Supporting Information (SI)

High magnetic coercive field in Ca-Al-Cr substituted strontium hexaferrite

Marian Stingaciu,[a,§] Durgamadhab Mishra[b,c] César de Julián Fernández,[c] Riccardo Cabassi,[c] Anna Zink Eikeland,[d] Mogens Christensen[d] and Stefano Deledda[a,*]

[a] *Institute for Energy Technology, Instituttveien 18, NO-2007 Kjeller, Norway*

[b] *Department of Physics, IIT Jodhpur, Karwad 342037 Rajasthan, India*

[c] *Institute of Materials for Electronics and Magnetism - CNR, Parco Area delle Scienza 37/A, 43124-Parma, Italy*

[d] *Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University Langelandsgade 140, DK-8000 Aarhus C, Denmark*

[§] Present Address: *Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University Langelandsgade 140, DK-8000 Aarhus C, Denmark*

* Corresponding author: stefano.deledda@ife.no

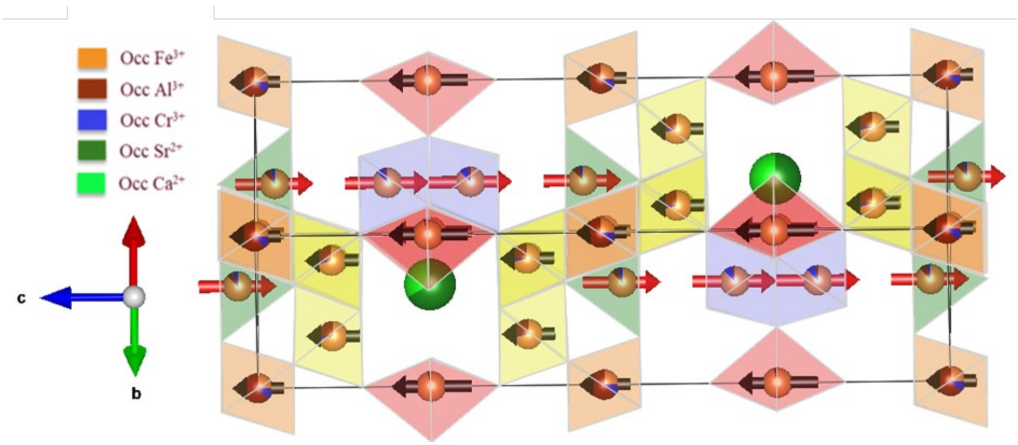

Figure S1. The crystal and magnetic structure of sample $Sr_{0.67}Ca_{0.33}Fe_9Al_{2.5}Cr_{0.5}O_{19}$.

Figure S2 shows the comparison of magnetic hysteresis loops of $SrFe_{12}O_{19}$ and $SrFe_9Al_3O_{19}$. The Al substitution shows a drop in saturation magnetization from 65.6 Am^2/kg to 23 Am^2/kg (at an applied field of 5 T) and corresponding increase in coercive field from 0.59 T to 1.08 T.

