**Supplementary Information**

**"Investigation of Ferrimagnetism and Ferroelectricity in $Al_xFe_{2-x}O_3$ Thin Films"**

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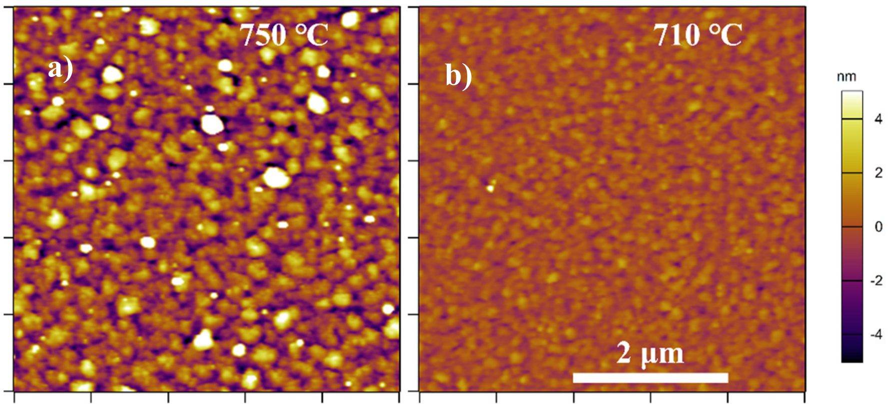


**Figure S1.** AFM topography images of 0.5-AFO films, displaying the effect of substrate temperature during the film deposition. The length and color scaling has been kept same for both the images. The films grown at 750 °C **(a)** have higher roughness of around 3 nm and larger grain size, as compared to films grown at 710 °C **(b)** (film roughness ~ 0.6 nm).

