

Phase equilibria in the system Hf–Zr–Ge at 1350 °C

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Abstract

The Hf–Zr–Ge system was studied for the isothermal section at 1350 °C. The homogeneity ranges of the various ternary solid solutions of binary Hf–Ge and Zr–Ge compounds were determined. X-ray powder diffraction (XRD) as well as optical microscopy was used for initial sample characterisation and electron probe microanalysis (EPMA) of the annealed samples was used to determine the exact phase compositions in the ternary system. The lattice parameters of the various ternary solid solutions were determined as a function of composition. No ternary compound was found to exist in the section at 1350 °C.

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1. Introduction

The investigation of the Hf–Zr–Ge system is part of a study of ternary systems with two early transition metals together with germanium, gallium and arsenic. The principal aim of this study is the detailed investigation of substitution and partial ordering in the corresponding ternary solid solutions. As there has been no investigation of the ternary system Hf–Zr–Ge up to now, an experimental study of the isothermal section of this system at 1350 °C was performed during our study and is presented here.

The binary systems Hf–Ge [1] and Zr–Ge [2] have been investigated previously. In the system Hf–Ge seven binary compounds have been reported: Hf₃Ge [3], Hf₂Ge [3], Hf₅Ge₃ [4], Hf₃Ge₂ [3], Hf₅Ge₄ [5], HfGe [1] and HfGe₂ [4]. A review article regarding phase equilibria in this system has been published by Gokhale and Abbaschian [1]. According to these authors, most structures are well known except for HfGe.

In the system Zr–Ge five binary compounds are known: Zr₃Ge [6], Zr₅Ge₃ [6], Zr₅Ge₄ [6], ZrGe [6] and ZrGe₂ [6]. An assessed version of the phase diagram was given by Abriata and Bolcich [2]. According to these authors, the phases in this system are well known although there are uncertainties left regarding the solubility ranges of ZrGe and Zr₃Ge. Structural data of binary Hf–Ge and Zr–Ge compounds are listed in Table 1.

The system Hf–Zr [7] shows a complete solid solubility of Hf and Zr in the room temperature modification (Mg-type, *hP2*) as well as in the high temperature modification (W-type, *cI2*). As three binary compounds in the Zr–Ge system (ZrGe₂, Zr₅Ge₃ and Zr₃Ge) have an isostructural counterpart in the Hf–Ge system, extended or even complete solid solutions can be expected.

2. Experimental

All samples were prepared from hafnium chips (99.9% metals basis, Alfa, Karlsruhe, Germany; the nominal amount of 2 at.% zirconium has been considered for the composition calculation), zirconium rods (99.6%, U.S.I. reactor grade) and germanium pieces (99.999%, Ventron, New Jersey, USA). Calculated amounts of the metals were weighted to an accuracy of 0.05 mg and arc melted on a water-cooled copper plate under an argon atmosphere. Zirconium was used as a getter material within the arc chamber. The samples with a total mass of 1200 mg were re-melted two to four times for homogenisation. The metals were subsequently placed in a tantalum crucible which was welded with a tantalum cap in the arc furnace under an argon atmosphere of 0.5 bar.

A series of 31 samples covering the whole composition range was prepared. The samples were annealed at 1350 °C for 48 h in a high temperature resistance furnace. Finally, the samples were quenched in a water-cooled steel vessel and weighed back in order to check for weight losses during annealing.

Because of the relatively high vapour pressure of germanium it was not possible to melt the metals without a considerable mass loss (up to 2 wt.%) due to evaporation of germanium. It was tried to compensate this loss (of germanium) by adding some extra germanium before every re-melting process. For the calculation of the nominal sample composition we assumed that the weight loss during the arc melting is derived only from the loss of germanium. Apparently, this assumption was not always correct, as reflected by the EPMA-results listed in Table 2.

