Supporting Information

Observation of Piezoelectricity in Lead-free $Cs_2AgBiBr_6$ Perovskite: A New Entrant in Energy Harvesting Arena

Tufan Paul[1#], Aditi Sahoo[2#], Soumen Maiti[3], Suvankar Mandal[4], Souvik Bhattacharjee[4], Avisek Maiti[5], Kalyan Kumar Chattopadhyay*[1, 4]

[1]*School of Material Science and Nanotechnology, Jadavpur University, Kolkata-700032, India*

[2]*CSIR- Central Glass and Ceramic Research Institute, Kolkata-700032, India*

[3]*St Thomas College of Engineering & Technology, Kolkata, 700023, India*

[4]*Department of Physics, Jadavpur University, Kolkata, 700032, India*

[5] *S. N. Bose National Centre for Basic Sciences, Salt Lake, Kolkata 700106, India*

*Corresponding author Email: kalyan_chattopadhyay@yahoo.com

Current affiliation: Institut national de la recherche scientifique (INRS), EMT Centre, Varennes, Quebec J3X 1S2, Canada

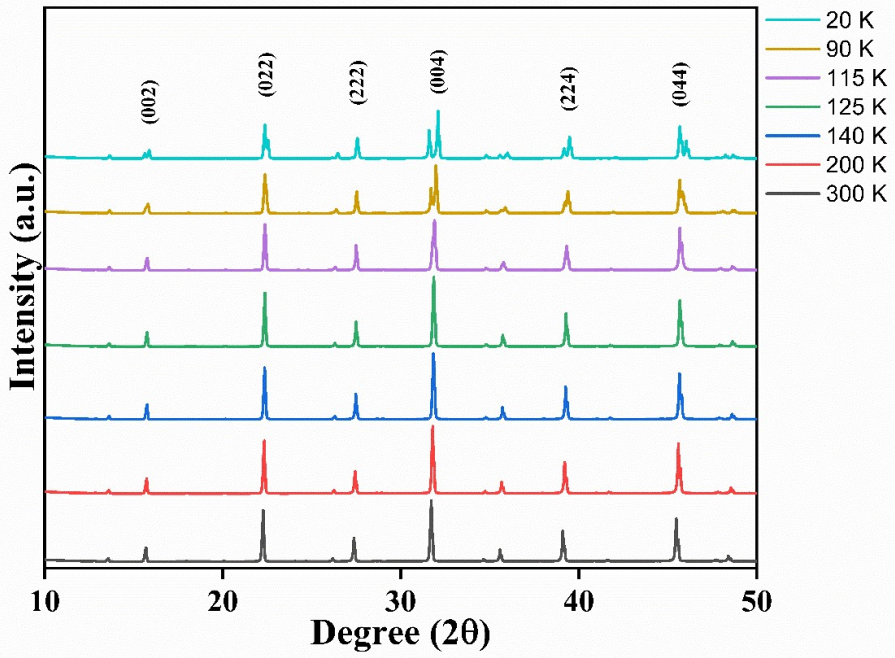

Figure S1: *Low temperature dependent XRD of $Cs_2AgBiBr_6$.*

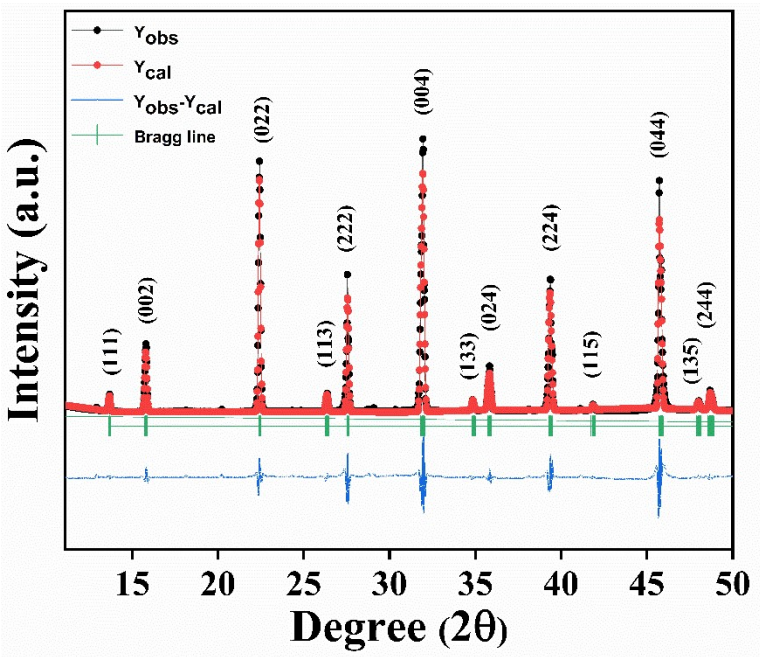

Figure S2: *Refined XRD data of $Cs_2AgBiBr_6$ at 115 K in tetragonal lattice system with I4/m space group.*

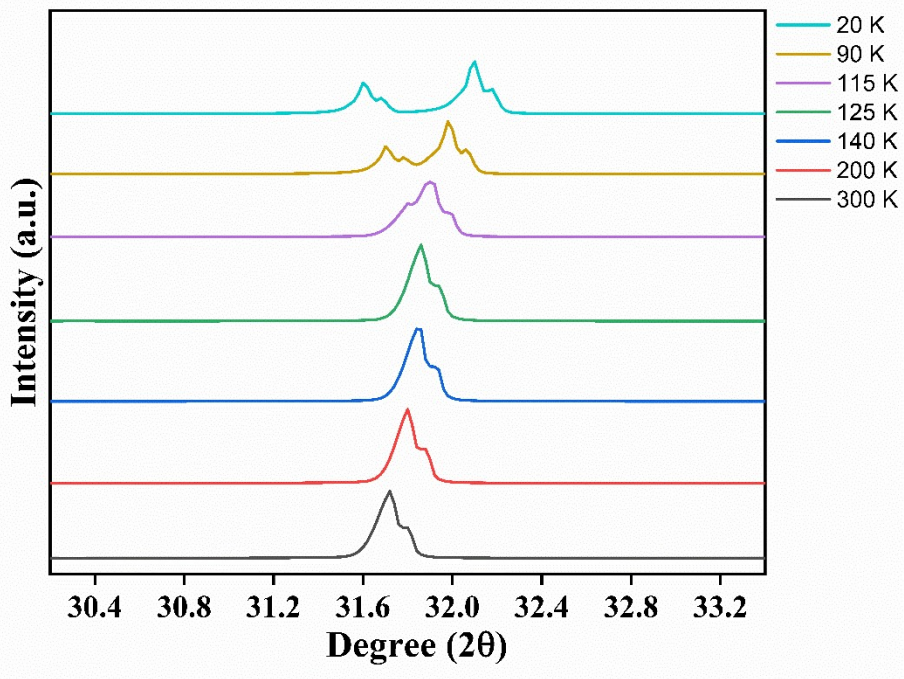

Figure S3: *Low temperature XRD of $Cs_2AgBiBr_6$ at the phase transition region.*

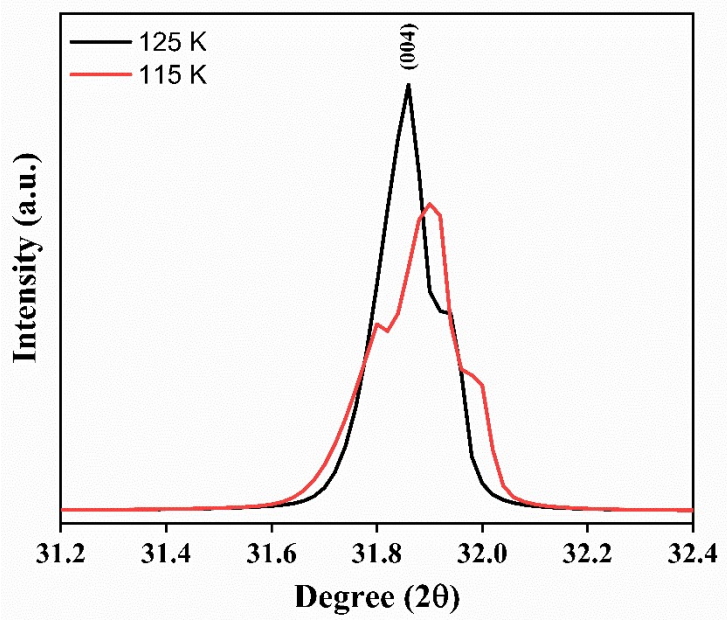

Figure S4: *Zoom view of 31.73° peak at low temperature XRD of* $Cs_2AgBiBr_6$.

