Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Exchange bias mediated self-biased magnetoelectric coupling in Co-$BaTiO_3$ composites

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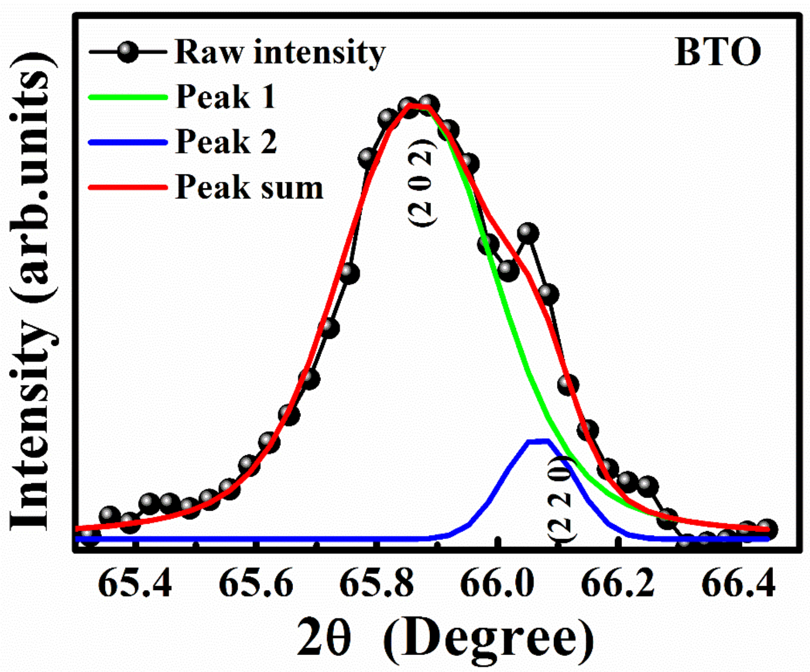

