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Crystal structures of (barium, europium) platinum trigermanium, $Ba_{1-x}Eu_xPtGe_3$ (x = 0, 0.27, 1)

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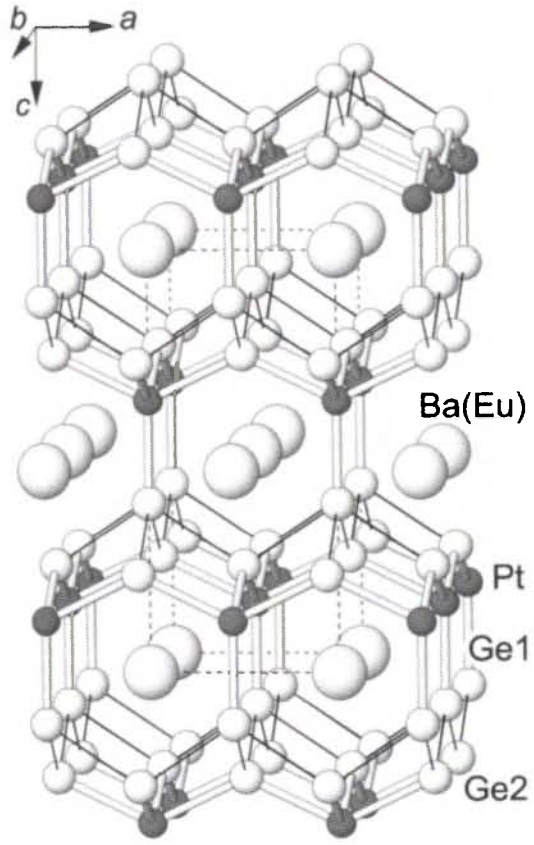

Abstract

$BaGe_3Pt$, tetragonal, *I4mm* (no. 107), a = 4.5636(2) Å, c = 10.2341(6) Å, V = 213.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.030, $wR_{ref}(F^2)$ = 0.074, T = 293 K.

$Ba_{0.73}Eu_{0.27}Ge_3Pt$, tetragonal, *I4mm* (no. 107), a = 4.5432(1) Å, c = 10.1763(2) Å, V = 210.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.061, T = 293 K.

$EuGe_3Pt$, tetragonal, *I4mm* (no. 107), a = 4.4633(1) Å, c = 10.0625(4) Å, V = 200.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.018, $wR_{ref}(F^2)$ = 0.035, T = 293 K.

Source of material

A series of $Ba_{1-x}Eu_xPtGe_3$ samples with x = 0, 0.27 and 1 was synthesized by melting mixtures of the elemental components in a high-frequency oven. Dendritic pieces of barium (99.9 %, Alfa Aesar) and europium (99.9 %, Ames), platinum wire (99.9 %, ChemPur) and germanium fragments (99.999 %, ChemPur) were used. Homogenization was achieved by annealing at 800 °C for 200 h and followed by quenching in cold water. Single crystals were separated from the ingots by mechanical fragmentation. Further details of the sample characterization (X-ray absorption spectra, measurements of magnetic susceptibility and electrical resistivity) and respective results are available in the CIF.

Experimental details

Samples were investigated by X-ray powder diffraction (Huber Image Plate Guinier camera G670, Cu$K_{\alpha 1}$ radiation, λ = 1.54056 Å, 5° ≤ 2θ ≤ 100°, LaB_6 as internal standard, a = 4.1569 Å). Crystal structure refinements were performed using single crystal X-ray diffraction data. Interatomic distances were calculated with the resulting positional parameters and lattice parameters as refined from X-ray powder diffraction data.

Discussion

The continuous solid solution $Ba_{1-x}Eu_xPtGe_3$ ($0 < x < 1$) was investigated and the crystal structures of the boundary phases and of an intermediate composition were refined using single crystal X-ray diffraction data. The unit cell parameters within the homogeneity range decrease linearly with increasing Eu content. The c/a ratio of about 2.24 remains practically constant in the whole concentration interval. All Pt atoms in the structure of $BaPtGe_3$ are five-fold coordinated by Ge species in form of a tetragonal pyramid with d(Pt—Ge) = 2.526(1) Å and 2.533(4) Å to the atoms in the basis (4 × Ge2) and in the top (1 × Ge1), respectively. The environments of the crystallographically independent germanium sites exhibit pronounced differences. The coordination of Ge1 atoms is similar to those of Pt (tetragonal pyramid with four Ge1 at 2.731(2) Å and one Pt), whereas the Ge2 atoms are tetrahedrally coordinated by two Ge1 and two Pt atoms. Comparing these values with the sum of the Pauling's single bond radii assumed for Pt and Ge (1.30 Å + 1.22 Å = 2.52 Å) [1] and with the interatomic distances in elemental germanium (2.45 Å) [2] one can consider strong Pt—Ge bonds and weak Ge—Ge interactions. The Ba—Pt distances vary between 3.564(7) Å and 3.663(2) Å, the Ba—Ge interactions cover the range from 3.384(1) Å to 3.457(2) Å. All interatomic distances in $EuPtGe_3$ are in average 0.05 Å – 0.10 Å shorter than those in the barium phase: d(Pt—Ge1) = 2.445(2) Å, d(Pt—Ge2) = 2.488(1) Å, d(Ge—Ge2) = 2.681(1) Å, d(Eu—Pt) = 3.488(1) Å – 3.547(1) Å, d(Eu—Ge) = 3.299(6) Å – 3.415(1) Å.

