Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

DFT calculations and giant dielectric responses in $(Ni_{1/3}Nb_{2/3})_xTi_{1-x}O_2$

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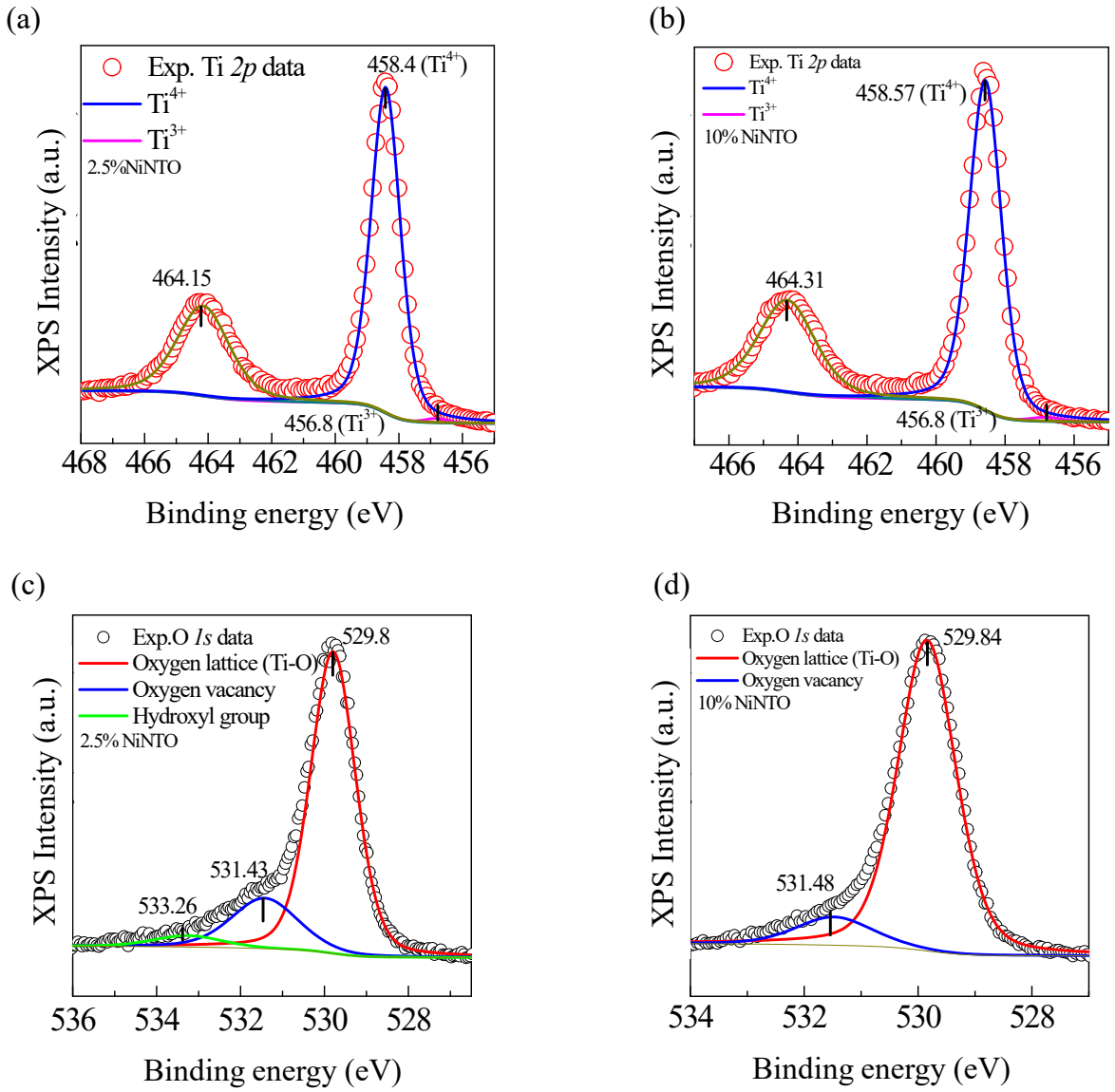

Fig. S1 Valence states of Ti *2p* for (a) 2.5%NiNTO and (b) 10%NiNTO and valence state of O *1s* for (c) 2.5%NiNTO and (d) 10%NiNTO.