Figure S1. *Deconvoluted XRD peak of BTO*

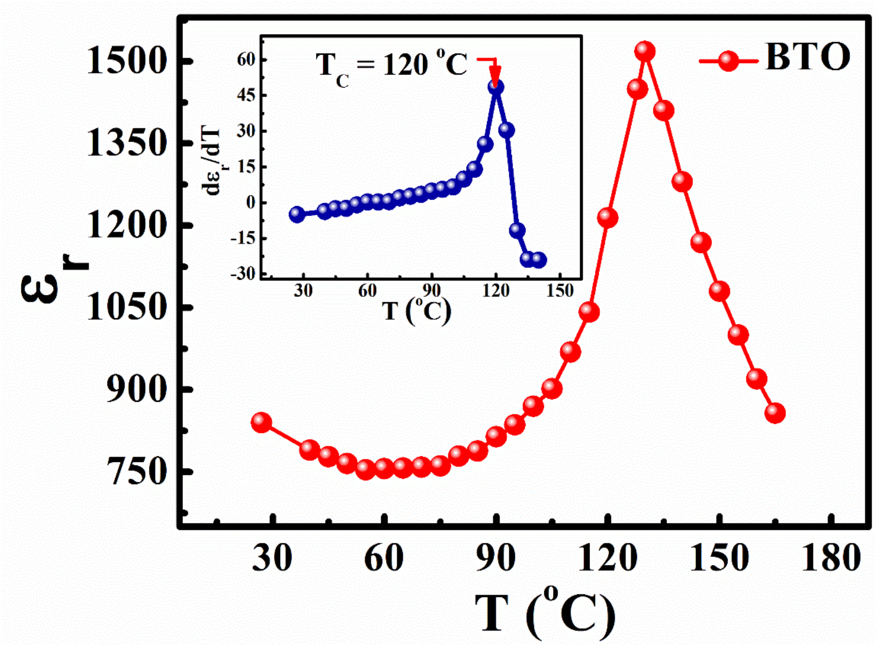

Figure S2. *Temperature-dependent dielectric measurement of sintered BTO*

Absolute field error correction

In the present manuscript, all the magnetic characterizations were carried out using a physical property measurement system (PPMS-DynaCool, QD, USA) equipped with a 9 Tesla (T) magnet. The origin of the remanent field and methods for its mitigation are outlined in the website of QD (see the QD Application Note 1070-207, https://www.qdusa.com/siteDocs/appNotes/1070-207.pdf). It is possible to characterize these remnant fields using a standard paramagnetic test sample (see the QD Application Note 1500-021, Correcting for the absolute field error using the Pd standard, https://www.qdusa.com/siteDocs/appNotes/1500-021.pdf). For mitigating the magnetic field artifacts in measurements, the authors have carried out the M(T) and M(H) measurements of the standard paramagnetic test sample, Palladium (Pd), to directly calculate the susceptibility and true magnetic field. This procedure is invariably conducted during every restart of the PPMS system after the shutdown.

Fig. S3 shows the M(T) measurements of Pd at ±1T field in zero field cooled (ZFC) and field cooled (FC) modes within a temperature range of 290 K to 302 K. From the figure, it is clear that ZFC and FC data at ±1T field produces almost same magnetization values for paramagnetic Pd sample. The obtained χ at 298 K is ~ 5.30× 10^{-6} emu/g. Oe. Figs. S4(a) and (b) depict the M(H) data of Pd taken at 298 K and its zoomed-in portion, respectively. From Fig. S4(b), it is clear that at low fields, the moment is hysteretic. At zero reported field, the moment is not zero as would be expected for a perfect paramagnet. Here, a remanent field of ~ 20.33 Oe is obtained in the (-H) axis. From the

M(H) data, we can calculate the true field of the Pd standard using the equation, True field = $\frac{M}{\chi \text{ at } 298\text{ K}}$, where moment (M) is in emu/g.

