

# Variable Temperature Behaviour of the Hybrid Double Perovskite MA<sub>2</sub>KBiCl<sub>6</sub>

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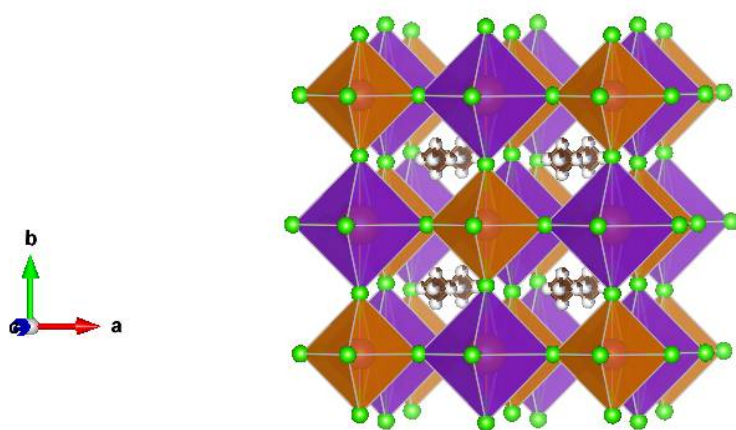
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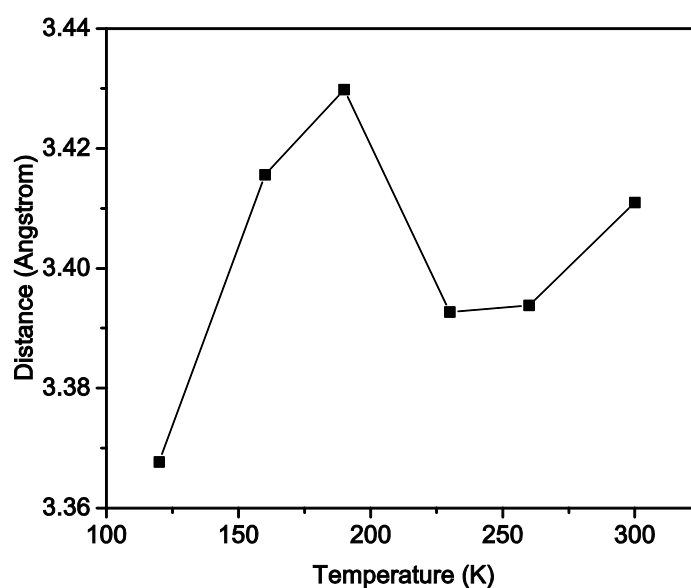
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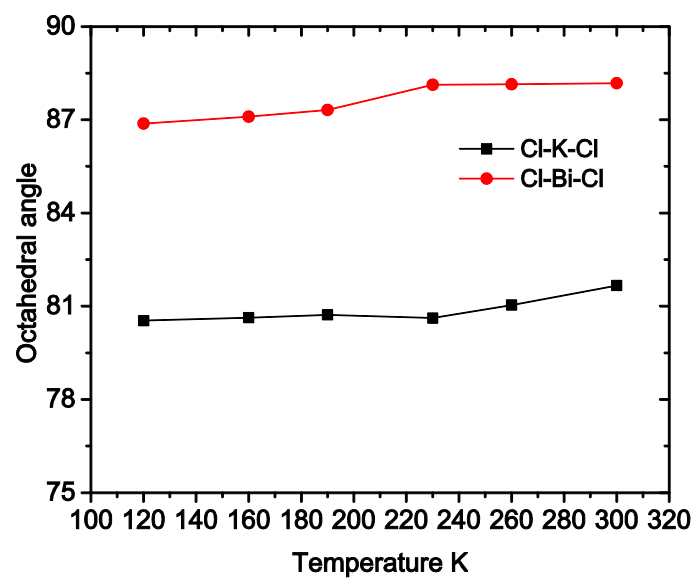
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**Figure S1.** The crystal structure of MA<sub>2</sub>KBiCl<sub>6</sub> double perovskite at 380 K. BiCl<sub>6</sub>: purple, KCl<sub>6</sub>: brown. MA cation is disordered in the cavity, H is omitted for illustration purpose.



