Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

SUPPORTING INFORMATION

Lead-Free Hybrid Ferroelectric Material Based on the Formamidine: $[NH_2CHNH_2]_3Bi_2I_9$.

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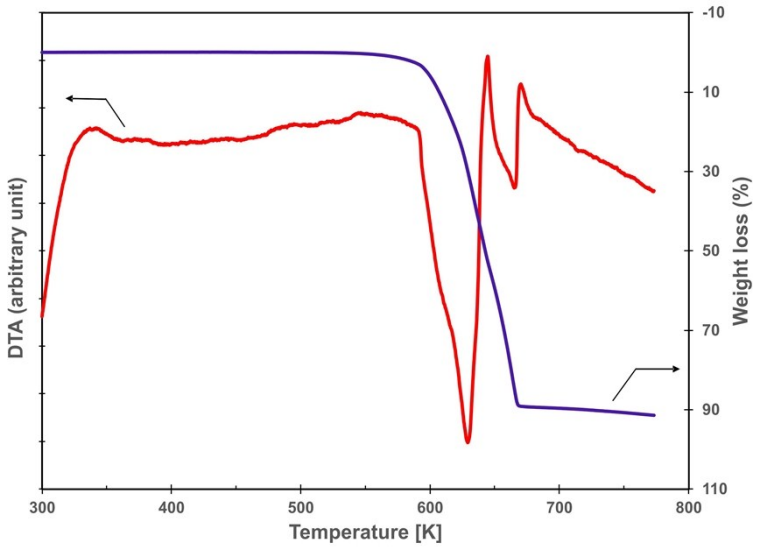

Fig S1. The TGA and DTA signals for $FA_3Bi_2I_9$

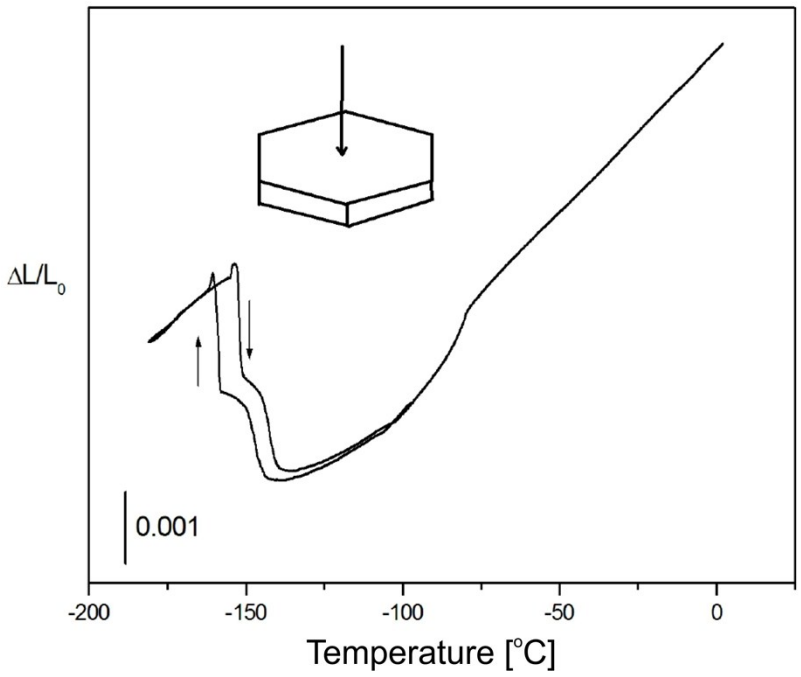

Fig. S2. The linear thermal expansion, $\Delta L/L_o$, measured for the crystal of FBI along the c-axis.