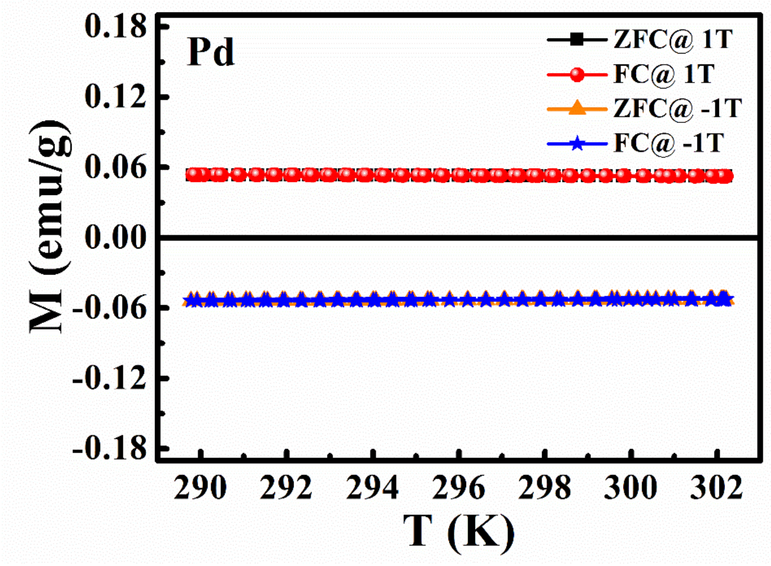

Figure S3. M(T) measurements taken at a field of ±1T

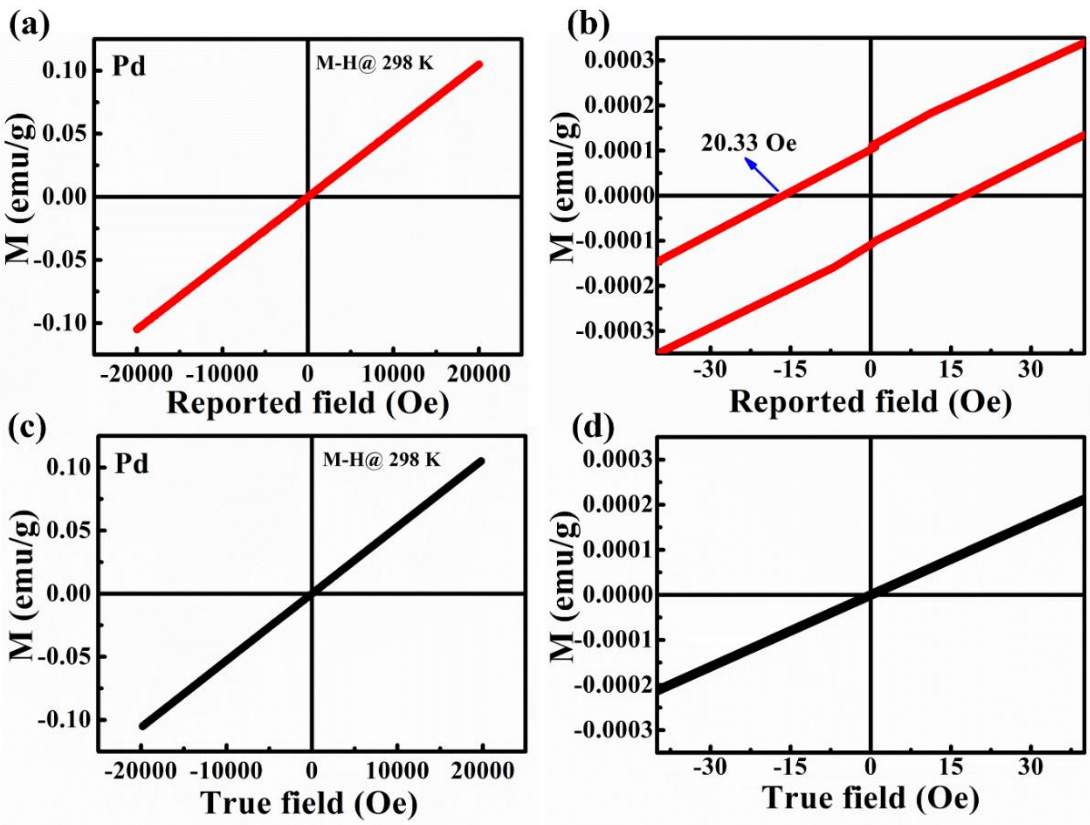

Figure S4. M(H) measurements at 298 K for standard paramagnetic Pd sample

In Fig. S4(c), M is plotted as a function of the calculated true field, and its zoomed-in portion is shown in Fig. S4(d). Then, there is no hysteresis formation in the M(H) data (see Fig.S4(d)). Hence the remanent field is avoided by considering the true field of the sample. So, correcting the absolute field error using the Pd standard is an excellent option to mitigate the remanent field.

