Appendix 1

Table S1. Selected crystallographic parameters from structure solution (SIR2014) and dynamical refinement (JAAN2006) of wenjiite.

Crystallographic information	
Cell content	$P_{1.6}Si_{5.4}Ti_{10}$
Space group	$P6_3/mcm$
a (Å)	7.30(10)
c (Å)	5.09(10)
Volume (Å^3)	235(6)
Structure solution parameters	
Data resolution (Å)	0.9
No. of sampled reflections	625
No. of independent reflections	67
Independent reflections coverage (%)	94
Global thermal factor U_{iso} (Å^2)	0.005
$R_{int}(F)$ (%)	21.51
$R_{sir}(F)$ (%)	23.58
Dynamical structure refinement parameters	
No. of zones used for refinement	93
No. of reflections (all)	1397
No. of reflections (>3σ)	1170
Refined thickness (Å)	416
*R*1(>3σ) (%)	12.58
wR1(>3σ) (%)	16.04
*R*1(all) (%)	19.70
*wR*1(>3σ) (%)	17.07
Goodness of fit	7.45

Table S2. Selected crystallographic parameters from structure solution (SIR2014) and dynamical refinement (JAAN2006) of kangjinlaite.

Crystallographic information	
Cell content	$P_{10.4}Si_{29.6}Ti_{44}$
Space group	*I*4/*mmm*
a (Å)	9.4(2)
c (Å)	13.5(3)
Volume (Å^3)	1190(40)
Structure solution parameters	
Data resolution (Å)	0.9
No. of sampled reflections	2101
No. of independent reflections	283
Independent reflections coverage (%)	100
Global thermal factor U_{iso} (Å^2)	-0.026
$R_{int}(F)$ (%)	25.60
$R_{sir}(F)$ (%)	34.33
Dynamical structure refinement parameters	
No. of zones used for refinement	111
No. of reflections (all)	4836
No. of reflections (>3σ)	3829
Refined thickness (Å)	651
*R*1(>3σ) (%)	14.94
wR1(>3σ) (%)	17.08
*R*1(all) (%)	21.77
*wR*1(>3σ) (%)	17.60
Goodness of fit	4.10

Table S3. X-ray powder diffraction data obtained by simulation for wenjiite

I/meas	*h*	*k*	*l*	2θ (°)	*d* (Å)
0.17	1	0	0	14.00	6.32
5.82	1	1	0	24.37	3.65
3.94	2	0	0	28.21	3.16
4.86	1	1	1	30.10	2.97
10.52	0	0	2	35.24	2.55
31.33	**2**	**1**	**0**	**37.61**	**2.39**
16.77	**1**	**0**	**2**	**38.09**	**2.36**
100.00	**2**	**1**	**1**	**41.73**	**2.16**
38.90	**3**	**0**	**0**	**42.88**	**2.11**
80.22	**1**	**1**	**2**	**43.31**	**2.09**
2.48	2	0	2	45.73	1.98
2.33	2	2	0	49.93	1.83
1.45	3	1	0	52.12	1.75
1.60	2	1	2	52.49	1.74
4.71	2	2	1	53.28	1.72
4.97	3	1	1	55.38	1.66
1.16	3	0	2	56.66	1.62
3.18	4	0	0	58.34	1.58

