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Computational prediction of the electronic, thermodynamic and kinetic properties of new materials synthesized under high pressure

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Materials subjected to high pressures and temperatures sometimes change their properties unpredictably. Here, a metastable high-pressure phase of RhGe with a non-centrosymmetric crystal structure of the B20 type (SG $P2_13$) was studied both experimentally and by density-functional calculations.

Theoretically, we performed an evolutionary search for energetically favored polymorphs using the USPEX code and determined their stability regions on the $P-T$ phase diagram in quasi-harmonic approximation (QHA).

The experiments included synthesis under high-pressure–high-temperature conditions and examination of the obtained samples by means of differential scanning calorimetry (DSC). Before and after DSC, the X-ray diffraction analysis (XRD) of observed phases was carried out and the microstructure of the samples was investigated.

Low-energy polymorphs of RhGe and its isovalent analogue RhSi: Evolutionary search (T=0)

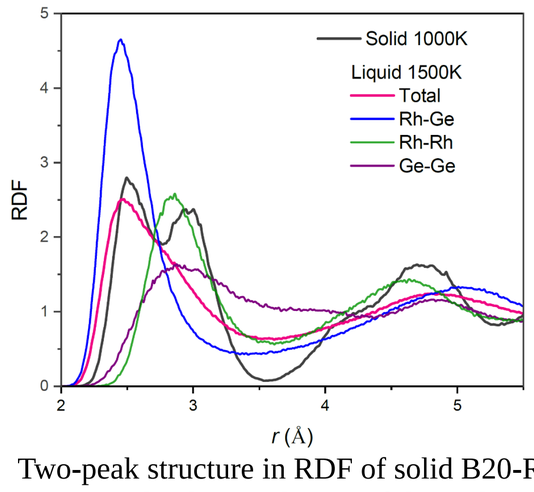
RhGe: only B31 and B20 phases are presently known. Can the intermediate monoclinic phase (#14) be obtained experimentally?

SG #	E_{at}	V_{at}	$\rho=1/V_{at}$	
62 (Pnma)	–6.4238	15.3813	0.0650	orth (B31) MnP
198 ($P2_13$)	–6.3850	14.8812	0.0672	cub (B20) FeSi
14 ($P2_1/c$)	–6.3820	14.8002	0.0676	mon
64 (Cmca)	–6.3622	14.8229	0.0675	orth

RhSi: all four phases are known. The densest B2 phase(#221) is stable only at very high pressures ~100 GPa

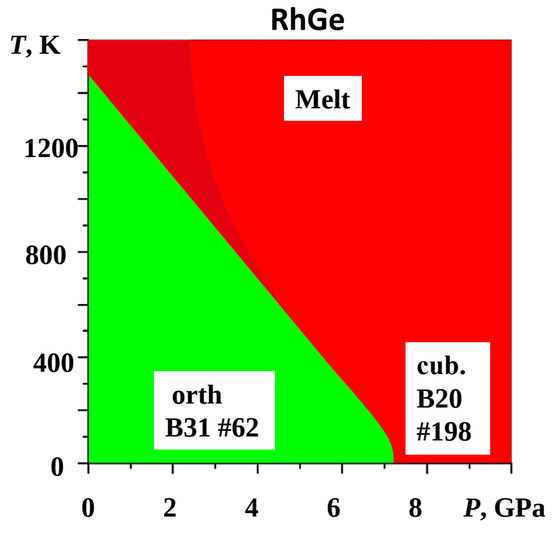
SG #	E_{at}	V_{at}	$\rho=1/V_{at}$	Symmetry
62 (Pnma)	–6.816	14.008	0.0714	orth (B31) MnP
198 ($P2_13$)	–6.798	13.272	0.0753	cub (B20) FeSi
14 ($P2_1/c$)	–6.783	13.546	0.0738	mon
221 (Pm3m)	–6.532	13.224	0.0756	cub (B2) CsCl

