Electronic Supplementary Information

Phonon Glass Behavior Beyond Traditional Cage Structures: Synthesis, Crystal and Electronic Structure, and Properties of KMg_4Sb_3

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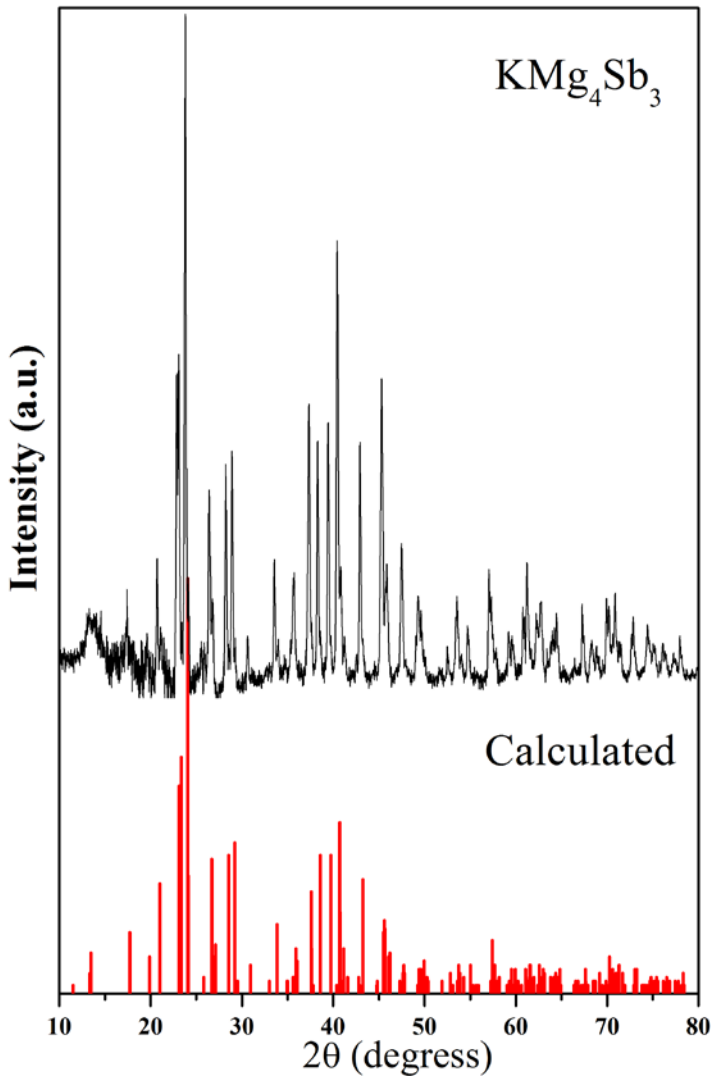

Figure S1. Calculated and experimental powder X-ray diffraction patterns of KMg_4Sb_3. Holder scattering was substracted from the experimental pattern.

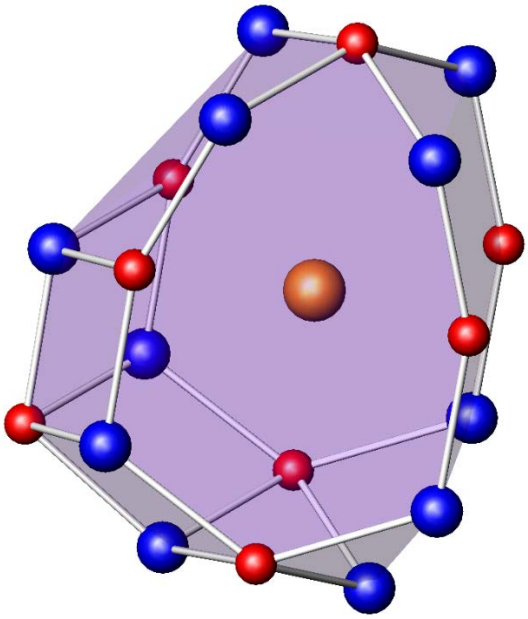

Figure S2. The nineteen-vertex open "cage" around K in KMg_4Sb_3. Large 8-memebred faces are visible. K: orange; Mg: blue; Sb: red.