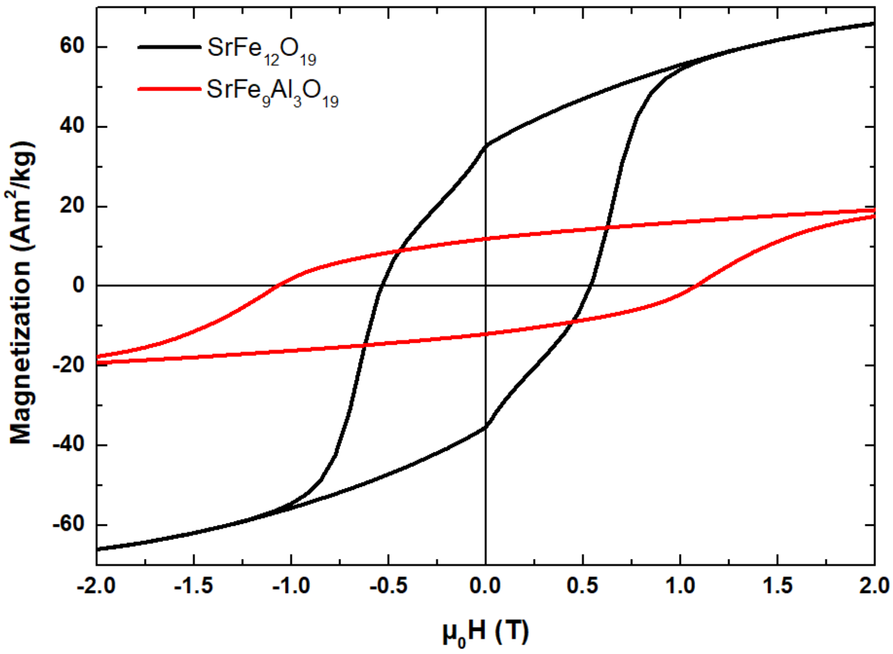

Figure S2. Hysteresis of sol-gel prepared $SrFe_{12}O_{19}$ and $SrFe_9Al_3O_{19}$.

There are two parameters, coercive field and switching field distribution, which are crucial in understanding the reversal mechanism of the samples. Ideally, one would like to have a high coercivity and narrow switching field distribution, which indicates a homogeneous single phase magnet. Therefore, the role of annealing is significant. Figures S3(a) and (b) show the hysteresis and first derivative of the hysteresis curves of $Sr_{0.67}Ca_{0.33}Fe_9Al_{2.5}Cr_{0.5}O_{19}$ samples annealed at 950° C and 1050° C, respectively. The sample annealed at 1050° C shows higher coercivity and slightly higher magnetization. This means, the sample has better crystallinity and homogeneity compared to sample annealed at 950° C. This is also evident from the first derivative of magnetization shown in Figure S3(b), where two peaks are observed in switching field distribution for sample annealed at 950° C annealed sample, whereas there is a single peak for 1050° C annealed sample with narrower distribution. The double peak feature indicates, secondary magnetic phases and inhomogeneities for low annealing temperature.

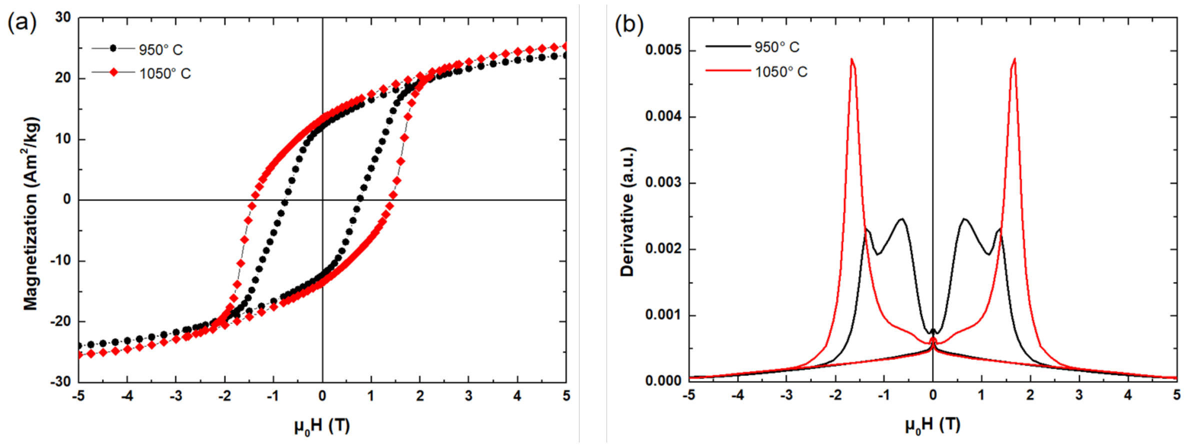

Figure S3. (a) Hysteresis of $Sr_{0.67}Ca_{0.33}Fe_9Al_{2.5}Cr_{0.5}O_{19}$ annealed at 950° C and 1050° C.