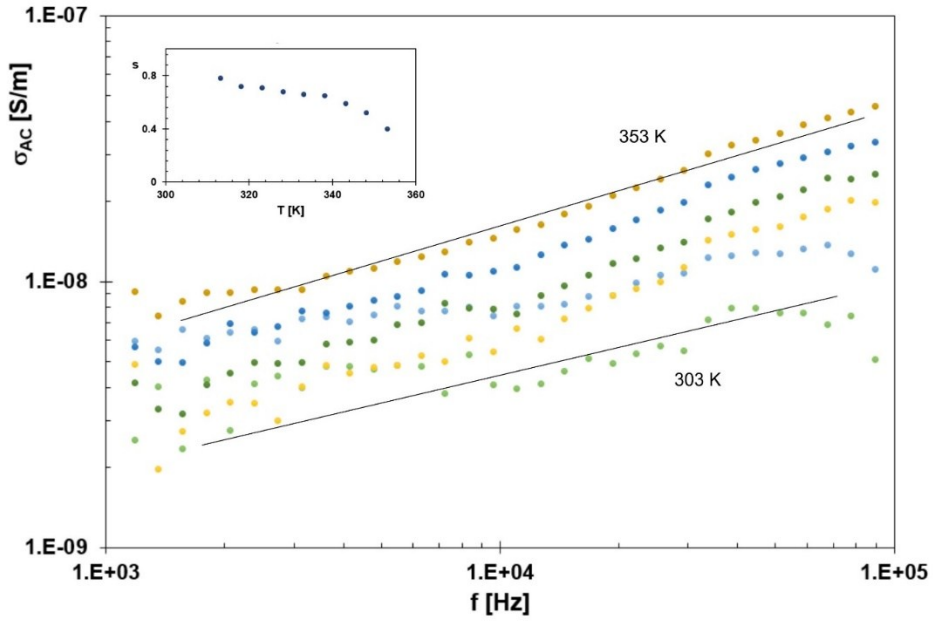

Fig. S3. Frequency dependence of the ac conductivity [S m^{-1}] in *log-log* scale, measured above room temperature. Inset:The temperature dependence of the s parameter for the frequency range 1–12 kHz,

In the log-log plot the $A\omega^s$dependence of conductivity is observed as a linear dependence of $\log\sigma$ *versus* $\log\omega$ The value of *s*, estimated on the basis of the Eq. (1) for frequencies below 100 kHz, is lower than 1. The values of *s* observed are characteristic of an activation process

of conductivity. The inset in Figure S3 shows the temperature dependence of the *s* parameter. The temperature characteristics of the *ac* conductivity contribution were clearly observed on heating a sample.

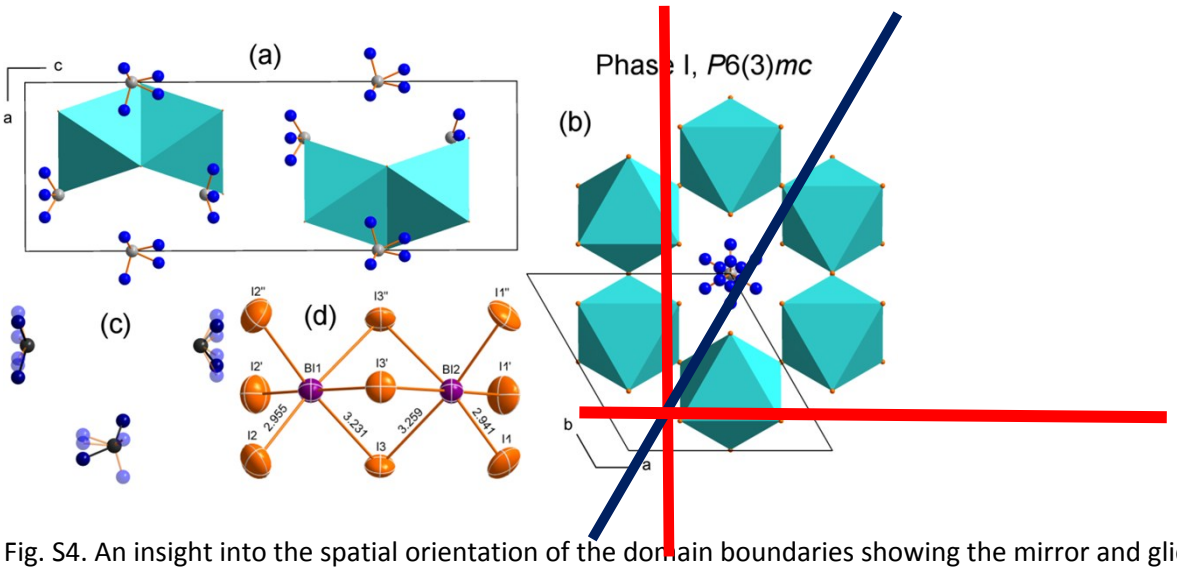

Fig. S4. An insight into the spatial orientation of the domain boundaries showing the mirror and glide planes of group $P6_3mc$ preserved in the phases II – IV marked in in red. The shear planes corresponding to the domain boundaries are marked in blue.

