Supporting Information

Electronic and plasmonic phenomena at nonstoichiometric grain boundaries in metallic $SrNbO_3$

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1. Strain mapping and EELS fitting

The bonding length (a_{exp}) is defined as the average distance between Nb and its four nearest neighbored cations, as schematically shown below in **Figure** S1(a). The strain mapping across the grain boundary is evaluated as the change of bonding length from the perfect crystal ($a_{perfect}$). The strain is calculated as the ratio of the changed and perfect bond lengths, that is $(a_{exp} - a_{perfect})/ a_{perfect}$. The atom positions from the HAADF image were measured by fitting the atom columns with a two-dimensional Gaussian peak using the Mac-TempasX software. Lastly, the strain is calculated using a customized Matlab code in **Figure** S1(b-c). The EELS O *K* edge was fitted by three Gaussian peaks as shown in Supplemental Materials **Figure** S3. The peak ratio in **Figure** 2(b) is calculated from the ratio of the integrated peaks *a* and *b*.

2. HAADF simulations of the grain boundary

The slight blurring of Sr columns localized at the GB might result from the displacement of Sr atoms by distortions along the electron beam direction (thickness direction). That is to say, the Sr atoms might be disorderly distorted and the blurring Sr columns are probably not periodic in the whole thickness range (*c* axis). For the proposed model in the DFT calculations, we simply the case to make it periodic in the thickness direction (*c* axis) to reduce the number of atoms in the model, as the non-stoichiometry of the Nb-rich GB is the main feature at the GB. To verify the assumption, a new atom model is built with the consideration of the nonperiodic Sr columns and the HAADF simulation is conducted as shown in **Figure** S6. The blurring contrast for the Sr columns with decreased intensity is similar to the experimental

results.

3. Calculation of optical properties

The loss function (LF), refractive index n, extinction coefficient κ, reflectivity R and absorption coefficient α are calculated from the dielectric functions based on the following equations:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \quad (1)$$

$$n = \sqrt{\frac{1}{2}[\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1]} \quad (2)$$

$$\kappa = \sqrt{\frac{1}{2}[\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1]} \quad (3)$$

$$R = \frac{[n-1]^2 + \kappa^2}{[n+1]^2 + \kappa^2} \quad (4)$$

$$\alpha = \frac{4\pi\kappa}{\lambda} \quad (5)$$

$$LF = -Im[\frac{1}{\varepsilon}] \quad (6)$$

The LF is shown in **Figure** 4. The refractive index n, extinction coefficient κ, reflectivity R and absorption coefficient α are shown in **Figure** 5 and **Figure** S9.

