



Crystal structure and physical properties of $\text{EPCo}_{4.7}\text{Ge}_9$ (EP = Sr, Ba, Eu)

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ABSTRACT

$\text{BaCo}_{4.7}\text{Ge}_9$ ($\text{BaCo}_{5-x}\text{Ge}_9$, $x = 0.29$) is a novel ternary compound which forms incongruently from the melt and crystallizes in a unique structure type (space group $Pnma$; $a = 1.39910(2)$, $b = 0.40218(2)$, $c = 1.69882(2)$ nm, $Z = 4$). Isotypic compounds were found with $\text{SrCo}_{4.7}\text{Ge}_9$ ($a = 1.39389(8)$, $b = 0.39665(1)$, $c = 1.67860(9)$ nm) and $\text{EuCo}_{4.7}\text{Ge}_9$ ($a = 1.3910(1)$, $b = 0.39425(2)$, $c = 1.6741(2)$ nm). Physical properties (electrical resistivity, specific heat, magnetic susceptibility) were studied for $\text{BaCo}_{4.7}\text{Ge}_9$ and $\text{EuCo}_{4.7}\text{Ge}_9$. $\text{BaCo}_{4.7}\text{Ge}_9$ shows metallic behaviour but neither a superconducting nor a magnetic phase transition was observed for temperatures as low as $T = 2$ K. Magnetic susceptibility and specific heat data of $\text{EuCo}_{4.7}\text{Ge}_9$, evidence the onset of antiferromagnetic order at 18.5 K. Both magnetic ordering and the effective magnetic moment derived verify the Eu^{2+} state with a total angular momentum $j = 7/2$.

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1. Introduction

As part of a systematic investigation of T -metal substitution in thermoelectric clathrates we have recently studied the phase relations involving the clathrate type I and clathrate type IX phases, $\text{Ba}_8\text{T}_x\text{Ge}_{46-x-y}\square_y$ and $\text{Ba}_6\text{T}_x\text{Ge}_{25-x}$, with $T = \text{Mn, Fe, Co}$ [1]. Particularly the system Ba–Co–Ge has been studied earlier [2,3] on alloys $\text{Ba}_8\text{Co}_x\text{Ge}_{46-x}$ ($x = 0, 4, 6$) annealed at 700 °C and two superconducting transitions (type II superconductors) were reported for $x = 0$ at $T_{\text{SC}} = 10$ K and 4 K, but Co-doping ($\text{Ba}_8\text{Co}_x\text{Ge}_{46-x-y}\square_y$; $x = 4, 6$) was said to suppress the 4 K transition completely and to reduce the T_{SC} from 10 to 7 K [2,3]. $\text{Ba}_8\text{Co}_x\text{Ge}_{46-x}$ alloys, however, were claimed to be multi-phase ((Ge) + unknown phase for $x = 0$ and (Ge) + CoGe_2 + unknown phase for $x = 4$ and 6), but neither contained a clathrate phase nor BaGe_2 (the latter phase superconducts below $T_{\text{SC}} = 4.93$ K). Our isothermal section covering phase equilibria at 800 °C around the two clathrate phases in the Ge-rich region of the Ba–Co–Ge system showed the existence of only one ternary compound labelled τ_1 at a composition $\text{Ba}_{6.79}\text{Co}_{30.4}\text{Ge}_{63.09}$ (from EPMA in at.%) without a sizeable homogeneity region [1]. It is therefore the aim of the present paper (i) to elucidate the crystal structure of the τ_1 -phase, (ii) to characterize its physical properties,

particularly with respect to superconductivity and (iii) to investigate the formation and physical properties of isotypic compounds with Sr and Eu.

2. Experimental

Alloys with a weight of 1–2 g were prepared by argon arc-melting (weight loss less than 0.1%) on a water-cooled copper hearth in Ti-gettered argon from elemental ingots with minimal purity of 99.9 mass%. A single crystal fragment, suitable for X-ray structure determination was broken from an arc-melted sample with nominal composition $\text{Ba}_{7.0}\text{Co}_{30.4}\text{Ge}_{62.6}$, which had been vacuum-sealed in a quartz tube and annealed for 14 days at 700–900 °C prior to quenching in cold water. Inspection on an AXS-GADDS texture goniometer assured high crystal quality, unit cell dimensions and Laue symmetry of the specimens prior to X-ray intensity data collection on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector and employing graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.071073$ nm). Orientation matrix and unit cell parameters for a cubic system were derived using the program DENZO [4]. No absorption correction was necessary because of the rather regular crystal shape and small dimensions of the investigated specimen. The structure was solved by direct methods and refined with the SHELXL-97 and SHELXS-97 programs [5].

