Supporting information

for

Ferroelectricity Induced by Cations of Nonequivalent Spins Disordered in the Weakly Ferromagnetic Perovskites, $YCr_{1-x}M_xO_3$ (M = Fe or Mn)

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3. Tabular column giving the details of the Rietveld refinement on the neutron diffraction data of $YCr_{0.5}Fe_{0.5}O_3$.

4. PUND measurements on $YCr_{0.5}Fe_{0.5}O_3$ verifying the intrinsic nature of polarization.

5. Magnetization and polarization data showing the polarization when Gd^{3+} ion in substitution at the A site of $Y_{1-x}Gd_xCrO_3$ systematically (where x= 0.2, 0.4, 0.6 and 0.8). These results show that ferroelectricity can be introduced in non-magnetic rare earth orthochromites not only by the spin disorder at the B-site but also by substituting a magnetic rare-earth at the A-site thereby inducing Magnetic Jahn-Teller effect.[1]

We have demonstrated the switching of polarization in Fig. 5(a). The experiment is performed by first applying a poling field (say positive) above the ordering temperature and poling the sample down to temperature below the magnetic ordering temperature (225 K). After shorting for a considerable time to remove the effects due to leakage and stray currents, we started measuring the pyrocurrent till a certain temperature (275 K). Now the sample is applied a negative poling field down to 175 K. The shorting time needs to be increased with every subsequent poling to get a proper switching of the polarity of pyroelectric current. The experiment is repeated down to 10 K. The obtained pyrocurrents are integrated together to obtain a switched polarization profile. To verify the magnetoelectric effect, we have also performed field dependent pyrocurrent measurements as shown in the inset of Fig. 5(a). Here, the sample is poled and fixed at a certain temperature below the T_N and then the current is measured in the presence of a ramping magnetic field. From time t = 0 s to 1500 s, there is no magnetic field and the current value stabilizes. At t = 1501 s, the field is ramped from 0 Oe to 30 kOe and the current values show an increase correspondingly. At t= 3000 s, the magnetic field is stable at 30 kOe and the current also settles down. The increase in the pyrocurrent due to the presence of magnetic field gives clear evidence for the magnetoelectric coupling. We have carried out frequency dependence of dielectric constant and loss with respect to temperature in $YCr_{0.5}Fe_{0.5}O_3$ using the Agilent 4294A Precision Impedance Analyzer as shown in Fig. S1. It can be seen that the dielectric constant is nearly independent of temperature till 175 K above which the Maxwell-Wagner relaxation regime sets it. Although the loss associated with the Maxwell-Wagner relaxation is large, the value of loss at T_N is small proving that the ferroelectric polarization in these materials at T_N is not arising from loss due to conductivity. A detailed explanation for characterization of ferroelectricity by PUND measurements is given elsewhere.[1] The PUND measurements in $YCr_{0.5}Fe_{0.5}O_3$ shows clearly that there is remanent polarization below T_N(Fig. S3). These measurements establish

that $YCr_{0.5}Fe_{0.5}O_3$ shows an remanent polarization of 0.01 $\mu C/cm^2$. This value is much lesser than the values obtained by pyroelectric measurements. This is due to the experimental limitation of not being able to apply a higher electric field owing to possible sample breakdown. However, the presence of remanence below T_N and the respective absence of it above T_N clearly demonstrate the magnetoelectricity.

In the case of $Y_{1-x}Gd_xCrO_3$, magnetoelectric coupling is clearly demonstrated(Fig. S4-S7). This is due to the magnetic interactions between Gd^{3+} ions and Cr^{3+} ions at the chromium ordering temperature. It is to be noted that the polarization values increase with increase in Gd ion concentration. The results show clearly that either magnetic interactions between the R^{3+} ion and Cr^{3+} ion causes ferroelectric polarization and hence multiferroicity. In the absence of a magnetic rare earth, the spin disorder at the B-site gives rise to magnetoelectric coupling as elucidated in $YCr_{1-x}M_xO_3$(M= Fe or Mn).