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Table 1
Binary phases reported in the systems Hf–Ge and Zr–Ge

Phase	Structure type	Pearson symbol, space group	Lattice parameter (Å)	Cell volume (Å ³)	Reference
Hf ₃ Ge	Ti ₃ P	<i>tP32, P4₂/n</i>	<i>a</i> = 10.92, <i>c</i> = 5.42	646.3	[3]
Zr ₃ Ge			<i>a</i> = 11.73(3), <i>c</i> = 5.474(3)	753.2	[6]
Hf ₂ Ge	CuAl ₂	<i>tI12, I4/mcm</i>	<i>a</i> = 6.596(3), <i>c</i> = 5.291(3)	230.2	[3]
Hf ₅ Ge ₃	Mn ₅ Si ₃	<i>hP16, P6₃/mcm</i>	<i>a</i> = 7.941(1), <i>c</i> = 5.542(2)	302.7	[4]
Zr ₅ Ge ₃			<i>a</i> = 8.029(2), <i>c</i> = 5.594(2)	312.3	[6]
Hf ₃ Ge ₂	U ₃ Si ₂	<i>tP10, P4/mbm</i>	<i>a</i> = 7.06, <i>c</i> = 3.72	185.4	[3]
Hf ₅ Ge ₄	Sm ₅ Ge ₄	<i>oP36, Pnma</i>	<i>a</i> = 7.017(1), <i>b</i> = 13.434(4), <i>c</i> = 7.105(1)	669.8	[5]
Zr ₅ Ge ₄	Zr ₅ Si ₄	<i>tP36, P4₁2₁2</i>	<i>a</i> = 7.238(2), <i>c</i> = 13.154(4)	689.1	[6]
HfGe	FeB	<i>oP8, Pnma</i>	–	–	[1] ^a
ZrGe			<i>a</i> = 7.068(2), <i>b</i> = 3.899(1), <i>c</i> = 5.396(1)	148.7	[6]
HfGe ₂	ZrSi ₂	<i>oC12, Cmcm</i>	<i>a</i> = 3.793(1), <i>b</i> = 14.882(5), <i>c</i> = 3.751(2)	211.7	[4]
ZrGe ₂			<i>a</i> = 3.810(3), <i>b</i> = 15.07(2), <i>c</i> = 3.769(2)	216.4	[6]

^a Not found in this work.

After the quenching, a pie slice shaped piece of the samples was cut off and incorporated into a mixture of resin and copper powder. The embedded samples were grinded and polished in order to perform optical microscopy as well as electron probe microanalysis (EPMA). For the investigation by optical microscopy a Zeiss Axiotech 100 microscope equipped for operation under polarised light was used.

The EPMA measurements were carried out on a Cameca SX 100 electron probe, using wavelength dispersive spectroscopy (WDS) for quantitative analysis and employing elemental hafnium (2 at.% zirconium), zirconium and germanium as standard materials. The measurements were carried out at 20 kV and 20 nA. Conventional ZAF correction was used to calculate the final composition.

The remaining parts of the samples were used to perform X-ray powder diffraction. For investigation of the lattice parameters, Guinier-Huber Image Plate techniques (Cu K α ₁, monochromated) as well as X-ray diffractometry in Bragg–Brentano geometry (Cu K α) have been used.

3. Results and discussion

The isothermal section as proposed from our experimental investigations is shown in Fig. 1 including all tie-lines and tie triangles as determined by EPMA. The exact compositions of the various phases are given in Table 2.

No samples were prepared in the most Ge-rich part of the phase diagram because of the anticipated problems in the sample preparation by arc furnace connected with the expected high Ge-loss. However, given the existence of a complete solid solution HfGe₂–ZrGe₂, the positions of the tie-lines in this corner are fixed anyhow.

Phase equilibria between the solid solution Hf_{1–x}Zr_xGe₂ and neighbouring phases were determined from samples with nominal compositions around 44 at.% (cf. Table 2) and thus only contain small amounts of Hf_{1–x}Zr_xGe₂. Consequently, the course of lattice parameters with composition was not evaluated for this phase.

The existence of the phase HfGe (FeB, *oP8, Pnma*) could not be confirmed in the current work, and the solubility limit of Hf in ZrGe was found to be approximately 12 at.% at 1350 °C.

