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Supporting information for article:

One-dimensional composite host–guest structure in BaVS₃

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Supporting information

S1. Experimental details for the BaVS₃ X-ray study at ten temperatures within the 10 – 295 K temperature range

Table S1 Experimental details for BaVS₃ at ten different temperatures

Temperature	10 K	40 K	70 K	100 K
Crystal data				
Chemical formula	BaVS ₃	BaVS ₃	BaS ₃ V	BaS ₃ V
Crystal system, space group	Monoclinic, <i>Im</i>	Monoclinic, <i>Im</i>	Monoclinic, <i>Cm</i>	Monoclinic, <i>Cm</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.456 (1), 6.764 (1), 11.188 (1)	11.458 (1), 6.764 (1), 11.190 (1)	11.496 (9), 6.742 (7), 5.597 (5)	11.485 (7), 6.751 (5), 5.597 (3)
α , β , γ (°)	90, 90.048 (9), 90	90, 90.045 (1), 90	90, 90.012 (6), 90	90, 90.011 (5), 90
<i>V</i> (Å ³)	866.94 (9)	867.25 (9)	433.8 (7)	434.0 (5)
<i>Z</i>	8	8	4	4
Radiation type	Synchrotron, λ = 0.70814 Å	Synchrotron, λ = 0.70814 Å	Synchrotron, λ = 0.70814 Å	Synchrotron, λ = 0.7 Å
Data collection				
No. of measured, independent and observed reflections	4005, 1187, 1186 [<i>I</i> > 3s(<i>I</i>)]	4010, 1185, 1185 [<i>I</i> > 2s(<i>I</i>)]	1782, 770, 769 [<i>I</i> > 3s(<i>I</i>)]	3199, 1935, 1934 [<i>I</i> > 3s(<i>I</i>)]
<i>R</i> _{int}	0.030	0.031	0.025	0.031
Range of <i>h</i> , <i>k</i> , <i>l</i>	<i>h</i> = -15 → 15, <i>k</i> = - 8 → 8, <i>l</i> = -11 → 11	<i>h</i> = -15 → 15, <i>k</i> = - 8 → 8, <i>l</i> = -11 → 11	<i>h</i> = -14 → 15, <i>k</i> = 0 → 8, <i>l</i> = -5 → 5	<i>h</i> = -17 → 17, <i>k</i> = - 9 → 9, <i>l</i> = -8 → 8
Refinement				

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2), S$	0.016, 0.027, 1.16	0.027, 0.036, 1.45	0.048, 0.065, 5.44	0.032, 0.045, 3.27
No. of reflections	1187	1185	770	1935
No. of parameters	110	110	53	59
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.37, -0.42	0.87, -1.07	2.26, -1.77	1.39, -1.76
Absolute structure	587 of Friedel pairs used in the refinement	586 of Friedel pairs used in the refinement	367 of Friedel pairs used in the refinement	806 of Friedel pairs used in the refinement
Absolute structure parameter	0.097 (19)	0.11 (2)	0.05 (5)	0.05 (4)

	150 K	200 K	220 K	240 K
Crystal data				
Chemical formula	BaVS ₃	BaVS ₃	BaVS ₃	BaVS ₃
Crystal system, space group	BaS ₃ : Orthorhombic, <i>Ccm2</i> ₁ ; V: Monoclinic, <i>C2/m</i> (*)	BaS ₃ : Orthorhombic, <i>Ccm2</i> ₁ ; V: Monoclinic, <i>C2/m</i> (*)	BaS ₃ : Orthorhombic, <i>Ccm2</i> ₁ ; V: Monoclinic, <i>C2/m</i> (*)	BaS ₃ : Orthorhombic, <i>Ccm2</i> ₁ ; V: Monoclinic, <i>C2/m</i> (*)
<i>a, b, c</i> (Å)	11.5839 (7), 6.7016 (5), 5.5956 (3)	11.5729 (7), 6.7116 (5), 5.6015 (3)	11.593 (7), 6.708 (5), 5.604 (3)	11.585 (7), 6.724 (5), 5.610 (2)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90
<i>V</i> (Å ³)	434.39 (5)	435.08 (5)	435.8 (5)	437.0 (4)
<i>Z</i>	4	4	4	4
Radiation type	Synchrotron, $\lambda =$ 0.70814 Å	Synchrotron, $\lambda =$ 0.693 Å	Synchrotron, $\lambda =$ 0.70814 Å	Synchrotron, $\lambda =$ 0.7 Å
Data collection				
No. of measured, independent and observed reflections	3834, 1409, 1409 [<i>I</i> > 3s(<i>I</i>)]	3593, 2206, 2191 [<i>I</i> > 3s(<i>I</i>)]	3944, 1464, 1464 [<i>I</i> > 3s(<i>I</i>)]	2084, 1751, 1724 [<i>I</i> > 3s(<i>I</i>)]
<i>R</i> _{int}	0.023	0.021	0.014	0.018