The substitution of Ca is expected to affect the coercivity. It was previously shown that Ca substitution leads to larger magneto crystalline anisotropy [27]. In our case we observed only small increase in coercivity due to addition of Ca. Figure S4 (a) and (b) show the comparison of hysteresis for samples $SrFe_9Al_3O_{19}$ and $SrFe_9Al_{1.5}Cr_{1.5}O_{19}$ before and after Ca substitution. The Ca substitution does not have effect on saturation magnetization, without any definite trend. The switching field distribution shown in Figure S4 (c) and (d) has a small but significant change due to Ca substitution. For both samples after Ca substitution the peak shifts to higher field indicating an improvement in anisotropy as expected before. The peaks are also narrower and sharper compared to unsubstituted ones, indicating better chemical homogeneities.

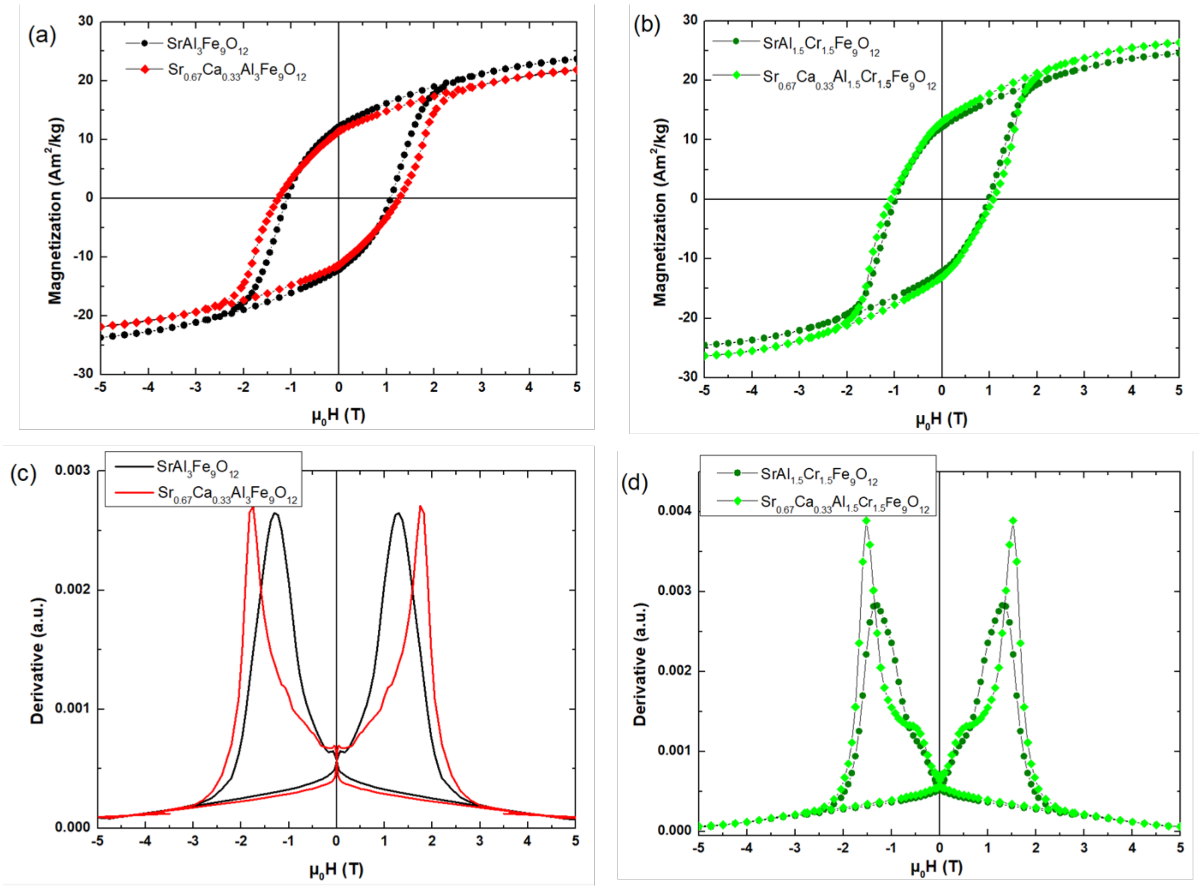

Figure S4. Hysteresis of samples with and without Ca substitution for (a) Cr-unsubstituted sample and (b) Crsubstituted sample. (c) and (d) First derivative (Switching field distributions) of corresponding samples.