Hf₅Ge₄ and Zr₅Ge₄ both exhibit extended solubility ranges in the ternary. XRD results show that the orthorhombic phase Hf_{5–x}Zr_xGe₄ is stable up to approximately 20 at.% Zr (corre-

sponding to the composition Hf_{3.2}Zr_{1.8}Ge₄) while the tetragonal modification Zr_{5–x}Hf_xGe₄ is stable up to approximately 34 at.% Hf (corresponding to the composition Zr_{1.94}Hf_{3.06}Ge₄). It was not possible to prepare a sample showing the orthorhombic and tetragonal modification in equilibrium with each other. The respective two- and three-phase fields are presumably very small as indicated by the dashed lines in Fig. 1. The lattice parameters of the two modifications Hf_{5–x}Zr_xGe₄ (orthorhombic) and Zr_{5–x}Hf_xGe₄ (tetragonal) are shown in Figs. 2 and 3, respectively. The determined lattice parameters show good linearity with rising Zr-content and show satisfying agreement with the literature data [5,6].

EPMA data clearly show the presence of a phase situated between Hf₅Ge₄ and Hf₅Ge₃ with the approximate composition Hf₃Ge₂ and a ternary solubility limit of approximately 16 at.% Zr (compare Fig. 1). The U₃Si₂-type structure reported by Rossteutscher and Schubert [8] could be confirmed for this phase. The

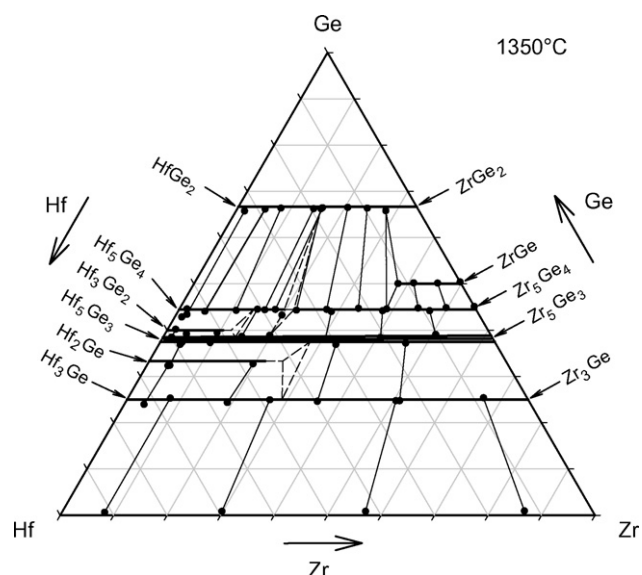


Fig. 1. Isothermal section of Hf–Zr–Ge at 1350 °C. Black dots indicate phase compositions measured by EPMA.