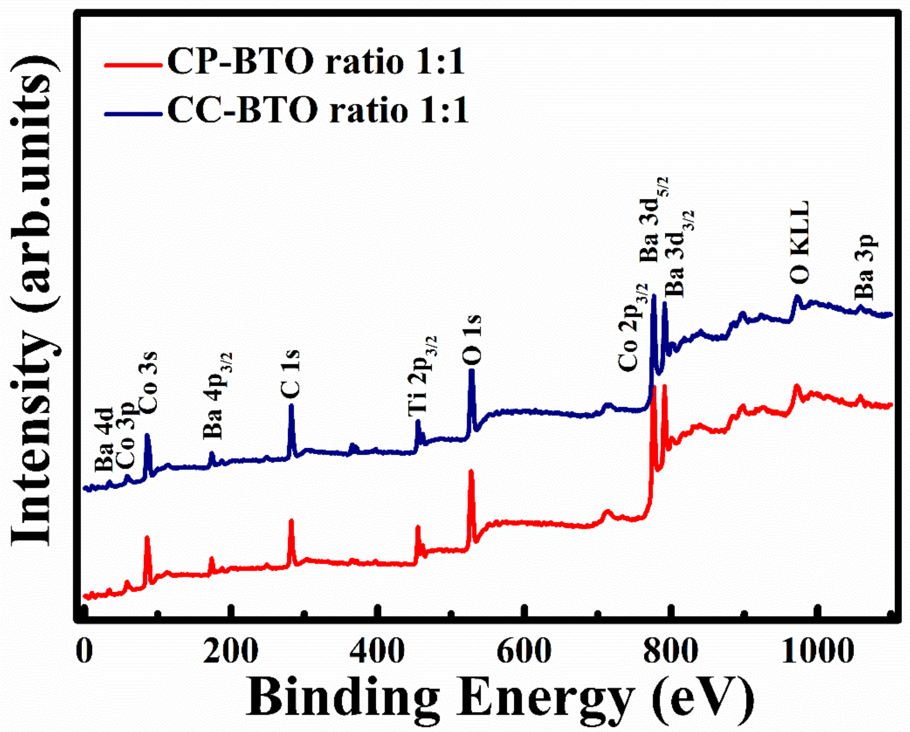

Figure S5. *XPS survey spectra of CP-BTO ratio 1:1 and CC -BTO ratio 1:1*

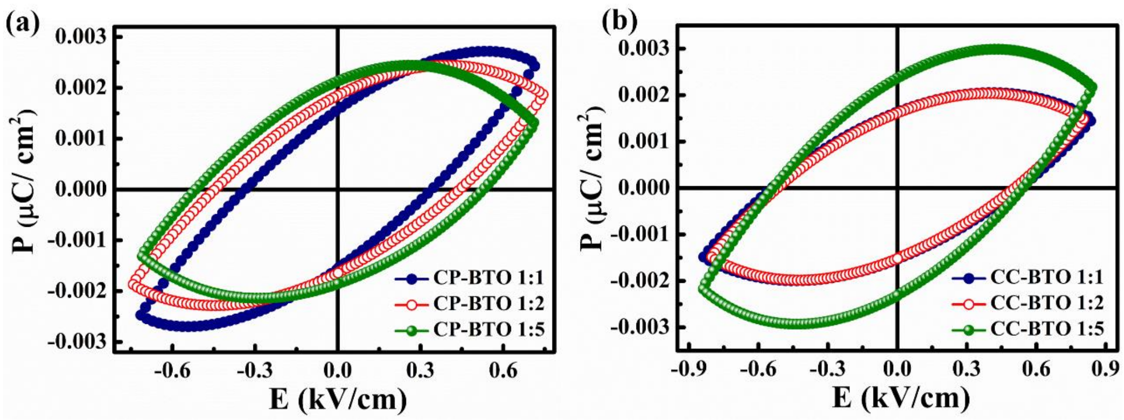

Figure S6. *P-E loops of ME composites (a) CP-BTO, and (b) CC-BTO*

The observed ferroelectricity in the ME composites is low and P-E loop looks like leaky, which is due to the nanosized BTO present in the sample. To emphasize the ferroelectricity of BTO nanoparticles, we have tested the P-E loop of BTO nanoparticles and which shows low remanent polarization similar to the ME composites (see Fig. R3(a)). On the other hand, the sintered BTO at 1200 °C shows large remanent polarization of 16.9 μC/cm^2 (see Fig. R3(b)), which is in good agreement with the previous report [16]. The nanostructured BTO exhibits very leaky dielectric nature compared to sintered bulk BTO, which is a consequence of the finite size effect in ferroelectrics. The volume of grain boundary increases as the grain size decreases. The grain boundary possesses several defects and has low permittivity, thereby possessing poor ferroelectricity [17],[18]. On the other hand, the grain size increases with sintering and reduces the grain boundary volume, and get food ferroelectric nature. Similar P-E loops were previously reported in nanomaterials [19], [20]. Thus, the leaky behavior of P-E hysteresis loops of Co-BTO composites is due to the smaller size of grains in BTO present in the samples [20].