Note: Bold – most intense reflections

Table S4. X-ray powder diffraction data obtained by simulation for kangjinlaite

I/meas	*h*	*k*	*l*	2θ (°)	*d* (Å)
0.79	1	0	1	11.46	7.71
1.70	0	0	2	13.11	6.75
6.10	1	1	0	13.31	6.65
0.54	1	1	2	18.72	4.74
0.47	2	0	0	18.87	4.70
0.09	1	0	3	21.88	4.06
0.04	2	1	1	22.13	4.01
0.36	2	0	2	23.04	3.86
0.02	0	0	4	26.39	3.38
3.52	2	2	0	26.80	3.32
1.13	2	1	3	29.04	3.07
7.01	3	0	1	29.24	3.05
0.04	1	1	4	29.66	3.01
2.17	2	2	2	29.94	2.98
0.15	3	1	0	30.04	2.97
4.99	2	0	4	32.64	2.74
0.94	3	1	2	32.90	2.72
4.42	1	0	5	34.54	2.60
4.27	3	0	3	34.86	2.57
1.81	3	2	1	35.03	2.56
2.65	2	2	4	37.97	2.37
35.35	**4**	**0**	**0**	**38.27**	**2.35**
84.51	**2**	**1**	**5**	**39.64**	**2.27**
100.00	**3**	**2**	**3**	**39.93**	**2.26**
14.20	0	0	6	40.04	2.25
11.10	4	1	1	40.08	2.25
33.44	**3**	**1**	**4**	**40.40**	**2.23**
39.93	**4**	**0**	**2**	**40.62**	**2.22**
63.48	**3**	**3**	**0**	**40.69**	**2.22**
10.55	1	1	6	42.38	2.13
19.64	3	3	2	42.93	2.11
1.50	4	2	0	43.00	2.10
36.68	**3**	**0**	**5**	**44.25**	**2.05**
5.44	4	1	3	44.51	2.03
13.22	2	0	6	44.61	2.03
3.69	4	2	2	45.14	2.01
7.97	4	0	4	47.08	1.93
0.70	1	0	7	48.13	1.89
2.41	3	2	5	48.50	1.88

0.51	2	2	6	48.84	1.86
2.85	5	0	1	48.87	1.86
0.08	4	3	1	48.87	1.86
2.10	3	3	4	49.15	1.85
0.12	5	1	0	49.40	1.84
2.30	3	1	6	50.86	1.79
1.51	4	2	4	51.16	1.78
0.55	5	1	2	51.34	1.78
2.19	2	1	7	52.14	1.75
3.63	4	1	5	52.49	1.74
13.53	5	0	3	52.73	1.74
5.65	4	3	3	52.73	1.74
0.45	5	2	1	52.84	1.73
0.02	0	0	8	54.32	1.69
5.30	4	4	0	55.23	1.66
0.04	3	0	7	55.94	1.64
0.98	1	1	8	56.19	1.64
0.98	5	2	3	56.50	1.63
1.15	4	0	6	56.59	1.63
0.12	5	1	4	56.86	1.62
8.43	4	4	2	57.03	1.61
0.00	5	3	0	57.09	1.61
1.09	2	0	8	58.03	1.59
3.55	3	3	6	58.41	1.58
1.60	5	3	2	58.85	1.57
15.83	6	0	0	58.90	1.57
1.92	3	2	7	59.58	1.55
1.74	4	3	5	59.90	1.54
3.72	5	0	5	59.90	1.54

Note: Bold – most intense reflections

Table S5. Coordinates and equivalent displacement parameters (U_{iso} Å^2) of atoms in wenjiite

Label	Williams[1]	x/*a*	y/*b*	z/*c*	U_{iso}	occupancy	multiplicity
Ti1	Ti^{4d}	⅔	⅓	0	0.0053(8)	1	4
Ti2	Ti^{6g}	0.7614(3)	0	0.25	0.0060(7)	1	6
Si1	Si	0.5981(6)	0.5981(6)	0.25	0.0071(9)	0.77	6
P1	—	0.5981(6)	0.5981(6)	0.25	0.0071(9)	0.23	6
Si2	*Z*	0	0	0	0.020(4)	0.385	2
P2	—	0	0	0	0.020(4)	0.115	2

Note: 1. Site designation from Williams et al. (2000a,b)

Table S6. Coordinates and equivalent displacement parameters (U_{iso} Å^2) of atoms in kangjinlaite

Label	x/*a*	y/*b*	z/*c*	U_{iso}	occupancy	multiplicity
Ti1	0.1811(3)	0.1811(3)	0	0.005	1	8
Ti2	0.5	0.1654(3)	0.10097(16)	0.005	1	16
Ti3	0.2509(3)	0	0.18651(15)	0.005	1	16
Ti4	0.5	0.5	0.1661(3)	0.005	1	4
Si1	0.3720(4)	0.3720(4)	0	0.005	0.74	8
P1	0.3720(4)	0.3720(4)	0	0.005	0.26	8
Si2	0	0	0.1030(5)	0.005	0.74	4
P2	0	0	0.1030(5)	0.005	0.26	4
Si3	0.2937(3)	0.2937(3)	0.1742(2)	0.005	0.74	16
P3	0.2937(3)	0.2937(3)	0.1742(2)	0.005	0.26	16
Si4	0.3595(6)	0	0	0.005	0.74	8
P4	0.3595(6)	0	0	0.005	0.26	8
Si5	0.5	0	0.25	0.005	0.74	4
P5	0.5	0	0.25	0.005	0.26	4