**Figure S2.** Distance between N-Cl of the hydrogen bond N-H...Cl as a function of temperature.



**Figure S3.** Octahedral angles variation with respect to temperature. Only one set of angles for each octahedra are shown (the total angle =  $180^\circ$  when plus the other set of angles). Smaller angle away from  $90^\circ$  means more distortion.

**Table S1.** Atomic coordinates and ADPs at 380K.

Atom	Wyckoff position	x	y	z	Beq
Bi	48d	0	0.5	0.5	0.0514(8)
K	48d	0.5	0.5	0.5	0.063(3)
Cl	8d	0.2357(7)	0.5	0.5	0.125(3)
	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>		
Bi	0.0514(8)	0.0514(8)	0.0514(8)		
K	0.063(3)	0.063(3)	0.063(3)		
Cl	0.055(4)	0.161(6)	0.161(6)		

**Table S2.** Experimental details for the HT phase (refinement using OLEX2).

<b>Composition</b>	C <sub>2</sub> N <sub>2</sub> H <sub>12</sub> KBiCl <sub>6</sub>
<b>Chemical formula weight</b>	472.78
<b>Temperature</b>	380.00(14) K
<b>space group</b>	<i>Fm</i> $\bar{3}$ <i>m</i>
<b>a (Å)</b>	11.4326(2)
<b>Volume (Å<sup>3</sup>)</b>	1494.30(9)
<b>Z</b>	4
<b>mu</b>	13.095
<b>Absorpt correction Tmax</b>	0.986
<b>Absorpt correction Tmin</b>	0.981
<b>Absorpt correction type</b>	analytical
<b>Crystal colour primary</b>	colourless
<b>Experimental crystal density diffractions</b>	2.048
<b>Experimental crystal F000</b>	816
<b>Crystal size (mm)</b>	0.1417 × 0.1009 × 0.0935
<b>h</b>	-14 < h < 15
<b>k</b>	-15 < k < 14
<b>l</b>	-14 < l < 14
<b>Diffraction reflections number</b>	4380
<b>Diffraction reflections theta full</b>	25.242
<b>Diffraction reflections theta max</b>	27.925
<b>Diffraction reflections theta min</b>	3.086
<b>Diffraction detector</b>	CCD plate
<b>Diffraction detector area resol mean</b>	16.1183
<b>Diffraction measurement device</b>	four-circle diffractometer
<b>Diffraction measurement device type</b>	Xcalibur, Eos, Gemini ultra
<b>Diffraction measurement method</b>	\w scans
<b>Diffraction radiation monochromator</b>	graphite
<b>Diffraction radiation type</b>	MoK\alpha
<b>Diffraction radiation wavelength Å</b>	0.71073
<b>Reflections number gt</b>	121
<b>Reflections number total</b>	125

Reflections completeness	100
Reflections threshold expression	$I > 2\sqrt{s(I)}$
Refine Diffraction density max	1.846
Refine Diffraction density min	-0.817
Refine Diffraction density rms	0.286
Refine ls extinction coefficient	0.0010(5)
Refine ls extinction expression	$Fc^* = kFc[1 + 0.001 \times Fc^2 \sqrt{I^3/\sin(2\theta)}]^{-1/4}$
Refine ls extinction method	SHELXL-2014/7
Refine ls goodness of fit ref	1.433
Refine ls number parameters	7
Refine ls number Reflections	125
Refine ls number restraints	0
Refine ls R factor all	0.0471
Refine ls R factor gt	0.0458
Refine ls restrained S all	1.433
Refine ls shift/su max	0
Refine ls shift/su mean	0
Refine ls structure factor coef	Fsqd
Refine ls weighting details	$W = 1/[\sqrt{s^2(Fo^2) + (0.0794P)^2}]$ where $P = (Fo^2 + 2Fc^2)/3$
Refine ls weighting scheme	calc
Refine ls wR factor gt	0.1287
Refine ls wR factor ref	0.129

Table S3. Bond lengths (Å) and angles (°) at different temperatures.

