Planar vs. Puckered Nets in the Polar Intermetallic Series EuGa*Tt* (*Tt* = Si,Ge,Sn)

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Supplementary Material

S1. Alternative Synthetic Approaches and Characterization

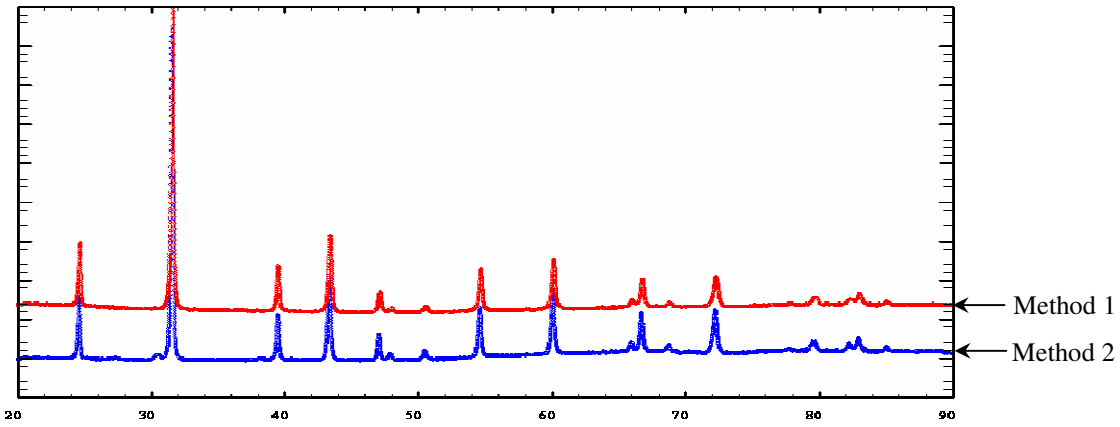
A certain amount of weight loss is inevitable during arc-melting (ca. 0.4-0.7 wt % loss out of total 1 ± 0.2 g samples), although low current was used (20 A) for these experiments due to potential volatility of Eu. Based on the X-ray diffraction analysis and chemical analysis (e.g. EDS), all of the compounds crystallized in single phase products with equiatomic compositions.

In addition, all three compounds were prepared in sealed Ta tubes using a high-frequency (HF) induction furnace or a conventional tube furnace at elevated temperatures. However, this approach did not generally obtain a homogeneous product or better crystallinity for the target compositions. No difference was observed between products from arc-melting and sealed tubes in terms of the crystal structure and the composition for EuGaGe. It is possible that optimizing synthetic or annealing temperatures could be achieved to obtain homogeneous target compounds, but the arc-melted products provided samples suitable for subsequent characterization. However, at this time, we are not certain whether observed, mixed-phase products are due to inaccurate temperature profiles or intrinsic properties of the components. Moreover, unlike EuPtGe where Eu boils (1537 °C) even before Pt melts (1769 °C) resulting in inaccurate compositions of the product, the melting points of Si, Ga, Ge and Sn are lower than the boiling point of Eu. Thus, weight loss of products seems to occur mainly after each ternary compound was produced.

Experimental methods and powder X-ray patterns, which are not included in a manuscript, are summarized below for comparison.

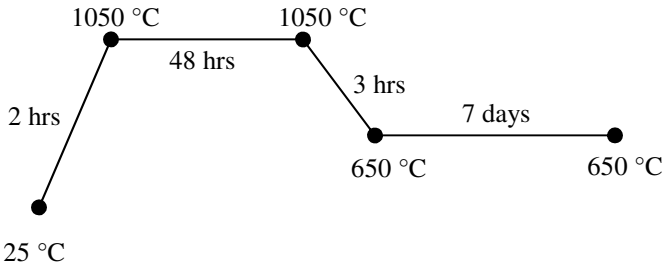
<u>EuGaSi</u>

- Method 1: arc-melting (20 A)
- Method 2: HF induction furnace (1500 °C, 15 min)
- Powder X-ray pattern comparison: Two patterns are almost identical except small peaks around $2\theta = 31°$ and 38° in method 2. Method 1 gives a single phase product.