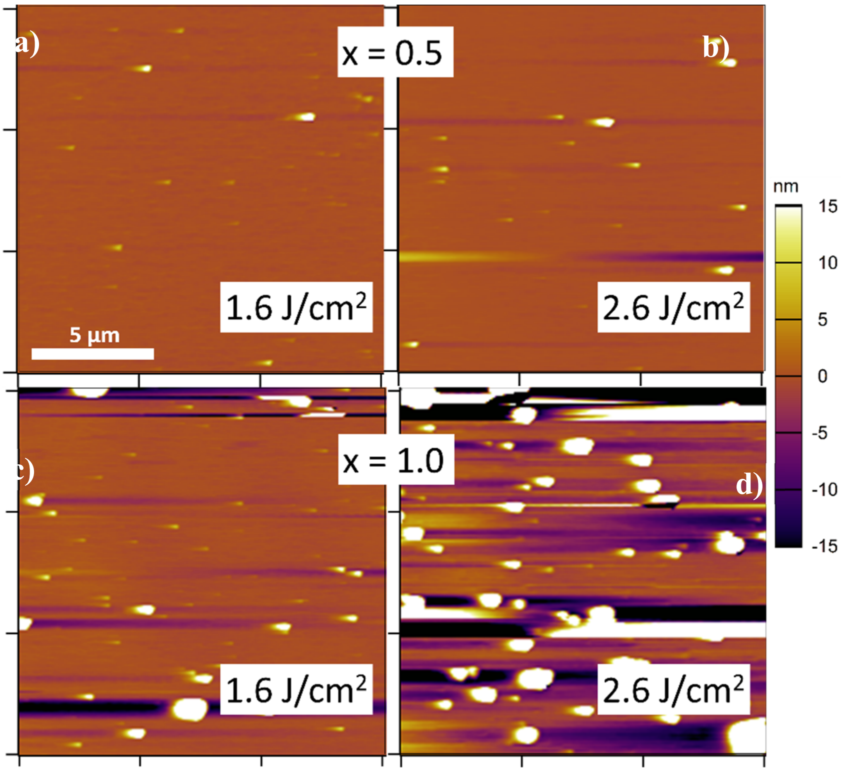


**Figure S2.** AFM topography images displaying the effect of laser fluence on the droplet formation in the films. The laser fluence used for each film is displayed over the figure in units of J/cm$^2$. The length and color scaling has been kept same for all the AFM images. **a)** and **b)** compare the effect for 0.5-AFO, while **c)** and **d)** compare for the 1-AFO films. It can be seen that for lower Al composition ($x$ = 0.5), the droplet formation is minimum for both the laser fluence considered. However, for composition with higher Al content ($x$ = 1), there is tremendous increase in droplet formation upon increase in laser fluence. This clearly establishes that the targets with higher Al-content are more prone to droplet formation.

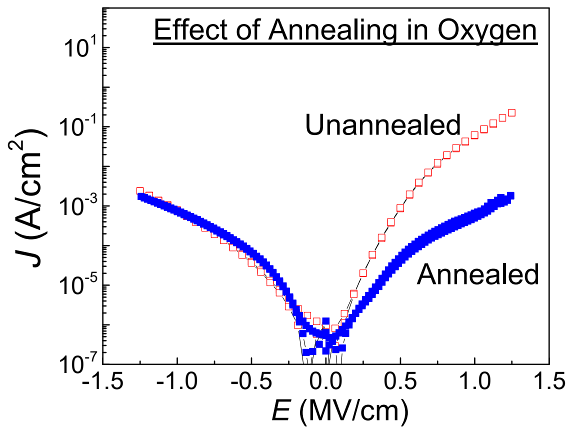


**Figure S3.** Leakage current density ($J$) versus electric field ($E$) plot comparing 0.5-AFO films with and without successive annealing at 600°C for 30 minutes under 100 Torr oxygen, inside the PLD chamber. It can be seen that the unannealed films are more leaky compared to the annealed films.