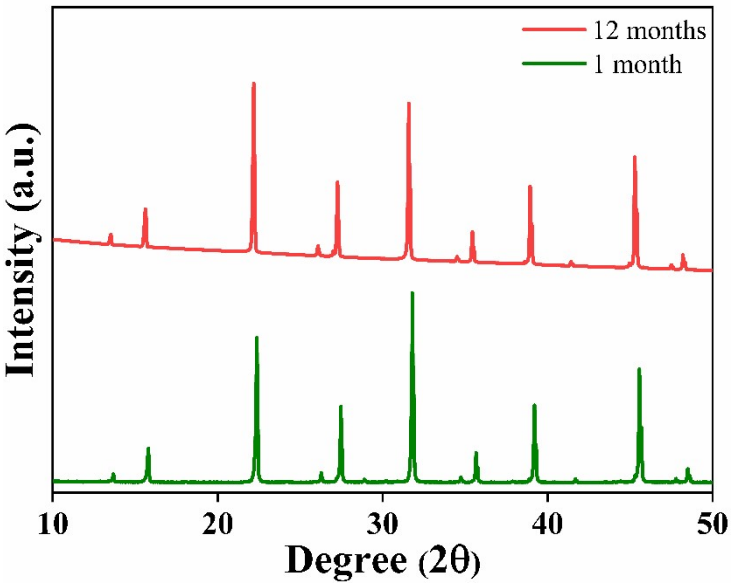

Figure S5: *Time dependent XRD stability of* $Cs_2AgBiBr_6$.

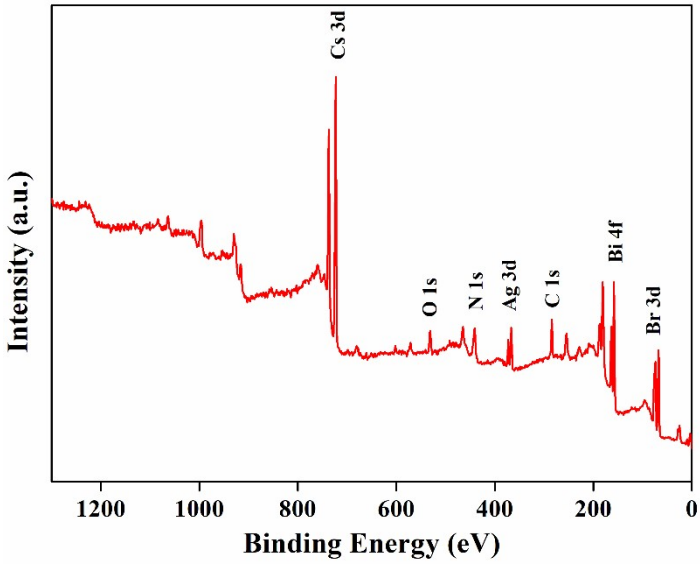

Figure S6: *XPS survey scan of* $Cs_2AgBiBr_6$.

Table S1*: Comparison of Piezoresponse of various halide perovskites*

S. No.	Material	Maximum piezoelectric Amplitude response	Applied electric bias	Reference
1.	$FASnI_3$	~400 pm	± 10 V	1
2.	γ-$CsPbI_3$	~350 pm	± 10 V	2
3.	$CsGeBr_3$	~70 pm	± 8 V	3
4.	$PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =5)	~400 pm	± 10 V	4
5.	$MAPb(I_{1-x}Br_x)_3$	~90 pm	± 5 V	5
6.	$DMAACdCl_3$	~175 pm	± 60 V	6
7.	$(TMAEA)Pb_2Cl_6$	~600 pm	± 20 V	7
8.	**$Cs_2AgBiBr_6$**	**~272 pm**	**± 20 V**	**this work**