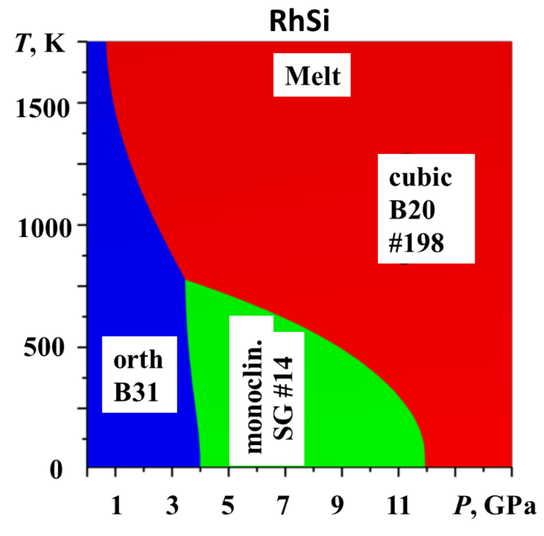
AIMD simulation of B20-RhGe



Two-peak structure in RDF of solid B20-RhGe is not resolved in total RDF of the melt

(P, T) phase diagrams calculated in QHA

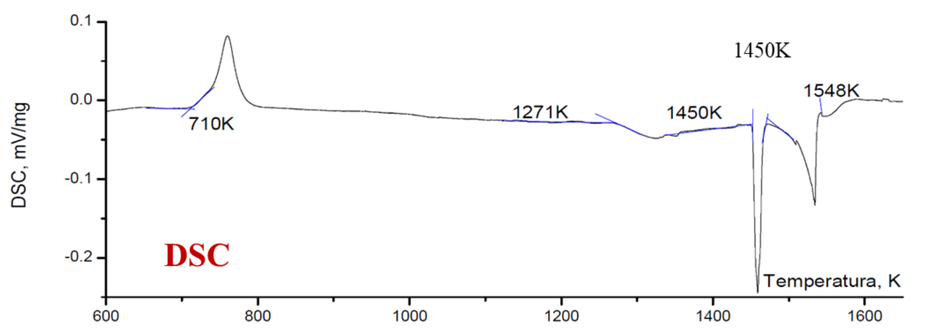


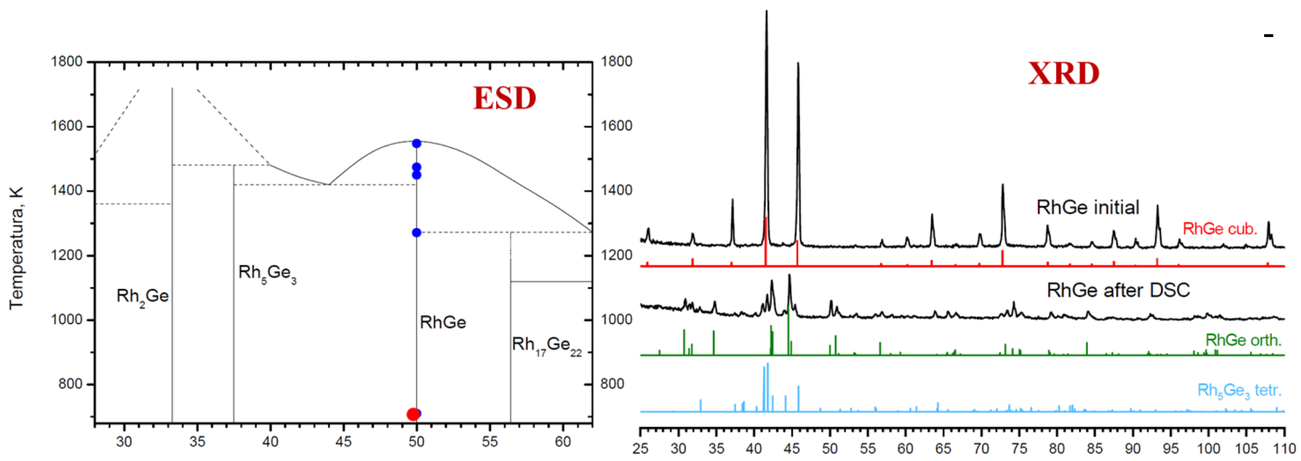


The results of calculations

1. B31-RhGe is a ground state. The denser B20-RhGe phase becomes stable from ~7 GPa.
2. As temperature increases, B20-RhGe forms at progressively lower pressures.
3. The monoclinic phase $P2_1/c$ (#14) is not realized in RhGe at moderate P.

