Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

for

High-Pressure Single Crystal X-ray Diffraction Study of Thermoelectric ZnSb and β-Zn_4Sb_3

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Experimental details

All the pressure points measured for ZnSb and Zn_4Sb_3 in two different pressure media, a hydrostatic Ethanol:Methanol mixture and a non-hydrostatic Silicon Oil, are listed in Table S1. The cif-files for corresponding structures have been deposited in the Cambridge Crystallographic Data Centre (CCDC). The deposited structures for Zn_4Sb_3 have constrained Zn occupancies, see the manuscript for more details on the model.

In the manuscript all the plots are for the hydrostatic studies, and here in the supporting information, the equivalent plots for the non-hydrostatic studies are shown.

TABLE S1 The different data sets measured on ZnSb and Zn_4Sb_3 in two different pressure media, a hydrostatic Ethanol:Methanol mixture and a non-hydrostatic Silicon Oil.

Data set no.	ZnSb Silicon oil (SiO)		ZnSb Ethanol:Methanol (E:M) mixture		Zn_4Sb_3 Silicon oil (SiO)		Zn_4Sb_3 Ethanol:Methanol (E:M) mixture	
	Pressure (GPa)	CCDC No.	Pressure (GPa)	CCDC No.	Pressure (GPa)	CCDC No.	Pressure (GPa)	CCDC No.
0	Ambient	1486310	Ambient	1486319	Ambient	1486290	Ambient	1486273
1	0.403(15)	1486311	1.37(2)	1486320	0.072(14)	1486291	1.04(2)	1486274
2	1.25(2)	1486312	2.69(4)	1486321	0.80(2)	1486292	1.81(3)	1486275
3	3.38(5)	1486313	5.13(8)	1486322	1.12(2)	1486293	2.73(5)	1486276
4	3.93(6)	1486314	6.32(10)	1486323	1.49(3)	1486294	3.31(5)	1486277
5	6.69(10)	1486315	7.14(11)	1486324	1.84(3)	1486295	4.78(7)	1486278
6	7.88(14)	1486316	7.99(12)	1486325	1.97(3)	1486296	6.34(10)	1486279
7	9.57(15)	1486317	9.13(14)	1486326	2.45(4)	1486297	7.02(11)	1486280
8	11.0(2)	1486318	9.5(2)	1486327	3.88(6)	1486298	7.59(12)	1486281
9	12.4(2)		10.3(2)	1486328	4.17(6)	1486299	8.13(12)	1486282
10	10.9(2)		11.2(2)	1486329	4.31(7)	1486300	8.47(13)	1486283
11			12.8(2)	1486330	5.18(8)	1486301	8.89(14)	1486284
12			14.4(2)		6.03(9)	1486302	9.25(14) → 7.45(13)	1486285
13					7.01(11)	1486303	7.69(13)	1486286
14					7.47(11)	1486304	8.69(14)	1486287
15					8.28(10)	1486305	9.5(2)	1486288
16					8.46(13)	1486306	10.2(2)	1486289
17					9.8(2)	1486307	10.7(2)	
18					10.3(2)	1486308		
19					10.6(2)	1486309		
20					12.7(2)			
21					10.0(2)			

TABLE S2 Equation of state for ZnSb from different EoS models for non-hydrostatic and hydrostatic conditions named SiO and E:M, respectively. K_0' from 2nd order EoS models are fixed values from EoSFIT7 and therefore not listed with uncertainties.

Model	V_0 (Å^3)		K_0 (GPa)		K_0'		χ^2	
	SiO	E:M	SiO	E:M	SiO	E:M	SiO	E:M
Murnaghan	387.0(2)	387.02(15)	84(6)	46(1)	0.5(8)	7.6(5)	4.266	3.762
Birch-Murnaghan, 3rd order	387.0(2)	387.03(15)	83(3)	44(2)	1.1(5)	9.2(9)	4.055	3.776
Birch-Murnaghan, 2nd order	387.6(3)	386.7(4)	70(2)	57(2)	4.0	4.0	13.790	25.066
Vinet, 3rd order	387.0(2)	387.02(15)	84(8)	45(2)	0.5(8)	8.7(6)	4.270	3.761
Vinet, 2nd order	387.1(2)	386.4(6)	82(1)	67(3)	1.0	1.0	3.886	68.287
Natural strain, 3rd order	387.0(2)	387.03(16)	84(4)	43(2)	0.6(7)	11.0(9)	4.236	3.913
Natural strain, 2nd order	387.2(2)	386.5(5)	78(1)	64(2)	2.0	2.0	5.643	49.597
Tait, 3rd order	387.0(2)	387.02(15)	84(4)	45(1)	0.5(8)	8.1(5)	4.257	3.763

ZnSb

TABLE S3 Fitting results using the 3rd order Vinet equation for ZnSb and β-Zn_4Sb_3 under non-hydrostatic conditions in silicon oil.