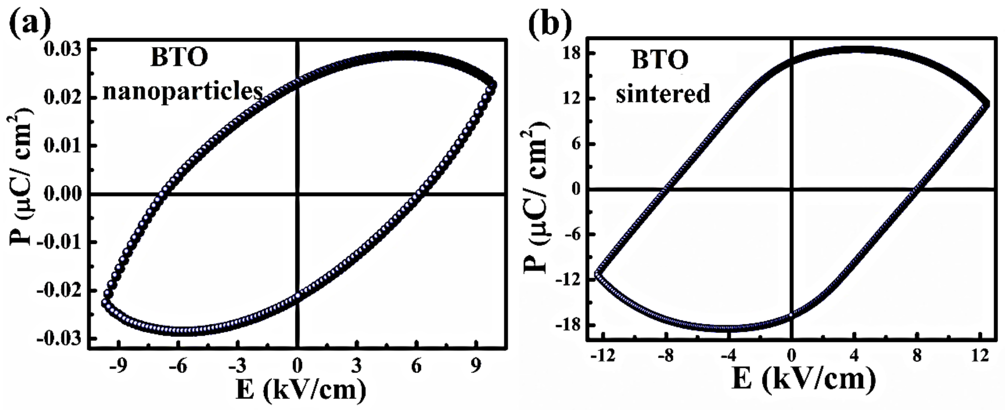

Figure S7. *P-E loop of pelletized BTO (a) before sintering, and (b) after sintering*

In the present study, BTO nanoparticles as such were added for preparing the ME composites so that leaky P-E loops are obtained for ME composites, as similar to BTO nanoparticles.

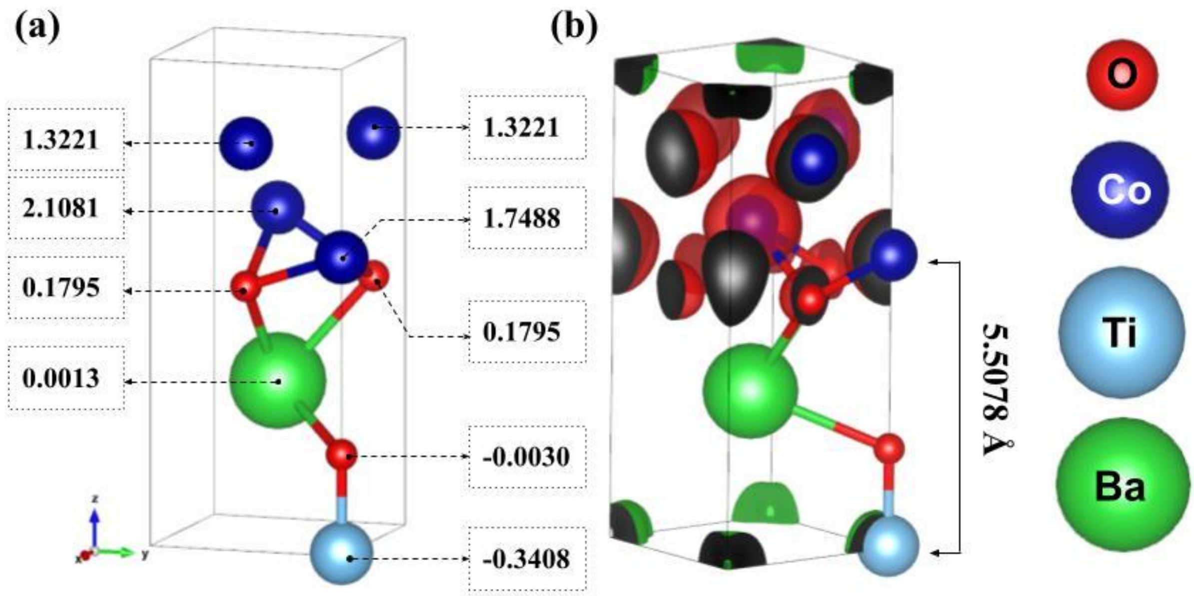

Figure S8. *(a) The localized magnetic moments in the 1BTO:1CO system (b) The spin polarized electron density on 1BTO:1CO system. Here red indicates a spin-up state and green indicates a spin-down state.*