Table S1. Refined atomic coordinates and isotropic displacement parameters for KMg_4Sb_3 and $A_2Mg_5Sb_4$ (A = Rb, Cs).

Atoms	Wyckoff	***x/a***	***y/b***	***z/c***	*s.o.f.*	U_{eq} (Å^2) [a)]
			KMg_4Sb_3			
K1	4*c*	0	0.8245(1)	0.25	1	0.0149(3)
Mg1	8*f*	0	0.1799(1)	0.0555(1)	1	0.0081(3)
Mg2	8*f*	0	0.53559(1)	0.1277(1)	1	0.0083(3)
Sb1	8*f*	0	0.36512(2)	0.05436(2)	1	0.00625(9)
Sb2	4*c*	0	0.08984(3)	¼	1	0.0066(1)
			$Rb_2Mg_5Sb_4$			
Rb1	8*e*	0.21608(6)	0	0	1	0.0086(2)
Mg1	8*g*	0.1395(2)	0.3734(4)	¼	1	0.0069(6)
Mg2	8*f*	0	0.6388(4)	0.1121(2)	1	0.0061(6)
Mg3	4*c*	0	0.0018(6)	¼	1	0.0082(9)
Sb1	8*g*	0.33990(4)	0.24637(7)	¼	1	0.0048(2)
Sb2	8*f*	0	0.26512(7)	0.09321(4)	1	0.0048(2)
			$Cs_2Mg_5Sb_4$			
Cs1	8*e*	0.22074(9)	0	0	1	0.0119(4)
Mg1	8*g*	0.1396(5)	0.3758(8)	¼	1	0.0114(14)
Mg2	8*f*	0	0.6448(8)	0.1116(5)	1	0.0118(14)
Mg3	4*c*	0	0.006(1)	¼	1	0.0135(19)
Sb1	8*g*	0.34127(9)	0.249(2)	¼	1	0.0089(4)
Sb2	8*f*	0	0.2698(2)	0.09476(9)	1	0.0095(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor

Table S2. Selected interatomic distances (Å) in for KMg_4Sb_3 and $A_2Mg_5Sb_4$ (A = Rb, Cs).

Atom pairs	Distances (Å)	Atom pairs	Distances (Å)
	KMg_4Sb_3		
K1 – Sb1× 4	3.530(1)	Mg1 – Sb1× 2	2.830(1)
Sb2	4.082(2)	Sb1	2.849(2)
Mg1× 2	4.021(2)	Sb2	2.911(2)
Mg1× 4	4.116(2)	Mg2 – Sb1	2.793(2)
Mg2	4.309(2)	Sb1	2.842(2)
		Sb2× 2	2.955(1)
	$Rb_2Mg_5Sb_4$		
Rb1 – Sb1× 2	3.894(3)	Mg2– Sb1× 2	2.885(3)
Sb1× 2	4.125(3)	Sb2	2.790(4)
Sb2× 2	3.705(2)	Sb2	2.930(4)
Mg1× 2	3.902(3)	Mg3– Sb1× 2	2.889(3)
Mg2× 2	4.129(3)	Sb1× 2	2.906(4)
Mg1– Sb1	2.797(4)		
Sb1	2.926(4)		
Sb2× 2	2.870(3)		
	$Cs_2Mg_5Sb_4$		
Cs1 – Sb1× 2	3.933(1)	Mg2– Sb1× 2	2.891(5)
Sb1× 2	4.152(1)	Sb2	2.812(7)
Sb2× 2	3.797(1)	Sb2	2.941(7)
Mg1× 2	3.905(4)	Mg3– Sb1× 2	2.894(7)
Mg2× 2	4.111(3)	Sb1× 2	2.913(7)
Mg1– Sb1	2.826(7)		
Sb1	2.929(7)		
Sb2× 2	2.875(5)		