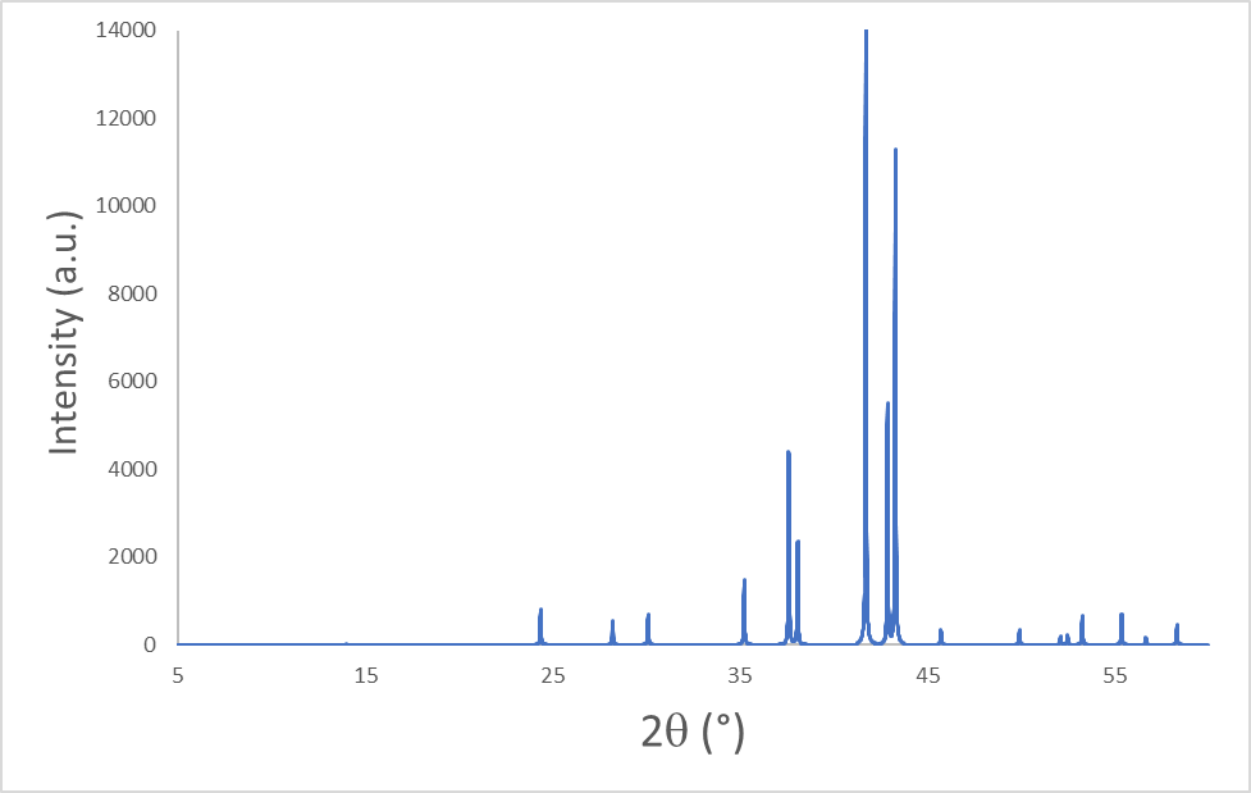

Figure S1. Simulated X-ray powder pattern of wenjiite with $CuK\alpha_1$ radiation