Table 2
Experimental phase compositions of various samples determined by EPMA

Nominal sample composition ^a	Phase field	Phase compositions determined by EPMA
Hf _{54.4} Zr _{2.2} Ge _{43.4}	(Hf _{5-x} Zr _x Ge ₄)	(Hf _{5-x} Zr _x Ge ₄): Hf _{54.2(1)} Zr _{16.7(1)} Ge _{44.1(1)}
Hf _{48.5} Zr _{2.5} Ge ₄₉	[(Hf _{1-x} Zr _x Ge ₂) + (Hf _{5-x} Zr _x Ge ₄)]	(Hf _{1-x} Zr _x Ge ₂): Hf _{32.6(1)} Zr _{1.6(1)} Ge _{65.8(1)}
Hf _{50.0} Zr _{5.6} Ge _{44.4}	[(Hf _{1-x} Zr _x Ge ₂) + (Hf _{5-x} Zr _x Ge ₄)]	(Hf _{1-x} Zr _x Ge ₂): Hf _{28.6(1)} Zr _{5.3(2)} Ge _{66.1(2)}
Hf _{43.4} Zr _{10.9} Ge _{45.7}	[(Hf _{1-x} Zr _x Ge ₂) + (Hf _{5-x} Zr _x Ge ₄)]	(Hf _{1-x} Zr _x Ge ₂): Hf _{25.5(1)} Zr _{8.1(2)} Ge _{66.4(2)}
Hf _{37.9} Zr _{16.2} Ge _{45.9}	[(Hf _{1-x} Zr _x Ge ₂) + (Hf _{5-x} Zr _x Ge ₄)]	(Hf _{1-x} Zr _x Ge ₂): Hf _{19.5(1)} Zr _{14.3(1)} Ge _{66.2(1)}
Hf _{37.3} Zr _{18.3} Ge _{44.4}	[(Hf _{1-x} Zr _x Ge ₂) + (Hf _{5-x} Zr _x Ge ₄)]	(Hf _{1-x} Zr _x Ge ₂): Hf _{17.7(2)} Zr _{15.8(1)} Ge _{66.5(3)}
Hf _{33.8} Zr _{22.6} Ge _{43.6}	[(Hf _{1-x} Zr _x Ge ₂) + (Zr _{5-x} Hf _x Ge ₄)]	(Hf _{1-x} Zr _x Ge ₂): Hf _{18.1(3)} Zr _{15.6(4)} Ge _{66.3(4)}
Hf _{27.8} Zr _{27.8} Ge _{44.4}	[(Hf _{1-x} Zr _x Ge ₂) + (Zr _{5-x} Hf _x Ge ₄)]	(Hf _{1-x} Zr _x Ge ₂): Hf _{13.0(1)} Zr _{20.5(3)} Ge _{66.5(2)}
Hf _{22.2} Zr _{33.3} Ge _{44.5}	[(Hf _{1-x} Zr _x Ge ₂) + (Zr _{5-x} Hf _x Ge ₄)]	(Hf _{1-x} Zr _x Ge ₂): Hf _{9.4(1)} Zr _{24.2(1)} Ge _{66.4(1)}
Hf _{16.6} Zr _{38.7} Ge _{44.7}	[(Hf _{1-x} Zr _x Ge ₂) + (Zr _x Hf _{1-x} Ge) + (Zr _{5-x} Hf _x Ge ₄)]	(Hf _{1-x} Zr _x Ge ₂): Hf _{6.2(1)} Zr _{28.0(2)} Ge _{65.8(2)}
Hf _{11.1} Zr _{44.4} Ge _{44.5}	[(Zr _x Hf _{1-x} Ge) + (Zr _{5-x} Hf _x Ge ₄)]	(Zr _x Hf _{1-x} Ge): Hf _{8.8(5)} Zr _{41.0(3)} Ge _{50.2(2)}
Hf _{5.5} Zr _{49.8} Ge _{44.7}	[(Zr _x Hf _{1-x} Ge) + (Zr _{5-x} Hf _x Ge ₄)]	(Zr _x Hf _{1-x} Ge): Hf _{4.4(4)} Zr _{45.5(4)} Ge _{50.1(1)}
Zr _{55.8} Ge _{44.2}	[(Zr _x Hf _{1-x} Ge) + (Zr _{5-x} Hf _x Ge ₄)]	(Zr _x Hf _{1-x} Ge): Hf _{0.2(1)} Zr _{49.6(2)} Ge _{50.4(1)}
Hf _{54.9} Zr _{2.2} Ge _{42.9}	[(Hf _{5-x} Zr _x Ge ₄) + (Hf _{5-x} Zr _x Ge ₂)]	(Hf _{5-x} Zr _x Ge ₄): Hf _{54.0(4)} Zr _{1.4(1)} Ge _{44.6(4)}