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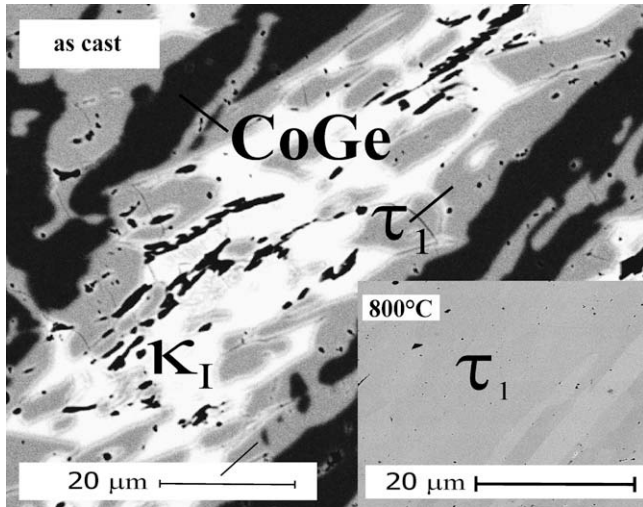


Fig. 1. Micrograph of alloy $Ba_{7.0}Co_{30.4}Ge_{62.6}$; as cast (main BSE image), annealed at $800\text{ }^{\circ}C$ (inset).

X-ray examination of polycrystalline materials was performed at room temperature in a Guinier-Huber X-ray camera with an Image Plate recording system ($CuK_{\alpha 1}$) employing an internal standard of 99.9999 mass% pure Si ($a_{Si} = 0.5431065\text{ nm}$). Quantitative Rietveld refinement of single-phase samples was performed by means of the FULLPROF program [6]. As cast and annealed samples were polished via standard procedures and have been examined by optical metallography and scanning electron microscopy (SEM). Specimen composition was determined by Electron Probe Microanalysis (EPMA) on a Carl Zeiss DSM 962 instrument equipped with a link EDX system operated at 20 kV and $60\text{ }\mu A$.

A superconducting quantum interference device (SQUID) served for the determination of the magnetization from 2 K up to 300 K in fields up to 6 T, respectively. Specific heat measurements on samples of about 1 g were performed at temperatures ranging from 2 K up to 120 K by means of a quasi-adiabatic step heating technique. The electrical resistivity of bar shaped samples was measured using a four-probe a.c. bridge-method in the temperature range from 2 K to room temperature.

Table 1a

X-Ray single crystal data for $BaCo_{4.7}Ge_9$ (standardized with program Structure Tidy [10]; room temperature data, redundancy >8); space group $Pnma$; No. 62.

Parameter/compound	$Ba_7Co_{30}Ge_{63}^a$
Composition from EPMA	$Ba_{6.79}Co_{30.12}Ge_{63.09}$
Composition from refinement	$Ba_{6.80}Co_{32.04}Ge_{61.16}$
Formula from refinement	$BaCo_{4.7}Ge_9$
Crystal size	$40 \times 57 \times 60\text{ }\mu m^3$
a, b, c [nm]	1.3992(5), 0.40220(2), 1.6993(7)
a, b, c [nm], Si standard	1.39910(2), 0.40218(2), 1.69882(2)
μ_{abs} [mm^{-1}]	43.31
Data collection, 2θ range [$^{\circ}$];	$2 \leq 2\theta \leq 70$
ω -scans, scan width 2°	150 s/frame
Total number of frames & sets	671; 13 sets
Reflections in refinement	$1893 \geq 4\sigma(F_o)$ of 2357
Mosaicity	<0.52
Number of variables	93
$R_F^2 = \sum F_o^2 - F_c^2 / \sum F_o^2$	0.025
R_{int}	0.069
wR2	0.076
GOF	1.108
Extinction (Zachariasen)	0.0011 (1)
Residual density [e/nm^3];	max; min 2800; -1770

^a Nominal composition.

Table 1b

Atom parameters for $BaCo_{4.7}Ge_9$. All atoms in site 4c ($x, \frac{1}{4}, z$). Atomic displacement parameters are given in 10^2 nm^2 .

