goal is to identify new compounds, their properties, and confirm the structures, establishing the structure-design principle. Novel structures are needed to improve the performance and establish the fundamental structure-property relationship.

Methods

1. Powders are pressed, arc-melted, and sealed in fused silica tubes.
2. ½ of sample crushed in mortar and put in X-Ray Diffractometer.
3. Fused silica tube with sample added to ceramic furnace.
3. Other ½ of sample is set in epoxy, carbon-coated, analyzed with Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray Spectroscopy (EDX)

Data/Results

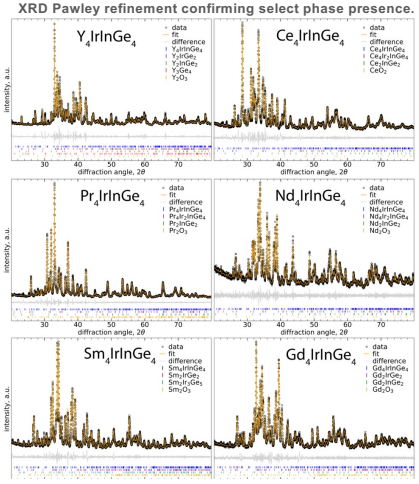
SEM images of select phases.



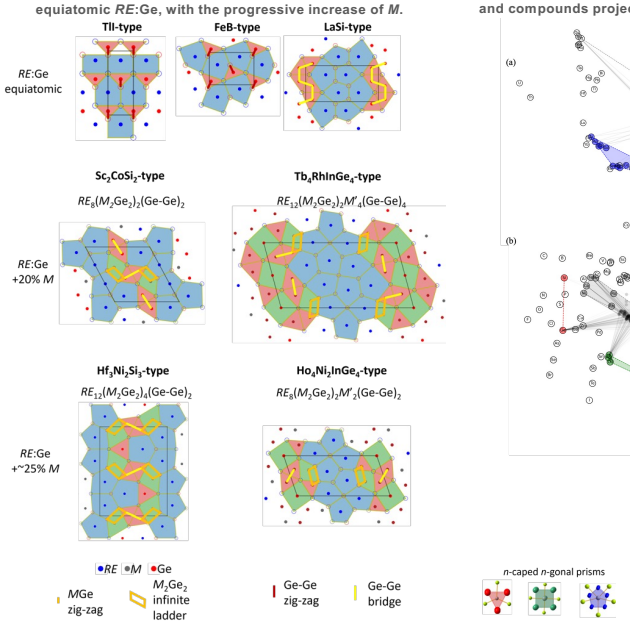
Common impurity table.

RE	Y	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er
RE$_4$IrInGe$_4$	+	+	+	+	+	+	+	+	+	+
RE$_4$Ir$_2$InGe$_4$	-	+	+	+	-	-	-	-	-	-
RE$_5$In$_2$Ge$_3$	-	-	-	-	-	-	+	+	+	-
RE$_2$InGe$_2$	+	-	-	-	+	+	+	+	-	+
RE$_2$InGe$_2$	+	+	+	+	-	+	-	+	+	-
RE$_5$Ge$_4$	+	-	-	-	-	-	-	-	+	+
*RE*Ge	-	-	-	-	-	-	+	+	+	+
RE$_5$Ir$_2$Ge$_6$	-	-	-	-	+	-	-	-	-	-
*RE*O$_2$	-	+	-	-	-	-	-	-	-	-
RE$_2$O$_3$	+	-	+	+	+	+	+	+	+	+

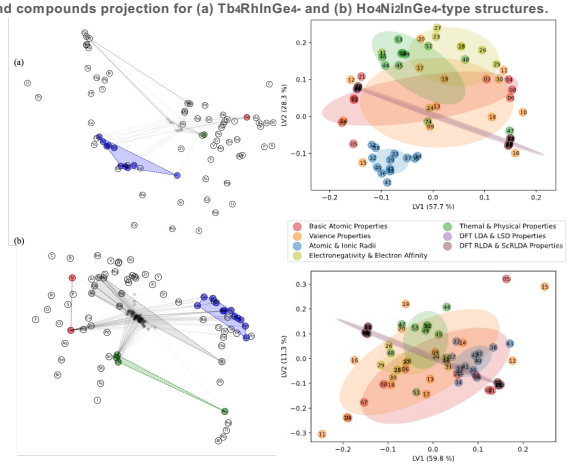
XRD Pawley refinement confirming select phase presence.



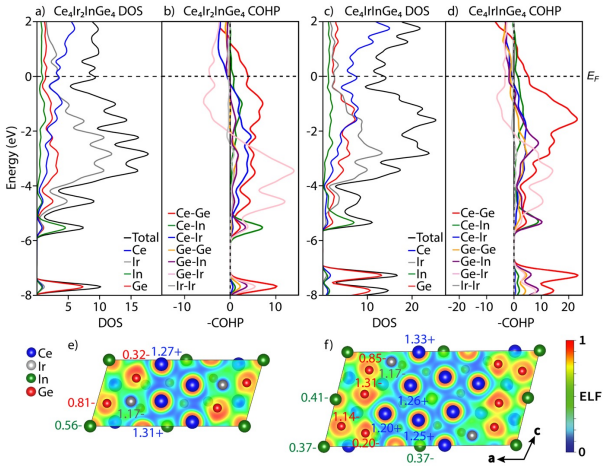
Structural evolution of prototypes adopted by compounds with equiatomic *RE*:Ge, with the progressive increase of *M*.



PLS-DA plot (left) and feature loadings of first two latent variables (right) for the element and compounds projection for (a) $Tb_4RhInGe_4$- and (b) $Ho_4Ni_2InGe_4$-type structures.



DFT calculations of $Ce_4Ir_2InGe_4$ and $Ce_4IrInGe_4$.



Conclusions

- 10 new compounds ($RE_4IrInGe_4$) were discovered.
- The quaternary systems equilibria is complex and require structural motif analysis to study the structure formation.
- Structural motifs include Ge-Ge bridges and M_2Ge_2 infinite ladders which are common for other ternary structures in the systems.
- The structural evolution can be approached through metal inclusions in the equiatomic *RE*:Ge structures.
- DFT calculations reveal importance of Ce-Ge and Ge-Ir bonding in the structure formation.

Future Directions

- Test compounds with different *M* (Os, Rh, Ru) to study structural distortions and their effects.
- Develop complete structure map for rational structure design.
- Correlate the structures with physical properties (electron transport properties in particular).

Acknowledgements

We thank for their support:

- Hunter College
- Macaulay Honors Program
- McNulty Scholars Program
- McNair Scholars Program