Hf _{56.7} Zr _{2.3} Ge _{41.0}	[(Hf _{3-x} Zr _x Ge ₂) + (Hf _{5-x} Zr _x Ge ₃)]	(Hf _{3-x} Zr _x Ge ₂): Hf _{58.3(1)} Zr _{1.5(2)} Ge _{40.2(1)}
Hf _{54.6} Zr _{4.9} Ge _{40.5}	[(Hf _{3-x} Zr _x Ge ₂) + (Hf _{5-x} Zr _x Ge ₃)]	(Hf _{3-x} Zr _x Ge ₂): Hf _{56.8(1)} Zr _{4.0(1)} Ge _{39.2(2)}
Hf _{49.8} Zr _{9.9} Ge _{40.3}	[(Hf _{3-x} Zr _x Ge ₂) + (Hf _{5-x} Zr _x Ge ₃)]	(Hf _{3-x} Zr _x Ge ₂): Hf _{50.9(5)} Zr _{9.6(3)} Ge _{39.5(5)}
Hf _{39.9} Zr _{20.0} Ge _{40.1}	[(Hf _{5-x} Zr _x Ge ₄) + (Hf _{5-x} Zr _x Ge ₃)]	(Hf _{5-x} Zr _x Ge ₄): Hf _{36.5(4)} Zr _{19.9(4)} Ge _{43.6(4)}
Hf _{29.9} Zr _{29.9} Ge _{40.2}	[(Zr _{5-x} Hf _x Ge ₄) + (Hf _{5-x} Zr _x Ge ₃)]	(Zr _{5-x} Hf _x Ge ₄): Hf _{27.3(5)} Zr _{28.7(5)} Ge _{44.0(2)}
Hf _{20.1} Zr _{40.1} Ge _{39.8}	[(Zr _{5-x} Hf _x Ge ₄) + (Hf _{5-x} Zr _x Ge ₃)]	(Zr _{5-x} Hf _x Ge ₄): Hf _{17.5(1)} Zr _{38.3(1)} Ge _{44.2(2)}
Hf _{10.0} Zr _{49.8} Ge _{40.2}	[(Zr _{5-x} Hf _x Ge ₄) + (Hf _{5-x} Zr _x Ge ₃)]	(Zr _{5-x} Hf _x Ge ₄): Hf _{8.8(1)} Zr _{47.0(1)} Ge _{44.2(1)}
Hf _{59.8} Zr _{5.0} Ge _{35.2}	[(Hf _{5-x} Zr _x Ge ₃) + (Hf _{2-x} Zr _x Ge)]	(Hf _{5-x} Zr _x Ge ₃): Hf _{59.1(1)} Zr _{4.0(2)} Ge _{36.9(3)}
Hf _{64.6} Zr _{5.0} Ge _{30.4}	[(Hf _{2-x} Zr _x Ge) + (Hf _{3-x} Zr _x Ge)]	(Hf _{2-x} Zr _x Ge): Hf _{63.8(2)} Zr _{4.0(2)} Ge _{32.2(2)}
Hf _{50.0} Zr _{20.0} Ge _{30.0}	[(Hf _{2-x} Zr _x Ge) + (Hf _{3-x} Zr _x Ge)]	(Hf _{2-x} Zr _x Ge): Hf _{47.5(2)} Zr _{19.8(3)} Ge _{32.7(3)}
Hf _{35.0} Zr _{35.0} Ge _{30.0}	[(Hf _{5-x} Zr _x Ge ₃) + (Hf _{3-x} Zr _x Ge)]	(Hf _{5-x} Zr _x Ge ₃): Hf _{30.0(3)} Zr _{33.1(2)} Ge _{36.9(2)}
Hf _{20.3} Zr _{50.9} Ge _{28.8}	[(Hf _{5-x} Zr _x Ge ₃) + (Hf _{3-x} Zr _x Ge)]	(Hf _{5-x} Zr _x Ge ₃): Hf _{16.8(1)} Zr _{46.0(2)} Ge _{37.2(3)}
Hf _{44.8} Zr _{14.9} Ge _{40.3}	[(Hf _{5-x} Zr _x Ge ₄) + (Hf _{5-x} Zr _x Ge ₃)]	(Hf _{5-x} Zr _x Ge ₄): Hf _{40.9(4)} Zr _{14.6(4)} Ge _{44.5(2)}
Hf _{74.9} Zr _{10.0} Ge _{15.1}	[(Hf _{3-x} Zr _x Ge) + (Hf _{1-x} Zr _x)]	(Hf _{3-x} Zr _x Ge): Hf _{66.8(4)} Zr _{7.9(4)} Ge _{25.3(4)}
Hf _{55.0} Zr _{30.0} Ge _{15.0}	[(Hf _{3-x} Zr _x Ge) + (Hf _{1-x} Zr _x)]	(Hf _{3-x} Zr _x Ge): Hf _{48.3(5)} Zr _{26.7(5)} Ge _{24.9(4)}
Hf _{30.0} Zr _{55.0} Ge _{15.0}	[(Hf _{3-x} Zr _x Ge) + (Hf _{1-x} Zr _x)]	(Hf _{3-x} Zr _x Ge): Hf _{24.8(5)} Zr _{50.4(5)} Ge _{24.8(4)}
