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The Tb–Hf–Si system at 873 K

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The isothermal cross-section of the phase diagram of the ternary Tb–Hf–Si system at 873 K was constructed. The formation of two compounds was established: $Tb_2Hf_3Si_4$ ($Sc_2Re_3Si_4$ type, $P4_12_12$, *tP*36, *Z* = 4; *a* = 0.72057(8), *c* = 1.3199(2) nm) and $(Tb_{0.7}Hf_{0.3})Si$ (CrB type, *Cmcm*, *oS*8, *Z* = 4; *a* = 0.42241(8), *b* = 1.0483(2), *c* = 0.38227(7) nm).

Terbium / Hafnium / Silicon / Phase diagram / Crystal structure

Introduction

The purpose of this work was to study the phase equilibria in the Tb–Hf–Si system at 873 K and to determine the crystal structure of new compounds. The binary Tb–Si and Hf–Si systems which limit the investigated ternary system have been well studied and the phase diagrams over the whole concentration region have been constructed in [1] and [2], respectively. No investigation of the binary Tb–Hf system has been published. Crystallographic data of the binary compounds reported in the Tb–Si and Hf–Si systems are listed in Table 1.

Experimental details

Six binary and 41 ternary alloys were prepared by arc-melting the elements under a purified argon atmosphere. Elements of the following purities were used: Tb, 99.9%; Hf, 99.9%; and Si, 99.999%. The samples were annealed at 873 K for 1000 h in evacuated quartz tubes and subsequently quenched in cold water. The mass of each sample was 1 g. Phase analysis was carried out using X-ray powder diffraction with Debye-Scherrer technique (non-filtered Cr *K* radiation). The programs LATCON [19] and PowderCell-2.4 [20] were used for calculations. The crystal structures were refined from X-ray powder diffraction patterns, recorded with a DRON-2.0 M (Fe *K*α radiation), HZG-4a (Cu *K*α), or XPERT PRO (Cu *K*α radiation) diffractometer using the program DBWS-9807 [21].

Results and discussion

During the investigation of the ternary Tb–Hf–Si system at 873 K we confirmed the existence and structure type of the following binary compounds: Tb_5Si_3 (structure type Mn_5Si_3), Tb_5Si_4 (Sm_5Ge_4), TbSi (FeB), $TbSi_{2-x}$ (AlB_2), $TbSi_{2-y}$ (α-$GdSi_2$), Hf_2Si ($CuAl_2$), Hf_5Si_3 (Mn_5Si_3), Hf_3Si_2 (U_3Si_2), Hf_5Si_4 (Zr_5Si_4), HfSi (FeB), and $HfSi_2$ ($ZrSi_2$).

The isothermal cross-section of the Tb–Hf–Si system at 873 K is shown in Fig. 1. The formation of two new compounds was established and their crystal structures were refined: $Tb_2Hf_3Si_4$ (structure type $Sc_2Re_3Si_4$) and $(Tb_{0.7}Hf_{0.3})Si$ (CrB type). Crystallographic data for the new ternary compounds are given in Table 2.

The structures of $Tb_2Hf_3Si_4$ and $(Tb_{0.7}Hf_{0.3})Si$ were refined on diffraction data from polycrystalline samples. The refinements were carried out with the full-profile Rietveld method. Cell parameters and atomic coordinates for the initial model were taken from the compounds $Sc_2Re_3Si_4$ and CrB [22]. The final refinements included scale factors, zero point, cell parameters, atomic coordinates, displacement parameters, pseudo-Voigt peak profile parameters, texture parameters. The atomic coordinates for $Tb_2Hf_3Si_4$ and $(Tb_{0.7}Hf_{0.3})Si$ are presented in Tables 3 and 4. Powder diagrams for some samples are shown in Figs. 2-4.

