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The Photoactive Nitrogen Impurity in Nitrogen-doped Zirconium Titanate (N-$ZrTiO_4$): A Combined Electron Paramagnetic Resonance and Density Functional Theory Study

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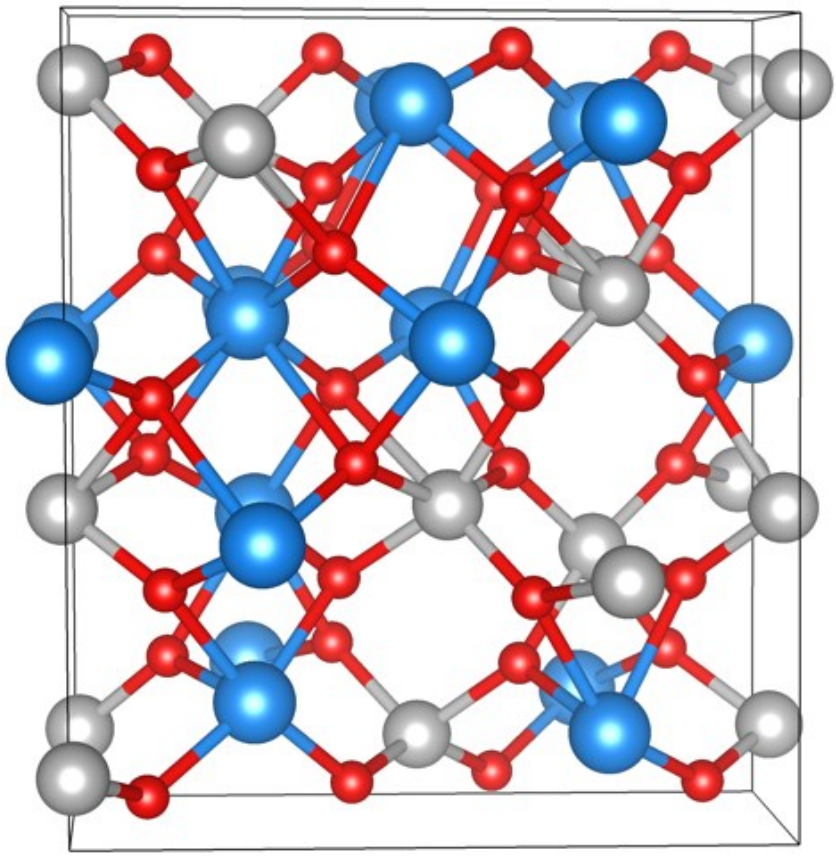

Figure S1: Optimized supercell of ZrTiO4. Gray spheres represent Ti atoms, light blue Zr and red O atoms.

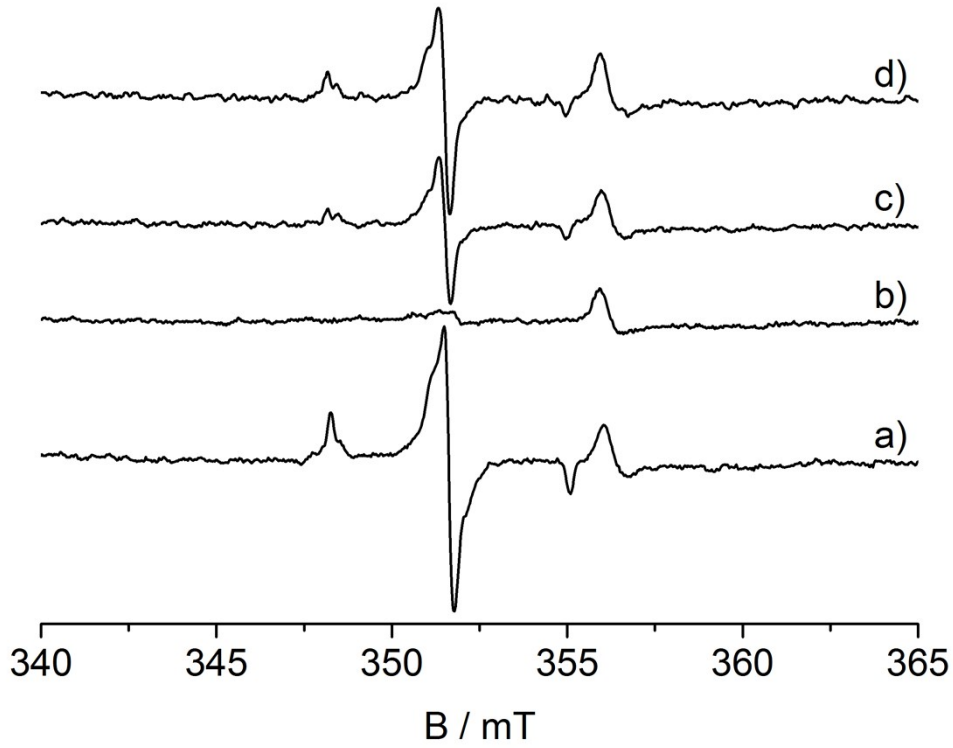

Figure S2. EPR spectra of the N-$ZrTiO_4$ sample. a) outgassed at RT. b) after annealing at 773K for 30 min. c) after oxidation at 773K for 60 min. in 50mabr of O_2. d) after oxidation at 773K for 180 min. in 50mabr of O_2. Spectra recorded at RT.

Figure S2 shows the effect of the thermal annealing in vacuum at 773K which causes a strong decrease of the EPR intensity of the specie $N^{\bullet}$ (Figure S2b). In this condition oxygen deplection occurs leaving two extra electrons per vacancy in the solid. Extra electrons are thus localized on the nitrogen states reducing the paramagnetic population in the doped solid. The whole process can be described by the following equation.

$$ZrTiO_4 \longrightarrow ZrTiO_{4-X} + \frac{X}{2} O_2 + {}^{x}V_{O}^{\bullet\bullet} + 2e^{-}$$

$$N^{\bullet}(\uparrow) + e^{-} \longrightarrow N^{-}(\uparrow\downarrow)$$

Upon the reoxidation at the same temperature the EPR signal increases, although the initial intensity is not fully recovered (Figure S2c). This fact can be ascribed to the difficult oxidation of a low surface area material as in the case of N-ZT (12 m^2/g). Indeed, performing an oxidation for a longer time than in the previous step (Figure S2d) an higher increase of the EPR signal is achieved.