Range of h, k, l	$h = -14 \rightarrow 14, k = -8 \rightarrow 8, l = -5 \rightarrow 5$	$h = -17 \rightarrow 16, k = -9 \rightarrow 9, l = -8 \rightarrow 8$	$h = -15 \rightarrow 15, k = -8 \rightarrow 8, l = -5 \rightarrow 5$	$h = -17 \rightarrow 17, k = -10 \rightarrow 10, l = -7 \rightarrow 8$
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.046, 0.072, 4.83	0.021, 0.026, 1.15	0.019, 0.040, 2.83	0.021, 0.033, 2.02
No. of reflections	1409	2206	1464	1751
No. of parameters	30	31	32	32
$\Delta\rho_{\max}, \Delta\rho_{\min} (\text{e } \text{\AA}^{-3})$	2.16, -1.62	0.62, -0.80	0.96, -0.72	1.27, -0.98
Absolute structure	653 of Friedel pairs used in the refinement	974 of Friedel pairs used in the refinement	668 of Friedel pairs used in the refinement	573 of Friedel pairs used in the refinement
Absolute structure parameter	0.02 (4)	0.17 (3)	0.28 (2)	0.20 (5)

	250 K	295 K
Crystal data		
Chemical formula	BaVS ₃	BaVS ₃
Crystal system, space group	BaS ₃ : Hexagonal, $P6_3/mmc$; V: Trigonal, $P-3m1$ (*)	BaS ₃ : Hexagonal, $P6_3/mmc$; V: Trigonal, $P-3m1$ (*)
$a, b, c (\text{\AA})$	6.7164 (2), 6.7164 (2), 5.6088 (2)	6.7180 (5), 6.7180 (5), 5.6150 (2)
$\alpha, \beta, \gamma (\text{^\circ})$	90, 90, 120	90, 90, 120
$V (\text{\AA}^3)$	219.12 (1)	219.46 (2)
Z	2	2
Radiation type	Synchrotron, $\lambda = 0.70814 \text{ \AA}$	Synchrotron, $\lambda = 0.6622 \text{ \AA}$
Data collection		
No. of measured, independent and observed reflections	2069, 196, 196 [$I > 3s(I)$]	2946, 173, 168 [$I > 2s(I)$]
R_{int}	0.034	0.038

Range of h, k, l	$h = -8 \rightarrow 8, k = -8 \rightarrow 8, l = -5 \rightarrow 5$	$h = -8 \rightarrow 8, k = -8 \rightarrow 8, l = -6 \rightarrow 6$
<hr/>		
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.146, 1.67	0.028, 0.063, 3.13
No. of reflections	196	173
No. of parameters	13	13
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	1.67, -1.94	0.76, -0.73

(*) The structure is considered as 1D commensurate composite consisting of the BaS₃ matrix and V-chains located in its hexagonal channels (Fig. 1).

A new multipurpose diffractometer PILATUS@SNBL (Dyadkin et al., 2016) has been used for the data collections.

S2. Examples of restrictions applied for atomic sites to provide the real symmetry of atoms in the BaVS₃ 1D commensurate composite structure at 295 K < T < 130 K.

S2.1. The hexagonal structure at T > T_s = 240 K.

The $P6_3/mmc$ and $P-3m1$ space group is constructed for the BaS₃ matrix and V-chain, respectively. The common space group $P3m1$ is used.

Example of the structure characteristic obtained at 250 K is shown.

Table S2 Positional parameters

Atom	Wyckoff letter	x	y	z	U_{eqv}
Ba1a	1b	0.3333	0.6667	0.5	0.0170(13)
Ba1b	1c	-0.3333	-0.6667	0	0.0170(13)
V1a	1a	0	0	-0.2593(16)	0.0339(19)
V1b	1a	0	0	0.2598(16)	0.0339(19)
S1a	3d	0.16378(19)	-0.16378(19)	0	0.018(3)
S1b	3d	-0.16378(19)	0.16378(19)	0.5	0.018(3)

Table S3 ADP harmonic parameters

Atom	U11	U22	U33	U12	U13	U23
Ba1a	0.0149(15)	0.0149(15)	0.021(3)	0.0074(7)	0	0
Ba1b	0.0149(15)	0.0149(15)	0.021(3)	0.0074(7)	0	0
V1a	0.040(2)	0.040(2)	0.021(4)	0.0201(11)	0	0
V1b	0.040(2)	0.040(2)	0.021(4)	0.0201(11)	0	0
S1a	0.018(3)	0.018(3)	0.025(6)	0.013(2)	0.0002(7)	-0.0002(7)
S1b	0.018(3)	0.018(3)	0.025(6)	0.013(2)	0.0002(7)	-0.0002(7)

Restrictions:

- (i) Identical ADP for Ba1a and Ba1b;
- (ii) Identical ADP for V1a and V1b;
- (iii) Identical ADP for S1a and S1b.