References:

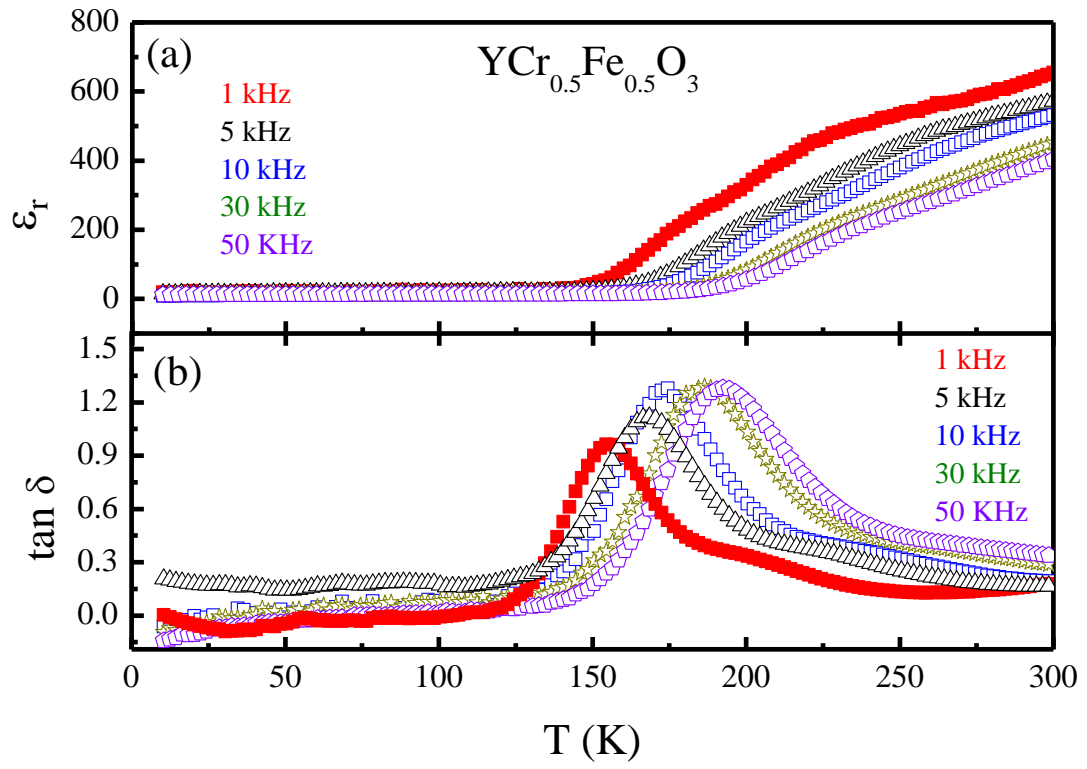(1) Rajeswaran, B.; Khomskii, D.I.; Zvezdin, A.K.; Sundaresan, A.; Rao, C.N.R.
arXiv:1201.0826v1 2012.

Fig. S1: Frequency dependence of dielectric constant and loss in $YCr_{0.5}Fe_{0.5}O_3$.
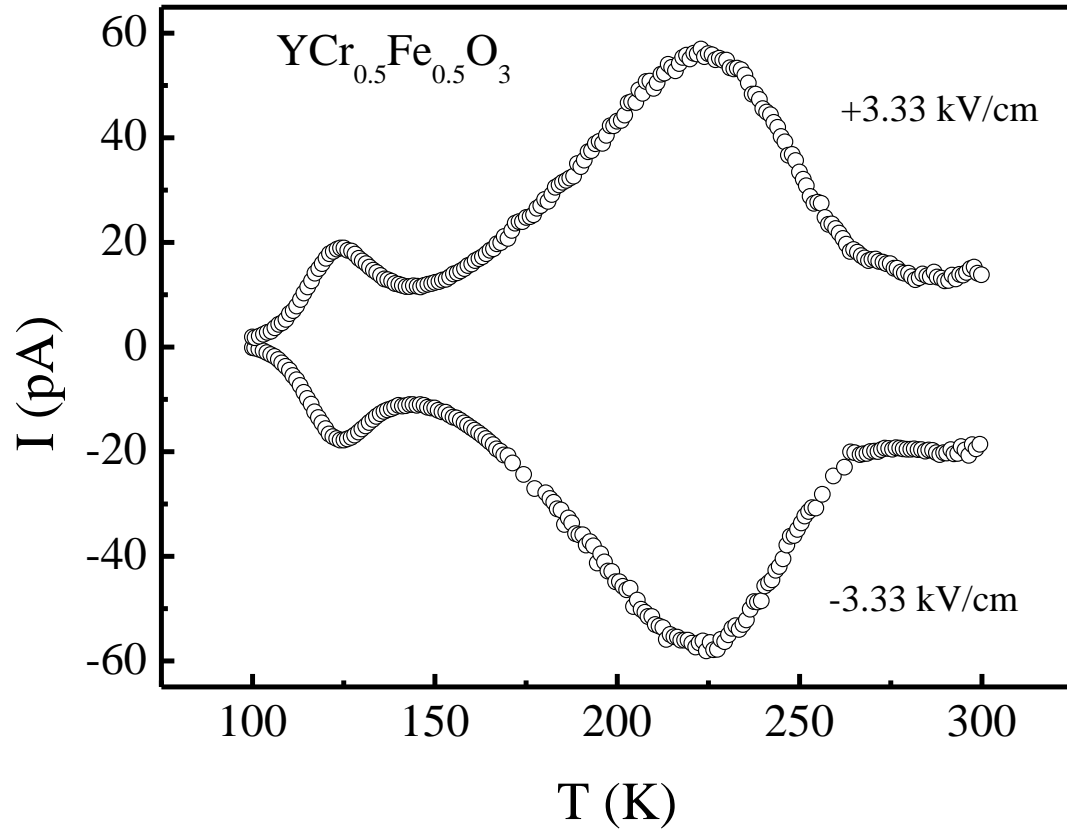
Fig. S2 : Pyroelectric current profile in $YCr_{0.5}Fe_{0.5}O_3$ (not corrected for leakage). It can be seen that there are two peaks one corresponding to magnetic ordering due to Cr-Fe spins and the other due to Cr-Cr ordering.