We also performed the temperature dependence of the magnetization (M-T) measured at 5 T of magnetic field on two samples, $Sr_{0.67}Ca_{0.33}Fe_9Al_{2.5}Cr_{0.5}O_{19}$ and $Sr_{0.67}Ca_{0.33}Fe_9Al_2Cr_1O_{19}$ from 10 K up to 320 K, as shown in Figure S5. The magnetization decreases gradually with temperature as expected for M-ferrites. We did not observe any magnetization around 260 K that could be correlated to the Morin transition of the hematite (α-Fe_2O_3), although x-ray diffraction pattern showed its presence. Most likely, the Morin transition is suppressed due to smaller volume present in the samples.

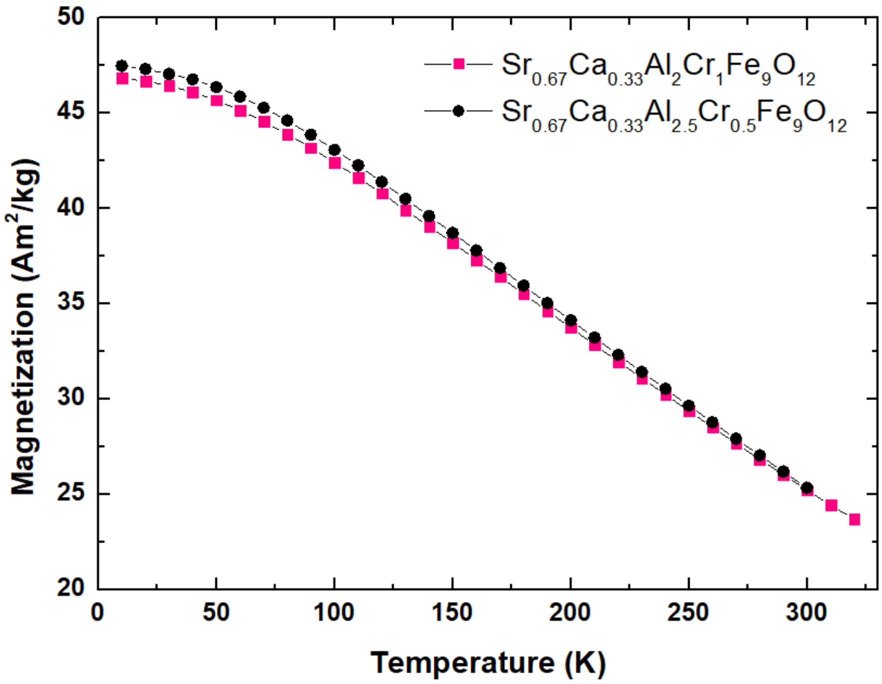

Figure S5. M-T of samples measured at 5 T applied field.

Table S1. Crystallographic parameters of $Sr_{0.67}Ca_{0.33}Fe_9Al_{3-x}Cr_xO_{19}$ (x=0, 0.5, 1.5, 2.5, 3.0)

Chemical formula	Crystal system	Space group	Cell param a=b (Å)	Cell param c (Å)	Volume (Å^3)
$Sr_{0.67}Ca_{0.33}Fe_9Al_{3.0}O_{19}$	Hexagonal	P 6_3/mmc	5.81301(4)	22.7889(2)	666.89(1)
$Sr_{0.67}Ca_{0.33}Fe_9Al_{2.5}Cr_{0.5}O_{19}$			5.82266(6)	22.7966(3)	669.33(1)
$Sr_{0.67}Ca_{0.33}Fe_9Al_{1.5}Cr_{1.5}O_{19}$			5.8377(2)	22.827(1)	673.72(2)
$Sr_{0.67}Ca_{0.33}Fe_9Al_{0.5}Cr_{2.5}O_{19}$			5.85721(1)	22.87699(8)	679.691(4)
$Sr_{0.67}Ca_{0.33}Fe_9Cr_{3.0}O_{19}$			5.86678(1)	22.89890(8)	682.568(4)