Equations: $x[S1b] = -x[S1a]$.

Fixed parameters: $z = 0.5$ for Ba1a and S1b; $z = 0$ for Ba1b and S1a.

Calculation of a shift (Δ) between origins characterising the BaS₃ hcp matrix and V-chain:

$$\Delta = (z[V1b] - z[V1a])/2$$

For T = 295 K: $\Delta = 0.2596(16)$

S2.2. The “orthorhombic” structure at 130 K < T ≤ T_s = 240 K

The Ccm2₁ and C12/m1 space group is constructed for the BaS₃ matrix and V-chain, respectively. The common space group C1m1 is used.

Example of the structure characteristic obtained at 220 K is shown.

Table S4 Positional parameters

Atom	Wyckoff letter	x	y	z	U _{eqv}
Ba1a	2a	-0.33471(3)	0	0.5046(4)	0.01489(16)
Ba1b	2a	0.33471(3)	0	0.0046(4)	0.01489(16)

V1a	2a	0.01545(6)	0	-0.25311(9)	0.0213(2)
V1b	2a	-0.01545(6)	0	0.25311(9)	0.0213(2)
S1a	2a	-0.16657(9)	0	0.0040(15)	0.0162(6)
S2a	4b	0.08293(7)	0.24697(8)	0.0193(13)	0.0114(5)
S1b	2a	0.16657(9)	0	0.5040(15)	0.0162(6)
S2b	4b	-0.08293(7)	-0.24697(8)	0.5193(13)	0.0114(5)

Table S5 ADP harmonic parameters

Atom	U11	U22	U33	U12	U13	U23
Ba1a	0.0146(3)	0.0141(3)	0.0160(3)	0	-0.0008(2)	0
Ba1b	0.0146(3)	0.0141(3)	0.0160(3)	0	-0.0008(2)	0
V1a	0.0212(4)	0.0301(5)	0.0125(4)	0	0.0011(4)	0
V1b	0.0212(4)	0.0301(5)	0.0125(4)	0	0.0011(4)	0
S1a	0.0107(9)	0.0153(9)	0.0226(13)	0	-0.0003(9)	0
S2a	0.0142(8)	0.0110(7)	0.0089(10)	-0.0017(3)	-0.0003(9)	0.0000(3)
S1b	0.0107(9)	0.0153(9)	0.0226(13)	0	-0.0003(9)	0
S2b	0.0142(8)	0.0110(7)	0.0089(10)	-0.0017(3)	-0.0003(9)	0.0000(3)

Restrictions:

- (i) Identical ADP for Ba1a and Ba1b;
- (ii) Identical ADP for V1a and V1b;
- (iii) Identical ADP for S1a and S1b;
- (iv) Identical ADP for S2a and S2b.

Equations: $x[V1b] = -x[V1a]$; $x[S1b] = -x[S1a]$; $x[S2b] = -x[S2a]$; $y[S2b] = -y[S2a]$; $z[V1b] = -z[V1a]$; $z[S1b] = z[S1a] + 0.5$; $z[S2b] = z[S2a] + 0.5$; $z[Ba1b] = z[Ba1a] - 0.5$; $x[Ba1b] = -x[Ba1a]$.

Fixed parameters: x and z of Ba1b are fixed as the origin; $U12[Ba1a] = U12[Ba1b] = U12[S1a] = U12[S1b] = 0$;

Calculation of a shift (Δ) between origins characterising the BaS₃ hcp matrix and V-chain:

$$\Delta = z[Ba1b] + 0.25$$

For T = 220 K: $\Delta = 0.2546(4)$.

S2.3. Complex twinning in monoclinic phases, which can be mistakenly considered as satellites