	ZnSb				β-Zn_4Sb_3	
	Non-hydrostatic SiO	Hydrostatic E:M	Jund *et al.*[1]	Balazyuk *et al.*[2]	Non-hydrostatic SiO	Hydrostatic E:M
a_0 (Å)	6.193(4)	6.1930(17)	6.2808	-	12.210(5)	12.1876(12)
b_0 (Å)	7.731(1)	7.7290(19)	7.8246	-	-	-
c_0 (Å)	8.088(3)	8.085(2)	8.2293	-	12.403(7)	12.3912(18)
K_0 (GPa)	84(8)	45(2)	47.18[a], 47.35[b]	54.75	66(5)	48(1)
K_0'	0.5(8)	8.7(6)	5.35	-	3(1)	6.1(5)
K_a (GPa)	176(25)	120(6)	133.4	162.4	174(13)	134(3)
K_b (GPa)	494(22)	152(7)	158.6	170.8	-	-
K_c (GPa)	191(15)	139(7)	136.2	160.9	240(30)	161(6)
K_a'	15(7)	28(3)	-	-	9(4)	16.0(12)
K_b'	-28(3)	27(2)	-	-	-	-
K_c'	12(4)	21(2)	-	-	11(8)	26(3)

[a] 3rd order Vinet equation, [b] elastic constants

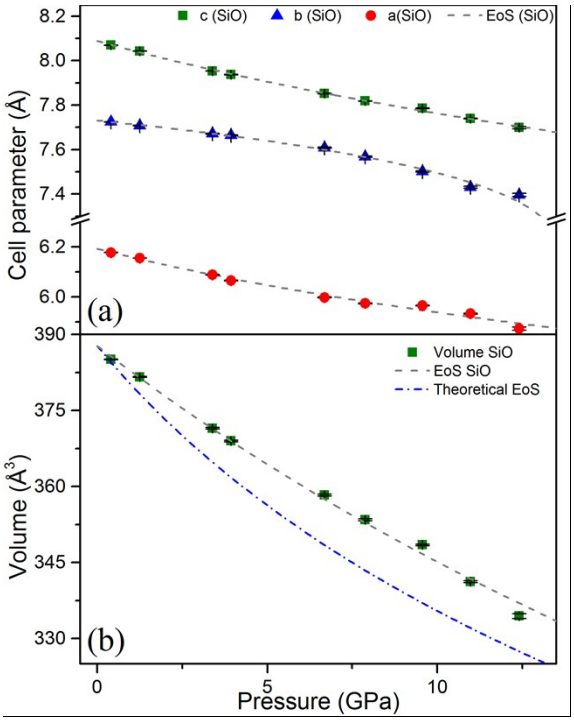

FIG. S1 ZnSb unit cell parameters as a function of pressure and fits to equation of states for ZnSb under non-hydrostatic conditions. (a) *a*-axis, *b*-axis and *c*-axis with the experimental 3rd order Vinet EoS fits. (b) Volumes with the experimental 3rd order Vinet EoS. The blue line is based on the experimental value for V_0 and the theoretical bulk modulus from Jund *et al*.[1]