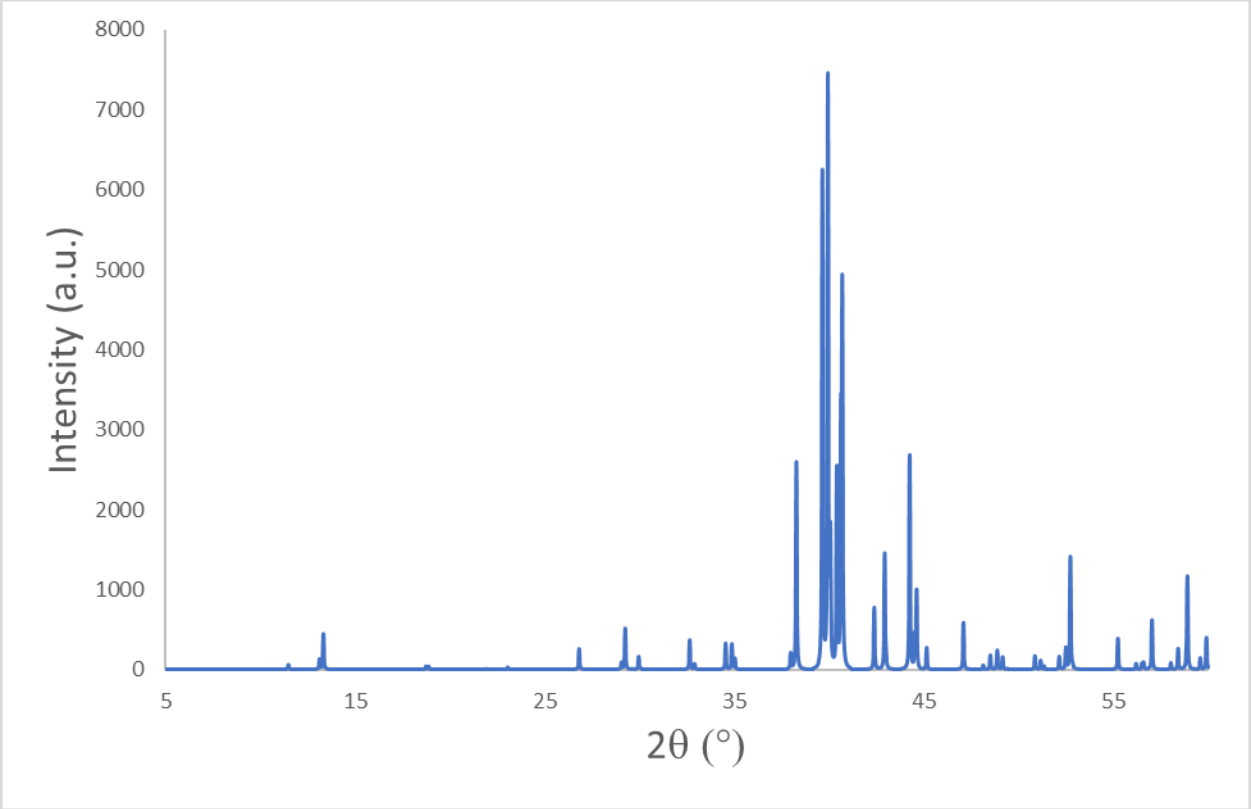

Figure S2. Simulated X-ray powder pattern of kangjinlaite with CuKα_1 radiation

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U												
	Reported as an occupant at the Ho site																
	Reported as an occupant at the Ge site																
	Reported as an occupant at both sites																
	Reported only in kangjinlaite																
	Reported only in $Eu_{11}As_{10}$																

Figure S3. The Periodic Table showing the 38 elements reported in compounds isostructural with $Ho_{11}Ge_{10}$, including kangjinlaite.

Appendix II

References for Figure 10

Cheung, Y.Y.J., Svitlyk, V. and Mozharivskyj, Y. (2011) Structure, magnetic and magnetocaloric properties of $RE_{11}Ge_8In_2$ (RE = Gd—Tm). Intermetallics 19, 276-281

Choi,W., Lee, J. Lee, Y., Ahn, K. and You, T.S. (2017) Single and double-doping effects on the thermoelectric properties of two Zintl compounds: $Eu_{11}Bi_{8.07(2)}Sn_{1.93}$ and $Eu_{10.74(2)}K_{0.26}Bi_{9.14(2)Sn0.86}$. Dalton Transactions, 2017, 46, 11840. DOI: 10.1039/c7dt02410j

Clark, H.L., Simpson, H.J., and Steinfink, H. (1970) The crystal structure of $Yb_{11}Sb_{10}$. Inorganic Chemistry, 9(8), 1962-194.