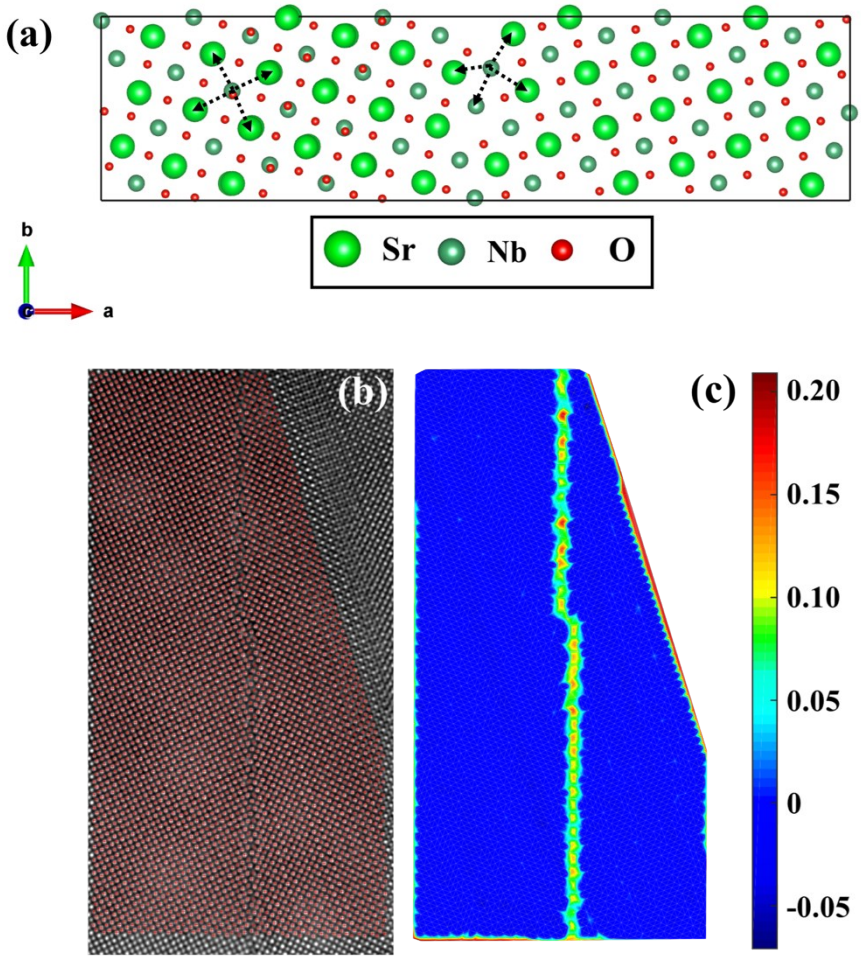

Figure S1. Strain mapping across the grain boundary of $SrNbO_3$. (a) Schematics of the bonding length for the calculation of strain mapping. The bonding in the perfect crystal and at the grain boundary are both indicated with black arrows. (b) Atomic resolution HAADF-STEM image of a $SrNbO_3$ grain boundary. The fitted atomic positions are overlaid with red crosses. (c) Calculated strain map corresponding to the left image. A large strain is localized in a narrow region at the grain boundary because of the structural discontinuity and distortions.

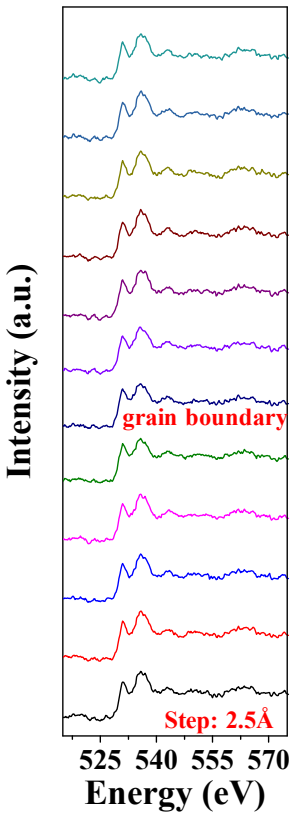

Figure S2. EELS line profiles of the O *K* edge across the grain boundary with a step size of 2.5 Å extracted from EELS mapping.

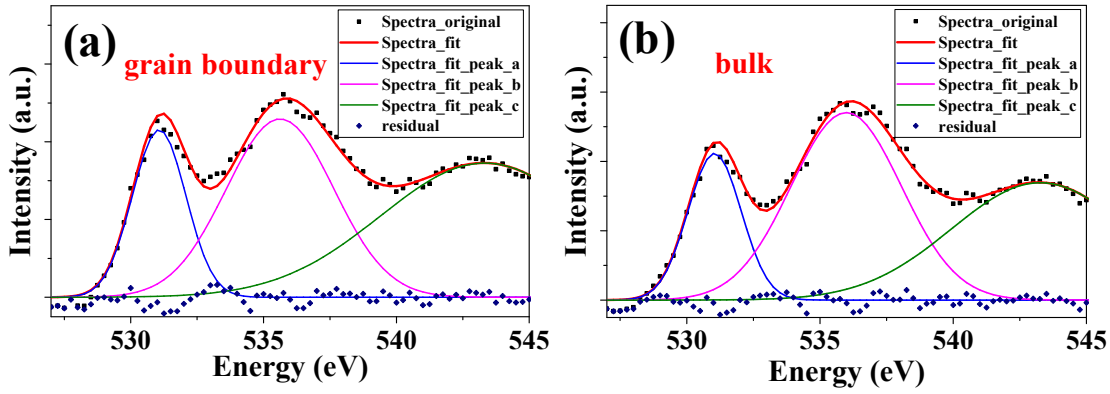

Figure S3. Fitted EELS O *K* edge by three Gaussian functions. (a) From bulk $SrNbO_3$. (b) From the $SrNbO_3$ GB.

