Electronic Supplementary Information

Reversible control of chromium valence in chemically reduced Cr-doped $SrTiO_3$ bulk powders

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Quantitative EPR Measurements. For quantitative measurements of EPR, the following protocol was used as described in [1]. All sample volumes were matched in the EPR tubes in order to ensure the same pathlength of absorption during the measurement. Samples were ground to ensure that no clumping of powders would affect the amount of sample in each tube. The use of a finger dewar ensured that each sample was in the same spot relative to the microwave frequency. All parameters for the measurement were held constant during measurement, and minor adjustments to the frequency were made in order to keep the quality factor constant between different samples.

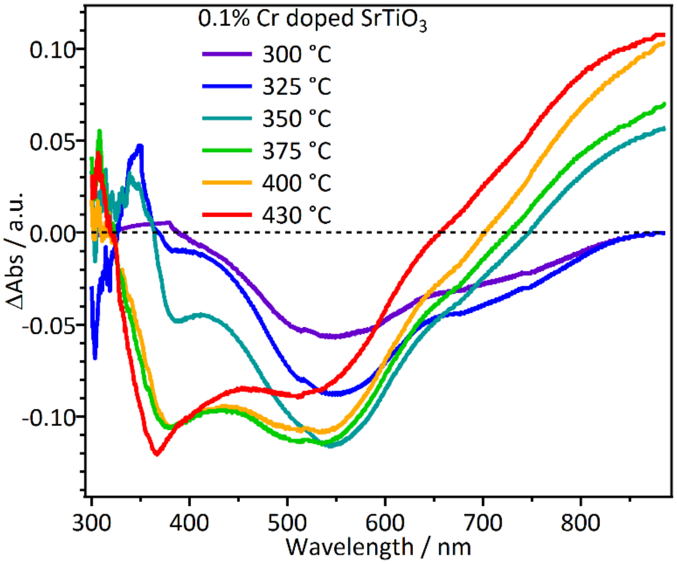

Fig 1. Change in the diffuse reflectance spectra from Cr:STO-ap to after reduction at different temperatures. The dashed black line is at zero.

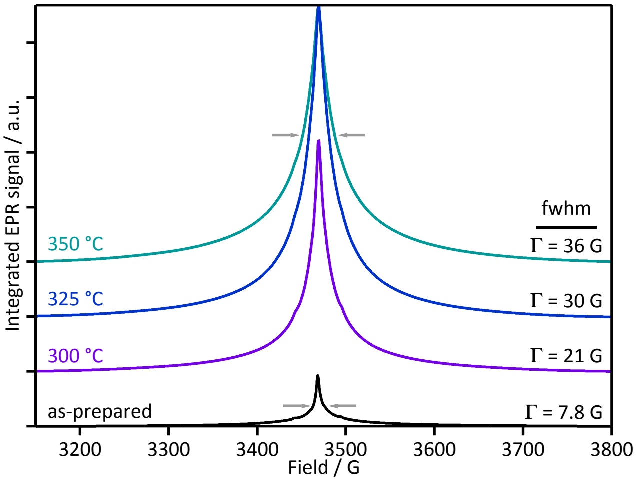

Fig 2. Integrated EPR signal of Cr:STO samples as-prepared and after $NaBH_4$ reduction at different temperatures.