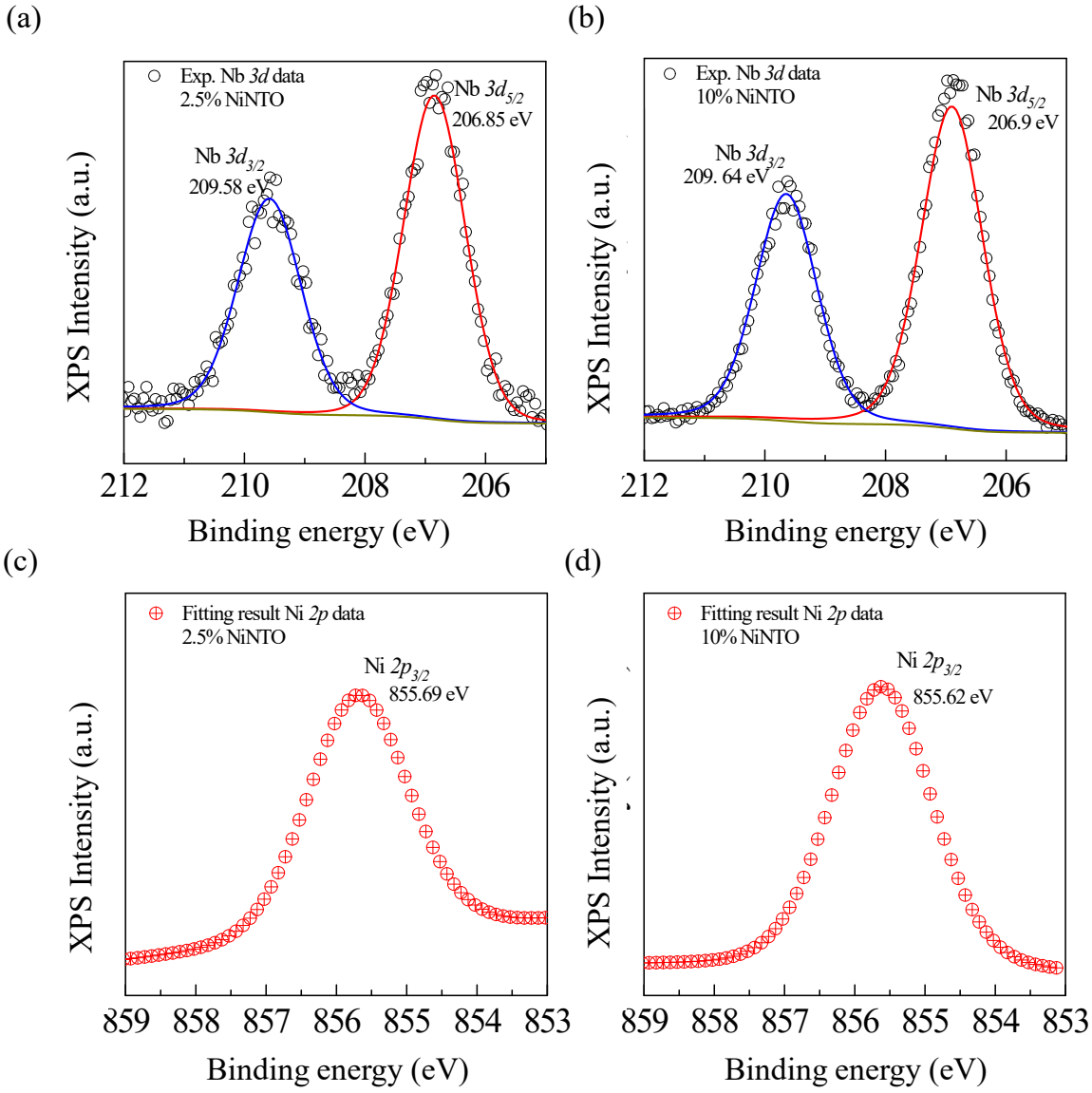

Fig. S2 Valence state of Nb *3d* for (a) 2.5%NiNTO and (b) 10%NiNTO and valence state of Ni *2p* for (c) 2.5%NiNTO and (d) 10%NiNTO.

Fig. S1(a)-(d) and S2(a)-(d) display the XPS spectra for the 2.5%NiNTO and 10%NiNTO samples, respectively. The XPS spectra for both samples encompass peaks corresponding to Ti 2p, O 1s, Nb 3d, and Ni 2p, commonly observed in co-doped TiO_2. The Ti 2p peaks for the 2.5%NiNTO sample, as shown in Fig. S1(a), are detected at binding energies of 464.15 eV and 458.4 eV, indicative of Ti^{4+} ions.[1, 2] In contrast, the Ti^{4+} peaks for the 10%NiNTO sample, presented in Fig. S2(b), emerge at binding energies of approximately 464.31 eV and 458.57 eV.[1, 2] Both the 2.5%NiNTO and 10%NiNTO samples exhibit Ti^{3+} at a consistent position of 456.8 eV. The Ti^{3+}/Ti^{4+} ratios for the 2.5%NiNTO and 10%NiNTO samples are found to be 1.05% and 1.23%, respectively. The defect equation describing the substitution of TiO_2 with Nb^{5+} is articulated as:

$$2TiO_2 + Nb_2O_5 \xrightarrow{4TiO_2} 2Nb_{Ti}^{\bullet} + 2Ti_{Ti}^{'} + 8O_0 + 0.5O_2 \quad \text{(S1)}$$

$$Ti^{4+} + e \rightarrow Ti^{3+} \quad \text{(S2)}$$

As depicted in Fig. S1(c) and (d), the O 1s peak at a binding energy of approximately 529.8 eV is evident for both the 2.5%NiNTO and 10%NiNTO samples, corresponding to the lattice oxygen (Ti-O). Another peak at roughly 531.4 eV signifies oxygen vacancies.[1, 2] The proportion of oxygen vacancies in the 2.5%NiNTO (19.28%) surpasses that in the 10%NiNTO (10.65%). Fundamentally, doping Ni^{2+} into the Ti^{4+} sites within the TiO_2 structure necessitates charge compensation via the formation of an oxygen vacancy, as illustrated by the following equation:

$$NiO \xrightarrow{TiO_2} Ni_{Ti}^{''} + V_o^{\bullet\bullet} + O_o \quad \text{(S3)}$$

The presence of the Nb element is evident, as illustrated in Fig. S2(a) and (b). Two peaks

for Nb 3d are located at approximately 209 eV and 206 eV, verifying the chemical valence state of +5.[3] Meanwhile, the XPS results for the Ni element, presented in Fig. S2(c) and (d), reveal a singular peak with a binding energy of roughly 855 eV, confirming the Ni^{2+} ions.[4]

References

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