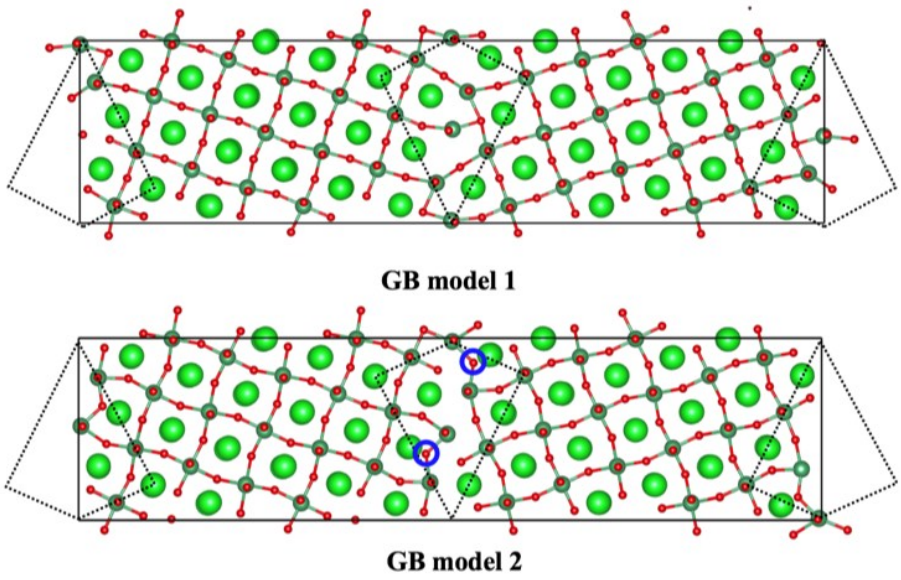

Figure S4. Grain boundary models with different oxygen configurations. The oxygen marked with blue circles in model 2 is not stable due to strong repulsive interaction. GB model 1 is used in the manuscript.