DSC thermogram, comparison with equilibrium state diagram (ESD) and XRD patterns before and after DSC

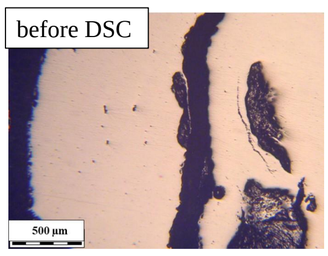


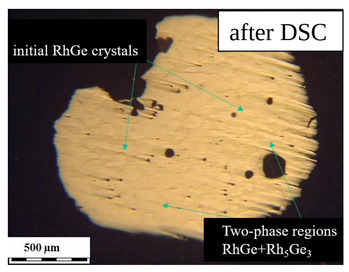


Results of calorimetric studies

- Temperatures of observed effects are plotted in the ESD (blue circles ●) for comparison
- 710 K: Exothermic transformation (●) B20-RhGe → B31-RhGe+$Rh_{17}Ge_{22}$+Rh_5Ge_3
- 1271 K: Peritectic decomposition $Rh_{17}Ge_{22}$ → RhGe + L
- 1450 K: Eutectic melting Rh_5Ge_3 + RhGe → L + RhGe
- 1548 K: Complete melting. After crystallization two phases B31-RhGe and Rh_5Ge_3 are formed (see micrographs below).

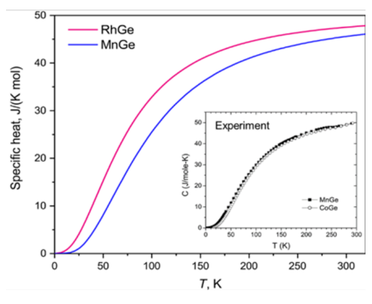
Microstructure of RhGe samples

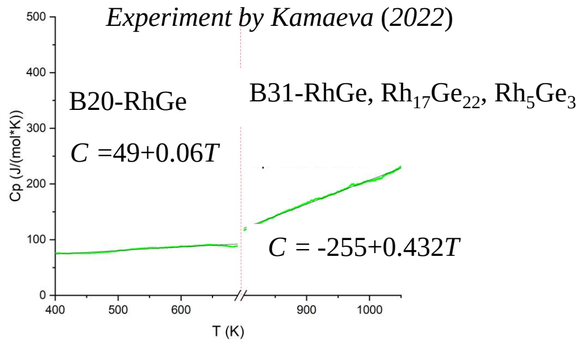




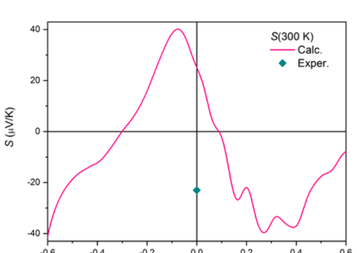
Specific heat

Theor. specific heat of RhGe & MnGe. Inset: experiment by Tsvyashchenko et al. (2012)





Calculated Seebeck coefficient



Green symbol: measurements by Sidorov et al. (2018)

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Papers:

1. M. Magnitskaya et al. *JMMM* **470**, 127 (2019)
2. N. Chtchelkatchev et al. *EPJST* **229**, 167 (2020)
3. L. Kamaeva et al. *J.All.Comp.* **888**,161565 (2021)

Summary

The calculations show that only two phases B31-RhGe and B20-RhGe exist at moderate pressures (no monoclinic phase). B20-RhGe can be synthesized at lower pressures of 4–5 GPa. This could reduce defects that occur during solidification under pressure, which is promising for the synthesis of single crystals.

The calorimetric measurements reveal that the behavior of the metastable RhGe phase is different from equilibrium phases. Its properties depend on the preparation method and sample prehistory.