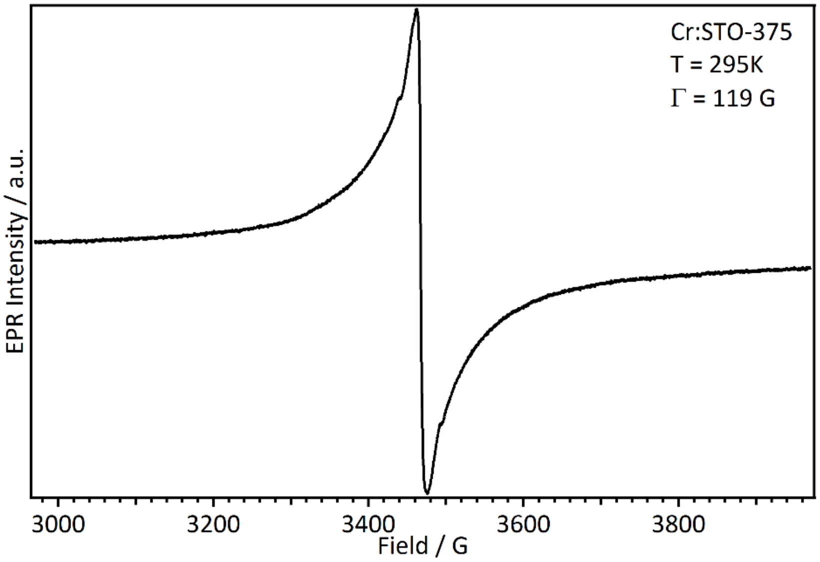

Fig 3. Room temperature EPR spectrum of Cr:STO-375.

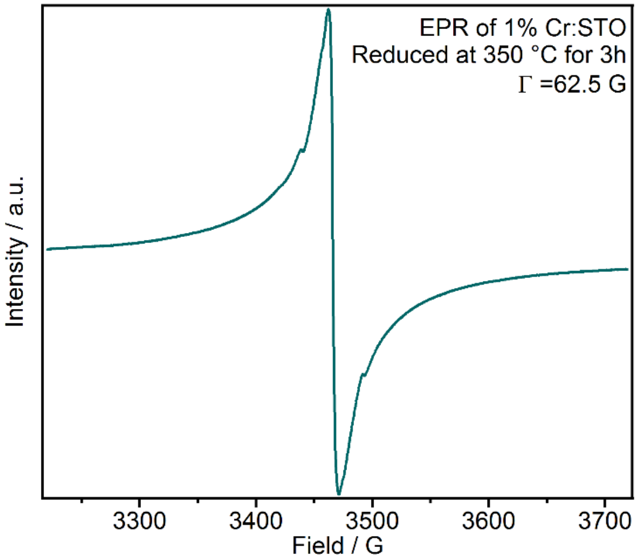

Fig 4. EPR spectrum of Cr:STO-350 after reduction for 3 h instead of 30 minutes.

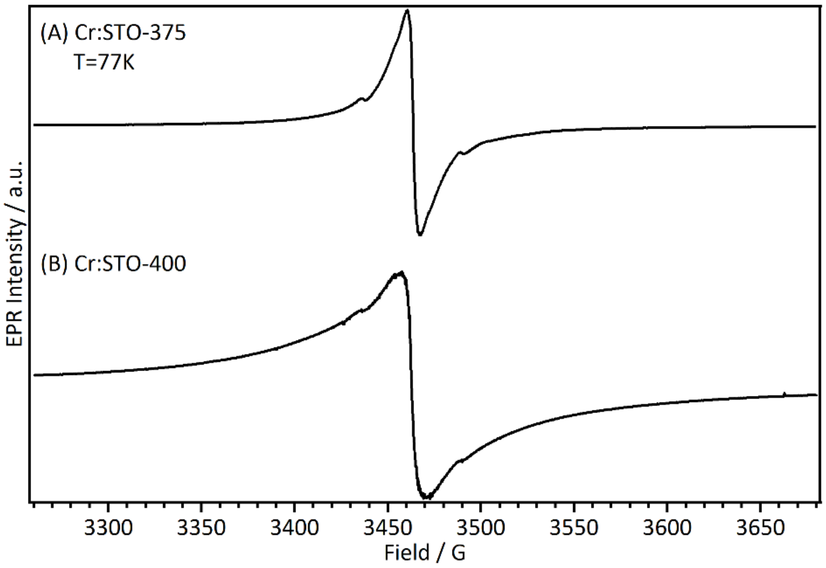

Fig 5. EPR spectroscopy of Cr:STO-325 (A) and Cr:STO-375 (B) at 77 K.