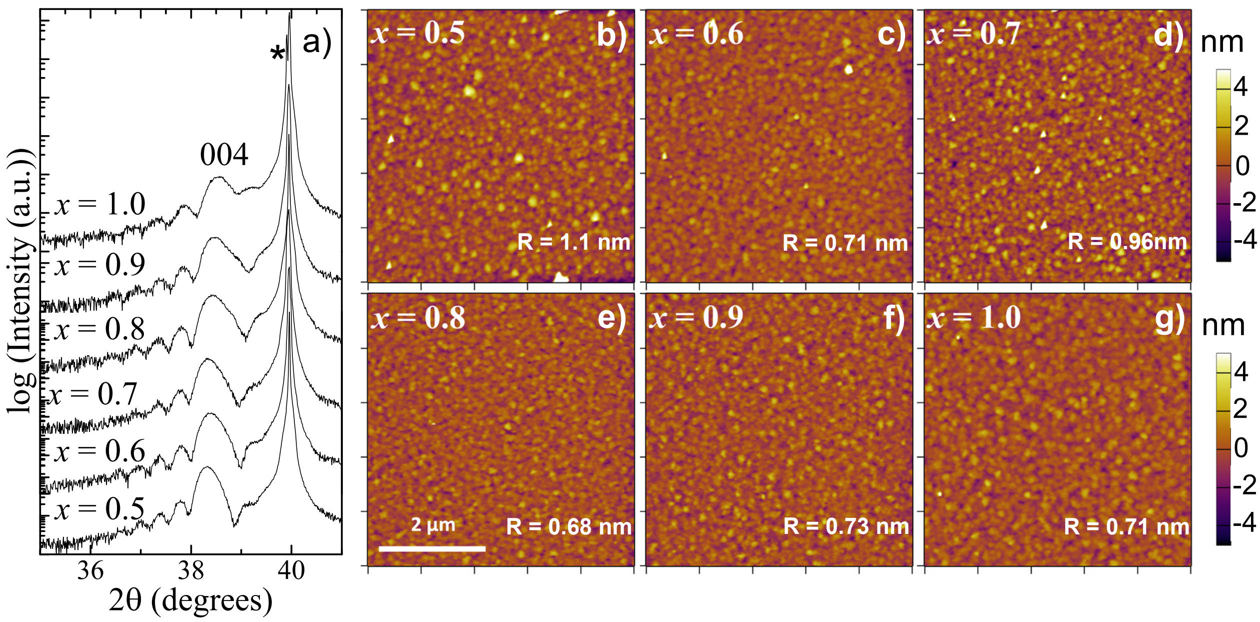


**Figure S4. a)** Out of plane *x*-ray diffraction pattern of the 004 peak of the films for different compositions studied. Observation of fringes in the 004 peak for all the compositions indicates the high flatness of the films. **(b-g)** Surface topography of the films of various compositions, imaged using AFM, confirming the low roughness of the films. 'R' indicates the RMS roughness, which is around 0.6 – 1.1 nm for all the films. The length and color scaling has been kept same for all the AFM images.

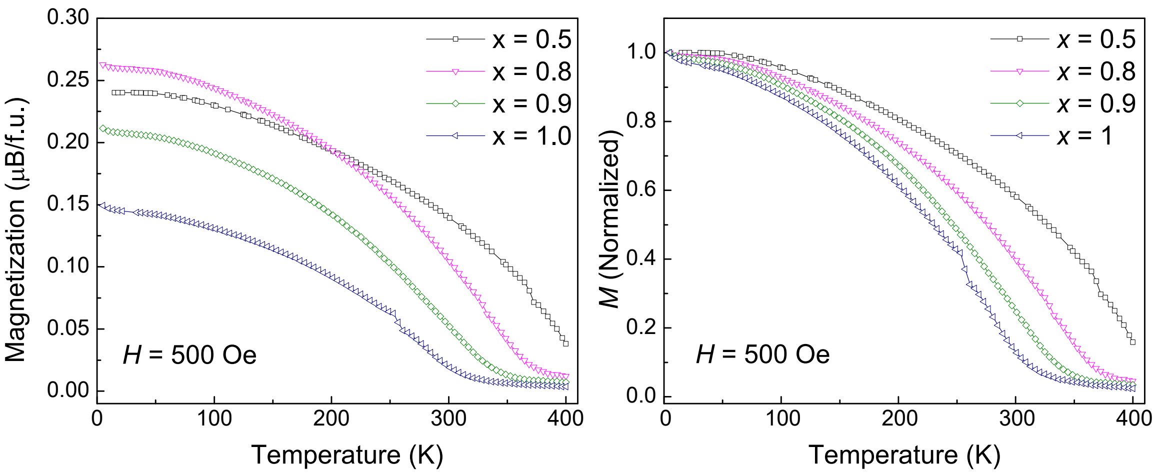


**Figure S5.** Magnetization vs. Temperature plot for films grown at 300 mTorr ($P_{O_2}$), showing lower Curie temperature than in figure 3, as well as decrease in Curie temperature with increasing *x*. It must be noted that the low temperature magnetization for *x* = 0.8 is still the highest among all the compositions, thereby clearly establishing that the maximum occupancy of Al in Al1 site is for this composition. For compositions above 0.8, the Al begins to occupy the Al2 sites also, thereby decreasing their magnetization. The normalized plot is also shown at the right, to depict the respective Curie temperatures more clearly. It is also interesting to note that the absolute value of magnetization at low temperatures has decreased with respect to films grown at 100 mTorr ($P_{O_2}$). In addition, the effect is more pronounced for $x \geq 0.8$.