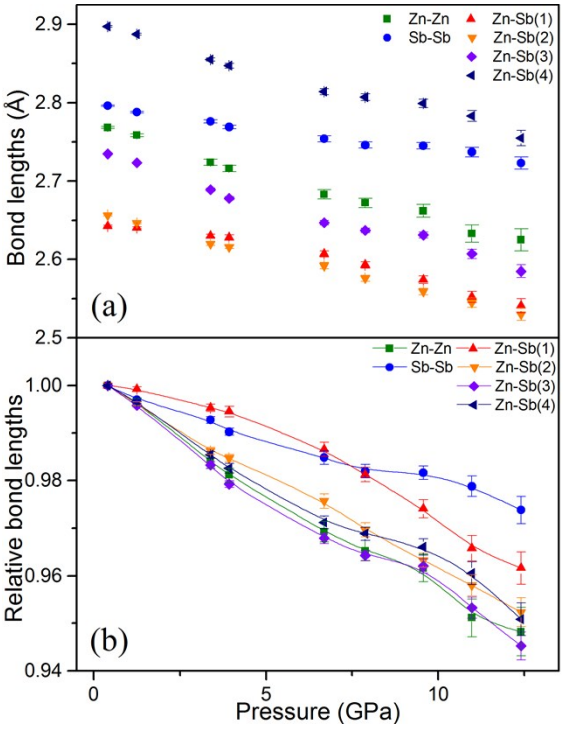

FIG. S2 (a) Sb-Sb and Zn-Zn interatomic distances in ZnSb under non-hydrostatic conditions. (b) The four different Zn-Sb interatomic distances in ZnSb.

There is a huge difference in bulk moduli between the non-hydrostatic and hydrostatic study, 84(8) GPa against 45(2) GPa, respectively. The non-hydrostatic study shows large anisotropy with K_b = 494(22) GPa, indicating that this direction is much less compressible than the *a*- and *c*-axes, K_a = 176(25) GPa and K_c = 191 (15) GPa. The discrepancy for K_b' in the SiO data is most likely due to the non-hydrostaticity of silicone oil at high pressures. The SiO study shows different behavior in the Zn-Zn and Sb-Sb distances than in the E:M study, which once again is due to the non-hydrostatic conditions.

Figure S3a shows the equivalent isotropic displacement parameters (ADPs), U_{eq}, as a function of pressure for ZnSb. The ADPs not only represent actual thermal vibrations of the atoms but also static and dynamic disorder and strain gradients over the sample as a consequence of non-hydrostatic pressure. In high-pressure studies U_{eq} normally decreases with pressure until the hydrostatic limit of the pressure medium is reached, after which it will increase. This increase in the ADPs is an indirect effect of peak broadening as described by Madsen *et al*.[3, 4] The peak broadening is seen in the peak shape parameters, e1-e3, as described by Kabsch.[5] For the E:M study the same diffractometer and therefore the same peak shape parameters were used as Madsen *et al*.[4] The mosaicity is described by two parameters; one for the average of the x- and y-directions, corresponding to e1 and e2, and another for the z-direction, corresponding to e3, Figure S3b. The integration box size also shown in the plots follow the same trend as the mosaicity descriptors. In the E:M study the increase of the U_{eq} starts at 6.3 GPa, which is lower than the reported hydrostatic limit at 9.8 GPa of the 1:4 ethanol:methanol mixture. In the SiO study a steady increase in U_{eq} is observed throughout the pressure range as a result of non-hydrostatic strain. The presence of non-hydrostatic strain is also seen in the peak shape parameters, e1-e3.