The solubility of the third component in the binary compounds of the Tb–Si and Hf–Si systems was determined. At 873 K the solid solutions based on the binary compounds Hf_5Si_3 and Tb_5Si_3 with hexagonal

Table 1 Crystallographic parameters of the binary compounds in the Tb–Si and Hf–Si systems.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, nm			Reference
				a	*b*	*c*	
Tb_5Si_3	Mn_5Si_3	*hP*16	$P6_3/mmc$	0.843	–	0.630	[1,3,4]
Tb_5Si_4	Sm_5Ge_4	*oP*36	*Pnma*	0.741	1.458	0.769	[1,5]
TbSi	FeB	*oP*8	*Pnma*	0.7919	0.3833	0.5703	[1,6,7]
Tb_2Si_3	V_2B_3	*oS*20	*Cmcm*	0.42178	2.3912	0.38230	[8]
$TbSi_{2-x}$ ($TbSi_{1.67}$)	AlB_2	*hP*3	*P*6/*mmm*	0.3846	–	0.4143	[1,9-11]
$TbSi_{2-y}$ ($TbSi_2$)	α-$GdSi_2$	*oI*12	*Imma*	0.398	0.407	1.337	[1,6,10,12]
Hf_2Si	$CuAl_2$	*tI*12	*I*4/*mcm*	0.6544	–	0.5173	[13,14]
Hf_5Si_3	Mn_5Si_3	*hP*16	$P6_3/mcm$	0.7840	–	0.5496	[14-16]
Hf_3Si_2	U_3Si_2	*tP*10	*P*4/*mbm*	0.6983	–	0.3672	[14,17]
Hf_5Si_4	Zr_5Si_4	*tP*36	$P4_12_12$	0.7030	–	1.2804	[14]
HfSi	FeB	*oP*8	*Pnma*	0.6855	0.3700	0.5220	[14]
$HfSi_2$	$ZrSi_2$	*oS*12	*Cmcm*	0.3677	1.4550	0.3649	[14,18]

Table 2 Crystallographic parameters of the ternary compounds in the Tb–Hf–Si system.

No.	Compound	Structure type	Pearson symbol	Space group	Cell parameters, nm		
					a	*b*	*c*
1	$Tb_2Hf_3Si_4$	$Sc_2Re_3Si_4$	*tP*36	$P4_12_12$	0.72057(8)	–	1.3199(2)
2	$(Tb_{0.7}Hf_{0.3})Si$	CrB	*oS*8	*Cmcm*	0.42241(8)	1.0483(2)	0.38227(7)

Table 3 Atomic coordinates for $Tb_2Hf_3Si_4$ (structure type $Sc_2Re_3Si_4$, Pearson symbol *tP*36, space group $P4_12_12$, $a = 0.72057(8)$, $c = 1.3199(2)$ nm, $Z = 4$; $R_B = 0.079$).

Atom	Wyckoff position	*x*	*y*	*z*	B_{iso}, 10^{-2} nm^2
Tb	8*b*	0.000(2)	0.342(2)	0.2122(7)	0.6(1)
Hf1	8*b*	0.156(1)	0.003(2)	0.375(2)	0.4(2)
Hf2	4*a*	0.167(2)	0.167(2)	0	0.4(2)
Si1	8*b*	0.279(7)	0.013(7)	0.177(4)	0.8(3)
Si2	8*b*	0.389(8)	0.324(9)	0.314(4)	0.8(3)