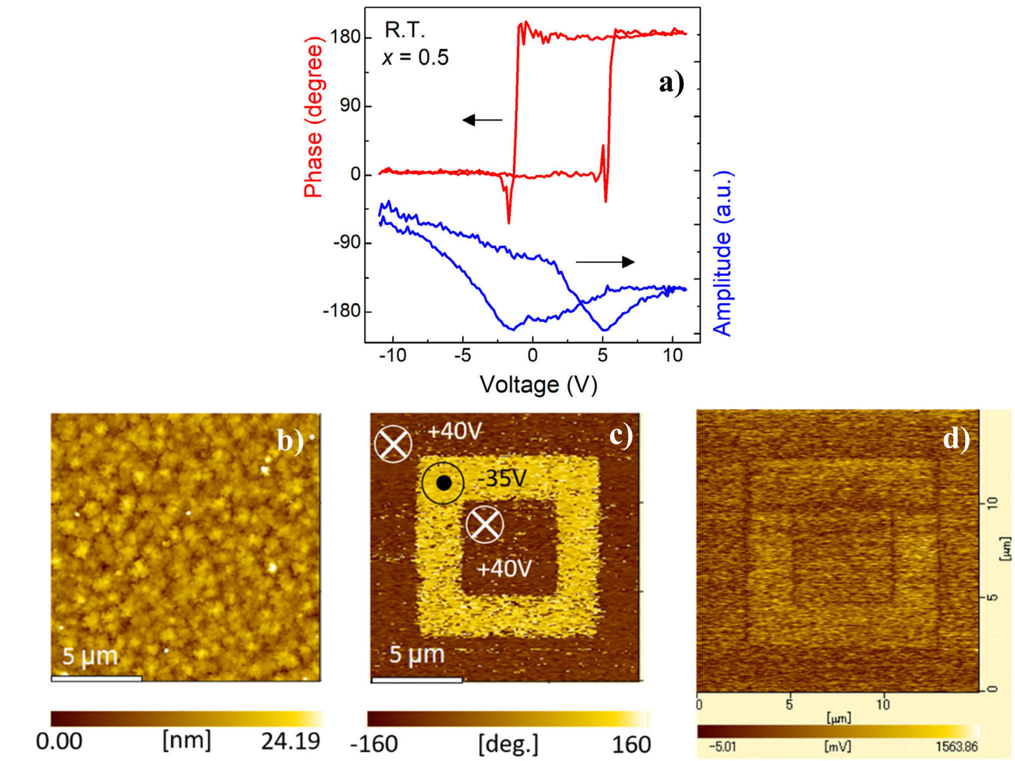


**Figure S6. (a)** The amplitude and phase curves of 0.5-AFO films, obtained from piezoresponse force microscopy (PFM), clearly depicting domain switching. **(b)** shows the surface topography of the films while **(c)** and **(d)** shows the PFM phase and amplitude response respectively of an electrically poled region. The films were differently poled at a rather high voltage of +40 V and -35 V in three regions as shown in **(d)**, in order to obtain contrast in the PFM. While the above PFM results strongly suggest the films to be ferroelectric in nature, only some films gave such good PFM response, which is why we opted for direct measurements using the ferroelectric tester.