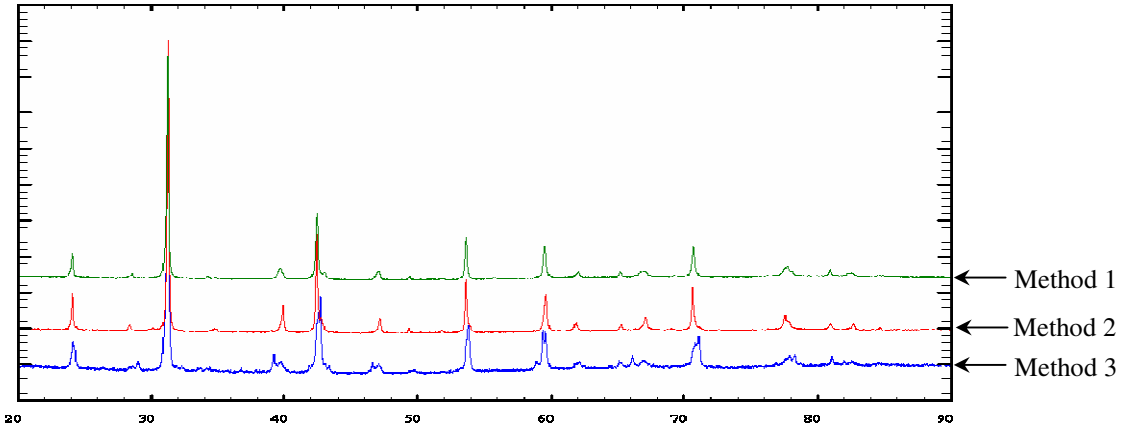


EuGaGe

- Method 1: arc-melting (20 A) + annealing (350°C, 7 days)
- Method 2: cylinder-furnace



- Method 3: HF induction furnace (1100°C, 15 min) + annealing (650°C, 3 hrs)
- Powder X-ray pattern comparison: Method 1 and 2 show almost identical single phase powder patterns. However, method 3 gives mixed phases.



EuGaSn

- Method 1: arc-melting (20 A)
- Method 2: HF induction furnace (950 °C, 15 min) + annealing (500°C, 2 hrs)
- Powder X-ray pattern comparison: Mixed phases are observed in methods 2. Method 1 gives a single phase of target compound.

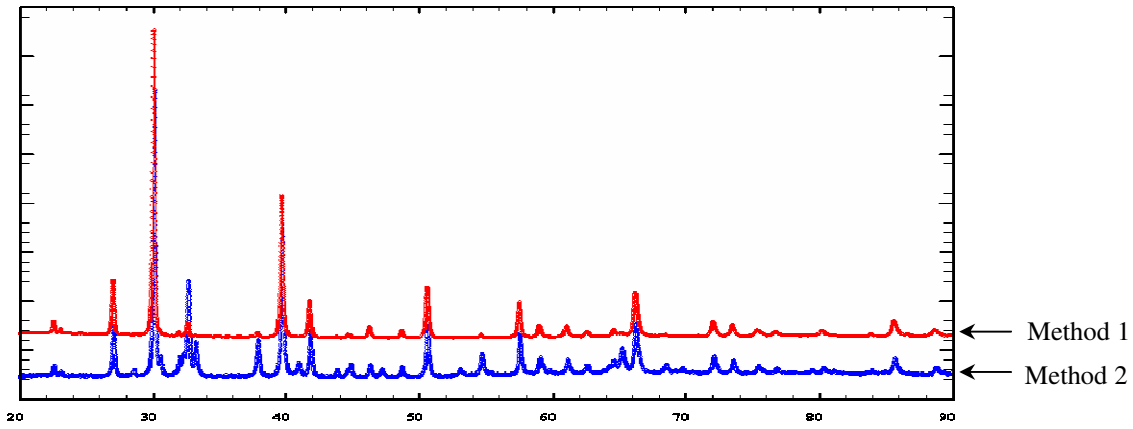


Table S2. Lattice constants as determined by single crystal and powder X-ray diffraction for EuGa*Tt* (*Tt* = Si, Ge, Sn).