Hf _{10.1} Zr _{75.4} Ge _{14.5}	[(Hf _{3-x} Zr _x Ge) + (Hf _{1-x} Zr _x)]	(Hf _{3-x} Zr _x Ge): Hf _{8.4(2)} Zr _{66.5(4)} Ge _{25.4(2)}
		(Hf _{5-x} Zr _x Ge ₄): Hf _{54.7(1)} Zr _{2.0(2)} Ge _{43.3(2)}
		(Hf _{5-x} Zr _x Ge ₄): Hf _{50.9(2)} Zr _{5.0(2)} Ge _{44.1(1)}
		(Hf _{5-x} Zr _x Ge ₄): Hf _{44.9(1)} Zr _{10.8(1)} Ge _{44.3(1)}
		(Hf _{5-x} Zr _x Ge ₄): Hf _{39.5(1)} Zr _{16.1(2)} Ge _{44.4(1)}
		(Hf _{5-x} Zr _x Ge ₄): Hf _{37.5(1)} Zr _{18.1(2)} Ge _{44.4(1)}
		(Zr _{5-x} Hf _x Ge ₄): Hf _{33.7(2)} Zr _{22.0(1)} Ge _{44.3(1)}
		(Zr _{5-x} Hf _x Ge ₄): Hf _{27.9(3)} Zr _{27.6(2)} Ge _{44.5(2)}
		(Zr _{5-x} Hf _x Ge ₄): Hf _{21.8(1)} Zr _{33.3(2)} Ge _{44.7(1)}
		(Zr _x Hf _{5-x} Ge): Hf _{11.8(1)} Zr _{38.1(1)} Ge _{50.1(1)}
	(Zr _{5-x} Hf _x Ge ₄): Hf _{16.6(4)} Zr _{38.8(4)} Ge _{44.6(1)}	
		(Zr _{5-x} Hf _x Ge ₄): Hf _{10.7(1)} Zr _{44.5(1)} Ge _{44.8(1)}
		(Zr _{5-x} Hf _x Ge ₄): Hf _{5.4(1)} Zr _{49.7(3)} Ge _{44.9(2)}
		(Zr _{5-x} Hf _x Ge ₄): Hf _{0.2(1)} Zr _{54.9(3)} Ge _{45.1(1)}
		(Hf _{3-x} Zr _x Ge ₂): Hf _{55.9(5)} Zr _{1.3(3)} Ge _{42.8(5)}
		(Hf _{5-x} Zr _x Ge ₃): Hf _{59.9(3)} Zr _{1.6(1)} Ge _{38.5(2)}
		(Hf _{5-x} Zr _x Ge ₃): Hf _{58.6(1)} Zr _{4.1(1)} Ge _{37.3(1)}
		(Hf _{5-x} Zr _x Ge ₃): Hf _{52.9(4)} Zr _{9.6(2)} Ge _{37.5(3)}
		(Hf _{5-x} Zr _x Ge ₃): Hf _{42.5(1)} Zr _{20.1(3)} Ge _{37.4(1)}
		(Hf _{5-x} Zr _x Ge ₃): Hf _{31.5(2)} Zr _{30.5(1)} Ge _{38.0(3)}
		(Hf _{5-x} Zr _x Ge ₃): Hf _{20.9(4)} Zr _{40.7(5)} Ge _{38.4(1)}
		(Hf _{5-x} Zr _x Ge ₃): Hf _{10.2(2)} Zr _{50.7(4)} Ge _{39.1(4)}
		(Hf _{2-x} Zr _x Ge): Hf _{63.3(3)} Zr _{4.3(3)} Ge _{32.4(1)}
		(Hf _{3-x} Zr _x Ge): Hf _{72.3(2)} Zr _{3.7(2)} Ge _{24.0(1)}
		(Hf _{3-x} Zr _x Ge): Hf _{56.6(4)} Zr _{19.1(5)} Ge _{24.3(2)}
		(Hf _{3-x} Zr _x Ge): Hf _{39.6(4)} Zr _{35.8(3)} Ge _{24.6(1)}
		(Hf _{3-x} Zr _x Ge): Hf _{24.2(1)} Zr _{51.1(1)} Ge _{24.7(1)}
		(Hf _{5-x} Zr _x Ge ₃): Hf _{46.7(2)} Zr _{14.6(4)} Ge _{38.7(2)}
		(Hf _{1-x} Zr _x): Hf _{91.4(4)} Zr _{8.0(2)} Ge _{0.6(5)}
		(Hf _{1-x} Zr _x): Hf _{69.3(4)} Zr _{29.8(4)} Ge _{0.9(3)}
		(Hf _{1-x} Zr _x): Hf _{42.5(3)} Zr _{56.7(4)} Ge _{0.8(4)}
		(Hf _{1-x} Zr _x): Hf _{12.7(5)} Zr _{86.4(2)} Ge _{0.9(1)}