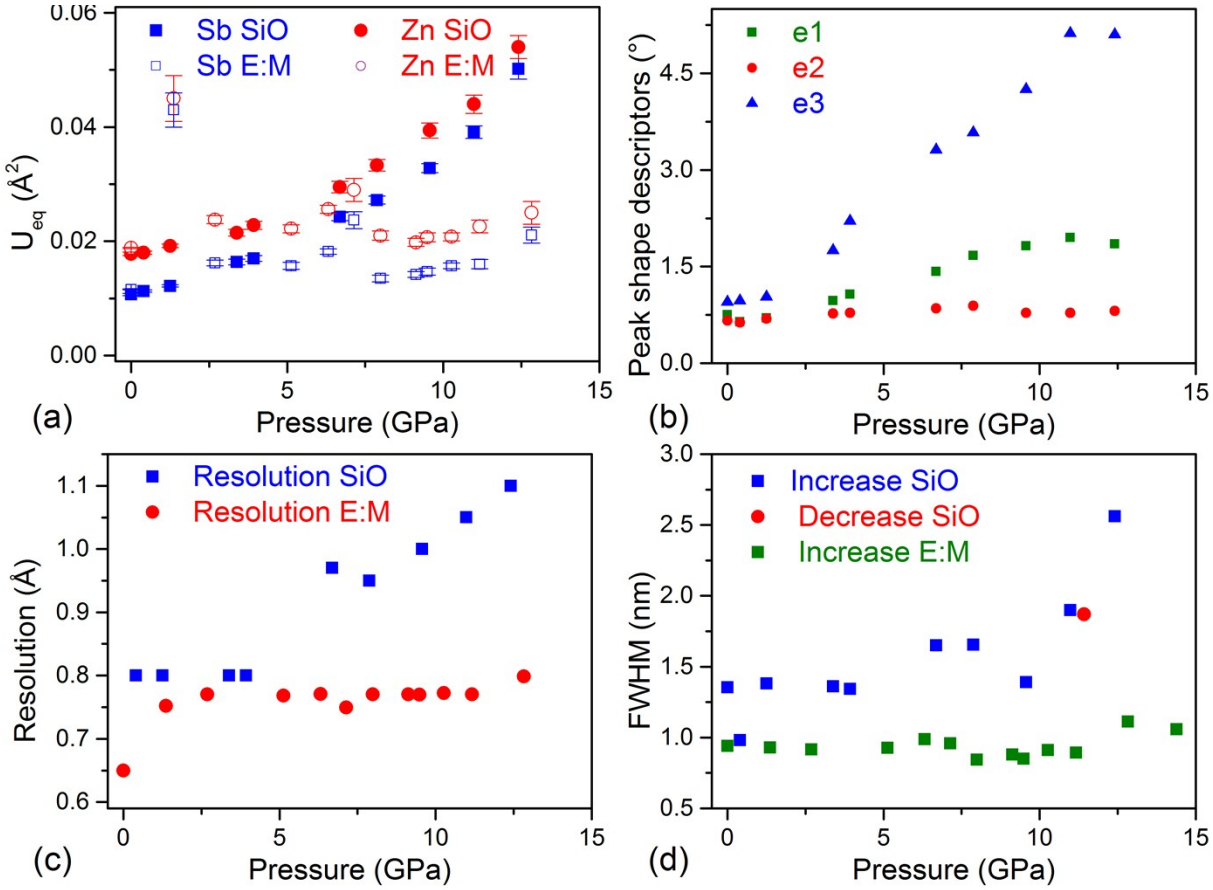

FIG. S3 a) ZnSb equivalent isotropic atomic displacement parameters, U_{eq}. b) peak shape parameters e1, e2 and e3 only for the non-hydrostatic study. c) the resolution for the single crystal data. d) FWHM of ruby fluorescence signals, where the red circle is the FWHM after heating of the DAC.

β-Zn_4Sb_3

In the non-hydrostatic SiO study the trends are somewhat diffuse, presumably due to the non-hydrostatic environment.

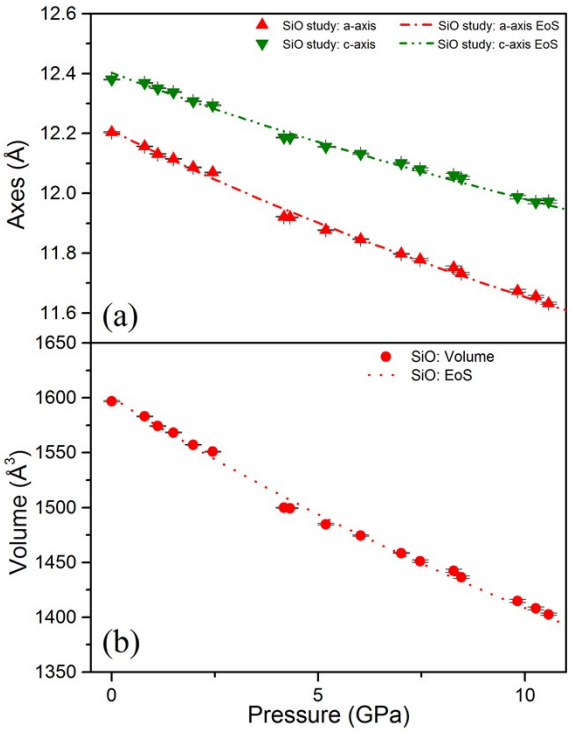

FIG. S4 Cell parameters and the EoS fit of Zn_4Sb_3 under non-hydrostatic conditions. (a) 3rd order Vinet model for the *a*- and *c*-axes. (b) 3rd order Vinet model of the volume.