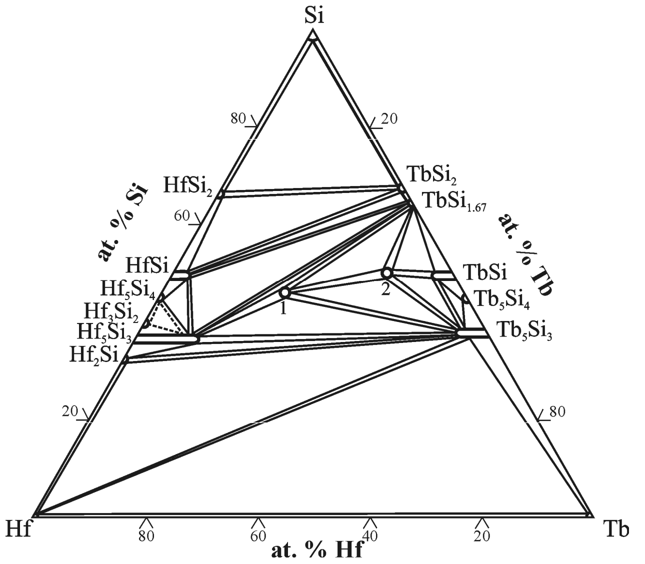
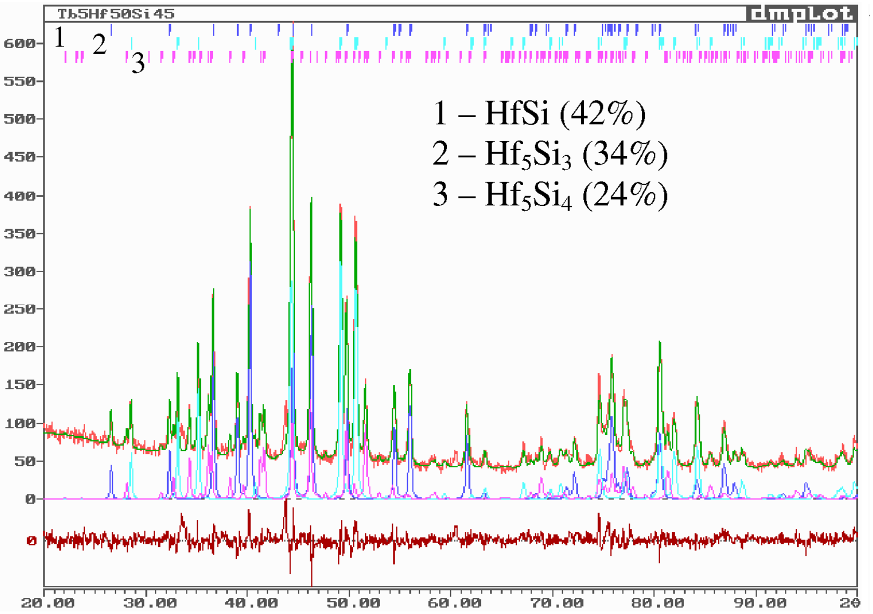
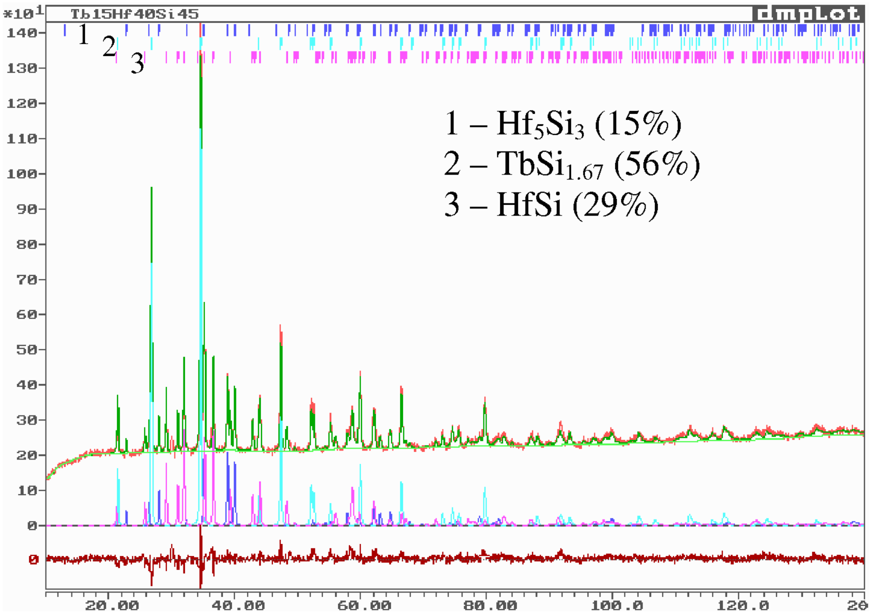


Fig. 1 Isothermal cross-section of the phase diagram of the ternary Tb–Hf–Si system at 873 K: 1 – $Tb_2Hf_3Si_4$, 2 – $(Tb_{0.7}Hf_{0.3})Si$.



HfSi (type FeB)	a = 0.69067(9), b = 0.37710(4), c = 0.52454(6) nm; R_B = 0.078
Hf_5Si_3 (type Mn_5Si_3)	a = 0.77937(8), c = 0.55324(6) nm; R_B = 0.081
Hf_5Si_4 (type Zr_5Si_4)	a = 0.70806(9), c = 1.2906(2) nm; R_B = 0.096