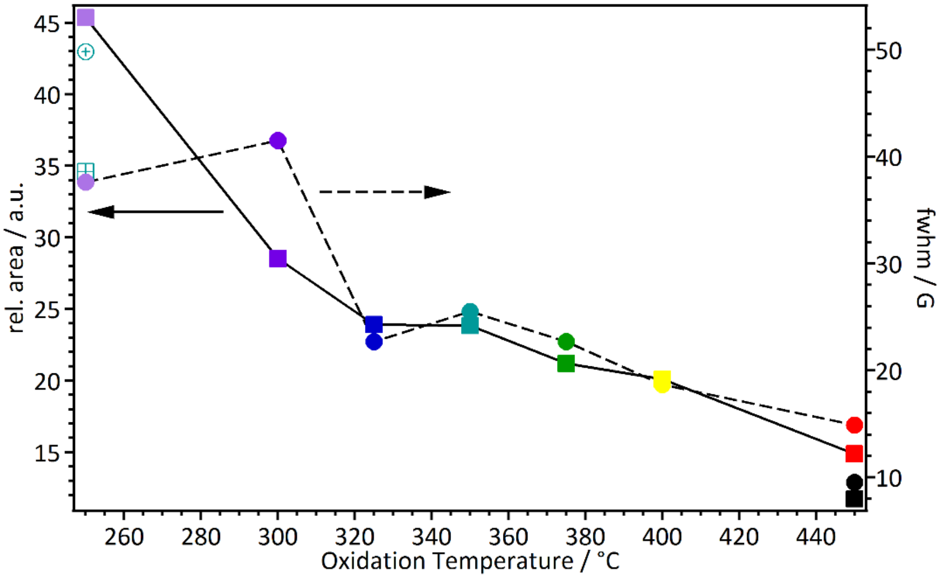

Fig 6. Area and full-width half max analysis for quantitative EPR measurements for oxidation of Cr:STO-350 (open markers) at different temperatures. As-prepared values added for reference.

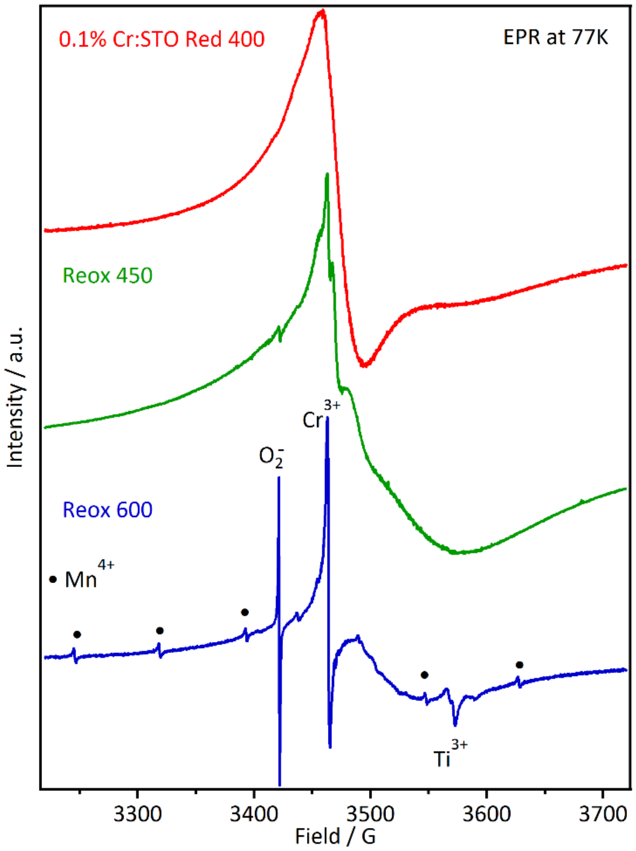

Fig 7. EPR spectra of 0.1% Cr:STO reduced at 400 °C and after oxidation at 450 and 600 °C. Spectra were collected at 77 K. Trace Mn^{4+} impurity was observed in the reox 600 sample. As the Ti^{3+} signal decreases in intensity, a feature at g=1.920 is visible which is consistent with a rhombic Ti^{3+} center in $SrTiO_3$ [2].