^a The nominal sample composition was calculated under the assumption that all weigh losses during sample preparation are due to loss of Ge.

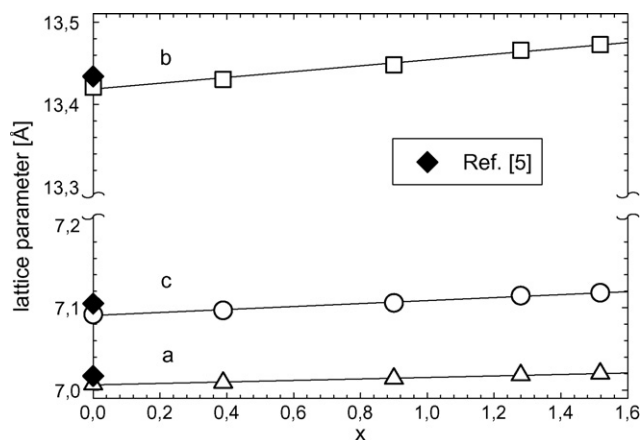


Fig. 2. Lattice parameters vs. composition for Me_5Ge_4 (*oP36*, *Pnma*), x corresponds to the formula $\text{Hf}_{5-x}\text{Zr}_x\text{Ge}_4$.

crystal structure of this phase is currently under investigation and will be published separately.

The two isostructural phases Hf_5Ge_3 and Zr_5Ge_3 again form a complete solid solution field. The lattice parameters are shown in Fig. 4. In contrast to the other phases discussed up to now, this phase field apparently shows a slight variability in the Ge-content. This is reflected by EPMA results (Fig. 1) as well as by the lattice parameters, which show different trends for samples from the Ge-poor and Ge-rich side of the phase field. The effect is also clearly seen in the unit cell volume (Fig. 5) which is generally higher for Ge-rich samples. Although no homogeneity range was reported for the two binary phases Hf_5Ge_3 and Zr_5Ge_3 in literature [4,6] our ternary data suggest binary homogeneity ranges and Fig. 1 was drawn accordingly.

The phase Hf_2Ge dissolves between about 20 and 30 at.% Zr. A sample in the three-phase field [$\text{Hf}_{5-x}\text{Zr}_x\text{Ge}_3 + \text{Hf}_{2-x}\text{Zr}_x\text{Ge} + \text{Hf}_{3-x}\text{Zr}_x\text{Ge}$] was not prepared and the corresponding tie triangle is consequently shown in dashed lines in Fig. 2.

There is a third complete solid solution in this ternary system, i.e. between Hf_3Ge and Zr_3Ge (both Ti_3P -structure type). EPMA data of samples in equilibrium with $\text{Hf}_{1-x}\text{Zr}_x\text{Ge}$ show a solubility of less than 1 at.% Ge for the binary Hf–Zr solid solution.