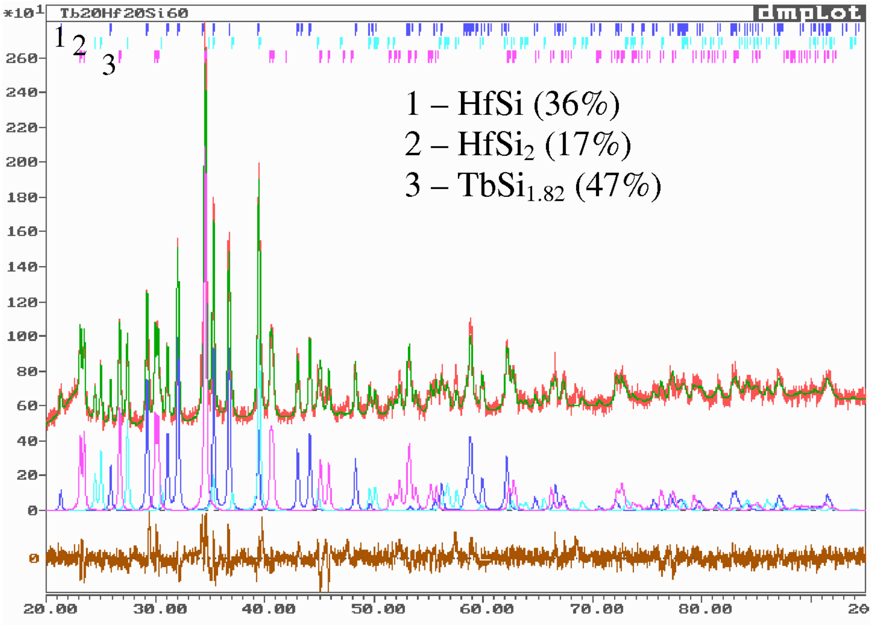
a



Hf_5Si_3 (type Mn_5Si_3)	a = 0.77847(8), c = 0.55230(9) nm; R_B = 0.177
$TbSi_{1.67}$ (type AlB_2)	a = 0.38382(2), c = 0.41263(3) nm; R_B = 0.146
HfSi (type FeB)	a = 0.69030(8), b = 0.37661(4), c = 0.52448(5) nm; R_B = 0.178

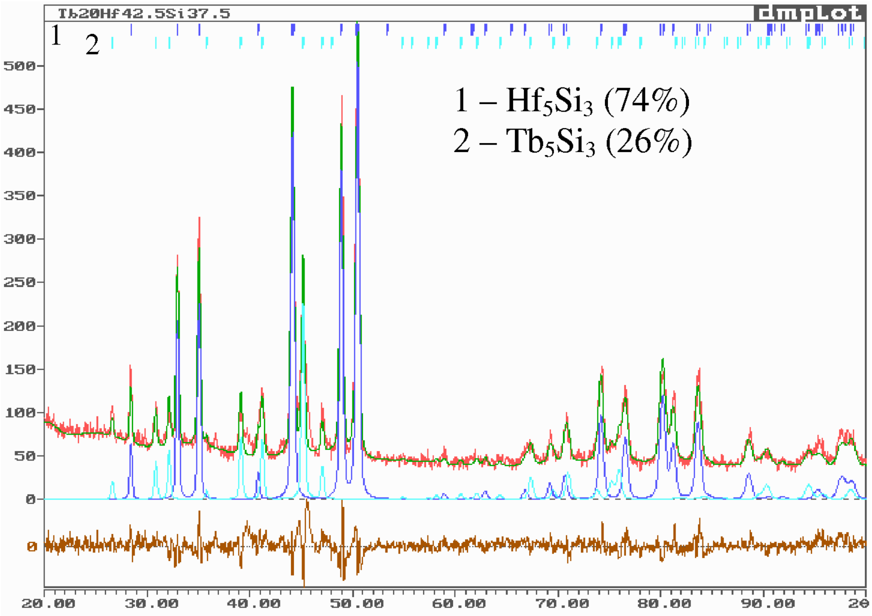
b

Fig. 2 X-ray diffraction powder patterns for samples $Tb_5Hf_{50}Si_{45}$ (Fe $K\alpha$ radiation, R_p = 0.071, R_{wp} = 0.093) (a) and $Tb_{15}Hf_{40}Si_{45}$ (Cu $K\alpha$ radiation, R_p = 0.027, R_{wp} = 0.035) (b).