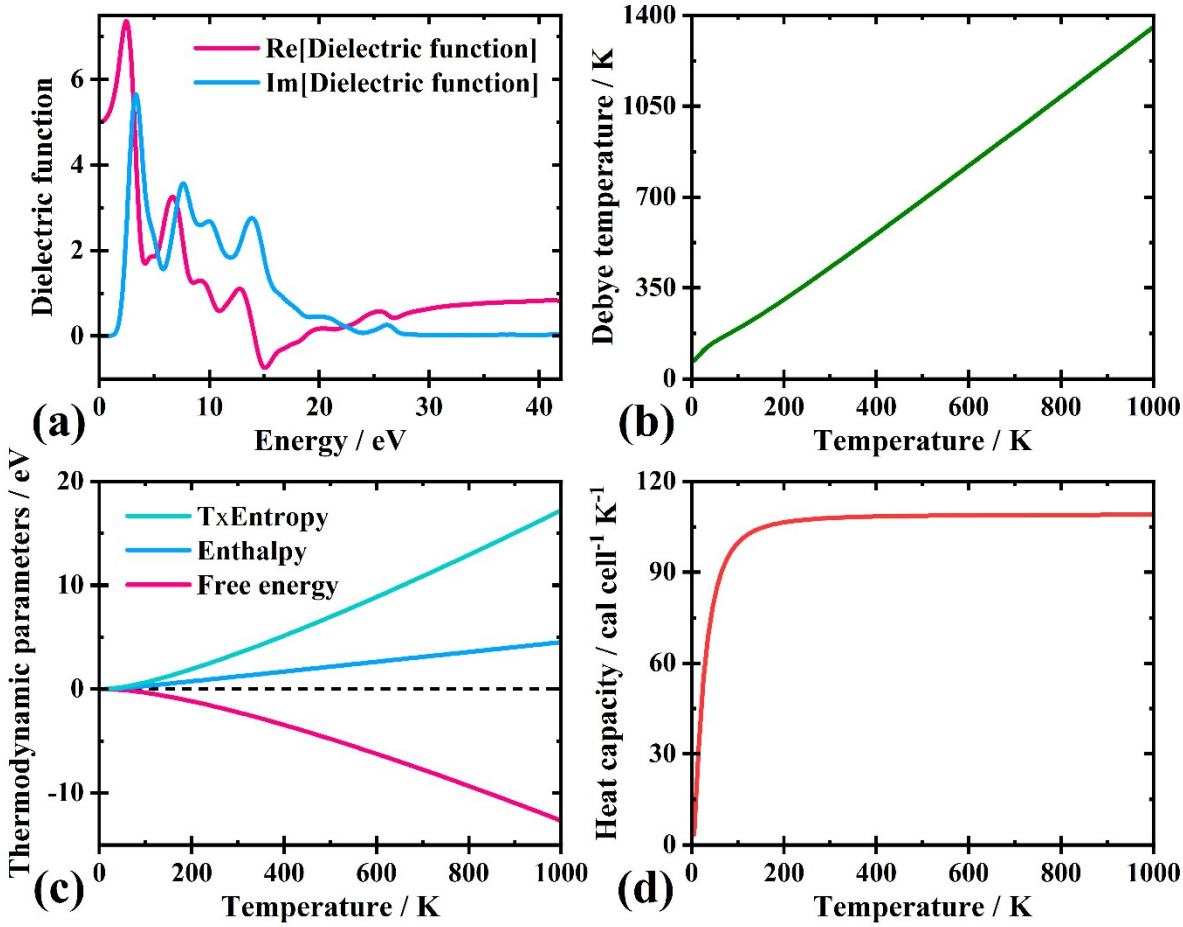

Figure S7: *(a) Energy dispersive real and imaginary parts of optical dielectric function; (b) Debye temperature versus absolute temperature* (T)*; (c)* $T \times$ *entropy, enthalpy, and free energy as a function of* T*; (d) heat capacity versus* T *plot.*