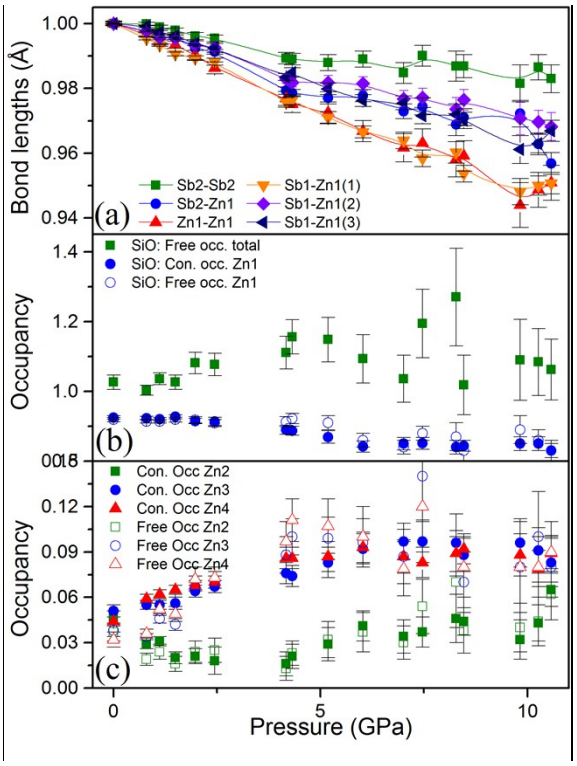

FIG. S5 (a) Relative bond lengths in Zn_4Sb_3 under non-hydrostatic conditions. The bonds at ambient pressure are 2.813(2), 2.674(1), 2.7670(3), 2.721(1), 2.789(2), and 2.778(2) Å for Sb2-Sb2, Sb2-Zn1, Zn1-Zn1, Sb1-Zn1(1), Sb1-Zn1(2), and Sb1-Zn1(3), respectively. (b) Total occupancy and Zn1 site occupancy. (c) Occupancy of the Zn2, Zn3 and Zn4 sites.

TABLE S4 Equation of state for Zn_4Sb_3 from different EoS models. K_0' from 2nd order EoS models are fixed values from EoSFIT7 and therefore not listed with uncertainties

Model	V_0 (Å^3)		K_0 (GPa)		K_0'		χ^2	
	SiO	E:M	SiO	E:M	SiO	E:M	SiO	E:M
Murnaghan	1593.7(5)	1600(2)	48(1)	66(5)	5.6(4)	3(1)	2.437	15.076
Birch-Murnaghan, 3rd order	1593.7(4)	1601(2)	48(1)	66(5)	6.1(5)	3(1)	2.198	15.328
Birch-Murnaghan, 2nd order	1593.1(7)	1602(1)	52.5(8)	62(2)	4.0	4.0	6.290	15.672
Vinet, 3rd order	1593.7(4)	1600(2)	48(1)	66(5)	6.1(5)	3(1)	2.156	15.191
Vinet, 2nd order	1592(1)	1599(1)	60(2)	72(2)	1.0	1.0	29.158	15.315
Natural strain, 3rd order	1593.8(4)	1600(2)	47(1)	66(5)	6.8(6)	3(1)	1.902	15.158
Natural strain, 2nd order	1592(1)	1600(1)	58(1)	68(2)	2.0	2.0	19.347	14.219
Tait, 3rd order	1593.7(4)	1600(2)	48(1)	66(5)	5.9(4)	3(1)	2.252	15.231

The equivalent isotropic ADP, U_{eq}, decreases with pressure in the Zn_4Sb_3 structure at low pressures in the non-hydrostatic SiO study, Fig. S6b. Around 5 GPa they start to increase indicating the transition to non-

hydrostatic conditions. This is confirmed by the full width half maximum (FWHM) plot for the ruby florescence, Fig. S6e, as well as in the mosaicity plot for the single crystal, Fig. S6d. For the hydrostatic E:M study all the parameters, U_{eq}, mosaicity and FWHM show in Fig. S6a, S6c and S6e, respectively, all show that the measurements are under hydrostatic conditions except above 10 GPa.