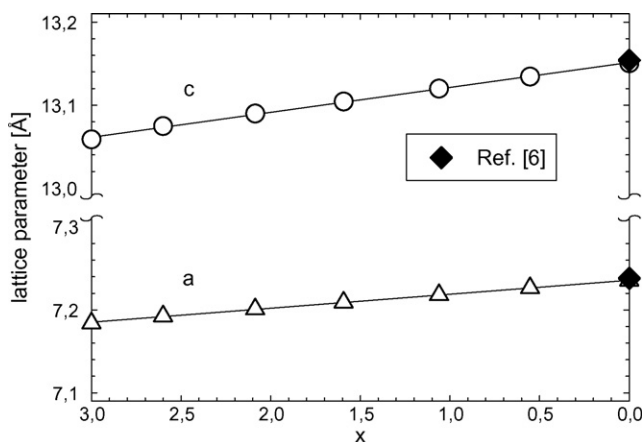


Fig. 3. Lattice parameters vs. composition for Me_5Ge_4 (*tP36*, *P41212*), x corresponds to the formula $\text{Zr}_{5-x}\text{Hf}_x\text{Ge}_4$.

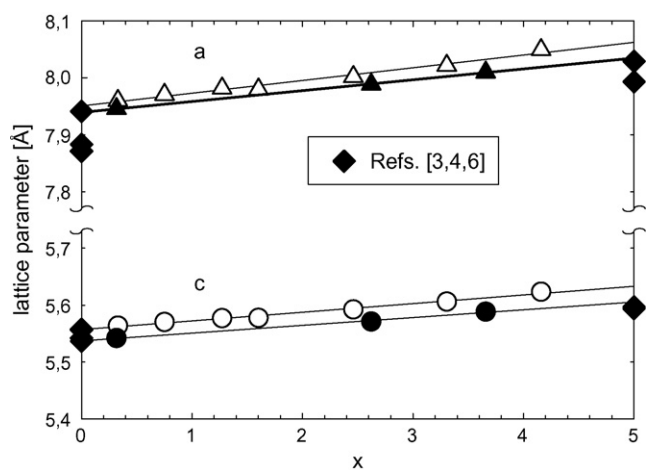


Fig. 4. Lattice parameters for the complete solid solution Me_5Ge_3 (*hP16*, *P63/mcm*) determined from Ge-rich (open symbols) and Ge-poor (full symbols) samples, x corresponds to the formula $\text{Hf}_{5-x}\text{Zr}_x\text{Ge}_3$.

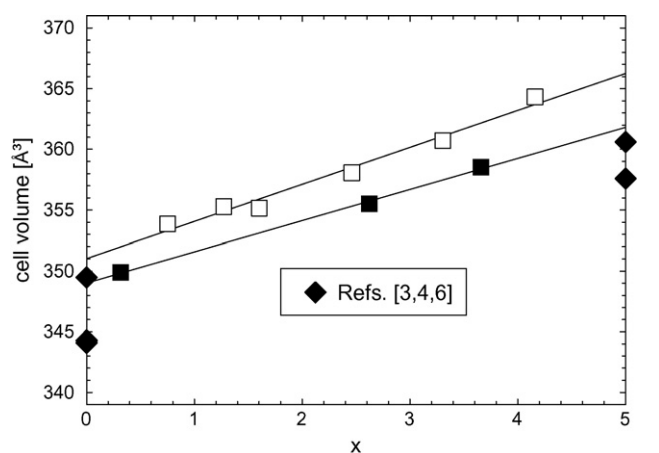


Fig. 5. Unit cell volume for the solid solution phase Me_5Ge_3 (*hP16*, *P63/mcm*) determined from Ge-rich (open squares) and Ge-poor (full squares) samples, x corresponds to the formula $\text{Hf}_{5-x}\text{Zr}_x\text{Ge}_3$.

As expected from the similarity of the two metals Hf and Zr, the ternary system Hf–Zr–Ge is dominated by extended solid solution phases, with no ternary phase existing in the investigated section at 1350 °C. An inconsistency to the existing binary phase diagram Hf–Ge [1] was observed for the phase HfGe which could not be found in the present study.

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