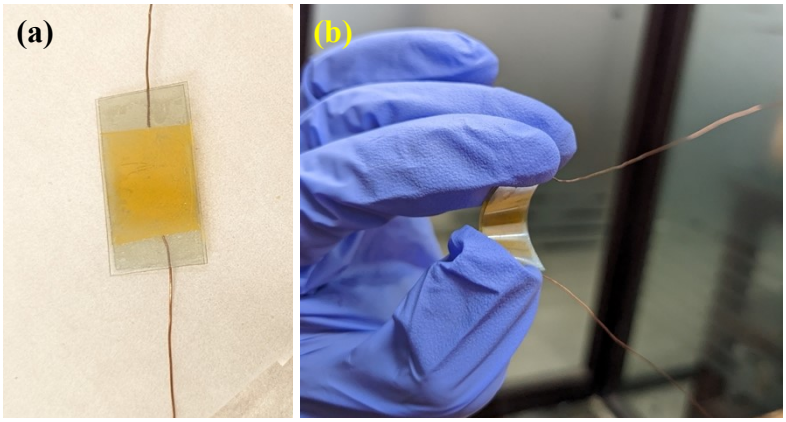

Figure S8: *Picture of the PNG device (a) without bending (b) with bending.*

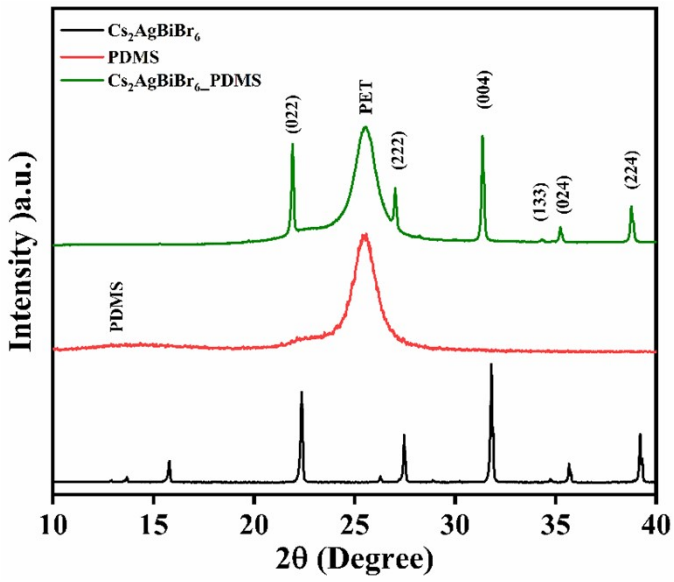

Figure S9: *XRD of pure PDMS, $Cs_2AgBiBr_6$ crystals with prepared film*

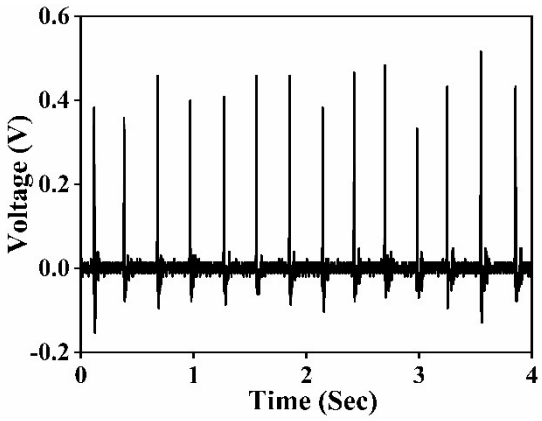

Figure S10: *Output performance registered from PDMS*

Group theoretical analysis using *VIBRATE!*

$Cs_2AgBiBr_6$
Hall Symbol: -F 4 2 3
Space Group: F m 3 m (O_h^5)
Space Group Number: 225
a = 11.2712
b = 11.2712
c = 11.2712
$\alpha = 90$
$\beta = 90$
$\gamma = 90$
Crystal System: Cubic
Setting: Standard
Point Group: m3m (O_h)