Table I Atomic positions(x, y, z) and Thermal parameters(B) of $YCr_{0.5}Fe_{0.5}O_3$ at 350 K and 2 K ([*]) as obtained from Rietveld refinement on Neutron data.

Site	Wyckoff Position	x	y	z	B($\mathring{A}^2$)
				$YCr_{0.5}Fe_{0.5}O_3$	
Y	4c	0.0671(1)	0.2500	0.9831(2)	0.42(2)
		0.0683(2)	0.2500	0.9824(3)	0.33(5)[*]
Fe/Cr	4b	0.00000	0.0000	0.50000	0.32(2)
		0.00000	0.0000	0.50000	0.05(4)[*]
O1	4c	0.4630(2)	0.2500	0.1079(3)	0.37(2)
		0.4619(3)	0.2500	0.1072(4)	0.06(4)[*]
O2	8d	0.6967(2)	-0.0555(1)	0.3080(2)	0.44(1)
		0.6966(2)	-0.0562(2)	0.3074(3)	0.23(4)*

Table 2- Lattice parameters and Reliability factors of $YCr_{0.5}Fe_{0.5}O_3$ at 350 K and 2 K as obtained from Rietveld refinement on Neutron data.

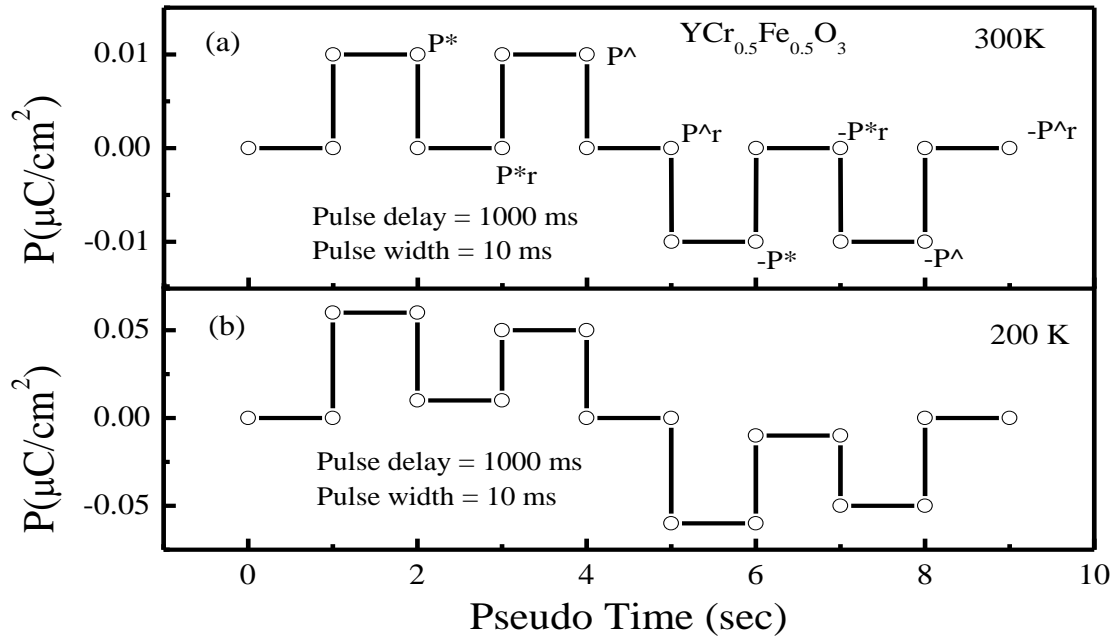| T(K)	a	b	c	χ^2	R_p (%)	R_{wp} (%)	R_B (%)	R_f (%)
350	5.5608(1)	7.5770(1)	5.2692(1)	9.76	7.68	8.46	3.21	2.27
2	5.5621(1)	7.5684(1)	5.2625(1)	5.59	9.98	10.5	1.85	1.41