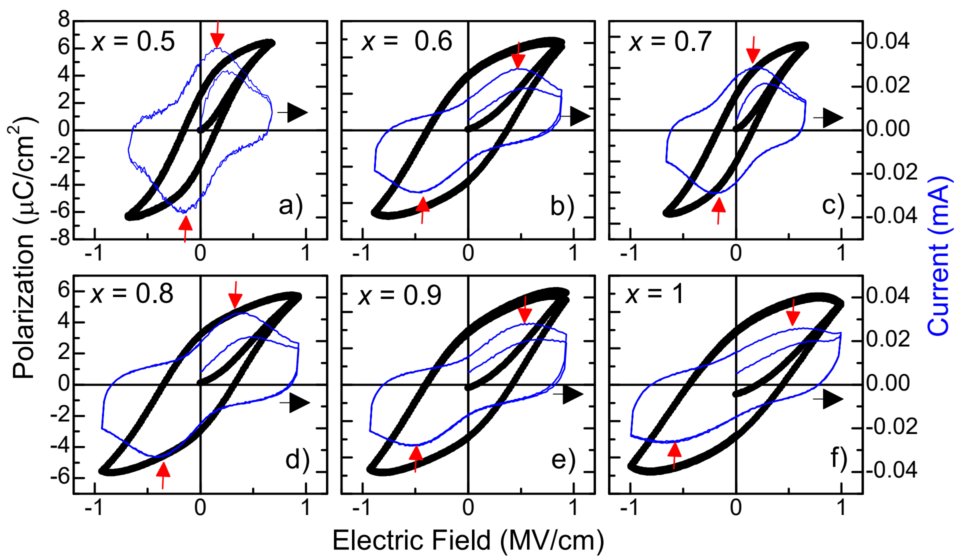


**Figure S7. (a-f)** Polarization vs Electric field (*PE*) and current dependence of electric field (*IE*) for various compositions of the film, collected at 10 kHz. The peak in the *IE* curve corresponding to ferroelectric switching is indicated by red arrows.

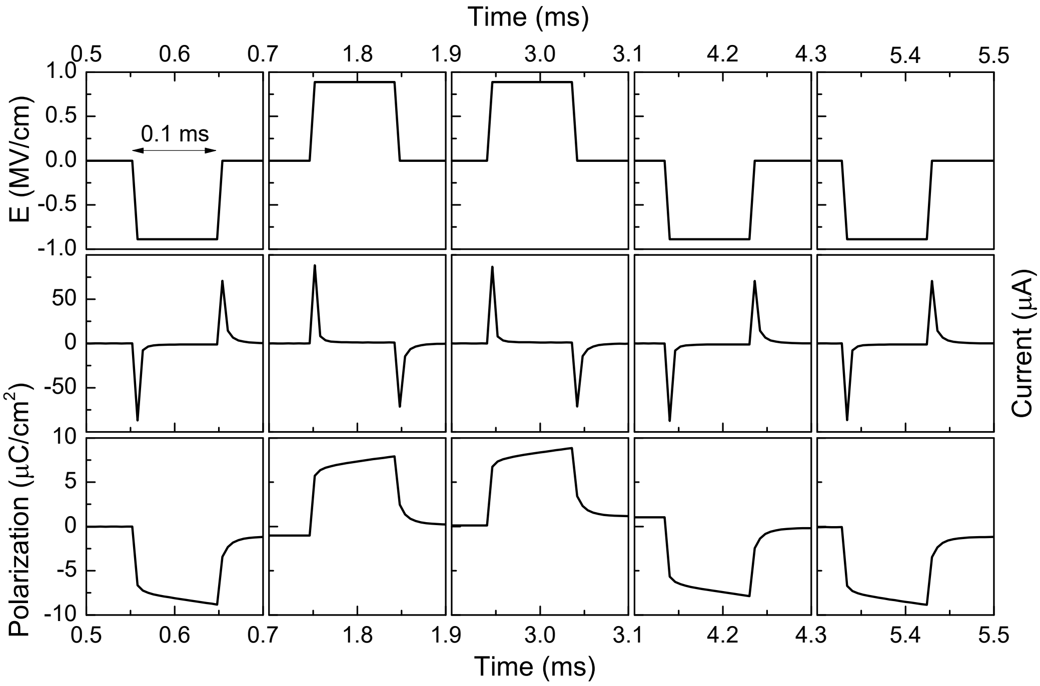


**Figure S8.** Applied electric field (top row) and resulting current flow (centre row) and polarization (bottom row) from a PUND measurement of 0.5-AFO at 300 K. Each pulse had a period of 0.1 ms, corresponding to a frequency of 10 kHz. The second and fourth pulses are the switching pulses, while the third and fifth are non-switching pulses. Appearance of large current even at the non-switching pulses indicate a major contribution from the extrinsic effects. This is the reason why we observe a very small remnant polarization from PUND measurement, which is the true intrinsic polarization.