Table S2. The atomic coordinates and refined occupancies of $Sr_{0.67}Ca_{0.33}Fe_9Al_{3-x}Cr_xO_{19}$ (x=0, 0.5, 1.5)

Composition $Sr_{0.67}Ca_{0.33}Fe_9Al_{3-x}Cr_xO_{19}$	Atom type	Atoms coordinates			Occupancies
		x	y	z	
X=0	Fe-Oh2	0	0	0	0.320(12)
	Al-Oh2	0	0	0	0.680(12)
	Fe-BP	0	0	0.25	0.962(14)
	Al-BP	0	0	0.25	0.038(14)
	Fe-Th	0.333333	0.666667	0.02749(10)	0.869(9)
	Al-Th	0.333333	0.666667	0.02749(10)	0.131(9)
	Fe-Oh1	0.333333	0.666667	0.18990(9)	0.953(9)
	Al-Oh1	0.333333	0.666667	0.18990(9)	0.047(9)
	Fe-Oh3	0.16861(19)	0.3372(4)	0.89110(6)	0.679(5)
	Al-Oh3	0.16861(19)	0.3372(4)	0.89110(6)	0.321(5)
X=0.5	Fe-Oh2	0	0	0	0.28(4)
	Cr-Oh2	0	0	0	0.06(5)
	Al-Oh2	0	0	0	0.66(7)
	Fe-BP	0	0	0.25	0.969(10)
	Al-BP	0	0	0.25	0.035(10)
	Fe-Th	0.333333	0.666667	0.02748(10)	0.91(2)
	Al-Th	0.333333	0.666667	0.02748(10)	0.13(3)
	Fe-Oh1	0.333333	0.666667	0.19010(10)	0.94(3)
	Cr-Oh1	0.333333	0.666667	0.19010(10)	0.01(4)
	Al-Oh1	0.333333	0.666667	0.19010(10)	0.07(5)
	Fe-Oh3	0.1680(2)	0.3360(4)	0.89104(6)	0.675(15)
	Cr-Oh3	0.1680(2)	0.3360(4)	0.89104(6)	0.073(19)
	Al-Oh3	0.1680(2)	0.3360(4)	0.89104(6)	0.25(2)
X=1.5	Fe-Oh2	0	0	0	0.41(4)
	Cr-Oh2	0	0	0	0.11(4)
	Al-Oh2	0	0	0	0.48(6)
	Fe-BP	0	0	0.25	0.98(3)
	Al-BP	0	0	0.25	0.086(5)
	Fe-Th	0.333333	0.666667	0.02741(5)	0.86(2)
	Cr-Th	0.333333	0.666667	0.02741(5)	0.05(3)
	Al-Th	0.333333	0.666667	0.02741(5)	0.11(3)
	Fe-Oh1	0.333333	0.666667	0.19042(5)	0.89(2)
	Cr-Oh1	0.333333	0.666667	0.19042(5)	0.08(3)
	Al-Oh1	0.333333	0.666667	0.19042(5)	0.05(4)
	Fe-Oh3	0.16840(10)	0.3368(2)	0.89110(3)	0.681(13)
	Cr-Oh3	0.16840(10)	0.3368(2)	0.89110(3)	0.202(16)
	Al-Oh3	0.16840(10)	0.3368(2)	0.89110(3)	0.12(2)

References

[27] L.A. Trusov, E.A. Gorbachev, V.A. Lebedev, A.E. Sleptsova, I.V. Roslyakov, E.S. Kozlyakova, A.V. Vasiliev, R.E. Dinnebier, M. Jansen, P.E. Kazin **Ca-Al double-substituted strontium hexaferrites with giant coercivity** Chem. Commun., 54 (2018), pp. 479-482.