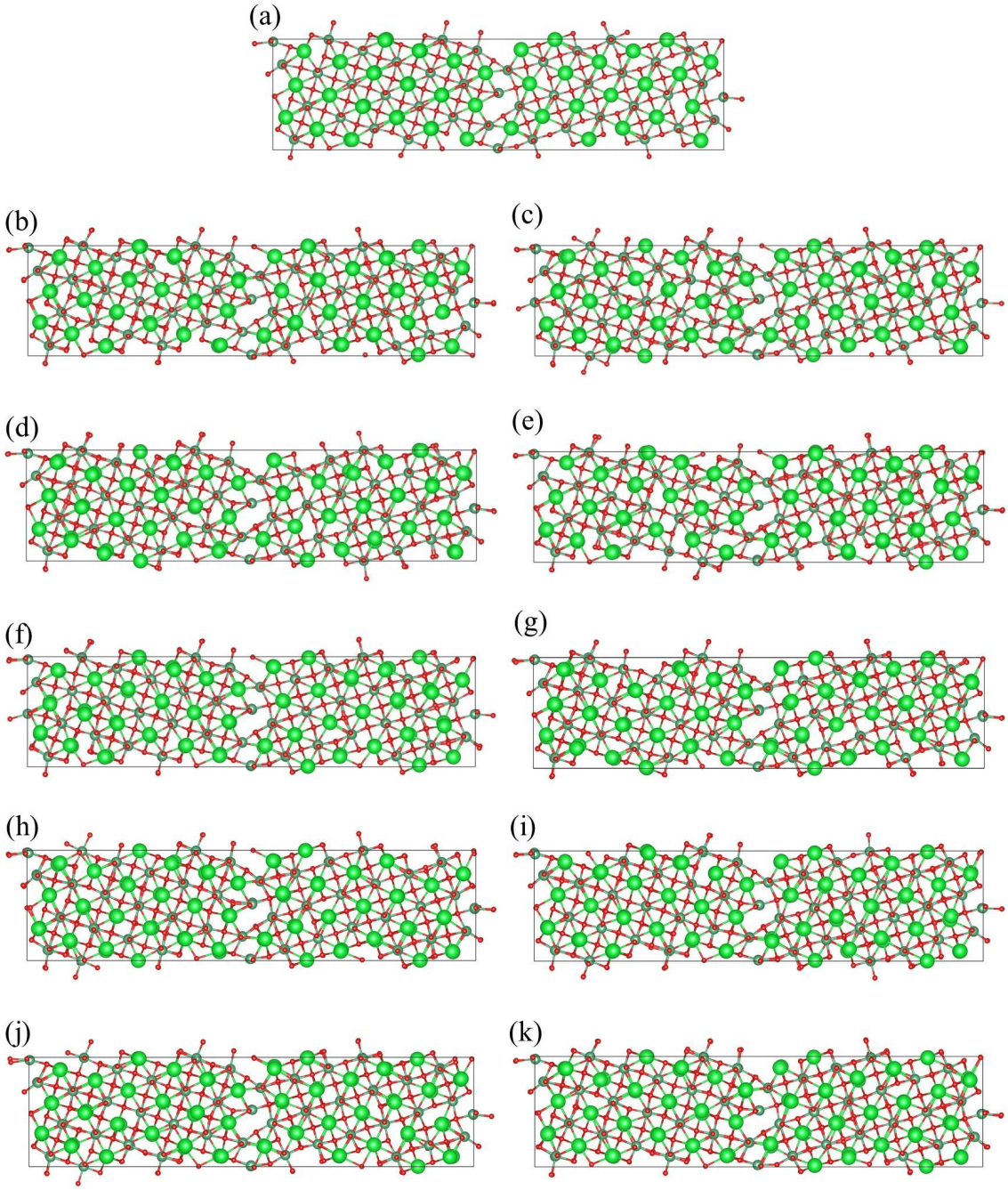

Figure S5. The ab initio MD simulation results of the GB model at a temperature of 300 K for 10000 fs. (a) initial structure at 0 fs, (b) 1000 fs, (c) 2000 fs, (d) 3000 fs, (e) 4000 fs, (f) 5000 fs, (g) 6000 fs, (h) 7000 fs, (i) 8000 fs, (j) 9000 fs, (k) 10000 fs.

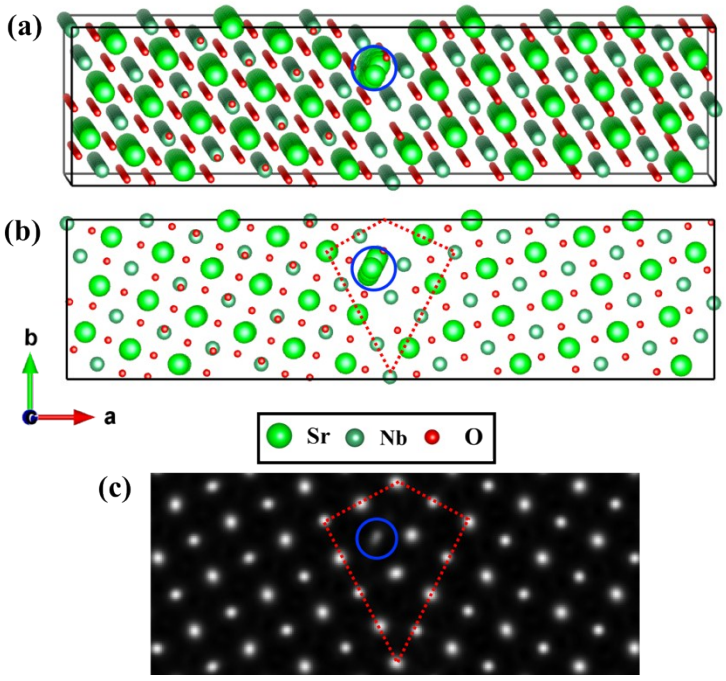

Figure S6. Atomic model of $SrNbO_3$ grain boundary in the perspective view (a) and projecting along *c* direction (b) with the consideration of random distortions of Sr columns along the thickness direction at the grain boundary. (c) HAADF simulations of the atom model in (b) conducted at accelerate voltage of 200 kV and convergence angle of 25 mrad, with the thickness of approximately 30 nm. The blurring Sr atom column with decreased intensity is indicated with blue circles.