Fig. S3 . PUND(Positive Up Negative Down) measurements in $YCr_{0.5}Fe_{0.5}O_3$ with an applied voltage of 150 V to verify the intrinsic nature of polarization. The remanent polarization is of the order of 0.01 $\mu C/cm^2$.
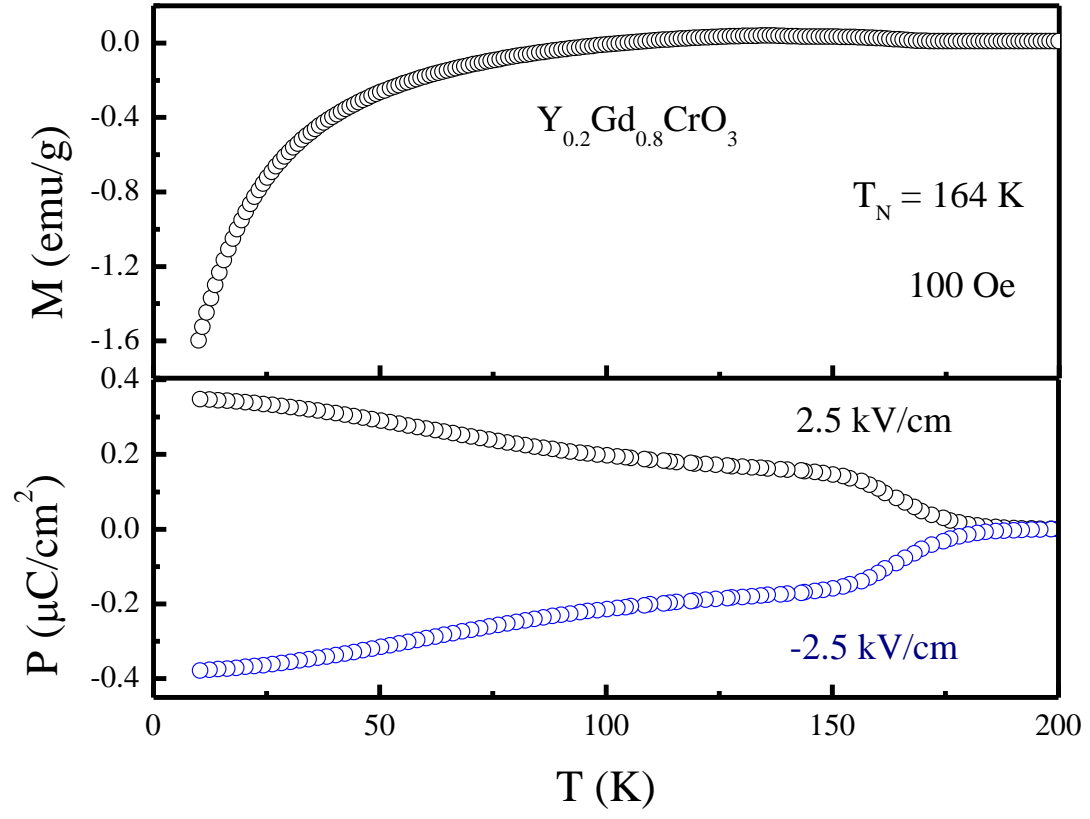
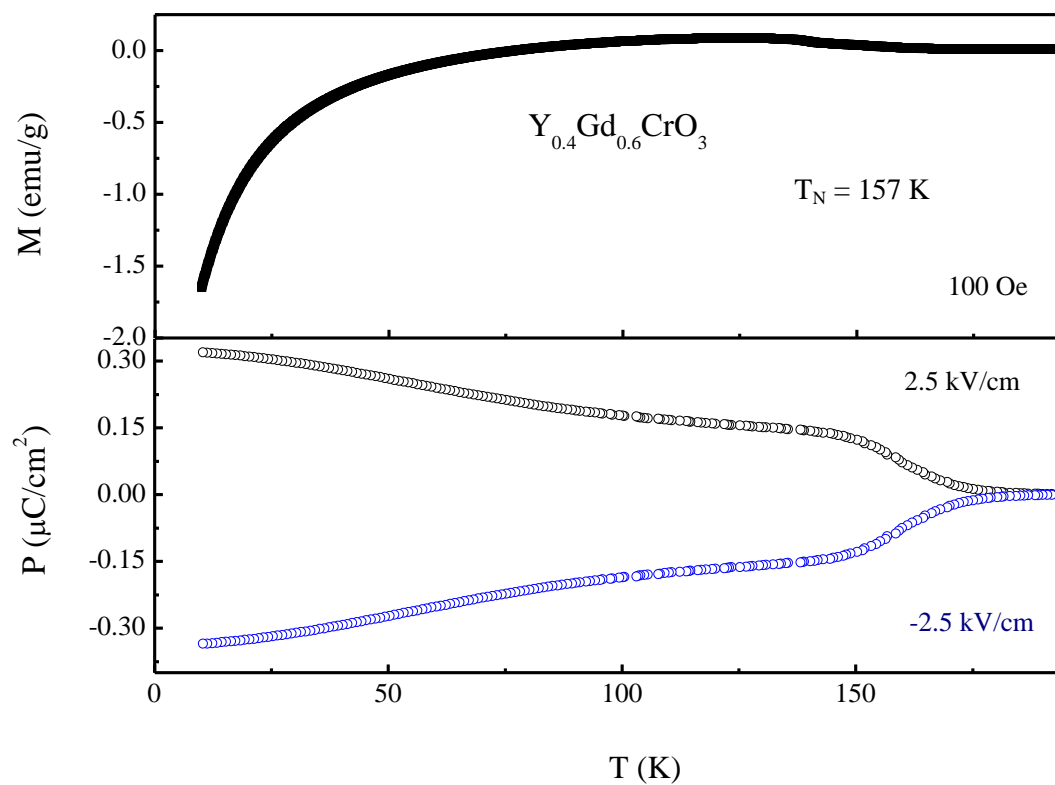Fig. S4: Magnetization and corresponding polarization at the Cr ordering temperature in $Y_{0.2}Gd_{0.8}CrO_3$.