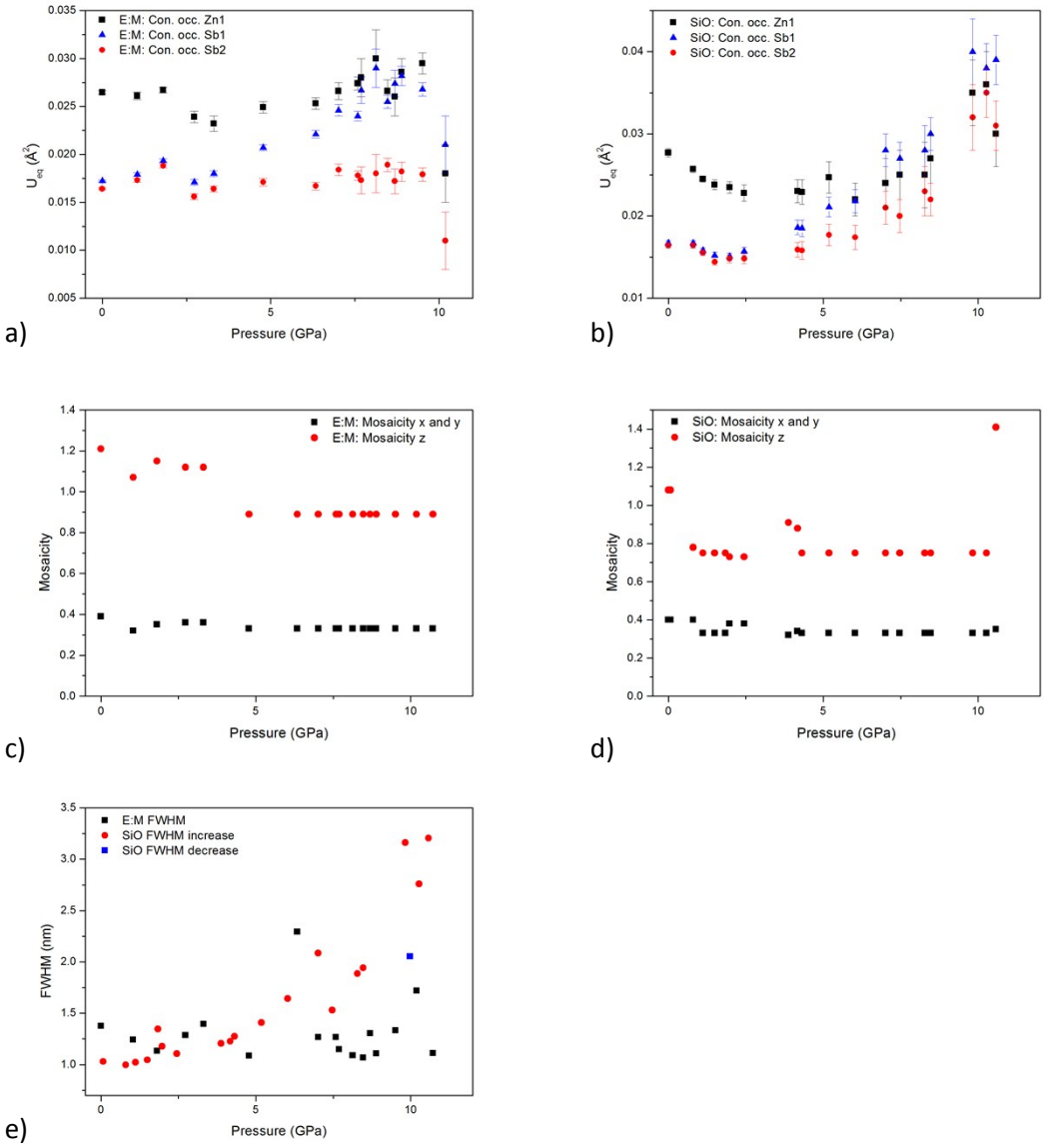

FIG. S6 a) Zn_4Sb_3 equivalent isotropic atomic displacement parameters, U_{eq}, for the hydrostatic study. b) Zn_4Sb_3 equivalent isotropic atomic displacement parameters, U_{eq}, for the non-hydrostatic study. c) Mosaicity for the hydrostatic Zn_4Sb_3 study. d) Mosaicity for the non-hydrostatic Zn_4Sb_3 study. e) FWHM of ruby fluorescence signals for both Zn_4Sb_3 studies.

References

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2. V. Balazyuk, A. Eremenko and N. Raransky, *Funct. Mater.*, 2008, **15**, 343-346.
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