The members of the series of $Ba_{1-x}Eu_xPtGe_3$ ($0 < x < 1$) adopt a tetragonal $BaNiSn_3$-type crystal structure [3], which represents an ordered variety of the well known $BaAl_4$ structure [4]. The finding of isotypic phases with composition 1:1:3 is remarkable since the $BaAl_4$-type variants with stoichiometry 1:2:2 are found to realize different arrangements. The structure of $BaPt_2Ge_2$ [5] is

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reported to adopt an inverse $BaCu_2Sb_2$ type [6], which can be described as an intergrowth of fragments of the $ThCr_2Si_2$ [7] and the $CaBe_2Ge_2$ structure types [8]. In contrast, the $EuPt_2Ge_2$ phase is assumed to be isotypic to an $LaPt_2Ge_2$ atomic arrangement [9] which is a monoclinically distorted variant of the $CaBe_2Ge_2$ type. The differences between these derivatives of the $BaAl_4$ structure type are mainly restricted to the ordering of atoms in the polyanionic framework corresponding to the aluminum sites of $BaAl_4$.

X-ray absorption spectra (XAS) of $EuPtGe_3$ indicate the presence of the europium mainly in the $4f^7$ (Eu^{2+}) configuration. This finding is in accordance with the results of magnetic susceptibility measurements. $EuPtGe_3$ exhibits a magnetic susceptibility $\chi(T)$ following a Curie-Weiss law over a wide temperature range. A fit for $T > 50$ K ($H = 10$ kOe) results in an effective magnetic moment $\mu_{eff} = 7.82\ \mu_B$ and a Weiss parameter $\Theta = -6.03(4)$ K (antiferromagnetic interactions), in good agreement with the properties expected for the $^8S_{7/2}$ state of the $4f^7$ configuration of Eu^{2+}.

1. Barium platinum trigermanium, $BaPtGe_3$

Table 1. Data collection and handling.

Crystal:	metallic platelet, size 0.012 × 0.030 × 0.040 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	624.85 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, ω/φ
$2\theta_{max}$:	67.28°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1190, 245
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 245
$N(param)_{refined}$:	15
Programs:	SHELXL-97 [10], WinCSD [11], ATOMS [12]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	2*a*	0	0	0.0069(4)	0.0078(5)	U_{11}	0.0051(7)	0	0	0
Pt	2*a*	0	0	0.6479(2)	0.0070(3)	U_{11}	0.0040(4)	0	0	0
Ge(1)	2*a*	0	0	0.4004(4)	0.0094(8)	U_{11}	0.006(1)	0	0	0
Ge(2)	4*b*	0	½	0.2537(2)	0.0062(7)	0.0101(8)	0.0049(7)	0	0	0

2. (Barium, europium) platinum trigermanium, $Ba_{0.73}Eu_{0.27}PtGe_3$

Table 3. Data collection and handling.

Crystal:	metallic platelet, size 0.015 × 0.030 × 0.065 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	647.7 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, ω/φ
$2\theta_{max}$:	65.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	872, 257
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 257
$N(param)_{refined}$:	15
Programs:	SHELXL-97 [10], WinCSD [11], ATOMS [12]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu	2*a*	0.27(6)	0	0	0.0061(4)	0.0060(5)	U_{11}	0.0062(6)	0	0	0
Ba	2*a*	0.73	0	0	0.0061	0.0060	U_{11}	0.0062	0	0	0
Pt	2*a*		0	0	0.6478(1)	0.0041(2)	U_{11}	0.0046(3)	0	0	0
Ge(1)	2*a*		0	0	0.4012(3)	0.0059(6)	U_{11}	0.0052(8)	0	0	0
Ge(2)	4*b*		0	½	0.2543(2)	0.0036(7)	0.0080(7)	0.0057(6)	0	0	0

3. Europium platinum trigermanium, $EuPtGe_3$

Table 5. Data collection and handling.

Crystal:	metallic, irregular, size 0.015 × 0.025 × 0.040 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	721.76 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, ω/φ
$2\theta_{max}$:	65.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	843, 241
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 241
$N(param)_{refined}$:	14
Programs:	SHELXL-97 [10], WinCSD [11], ATOMS [12]

Table 6. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu	2*a*	0	0	0.0080(2)	0.0088(2)	U_{11}	0.0063(5)	0	0	0
Pt	2*a*	0	0	0.64751(8)	0.0064(2)	U_{11}	0.0040(3)	0	0	0
Ge(1)	2*a*	0	0	0.4045(2)	0.0081(4)	U_{11}	0.0057(8)	0	0	0
Ge(2)	4*b*	0	½	0.2569(1)	0.0053(4)	0.0104(5)	0.0058(5)	0	0	0

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