Atomic Coordinates

24e	1	0.250310	0.000000	0.000000
24e	2	0.250310	0.500000	0.500000
24e	3	0.750310	0.000000	0.500000
24e	4	0.750310	0.500000	0.000000
24e	5	0.749690	0.000000	0.000000
24e	6	0.749690	0.500000	0.500000
24e	7	0.249690	0.000000	0.500000
24e	8	0.249690	0.500000	0.000000
24e	9	0.000000	0.250310	0.000000
24e	10	0.000000	0.750310	0.500000
24e	11	0.500000	0.250310	0.500000
24e	12	0.500000	0.750310	0.000000
24e	13	0.000000	0.749690	0.000000
24e	14	0.000000	0.249690	0.500000
24e	15	0.500000	0.749690	0.500000
24e	16	0.500000	0.249690	0.000000
24e	17	0.000000	0.000000	0.749690
24e	18	0.000000	0.500000	0.249690
24e	19	0.500000	0.000000	0.249690
24e	20	0.500000	0.500000	0.749690
24e	21	0.000000	0.000000	0.250310
24e	22	0.000000	0.500000	0.750310
24e	23	0.500000	0.000000	0.750310
24e	24	0.500000	0.500000	0.250310
4a	25	0.000000	0.000000	0.000000
4a	26	0.000000	0.500000	0.500000
4a	27	0.500000	0.000000	0.500000
4a	28	0.500000	0.500000	0.000000
4b	29	0.500000	0.000000	0.000000
4b	30	0.500000	0.500000	0.500000
4b	31	0.000000	0.000000	0.500000
4b	32	0.000000	0.500000	0.000000
8c	33	0.250000	0.250000	0.250000
8c	34	0.250000	0.750000	0.750000
8c	35	0.750000	0.250000	0.750000
8c	36	0.750000	0.750000	0.250000
8c	37	0.750000	0.750000	0.750000
8c	38	0.750000	0.250000	0.250000
8c	39	0.250000	0.750000	0.250000
8c	40	0.250000	0.250000	0.750000