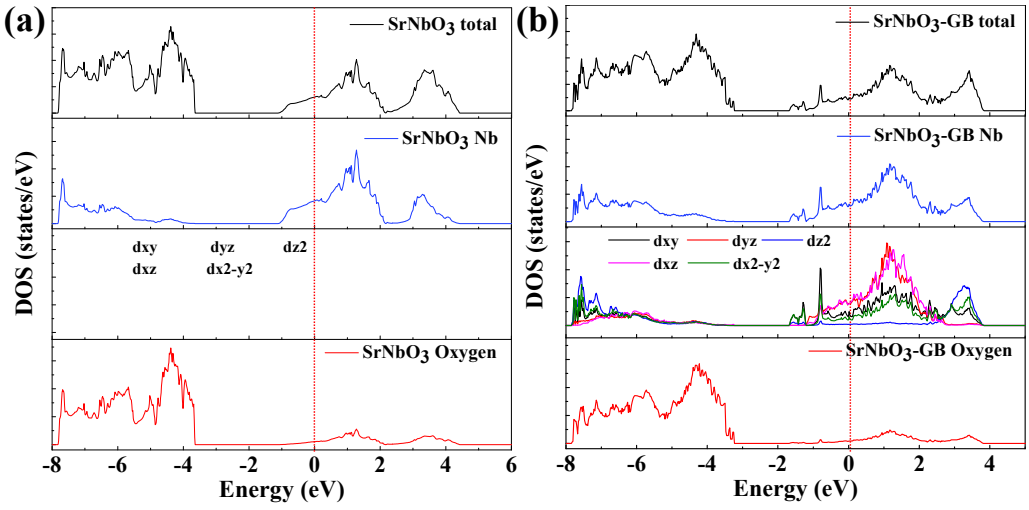

Figure S7. Total DOS, PDOS of Nb and O for $SrNbO_3$ bulk (a) and grain boundary (b), respectively.

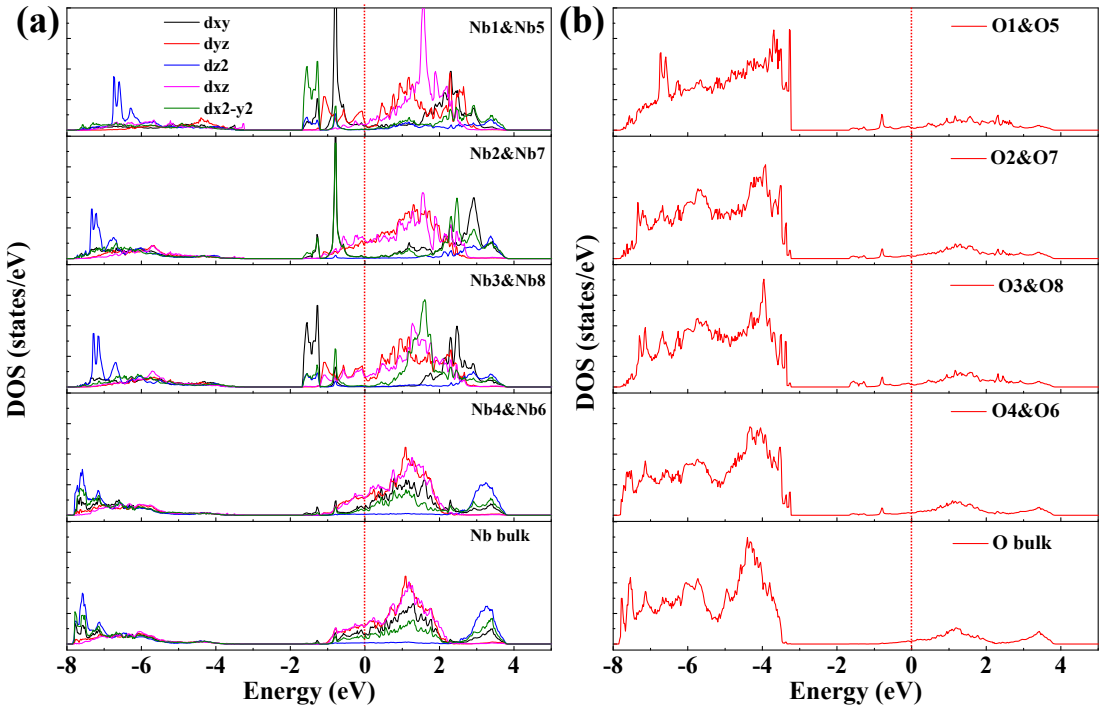

Figure S8. PDOS of different Nb atoms (a) and neighboring O atoms (b) extracted from the grain boundary.