Deller, K. and Eisenmann, B. (1976) Zur Kenntnis von $Ca_{11}Sb_{10}$ und $Ga_{11}Bi_{10}$. Zeitschrift für Naturforschung, 31b, 29-34.

Derrien, G., Tillard-Charbonnel, M., Manteghetti, A., Monconduit, L. and Belin, B. (2002) Synthesis and crystal structure of $M_{11}X_{10}$ compounds, M = Sr, Ba and X = Bi, Sb. Electronic requirements and chemical bonding. Journal of Solid State Chemistry, 164, 169-175

Ge, M.-H. and Corbett, J.D. (2012) Crystal structure of hendecaytterbium ditin octabismuthide, $Bi_8Sn_2Yb_{11}$. Zeitschrift für Kristallographie NCS, 227, 283-284. DOI 10.1524/ncrs.2012.0137

Jeon, B.-Y., Jeon, J., Lee, J., Kim, J., You, T.-S. (2015) Experimental and theoretical investigations for site preference and anisotropic size change of $RE_{11}Ge_4In_{6-x}M_x$ (RE = La, Ce; M = Li, Ge; x = 1, 1.96). Journal of Alloys and Compounds, 620, 269–276

Jeon, B.-Y., Nam, G., Lee, D.W., Ok, K.M., You, T.-S. (2016) $Ce_{11}Ge_{3.73(2)}In_{6.27}$: Solid-state synthesis, crystal structure and site-preference. Journal of Solid State Chemistry, 236, 195–202.

Kutar, B.Ya., Bodak, O.I., Zavodnik, V.E. (1985) The silicide $Sc_7Cr_{4+x}Si_{10-x}$ (x = 0.8): the first representative of a superlattice structure of the $Ho_{11}Ge_{10}$ type. Soviet Physics Crystallography, 30(5), 521-523 (translation of Kristallografia, 30, 899-903, 1985).

Kutar, B.Ya., Andrusyak, R.I. and Zavodnik, V.E. (1988) The germanides $Sc_7Mn_{4+x}Ge_{10-x}$ (x = 1.3) and $Sc_7Cr_{4+x}Ge_{10-x}$ ―new representatives of compounds with superstructure of the $Ho_{11}Ge_{10}$ type. Soviet Physics Crystallography, 33(1), 141-142 (translation of Kristallografia, 33, 240-241, 1988).

Kutar, B.Ya., Cerny, R., Mokrah, I.R., Yvona, K. (1996) $Sc_{11-x}Yb_xGe_{10}$ ($x \approx 5$) a substitution variant with $Ho_{11}Ge_{10}$ type structure showing partial order on the rare earth sites. Journal of Alloys and Compounds, 245, L21-L23.

Lee, J., Ahn, K., Kim, K., Jo, H., Yoon, J.S., Moon, D., Shin, W.H., Ok, K.M. and You, T.-S. (2019) Effect of rare-earth metals substitution for Ca on the crystal structure and thermoelectric properties of the $Ca_{11-x}RE_xSb_{10-y}$ system. Crystal Growth & Design, 19, 3498−3508.

Lee, J., Sa, H., Jo, H., Yoon, J.S., Moon, D., Ok, K.M. and You, T.-S. (2020) Site-Selective *n*-type "heavy" rare-earth-metal doping in the complex zintl phase $Ca_{11-x}RE_xSb_{10-y}$ (RE = Tb, Dy, Ho, Er, Tm). Crystal Growth & Design, 20, 4503−4511.

Liang, Y., Cardoso-Gil, R., Schnelle, W., Zhao, J.T. and Grin, Y. (2013) Synthesis, crystal structure and physical properties of $Yb_{11}Bi_{10-x}Sn_x$. Solid State Sciences, 18, 127-130.