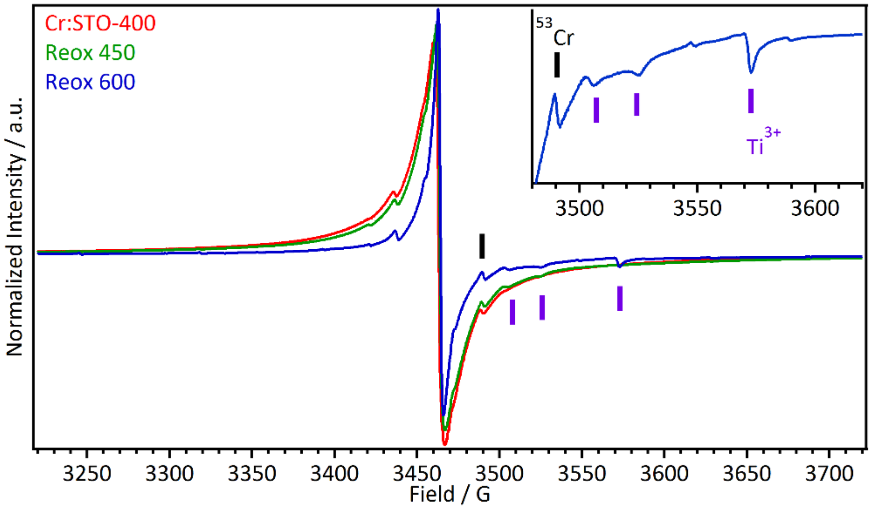

Fig 8. EPR spectra of Cr:STO-400 and after oxidation at 450 and 600 °C taken at 77 K.

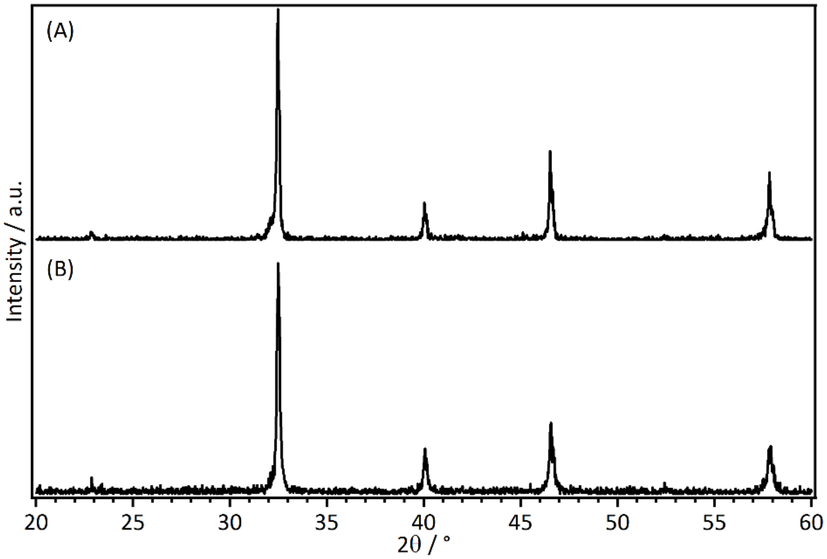

Fig 9. XRD patterns after reoxidation at 450 °C of (A) Cr:STO-350 and (B) Cr:STO-400.

References

[1] G. R. Eaton, S. S. Eaton, D. P. Barr and R. T. Weber, *Quantitative EPR*, Springer Vienna, 2010.

[2] O. F. Schirmer and K.A. Muller, *Phys. Rev. B*, 1973, **7**, 2986-2995.