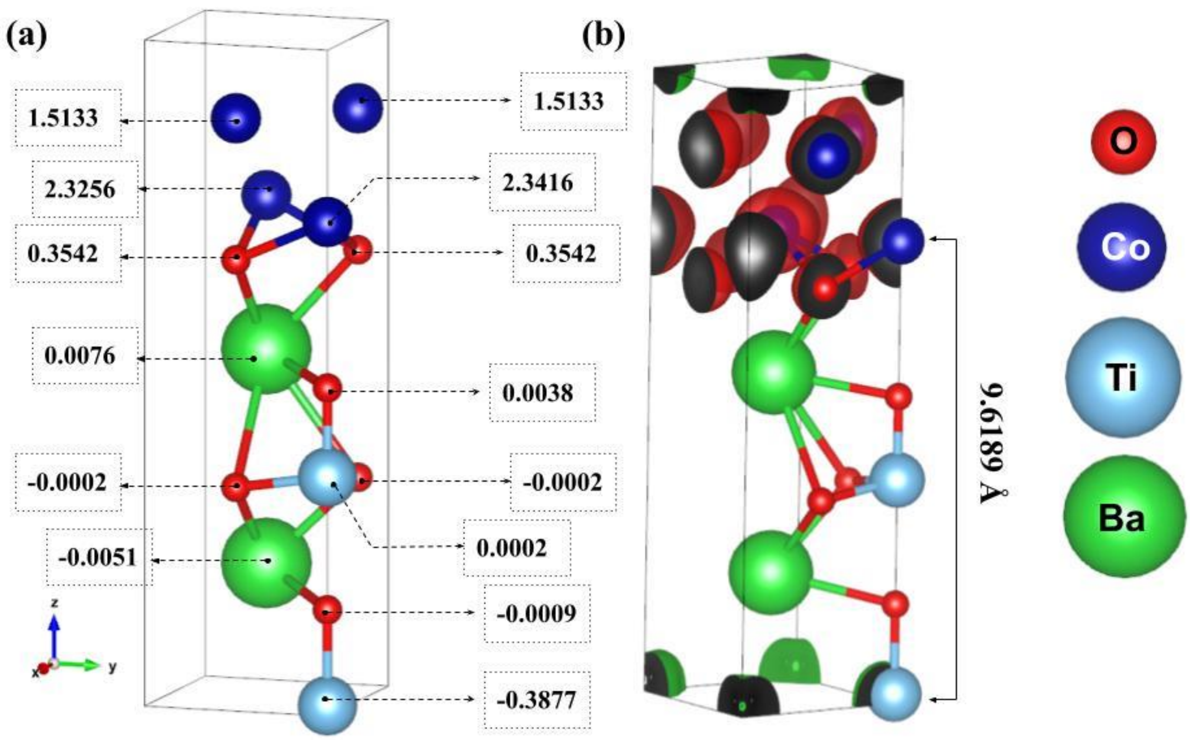

Figure S9. *(a) The localized magnetic moments in the 2BTO:1CO system (b) The spin polarized electron density on 2BTO:1CO system. Here red indicates a spin-up state and green indicates a spin-down state.*