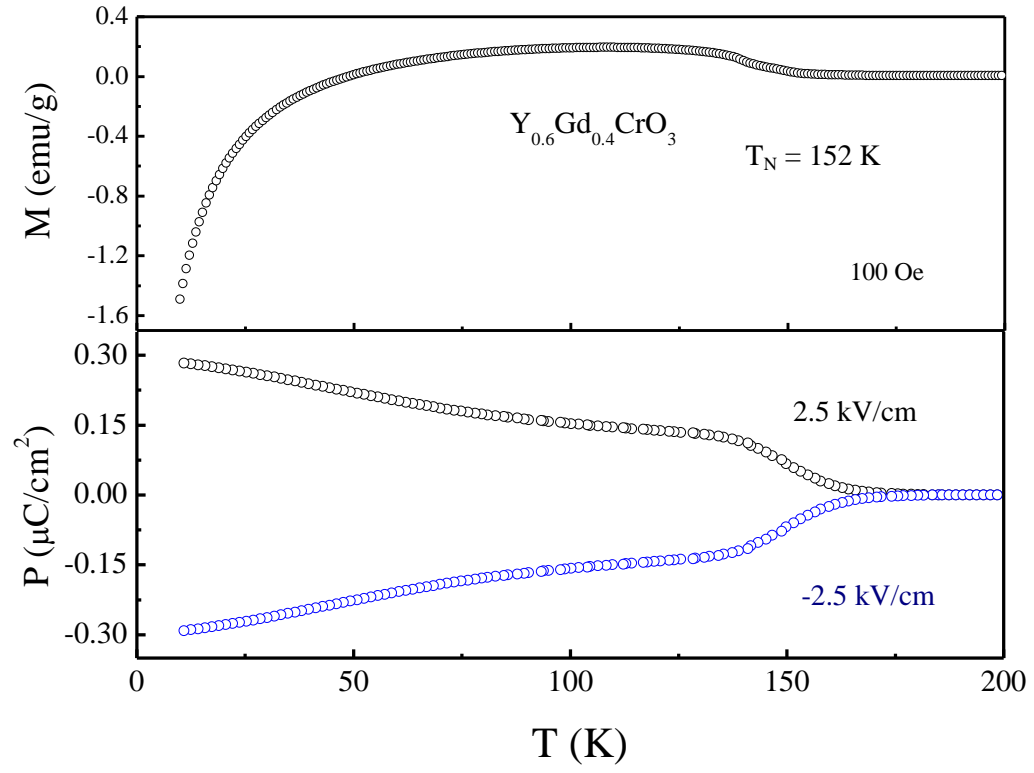Fig. S5 Magnetization and corresponding polarization at the Cr ordering temperature in $Y_{0.4}Gd_{0.6}CrO_3$.