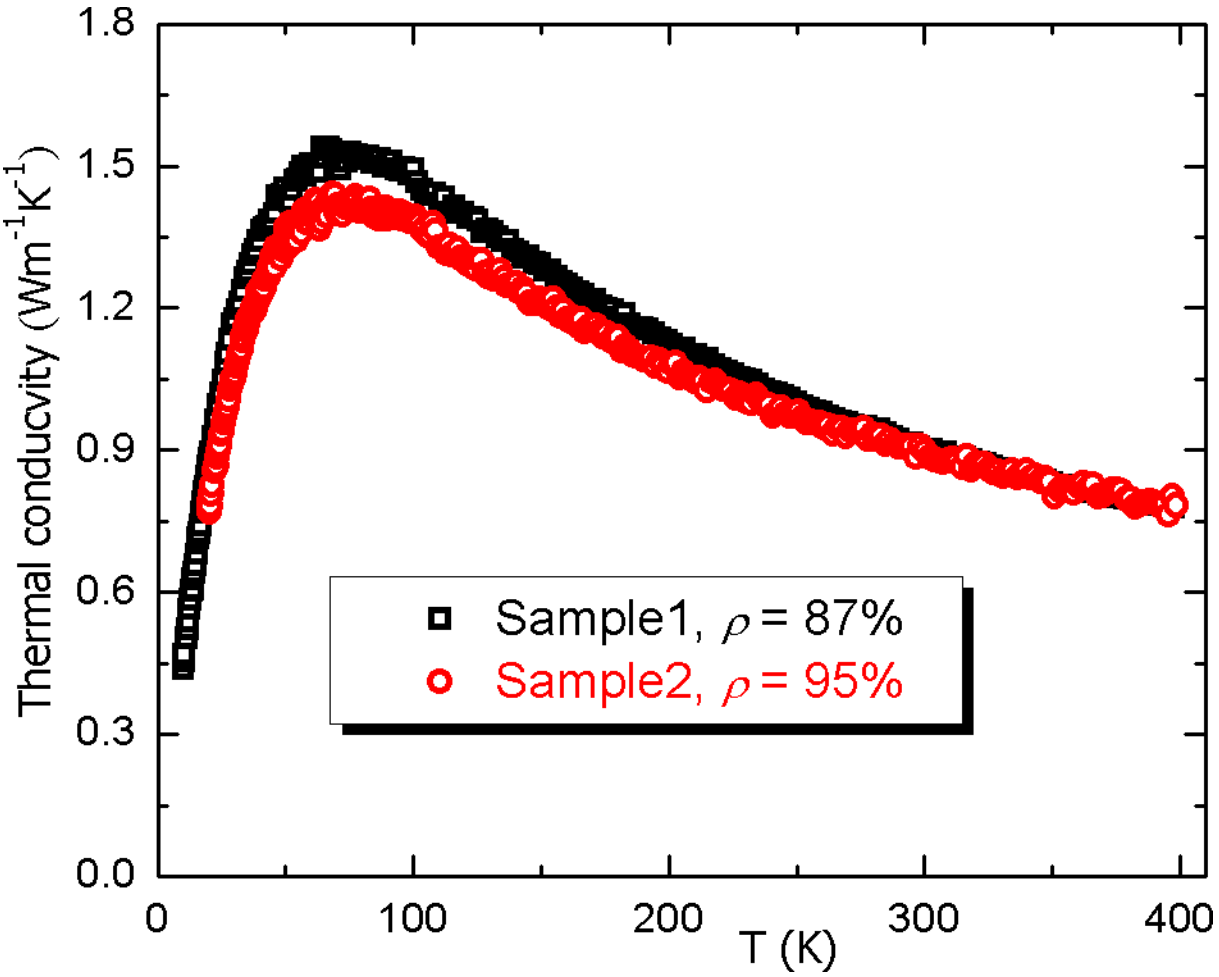

Figure S3. Temperature dependences of the total thermal conductivity for two samples of KMg_4Sb_3 with different densities.