Lattice Centring Operators

1: 0.0000000 0.5000000 0.5000000

2: 0.5000000 0.0000000 0.5000000

3: 0.5000000 0.5000000 0.0000000

4: 0.0000000 0.0000000 0.0000000

Non-Magnetic Case k =0

Symmetry Operators

R	t	x,y,z	Operator: 1 (E)
1 0 0	0.000		
0 1 0	0.000		
0 0 1	0.000		

R	t	-y,-z,x	Operator: 3 (C_3)
0 -1 0	0.000		
0 0 -1	0.000		
1 0 0	0.000		

R	t	z,-x,-y	Operator: 3 (C_3)
0 0 1	0.000		
-1 0 0	0.000		
0 -1 0	0.000		

R	t	-y,z,-x	Operator: 3 (C_3)
0 -1 0	0.000		
0 0 1	0.000		
-1 0 0	0.000		

R	t	-z,-x,y	Operator: 3 (C_3)
0 0 -1	0.000		
-1 0 0	0.000		
0 1 0	0.000		

R	t	-z,x,-y	Operator: 3 (C_3)
0 0 -1	0.000		
1 0 0	0.000		
0 -1 0	0.000		

R			t	y,-z,-x	Operator: 3 (C_3)
0	1	0	0.000		
0	0	-1	0.000		
-1	0	0	0.000		

R			t	z,x,y	Operator: 3 (C_3)
0	0	1	0.000		
1	0	0	0.000		
0	1	0	0.000		

R			t	y,z,x	Operator: 3 (C_3)
0	1	0	0.000		
0	0	1	0.000		
1	0	0	0.000		

R			t	-z,-y,-x	Operator: 2 (C_2)
0	0	-1	0.000		
0	-1	0	0.000		
-1	0	0	0.000		

R			t	z,-y,x	Operator: 2 (C_2)
0	0	1	0.000		
0	-1	0	0.000		
1	0	0	0.000		

R			t	-x,-z,-y	Operator: 2 (C_2)
-1	0	0	0.000		
0	0	-1	0.000		
0	-1	0	0.000		

R			t	-x,z,y	Operator: 2 (C_2)
-1	0	0	0.000		
0	0	1	0.000		
0	1	0	0.000		

R			t	-y,-x,-z	Operator: 2 (C_2)
0	-1	0	0.000		
-1	0	0	0.000		
0	0	-1	0.000		

R			t	y,x,-z	Operator: 2 (C_2)
0	1	0	0.000		
1	0	0	0.000		
0	0	-1	0.000		

R			t	-y,x,z	Operator: 4 (C_4)
0	-1	0	0.000		
1	0	0	0.000		

0 0 1 0.000

R **t** **y,-x,z** **Operator: 4 (C_4)**

0 1 0 0.000
-1 0 0 0.000
0 0 1 0.000

R **t** **x,-z,y** **Operator: 4 (C_4)**

1 0 0 0.000
0 0 -1 0.000
0 1 0 0.000

R **t** **x,z,-y** **Operator: 4 (C_4)**

1 0 0 0.000
0 0 1 0.000
0 -1 0 0.000

R **t** **z,y,-x** **Operator: 4 (C_4)**

0 0 1 0.000
0 1 0 0.000
-1 0 0 0.000

R **t** **-z,y,x** **Operator: 4 (C_4)**

0 0 -1 0.000
0 1 0 0.000
1 0 0 0.000

R **t** **-x,-y,z** **Operator: 2 (C_2)**

-1 0 0 0.000
0 -1 0 0.000
0 0 1 0.000

R **t** **x,-y,-z** **Operator: 2 (C_2)**

1 0 0 0.000
0 -1 0 0.000
0 0 -1 0.000

R **t** **-x,y,-z** **Operator: 2 (C_2)**

-1 0 0 0.000
0 1 0 0.000
0 0 -1 0.000

R **t** **-x,-y,-z** **Operator: 1 (i)**

-1 0 0 0.000
0 -1 0 0.000
0 0 -1 0.000

R **t** **y,-x,-z** **Operator: 4 (S_4)**

0 1 0 0.000

-1 0 0 0.000
0 0 -1 0.000

R **t** **-y,x,-z** **Operator: 4 (S_4)**

0 -1 0 0.000
1 0 0 0.000
0 0 -1 0.000

R **t** **-x,z,-y** **Operator: 4 (S_4)**

-1 0 0 0.000
0 0 1 0.000
0 -1 0 0.000

R **t** **-x,-z,y** **Operator: 4 (S_4)**

-1 0 0 0.000
0 0 -1 0.000
0 1 0 0.000

R **t** **-z,-y,x** **Operator: 4 (S_4)**

0 0 -1 0.000
0 -1 0 0.000
1 0 0 0.000

R **t** **z,-y,-x** **Operator: 4 (S_4)**

0 0 1 0.000
0 -1 0 0.000
-1 0 0 0.000

R **t** **-z,-x,-y** **Operator: 3 (S_6)**

0 0 -1 0.000
-1 0 0 0.000
0 -1 0 0.000

R **t** **-y,-z,-x** **Operator: 3 (S_6)**

0 -1 0 0.000
0 0 -1 0.000
-1 0 0 0.000

R **t** **y,z,-x** **Operator: 3 (S_6)**

0 1 0 0.000
0 0 1 0.000
-1 0 0 0.000

R **t** **-z,x,y** **Operator: 3 (S_6)**

0 0 -1 0.000
1 0 0 0.000
0 1 0 0.000

R **t** **y,-z,x** **Operator: 3 (S_6)**

0 1 0 0.000
0 0 -1 0.000
1 0 0 0.000

R t z,x,-y Operator: 3 (S_6)

0 0 1 0.000
1 0 0 0.000
0 -1 0 0.000

R t -y,z,x Operator: 3 (S_6)

0 -1 0 0.000
0 0 1 0.000
1 0 0 0.000

R t z,-x,y Operator: 3 (S_6)

0 0 1 0.000
-1 0 0 0.000
0 1 0 0.000

R t x,y,-z Operator: m (σ)

1 0 0 0.000
0 1 0 0.000
0 0 -1 0.000

R t -x,y,z Operator: m (σ)

-1 0 0 0.000
0 1 0 0.000
0 0 1 0.000

R t x,-y,z Operator: m (σ)

1 0 0 0.000
0 -1 0 0.000
0 0 1 0.000

R t z,y,x Operator: m (σ)

0 0 1 0.000
0 1 0 0.000
1 0 0 0.000

R t -z,y,-x Operator: m (σ)

0 0 -1 0.000
0 1 0 0.000
-1 0 0 0.000

R t x,z,y Operator: m (σ)