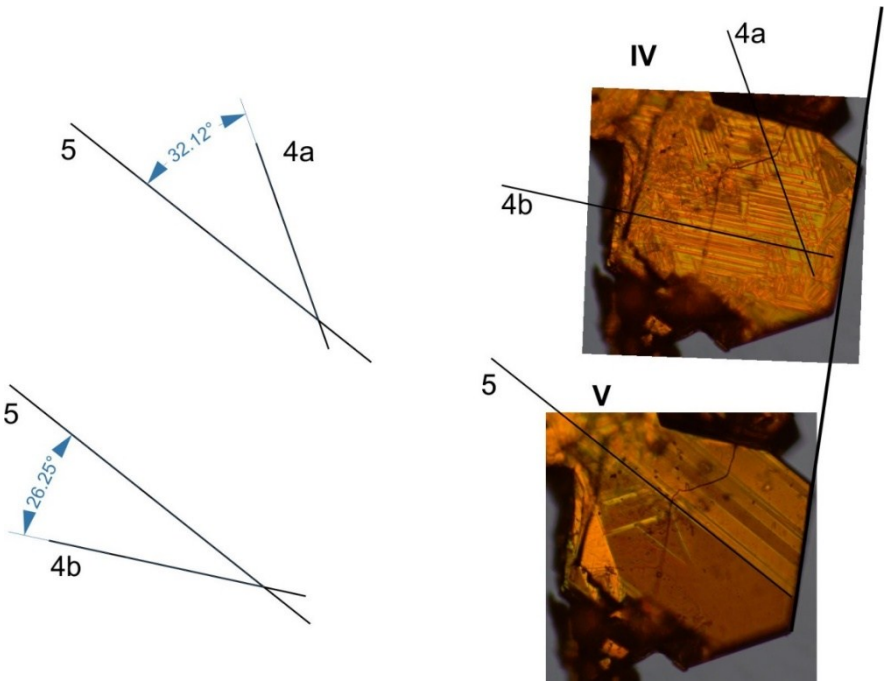

Fig.S5. Mutual orientation of domain walls in phase IV and V.

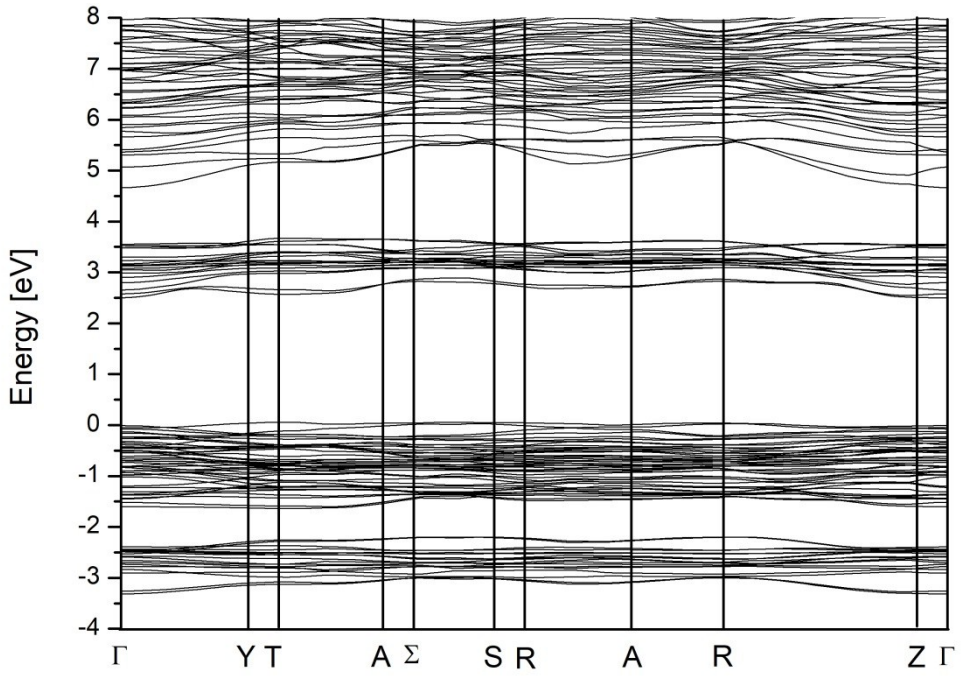

Fig. S6. Band structure of $FA_3Bi_2I_9$ calculated without SOC.

Table S1. Atomic displacements after the phase transition to Phase II (from AMPLIMODES [36]). NOTE: ux, uy and uz are given in relative units. |u| is the absolute distance given in Å. The displacements of terminal iodides are highlighted.

	Atomic Displacements

Wyckoff Positions		**Atom**	**ux**	**uy**	**uz**	**|u|**
4a	(0,y,z)	Bi1	0.0000	-0.0095	-0.0007	0.1444
4a	(0,y,z)	Bi2	0.0000	0.0092	-0.0010	0.1409
8b	(x,y,z)	I1	0.0033	-0.0190	0.0034	**0.2978**
4a	(0,y,z)	I2	0.0000	-0.0168	-0.0049	**0.2754**
4a	(0,y,z)	I3	0.0000	-0.0007	0.0077	0.1702
8b	(x,y,z)	I4	0.0018	-0.0010	-0.0042	0.0946
8b	(x,y,z)	I5	0.0001	0.0191	0.0036	**0.2989**
4a	(0,y,z)	I6	0.0000	0.0164	-0.0069	**0.2903**