Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2015

Electronic Supplementary Information (ESI) for

Atypical multiferroicity of HoCrO₃ in bulk and film geometry

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I. SURFACE CHARACTERIZATION

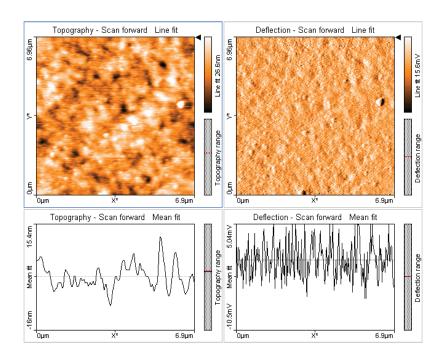


Figure S1: AFM image and depth profile of HoCrO₃ film.

AFM image shows nearly homogeneous surface topography as depicted in Fig. S1. The color bar indicates the Z-range or the depth profile.

II. ELECTRICAL CONNECTION FOR ELECTRIC POLARIZATION MEASUREMENT IN FILM

For P - E loop measurements in film, initially gold is coated on the Si substrate using a gold coater (Eiko IB-2 Ion coater, Japan) on which HoCrO₃ film is deposited. Schematic representation of the electrical connection is shown in Fig. S2.

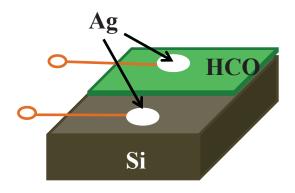


Figure S2: Schematic representation of the electrical connection for P-E loop measurement in film.

III. LOW TEMPERATURE STRUCTURE

Low temperature structure has been evaluated using Rietveld refinement of x-ray diffraction pattern. Fig. S3 shows satisfactory fit using Rietveld refinement of the diffraction pattern of HoCrO₃ measured at 80 K. The details of the structural parameters as obtained from the refinement are given in Table S1.

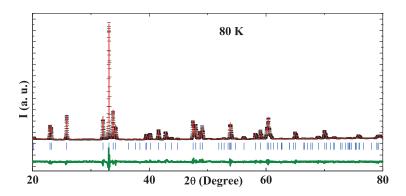


Figure S3: Rietveld refinement pattern of HoCrO₃. X-ray diffraction pattern recorded at 80 K temperature.

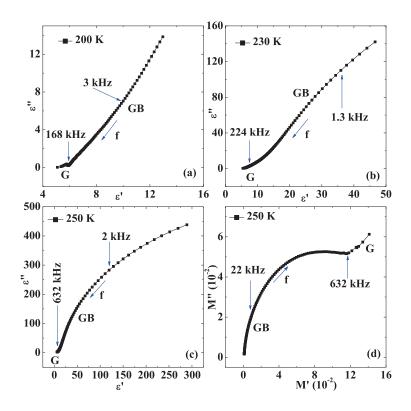


Figure S4: Cole-Cole plot at temperatures (a) 200 K, (b) 230 K, (c) 250 K and (d) complex-modulus plot at 250 K for bulk $HoCrO_3$.

IV. COLE-COLE PLOT

Rapid increase of dielectric permittivity in bulk HoCrO₃ is due to the different conduction mechanism involved in grain (G) and grain-boundary (GB). It is clear from the Fig. S4 a that f=1 kHz is at the tail of the grain-boundary arc of the complex-ε plot. This indicates the low frequency lines at temperatures greater than 200 K corresponds to extrinsic grain-boundary effect. Also it is clear from Figs. S4 b and c that with increase in temperature G arc decreases and GB arc increases. The high frequency components remains within G arc even at high temperature. This provides a conclusive proof of presence of grain-boundary led extrinsic effect at high temperatures for bulk HoCrO₃. As electric modulus shows real dielectric relaxation mechanism Fig. S4 d shows small G effect at high frequency range and large GB effect at low frequency range. So, the rapid increase in dielectric permittivity is

due to extrinsic grain-boundary effect.

V. RIETVELD REFINEMENT PARAMETERS

TABLE I: Rietveld refinement parameters obtained from x-ray diffraction data of $HoCrO_3$ using MAUD software package. The numbers in the parenthesis are the statistical errors in the last significant digits.

Lattice parameters			
T (K)	80 K	160 K	300K
a (Å)	5.5060(1)	5.5089(2)	5.2517(2)
b (Å)	5.2359(2)	5.2410 (1)	5.5207(1)
c (Å)	7.5218(1)	7.5310 (2)	7.5468 (1)
Space group	Pna_{21}	Pna_{21}	Pbnm
Atomic positions			
Ho (X)	0.0656(1)	0.0646(1)	-0.0192(1)
Ho (Y)	0.0175(2)	-0.0170(1)	0.0639(2)
Ho (Z)	0.1788(2)	0.4727(2)	0.25(0)
$\operatorname{Cr}(X)$	0.0104(2)	0.0023(1)	0.5(0)
$\operatorname{Cr}(Y)$	0.4830(2)	0.4892(2)	0 (0)
$\operatorname{Cr}(Z)$	-0.0831 (2)	-0.2802(1)	0 (0)
O1 (X)	0.4499 (1)	-0.0861(1)	0.0899(2)
O1 (Y)	-0.1144(2)	0.4155(2)	0.4599(2)
O1 (Z)	0.1634(2)	0.2278(2)	0.25(0)
O2(X)	0.0573(1)	0.0499 (2)	0.3265(2)
O2(Y)	0.4569 (1)	0.6003 (1)	0.1722 (1)
O2(Z)	0.4169 (2)	0.0119 (2)	0.0004(3)
O3 (X)	0.7028 (1)	0.2011 (1)	-
O3(Y)	0.6977(1)	0.1938 (2)	-
O3(Z)	0.4818 (2)	-0.2144 (2)	-
Reliability factors			
R_w (%)	5.9350	7.7348	5.7941
R_{wnb} (%)	6.1372	8.2315	8.2655
R_b (%)	4.5496	5.7376	4.0158
R_{exp} (%)	4.2661	3.5464	1.3623