	300 K	260 K	230 K	190 K	160 K	120 K
C-N	1.327(18)	1.36(18)	1.386(3)	1.434(2)	1.455(2)	1.472(3)
K-Cl	3.048(13)	3.046(14)	3.042(2)	3.072(2)	3.078(2)	3.081(3)
Bi-Cl	2.678(13)	2.675(14)	2.671(2)	2.694(2)	2.697(2)	2.699(3)
K-Cl-Bi	172.998(8)	172.553(8)	172.261(12)	161.054(12)	159.413(11)	157.979(12)

Table S4. Experimental details for the LT phase, refinement using JANA.

Composition	C <sub>2</sub> N <sub>2</sub> H <sub>12</sub> KBiCl <sub>6</sub>
Chemical formula weight	472.78
Temperature	180.00(14) K
space group	$R\bar{3}m$
a (Å)	7.7379(7)
c (Å)	21.1415(16)
Volume (Å <sup>3</sup> )	1096.26(16)
Z	3
mu	13.371
Absorpt correction Tmax	0.542
Absorpt correction Tmin	0.292

Absorpt correction type	analytical
Crystal colour primary	colourless
Experimental crystal density diffractions	2.3297
Experimental crystal F000	690
Crystal size (mm)	0.182 × 0.134 × 0.082
h	−5 < h < 9
k	−4 < k < 10
l	−24 < l < 26
Diffraction reflections number	1493
Diffraction reflections theta full	27.34
Diffraction reflections theta max	27.96
Diffraction reflections theta min	2.89
Reflections number gt	340
Reflections number total	340
Reflections completeness	100
Reflections threshold expression	$I > 3\sigma(I)$
Refine Diffraction density max	1.42
Refine Diffraction density min	−1.99
Refine ls extinction method	none
Refine ls goodness of fit ref	2.02
Refine ls number parameters	20
Refine ls number Reflections	340
Refine ls number restraints	0
Refine ls R factor all	0.0321
Refine ls R factor gt	0.0321
Refine ls shift/su max	0.0009
Refine ls shift/su mean	0.0003
Refine ls structure factor coef	F
Refine ls weighting details	$w = 1/(\sigma^2(F) + 0.0001F^2)$
Refine ls weighting scheme	sigma
Refine ls wR factor gt	0.0436
Refine ls wR factor ref	0.0436

Table S5. Atomic coordinates and ADPs at 180 K.

	Wyckoff	x	y	z	Beq	Occ
Bi	3a	0	0	0	0.0203(3)	1
K	3b	0.333333	0.666667	0.166667	0.0271(14)	1
Cl	36i	0.1084(6)	0.3299(6)	0.0698(2)	0.0444(18)	0.5
N	6c	0.666667	0.333333	0.0502(9)	0.043(5)	1
C	6c	0.666667	0.333333	0.1201(13)	0.089(12)	1
	U11	U22	U33	U12	U13	U23
Bi	0.0204(4)	0.0204(4)	0.0200(5)	0.01019(18)	0	0
K	0.0324(18)	0.0324(18)	0.016(2)	0.0162(9)	0	0
Cl	0.054(3)	0.0316(19)	0.041(2)	0.0160(16)	−0.0051(17)	−0.0131(16)

<b>N</b>	0.044(6)	0.044(6)	0.041(10)	0.022(3)	0	0
<b>C</b>	0.116(17)	0.116(17)	0.035(15)	0.058(9)	0	0