Fig. S6 :Magnetization and corresponding polarization at the Cr ordering temperature in $Y_{0.6}Gd_{0.4}CrO_3$.
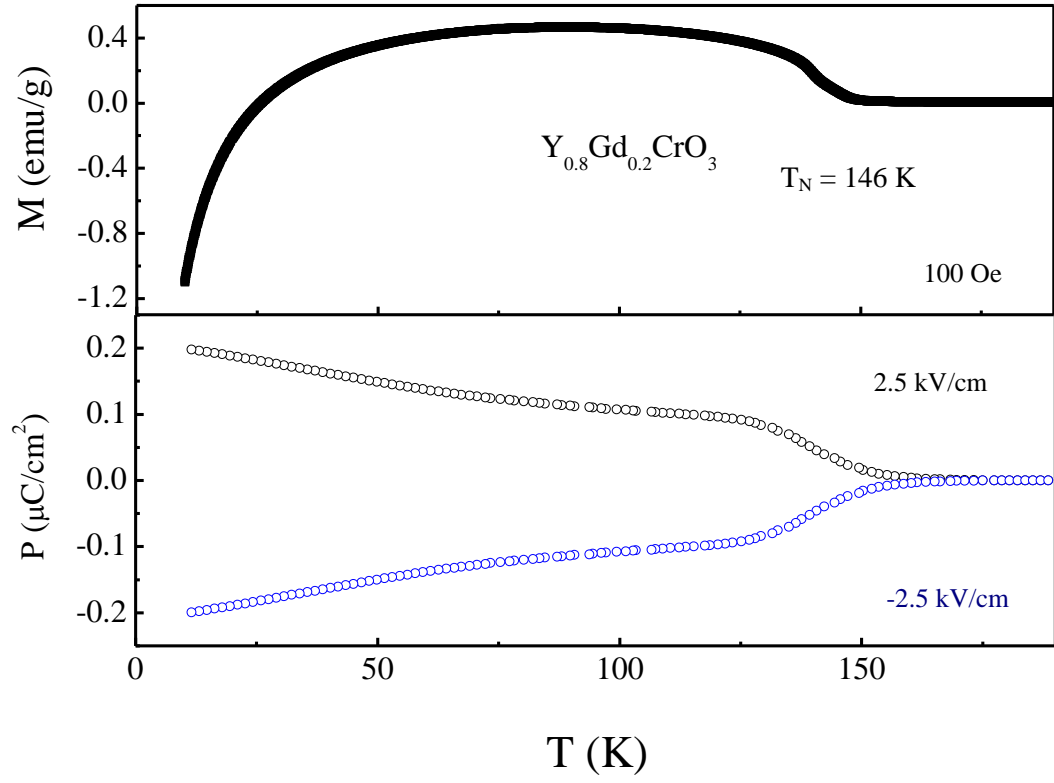
Fig. S7: Magnetization and corresponding polarization at the Cr ordering temperature in $Y_{0.8}Gd_{0.2}CrO_3$. It can be seen that there is a systematic decrease in the polarization values with the decrease in the relative proportion of the magnetic Gd^{3+} ion at the A-site.