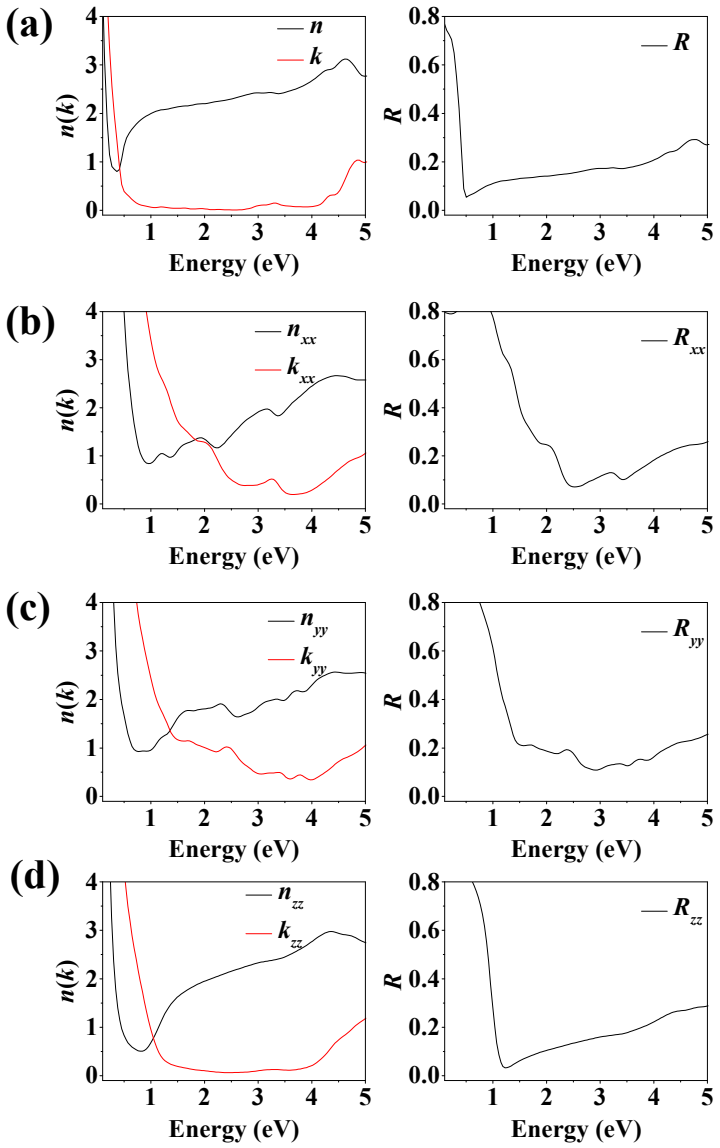

Figure S9. Optical properties calculated from dielectric functions for $SrNbO_3$ bulk (a) and grain boundary (b-d), corresponding to the absorption coefficients in Figure 5. The blue arrows indicate the absorption peaks of plasmon resonance. The black and red arrows indicate the absorption peaks of intraband and interband transitions, respectively.

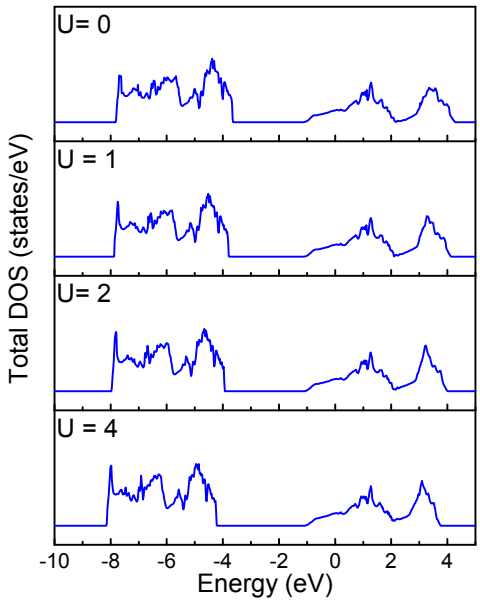

Figure S10. The total dos of bulk $SrNbO_3$ with different values of U.