HfSi (type FeB)	*a* =0.68966(8), *b* = 0.37706(4), *c* = 0.52391(5) nm; R_B = 0.096
HfSi$_2$ (type ZrSi$_2$)	*a* = 0.36782(6), *b* = 1.4584(3), *c* = 0.36416(6) nm; R_B = 0.126
TbSi$_{1.82}$ (type α-GdSi$_2$)	*a* = 0.39610(5), *b* = 0.40238(5), *c* = 1.3367(2) nm; R_B = 0.095

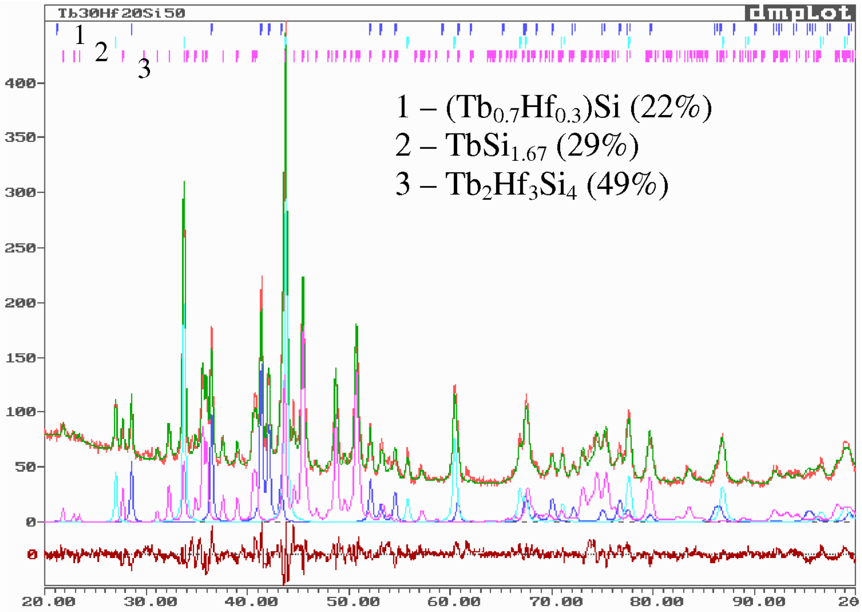
a



Hf$_5$Si$_3$ (type Mn$_5$Si$_3$)	*a* = 0.7868(1), *c* = 0.5544(1) nm; R_B = 0.079
Tb$_5$Si$_3$ (type Mn$_5$Si$_3$)	*a* = 0.8389(2), *c* = 0.6289(2) nm; R_B = 0.203

b

Fig. 3 X-ray diffraction powder patterns for samples Tb$_{20}$Hf$_{20}$Si$_{60}$ (Cu *K*α radiation, R_p = 0.044, R_{wp} = 0.058) (a) and Tb$_{20}$Hf$_{42.5}$Si$_{37.5}$ (Cu *K*α radiation, R_p = 0.086, R_{wp} = 0.112) (b).



$Tb_{0.7}Hf_{0.3}Si$ (type CrB)	a = 0.42192(8), b = 1.0477(2), c = 0.38254(7) nm; R_B = 0.086
$TbSi_{1.67}$ (type AlB_2)	a = 0.38435(5), c = 0.41343(7) nm; R_B = 0.051
$Tb_2Hf_3Si_4$ (type $Sc_2Re_3Si_4$)	a = 0.72057(8), c = 1.3199(2) nm; R_B = 0.079

Fig. 4 X-ray diffraction powder patterns for sample $Tb_{30}Hf_{20}Si_{50}$ (Fe $K\alpha$ radiation, R_p = 0.056, R_{wp} = 0.071).

Table 4 Atomic coordinates for $(Tb_{0.7}Hf_{0.3})Si$ (structure type CrB, Pearson symbol *oS*8, space group *Cmcm*, a = 0.42241(8), b = 1.0483(2), c = 0.38227(7) nm, Z = 4; R_B = 0.083).

Atom	Wyckoff position	x	y	z	B_{iso}, 10^{-2} nm^2
$Tb_{0.7}Hf_{0.3}$	4*c*	0	0.3574(6)	1/4	0.5(1)
Si	4*c*	0	0.083(2)	1/4	1.2(5)

Mn_5Si_3 structure type extend up to 12 at.% Tb and 6 at.% Hf, respectively, whereas the binary compounds HfSi and TbSi with orthorhombic FeB structure type dissolve not more than 5 at.% of the third component. The unit-cell parameters of the solid solutions based on the compounds Hf_5Si_3 and Tb_5Si_3 with structure type Mn_5Si_3 are shown in Fig. 5. It should be noticed that, according to the literature [16], the compound Hf_5Si_5 with structure type Mn_5Si_3 occurs only when stabilized by oxygen, nitrogen or carbon. The other compounds do not dissolve significant amounts of the third component. It should be emphasized, that there are no continuous solid solutions between the binary compounds TbSi and HfSi with orthorhombic FeB structure type, or Tb_5Si_3 and Hf_5Si_3 with hexagonal Mn_5Si_3 structure type.