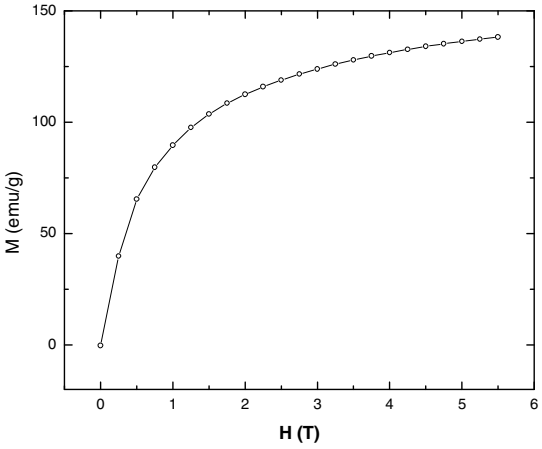
Compound	EuGaSi		EuGaGe		EuGaSn	
Analysis	$Eu_{1.00}Ga_{1.00}Si_{1.00}$		$Eu_{1.00}Ga_{1.00}Ge_{1.00}$		$Eu_{1.00}Ga_{1.00}Sn_{1.00}$	
	Single Crystal	Powder	Single Crystal	Powder	Single Crystal	Powder
a (Å)	4.1686(6)	4.1699(5)	4.2646(6)	4.2690(2)	4.5243(5)	4.5313(3)
c (Å)	4.5543(9)	4.5634(6)	18.041(5)	18.1237(2)	18.067(3)	18.0662(3)
c/*a* or 4*a*	1.0925	1.0944	1.0575	1.0613	0.9983	0.9967

Table S3. Anisotropic displacement parameters (Å^2) for EuGa*Tt* (*Tt* = Si, Ge, Sn). The exponent of the anisotropic displacement factor takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2\ hka^*b^*U_{12}\ ]$. For these space groups, U_{13} and $U_{23} = 0$.

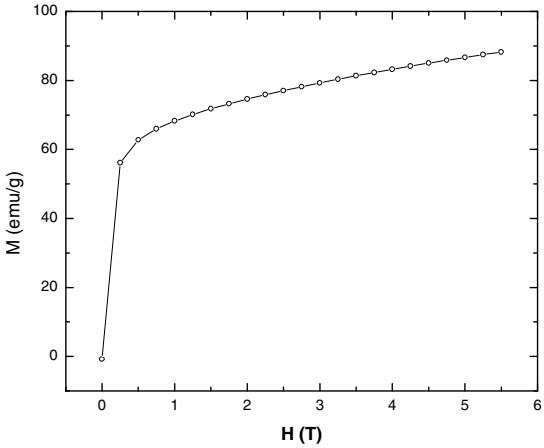
Atom	$U_{11} = U_{22}$	U_{33}	U_{12}
	EuGaSi		
Eu	0.011(1)	0.009(1)	0.005(1)
Ga/Si	0.010(1)	0.032(1)	0.005(1)
	EuGaGe		
Eu(1)	0.009(1)	0.011(1)	0.005(1)
Eu(2)	0.009(1)	0.010(1)	0.005(1)
Ga	0.008(1)	0.026(1)	0.004(1)
Ge	0.008(1)	0.014(1)	0.004(1)
	EuGaSn		
Eu(1)	0.013(1)	0.013(1)	0.006(1)
Eu(2)	0.010(1)	0.011(1)	0.005(1)
Ga	0.009(1)	0.024(1)	0.005(1)
Sn	0.009(1)	0.013(1)	0.005(1)

Figure S4. Magnetization measurements as a function of external field (0-5.5 T) at 2 K for EuGa*Tt* (*Tt* = Si, Ge, Sn).