Ba	Co5	Ge5
occ. 1.00(1)	occ. 0.715(4)	occ. 1.00(1)
x 0.28381(2)	x 0.03441(8)	x 0.26671(5)
z 0.81550(2)	z 0.08683(7)	z 0.17254(4)
U_{11} 0.0104(2)	U_{11} 0.0086(5)	U_{11} 0.0181(3)
U_{22} 0.0068(2)	U_{22} 0.0105(6)	U_{22} 0.0075(3)
U_{33} 0.0085(2)	U_{33} 0.0096(5)	U_{33} 0.0092(3)
U_{13} 0.0003(1)	U_{13} 0.0025(4)	U_{13} 0.0046(2)
Co1	Ge1	Ge6
occ. 1.00(1)	occ. 1.00(1)	occ. 1.00(1)
x 0.00801(6)	x 0.06051(5)	x 0.36531(4)
z 0.81696(5)	z 0.68755(4)	z 0.60199(4)
U_{11} 0.0075(3)	U_{11} 0.0097(3)	U_{11} 0.0062(3)
U_{22} 0.0067(3)	U_{22} 0.0165(3)	U_{22} 0.0113(3)
U_{33} 0.0069(3)	U_{33} 0.0066(3)	U_{33} 0.0103(3)
U_{13} 0.0003(3)	U_{13} 0.0012(2)	U_{13} -0.0012(2)
Co2	Ge2	Ge7
occ. 1.00(1)	occ. 1.00(1)	occ. 1.00(1)
x 0.00906(6)	x 0.06756(5)	x 0.37886(4)
z 0.55522(5)	z 0.40340(4)	z 0.03223(4)
U_{11} 0.0063(3)	U_{11} 0.0086(3)	U_{11} 0.0063(3)
U_{22} 0.0078(4)	U_{22} 0.0069(3)	U_{22} 0.0094(3)
U_{33} 0.0073(3)	U_{33} 0.0145(3)	U_{33} 0.0097(3)
U_{13} -0.0001(3)	U_{13} 0.0033(2)	U_{13} 0.0012(2)
Co3	Ge3	Ge8
occ. 1.00(1)	occ. 1.00(1)	occ. 1.00(1)
x 0.19554(6)	x 0.07045(5)	x 0.39399(5)
z 0.60504(5)	z 0.23042(4)	z 0.33498(4)
U_{11} 0.0061(3)	U_{11} 0.0105(3)	U_{11} 0.0085(3)
U_{22} 0.0076(4)	U_{22} 0.0074(3)	U_{22} 0.0094(3)
U_{33} 0.0074(3)	U_{33} 0.0120(3)	U_{33} 0.0203(3)
U_{13} 0.0004(3)	U_{13} -0.0038(2)	U_{13} 0.0022(2)
Co4	Ge4	Ge9
occ. 1.00(1)	occ. 1.00(1)	occ. 1.00(1)
x 0.20983(6)	x 0.25490(5)	x 0.56534(5)
z 0.02859(5)	z 0.46058(4)	z 0.54550(4)
U_{11} 0.0072(3)	U_{11} 0.0131(3)	U_{11} 0.0129(3)
U_{22} 0.0071(3)	U_{22} 0.0070(3)	U_{22} 0.0221(4)
U_{33} 0.0079(3)	U_{33} 0.0080(3)	U_{33} 0.0155(3)
U_{13} -0.0010(3)	U_{13} -0.0012(2)	U_{13} 0.0073(3)

3. Results and discussion

Micrographs show that the ternary compound $BaCo_{4.7}Ge_9$ (τ_1) forms incongruently. In the cast alloy $Ba_{7.0}Co_{30.4}Ge_{62.6}$ (see Fig. 1) primary crystals of CoGe (black phase) are surrounded by the gray phase τ_1 ; the last portion of liquid solidifies as clathrate I (κ_1 = white phase). After annealing at $800\text{ }^{\circ}C$ the sample is a single-phase ternary compound $BaCo_{4.7}Ge_9$ (compare inset in Fig. 1).

3.1. Crystal structure of $BaCo_{4.7}Ge_9$

Systematic extinctions ($hk0$) extinct for $h = 2n + 1$ and ($0kl$) extinct for $k + l = 2n + 1$, lead to $Pnma$, as the highest symmetric space group, for which determination of the atom arrangement was successful via direct methods revealing 15 independent atom sites in the unit cell. Search for higher symmetry (program PLATON) did not retrieve any further symmetry elements. Differences in X-ray scattering powers of Co- and Ge-atoms are sufficiently large to elucidate atom site occupation. Including Co5-atoms, for which a partial occupation (71%) was obvious from the large atom displacement factor (ADP), a fully ordered atom arrangement is obtained, which refines successfully to low residual values $R_F = 0.025$ at very small residual electron densities $< |2800| e^-/nm^3$ employing anisotropic thermal displacement factors for all atoms. Occupancies of all crystallographic sites were refined but except for Co5 did not reveal any significant deviations

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