The structure type $Sc_2Re_3Si_4$ is an ordered substitution variant of the Zr_5Si_4 type. The binary structure type Zr_5Si_4 is represented by a compound with composition R_5M_4 in such systems as {La,Ce,Pr,Nd}–Si and {Ti,Zr,Hf}–Si [23]. The superstructure $Sc_2Re_3Si_4$ is realized in the systems Sc–{V,Cr,Re}–Si and {Gd,Tb,Dy,Ho,Er}–Ti–Si [24].

The structure type CrB is one of the most common structure types of inorganic compounds. Two Wyckoff positions 4*c* of the space group *Cmcm* are occupied by larger and smaller atoms, respectively. This structure type is represented by binary (for example, {Eu,Dy,Ho,Er,Tm,Yb,Lu}Si or ZrSi [23]), ternary (for example, {La,Ce,Pr,Nd,Sm,Gd}$(Al_{0.5}Si_{0.5})$, $Tb(Al_{0.15}Si_{0.85})$ [25-27]), and quaternary compounds (for example, $(Tb_{0.70}Zr_{0.30})(Al_{0.17}Si_{0.83})$ [27]). We cannot exclude the existence of a small homogeneity range for the compound $(Tb_{0.7}Hf_{0.3})Si$ with CrB structure type.

One of the interesting features of the Tb–Hf–Si system is the coexistence of the binary compound Hf_5Si_4 with Zr_5Si_4 type and of the ternary compound

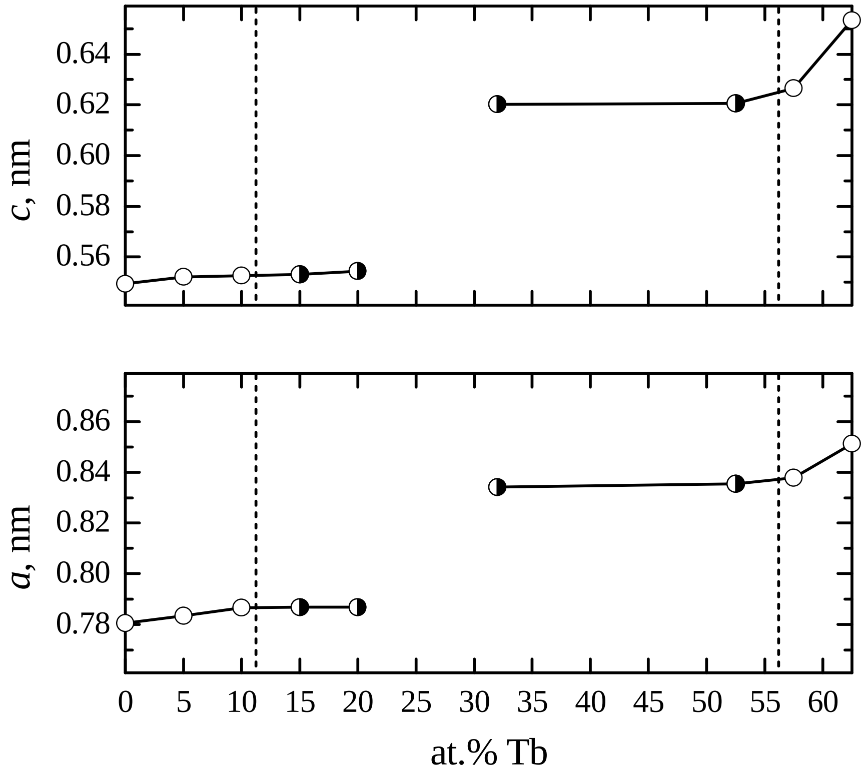


Fig. 5 Lattice parameters and cell volumes of the solid solutions based on the compounds Hf_5Si_3 and Tb_5Si_3 (structure type Mn_5Si_3) in the Tb–Hf–Si system.

$Tb_2Hf_3Si_4$ crystallizing with its ordered ternary substitution variant, the $Sc_2Re_3Si_4$ type. Phase equilibria between the compounds Hf_5Si_4 and $Sc_2Re_3Si_4$ are absent. Another interesting feature is the coexistence of the binary compound TbSi with FeB structure type and the ternary compound $(Tb_{0.7}Hf_{0.3})Si$ with CrB structure type.

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