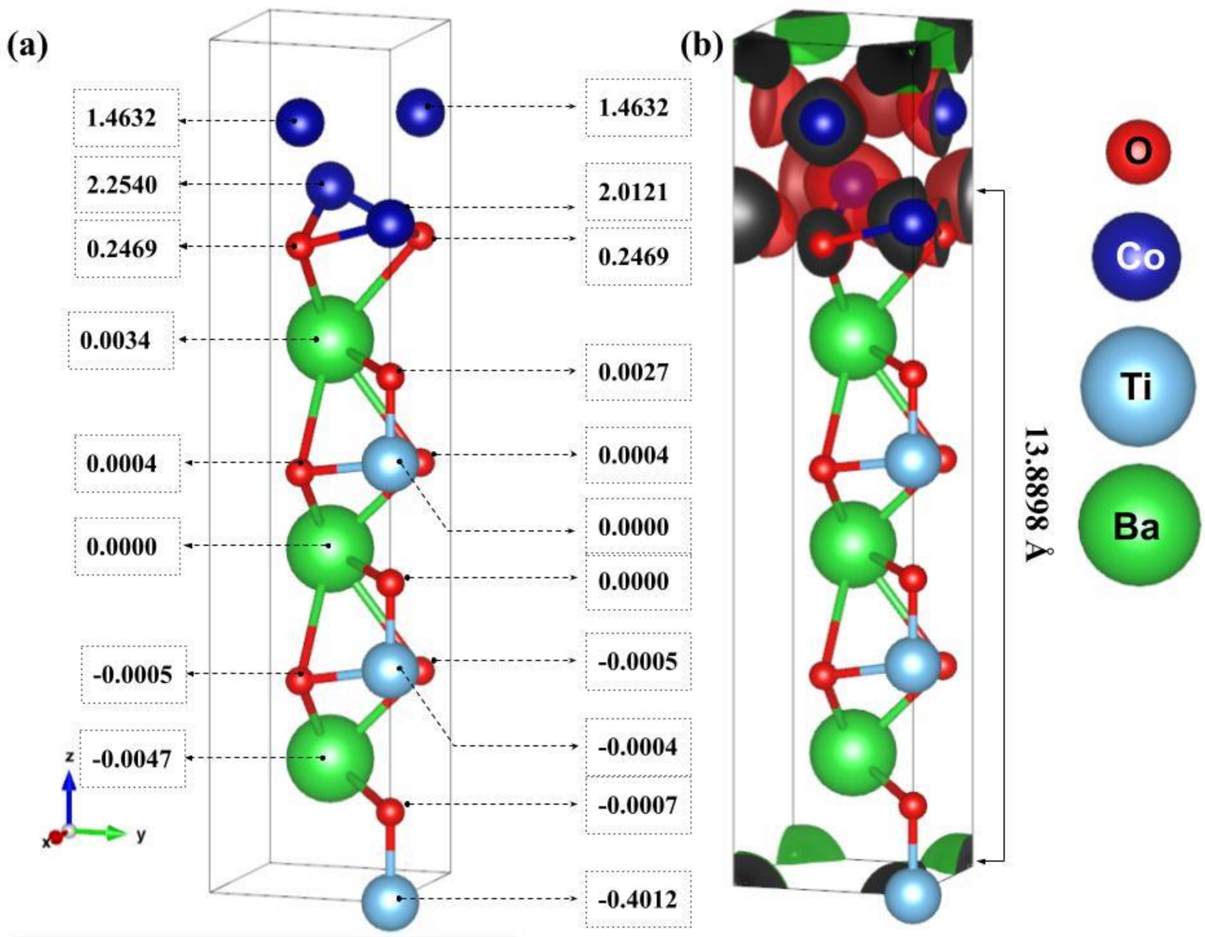

Figure S10. *(a) The localized magnetic moments in the 3BTO:1CO system (b) The spin polarized electron density on 3BTO:1CO system. Here red indicates a spin-up state and green indicates a spin-down state.*