1 0 0 0.000
0 0 1 0.000
0 1 0 0.000

R			t	x,-z,-y	Operator: m (σ)
1	0	0	0.000		
0	0	-1	0.000		
0	-1	0	0.000		

R			t	y,x,z	Operator: m (σ)
0	1	0	0.000		
1	0	0	0.000		
0	0	1	0.000		

R			t	-y,-x,z	Operator: m (σ)
0	-1	0	0.000		
-1	0	0	0.000		
0	0	1	0.000		

Reducible Characters List

Point Group = m3m (O_h)

1: (1) 30	2: (3) 0	3: (3) 0	4: (3) 0	5: (3) 0	6: (3) 0	7: (3) 0	8: (3) 0	9: (3) 0	10: (2) -2	11: (2) -2	12: (2) -2
13: (2) -2	14: (2) -2	15: (2) -2	16: (4) 4	17: (4) 4	18: (4) 4	19: (4) 4	20: (4) 4	21: (4) 4	22: (2) -6	23: (2) -6	24: (2) -6
25: (-1) -6	26: (-4) -4	27: (-4) -4	28: (-4) -4	29: (-4) -4	30: (-4) -4	31: (-4) -4	32: (-3) 0	33: (-3) 0	34: (-3) 0	35: (-3) 0	36: (-3) 0
37: (-3) 0	38: (-3) 0	39: (-3) 0	40: (m) 6	41: (m) 6	42: (m) 6	43: (m) 6	44: (m) 6	45: (m) 6	46: (m) 6	47: (m) 6	48: (m) 6

Character Table

	1	3	3	3	3	3	3	3	3	2	2	2	2	2	2	4	4	4	4	4	4	2	2	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	m	m	m	m	m	m	m	m	m
																									1	4	4	4	4	4	4	3	3	3	3	3	3	3	3									
A1g	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A2g	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1
Eg	2	-1	-1	-1	-1	-1	-1	-1	-1	0	0	0	0	0	0	0	0	0	0	0	0	2	2	2	2	0	0	0	0	0	0	-1	1	1	1	1	1	1	1	1	2	2	2	0	0	0	0	0	0
T1g	3	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1	3	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1	-1	-1	-1
T2g	3	0	0	0	0	0	0	0	0	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	3	-1	-1	-1	-1	-1	-1	0	0	0	0	0	0	0	0	0	-1	-1	-1	1	1	1	1	1	1
A1u	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
A2u	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	-1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1
Eu	2	-1	-1	-1	-1	-1	-1	-1	-1	0	0	0	0	0	0	0	0	0	0	0	0	2	2	2	-2	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	-2	-2	-2	0	0	0	0	0	0
T1u	3	0	0	0	0	0	0	0	0	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1	-3	-1	-1	-1	-1	-1	-1	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1
T2u	3	0	0	0	0	0	0	0	0	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-3	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0	1	1	1	-1	-1	-1	-1	-1	-1

Irreducible representations (Mulliken Notation)

$$\Gamma_{red} = A_{1g}+E_g +T_{1g}+2T_{2g}+5T_{1u}+T_{2u}$$

Irreducible representations (Bethe Notation)

$$\Gamma_{red} = \Gamma_1^+ + \Gamma_3^+ + \Gamma_4^+ + 2\Gamma_5^+ + 5\Gamma_4^- + \Gamma_5^-$$

Invariants

IR Active - Acoustic Modes (translations)

T_{1u} Γ_4^- (x,y,z)

Rotations

T_{1g} Γ_4^+ (R_x,R_y,R_z)

Raman Active

A_{1g} Γ_1^+ $x^2+y^2+z^2$

E_g Γ_3^+ ($2z^2-x^2-y^2$,x^2-y^2)

T_{2g} Γ_5^+ (xz,yz,xy)

Silent

T_{2u} Γ_5^-

References:

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4. Zhang, Q.; Solanki, A.; Parida, K.; Giovanni, D.; Li, M.; Jansen, T. L.; Pshenichnikov, M. S.; Sum, T. C. Tunable ferroelectricity in Ruddlesden–Popper halide perovskites. *ACS Appl. Mater. Interfaces* **2019**, 11(14), 13523-13532.
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