Mao, J. and Guloy, A.M. (2001) Synthesis, crystal structure and chemical bonding of a new La–

In–Ge ternary phase: $La_{11}In_6Ge_4$. Journal of Alloys and Compounds, 322, 135–142.

Markiv, V., Belyavina, N.N. and Kazachkova, S.S. (1989) Crystal structure of Sc_5Ga_4 and new compounds of the structural type $Ho_{11}Ge_{10}$. Russian Metallurgy, 1989(3), 191-194.

Nam, G. Choi, W., Lee. J., Lim, S.-J., Jo, H. Ok, K.M., Ahn, K. and You, T.-S. (2017) Effect of multisubstitution on the thermoelectric performance of the $Ca_{11-x}Yb_xSb_{10-y}Ge_z$ ($0 \le x \le 9$; $0 \le y \le 3$; $0 \le z \le 3$) system: Experimental and theoretical studies. Inorganic Chemistry, 56, 7099−7110.

Ovchinnikov, F., and Bobev, S. (2017) On the effect of Ga and In substitutions in the $Ca_{11}Bi_{10}$ and $Yb_{11}Bi_{10}$ bismuthides crystallizing in the tetragonal $Ho_{11}Ge_{10}$ structure type. Acta Crystallographica, C74, 269–273.

Rauscher, J.F., Kauzlarich, S.M., Ikeda, T. and G. J. Snyder,G.J. (2007) Synthesis, structure, and high temperature thermoelectric properties of $Yb_{11}Sb_{9.3}Ge_{0.5}$. Zeitschrift für Anorganische und Allgemeine Chemie, 633, 1587-1594.

Rehr, A. and Kauzlarich, S.M. (1994) $Sr_{11}Sb_{10}$. Acta Crystallographica, C50, 1859-1861.

Schmelczer, R., Schwarzenbach, D. and Hulliger, F. (1979) The Crystal structure of $Eu_{11}Sb_{10}$. Zeitschrift für Naturforschung, 34b, 1213-1217.

Smith, G.S., Johnson, Q. and Tharp, A.G. (1967) The crystal structure of $Ho_{11}Ge_{10}$. Acta Crystallographica, 23, 640-644.

Tyvanchuk, Yu., Duraj, R., Jaworska-Gołąb, T., Baran, S., Kalychak, Ya.M., J. Przewoźnik, J. and Szytuła, A. (2012) Structural chemistry and magnetic properties of $R_{11}M_4In_6$ (R = Gd, Tb, Dy, Ho, Er, Y; M = Si, Ge) compounds. Intermetallics, 25, 18-26.

Yue, C.-Y., Zhou, F.X., Wang, M.F., Zhang, H.-P. and Lei, X.-W. (2013) Synthesis, crystal

structure and chemical bonding of a new binary Lu–Sn phase: $Lu_{11}Sn_{10}$. Chinese Journal of Structural Chemistry, 32(6), 857─862.

Zaremba, V.I., Kaczorowskic, D., Nychyporuka, G.P., Rodewalda, U.Ch., Heyinga, B. and Pöttgen, R. (2006) Structure and magnetic properties of $Ce_3Ge_{0.66}In_{4.34}$ and $Ce_{11}Ge_{4.74}In_{5.26}$. Zeitschrift für Anorganische und Allgemeine Chemie, 632, 975-980.

Zeng, L., Hea, W., Wenjun Shen, W. and Lu, M. (2012) Crystal structure of new ternary compounds $Al_2R_{11}Ge_8$ (R = Y, Gd, Tb, Dy, Ho, Er) and thermal properties of $Al_2Er_{11}Ge_8$. Journal of Alloys and Compounds, 529, 158– 162.

Zhao, J.T. and Parthé, E. (1991) $Sc_{11}Al_2Ge_8$, a ternary substitution variant of the tetragonal $Ho_{11}Ge_{10}$ type. Acta Crystallographica,C47, 4-6.

Zhao, J.T., Chabon, B. and Parthé, E. (1988) $Sc_7Re_4Si_{10}$, a ternary substitution variant of the tetragonal $Ho_{11}Ge_{10}$ type. Acta Crystallographica,C44, 397-399.