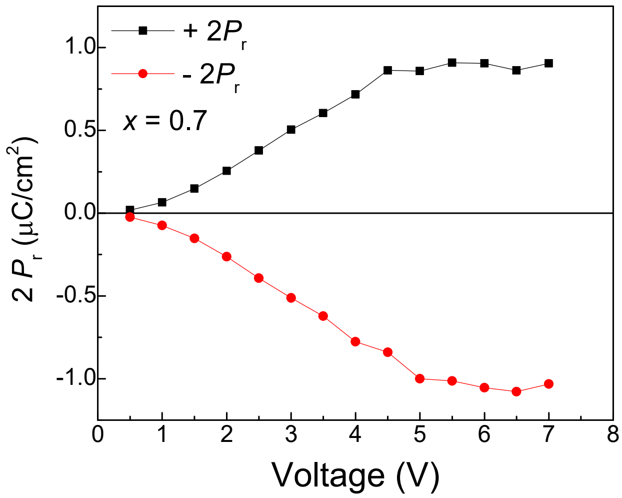


**Figure S9.** Remnant polarization as a function of pulse voltage, as obtained from the PUND measurement. We can clearly observe saturation in the polarization above 5 V, similar to conventional ferroelectrics.

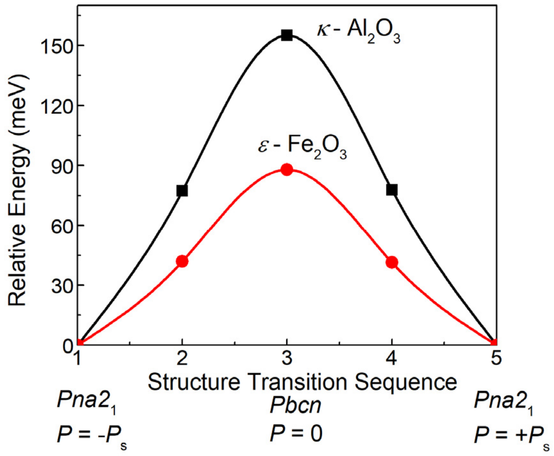


**Figure S10.** Variation of relative energies of $\kappa$-$Al_2O_3$ and $\varepsilon$-$Fe_2O_3$ during polarization switching through an intermediate centrosymmetric structure *Pbcn*.

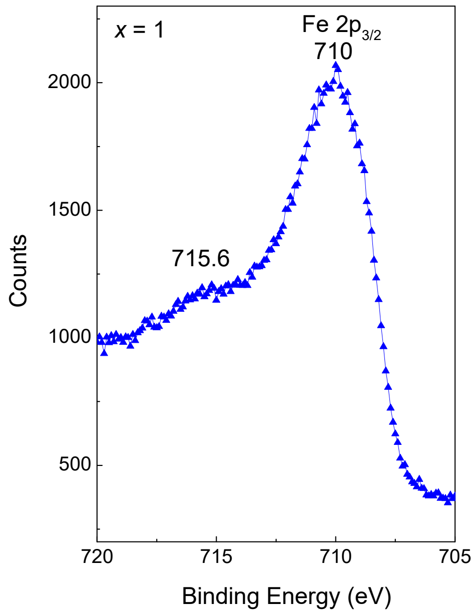


**Figure S11.** X-ray photoelectron spectrum of the Fe $2p_{3/2}$ line for 1-AFO film. For $Fe^{3+}$, we expect a peak at 711 eV and a satellite peak at 719 eV, whereas for $Fe^{2+}$, we expect a peak at 709.5 eV and a satellite peak at 716 eV (Eerenstein *et al.*, Science, 2005, Ref. 10 in the manuscript). While the broad peak at 710 in our film could indicate mixture of $Fe^{2+}/Fe^{3+}$ ions, the presence of satellite peak at 515.6 eV is a definite indicator for presence of $Fe^{2+}$ in our films. Cation charge deficiency caused due to presence of $Fe^{2+}$ ions may balance by formation of oxygen vacancies, which usually segregate near the domain boundaries.