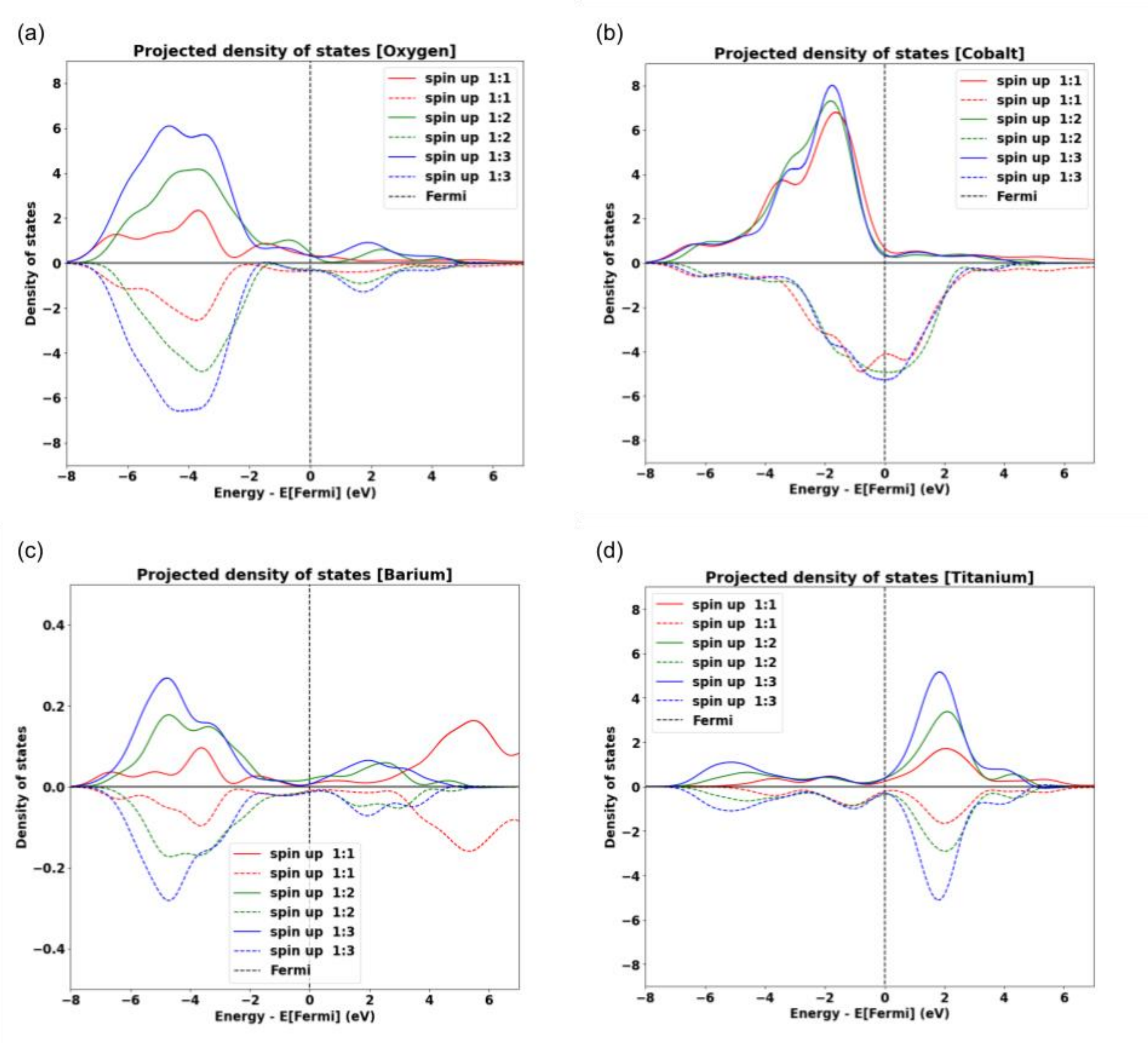

Figure *S11*. *The PDOS of the constituent elements: (a) oxygen (b) cobalt (c) barium and (d) titanium*