EuGaSi



EuGaGe



EuGaSn

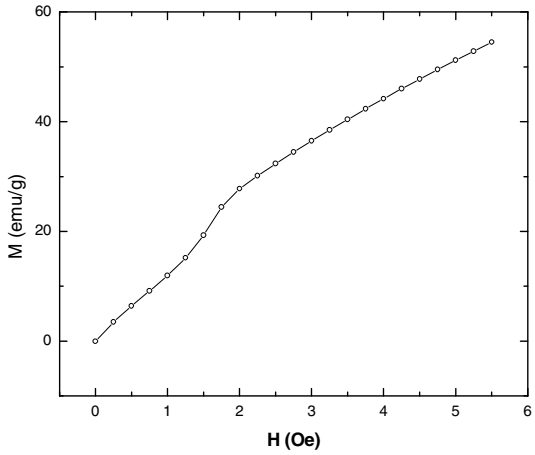


Figure S5. Electronic energy band structures of EuGaSi, model (1), with fatband contributions for p_x and p_y orbitals (top) and p_z orbitals (bottom) from Ga and Si, using the TB-LMTO-ASA method in the LSDA.

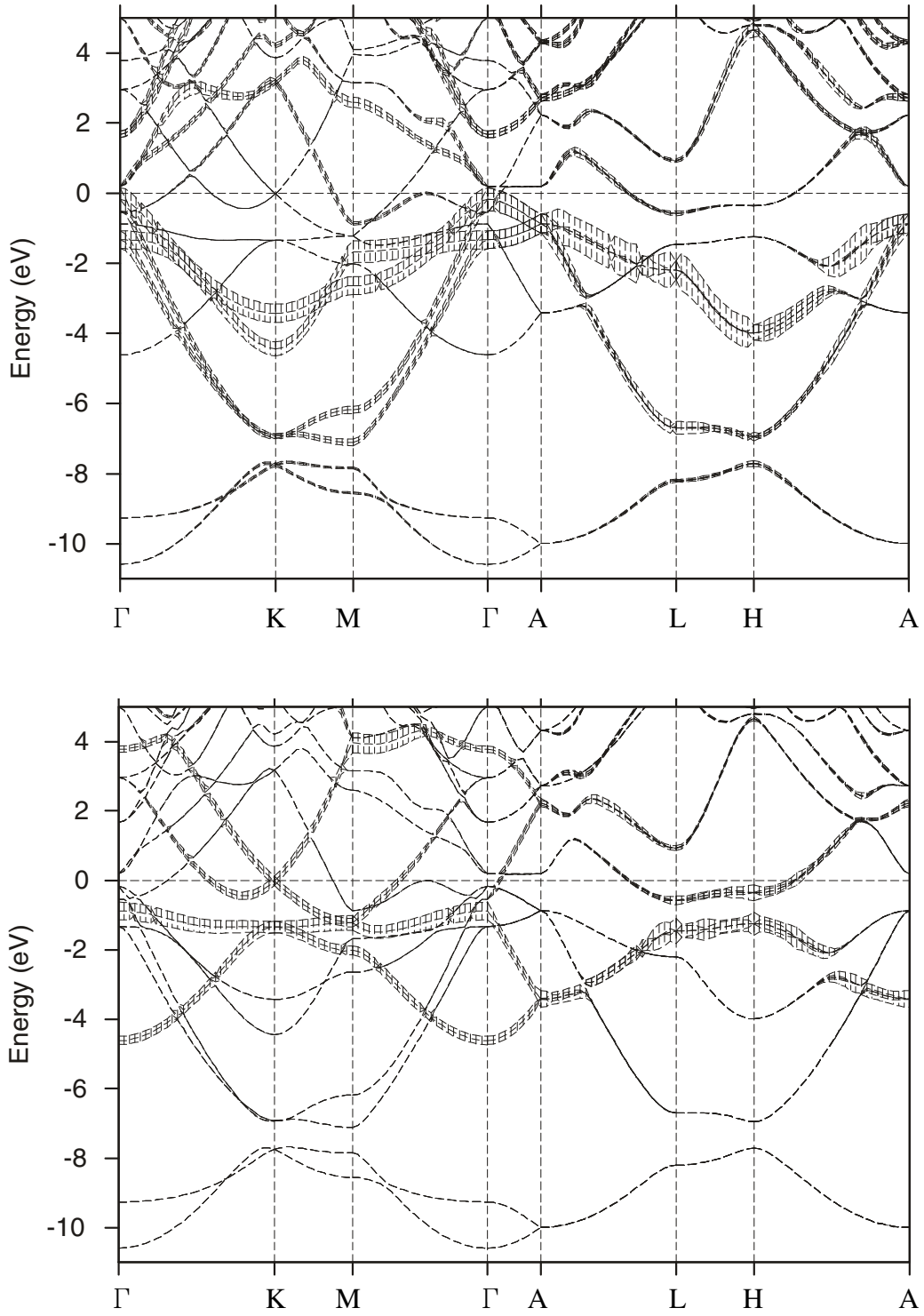


Figure S6. Electronic energy band structure of EuGaGe using the TB-LMTO-ASA method in the LSDA.

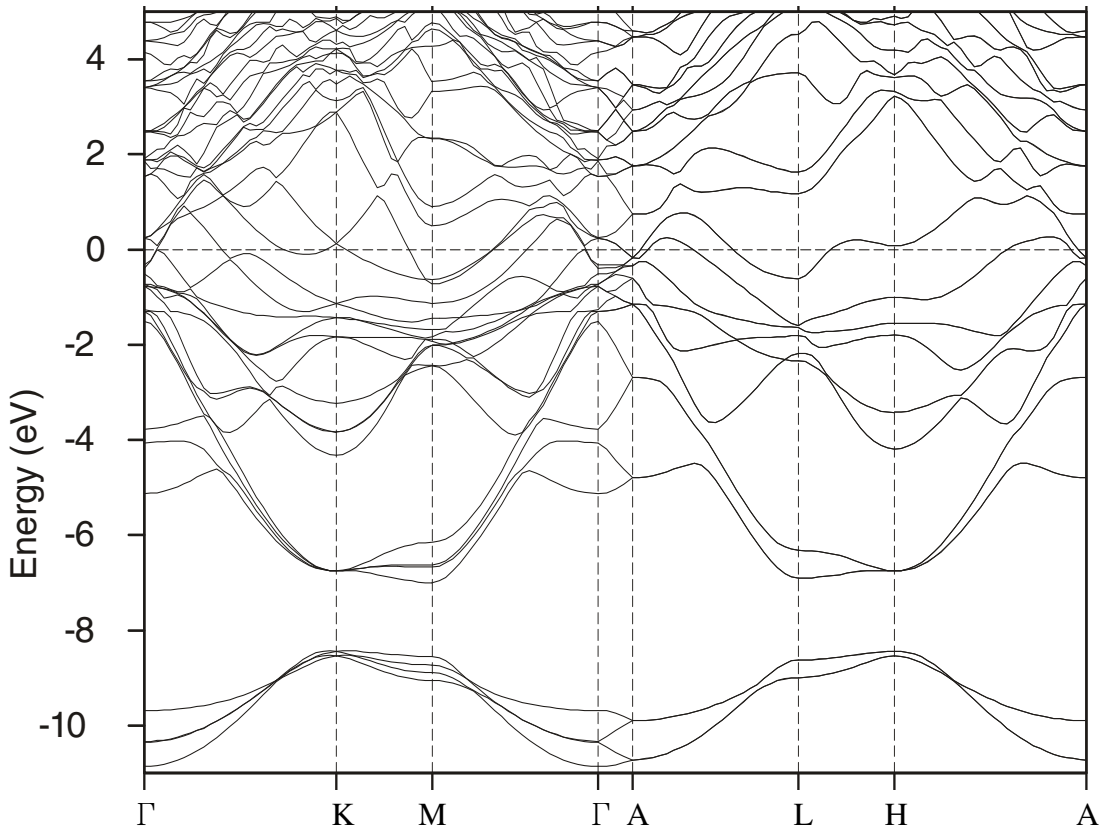


Figure S7. Electronic energy band structure of EuGaSn using the TB-LMTO-ASA method in the LSDA.