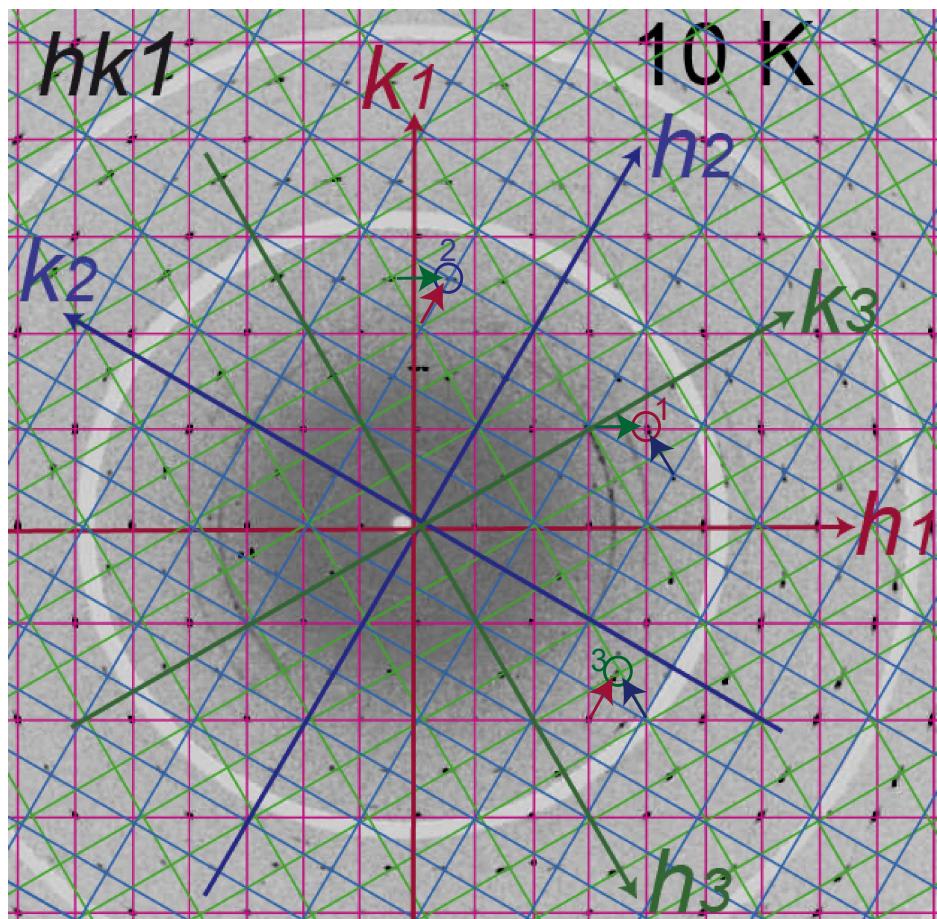


Figure S1 The *hk1* reciprocal space section of BaVS₃ at 10 K. Three reciprocal lattices (red, 1; green, 2; blue, 3) correspond to three twin components connected by the 3-fold axis normal to the plane. In each lattice, some systematic reflections can be indexed only with the pseudo vector $\mathbf{q}' = 0.5\mathbf{a} + 0.5\mathbf{b}$ (arrows). However, these reflections belong to another system as it is shown with the example of the (411) reflection indicated by circles.

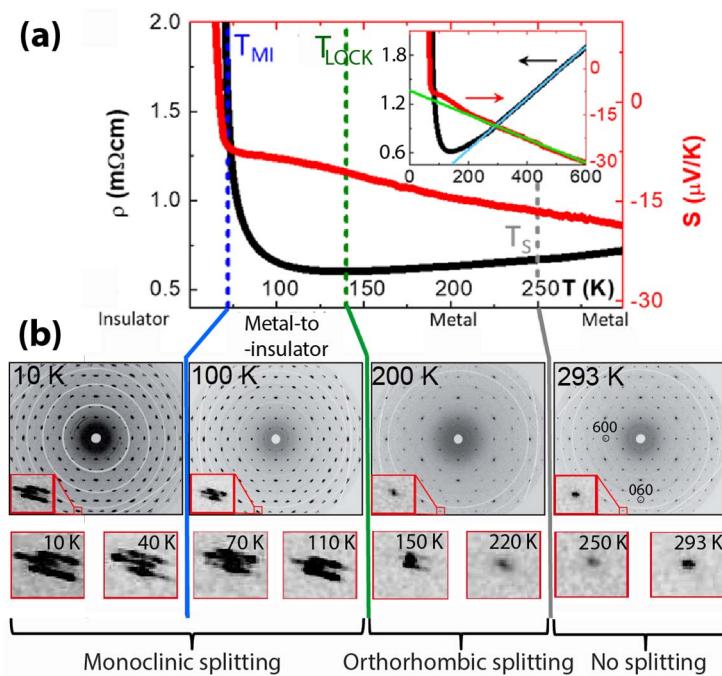


Figure S2 Correlation between the electrical resistivity, thermoelectric power and the fold of the splitting of the $hk0$ diffraction reflections between 10 and 293 K. Panel (a): Temperature dependence of the electrical resistivity (ρ , black line), and Seebeck coefficient (S , red line). Inset underlines the dependence. Blue and green straight lines are the guides for the eye. The plot is reproduced after Barišić (2004). Panel (b): Temperature dependent evolution of the X-ray reflections in the $hk0$ section of reciprocal space. The red frames show one, $hk0 = 370$, among other reflexes on an enlarged scale. The h and k axes correspond to the orthorhombic (monoclinic) setting in the reciprocal space.