**Supporting Information**

**Magnetism and site-selective substitution in arc melted perovskite titanates *A*TiO3–*δ* (*A* = Ca, Sr, Ba)**

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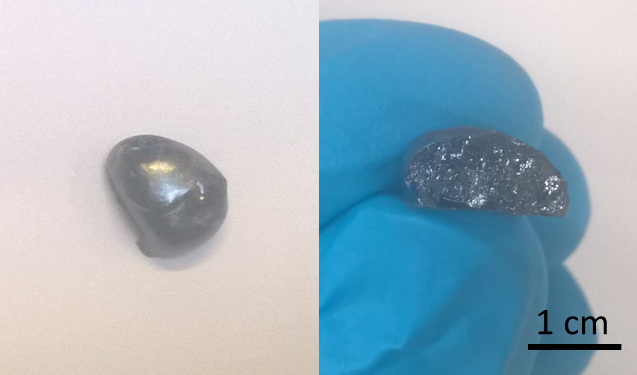
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**Supporting information S1. Songhak Yoon *et al.***

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**Supporting information Fig. S1.** Examplarily shown STO\_arc sample after arc-melting (left) and cross-section (right).

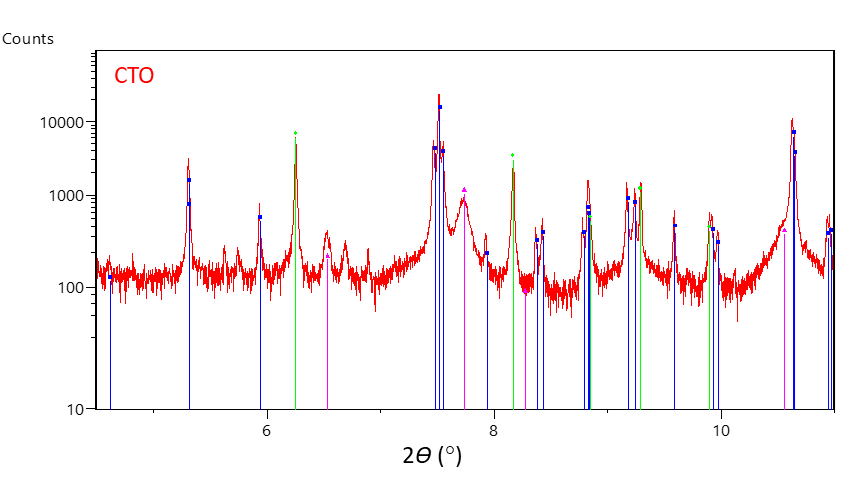
**Supporting information S2. Songhak Yoon *et al.***

**Supporting information Figure S2.** Reflection width of the main diffraction peaks before (black) and after (red) arc-melting ( = 0.35439 Å).

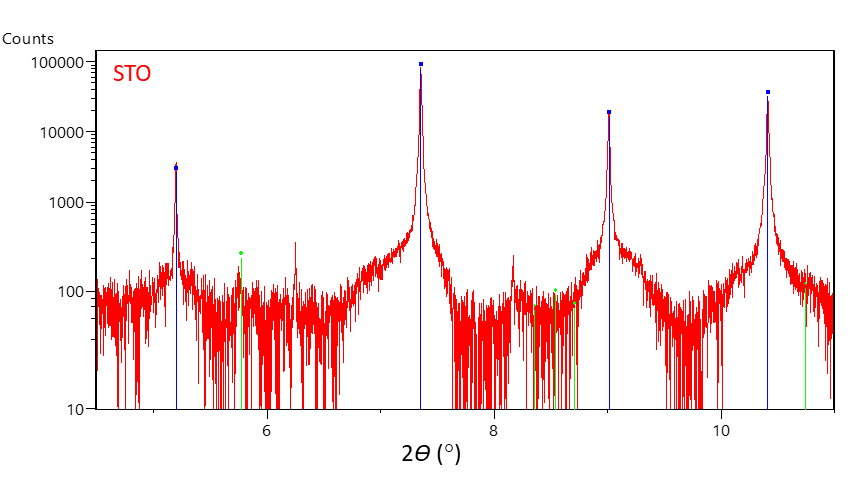
**Table S1**. The estimated full width at half maximum (FWHM) value.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample | FWHM(121) (°) | Sample | FWHM(011) (°) | Sample | FWHM(011) (°) |
| CTO | 0.0136 | STO | 0.0143 | BTO | 0.0177 |
| CTO\_arc | 0.0047 | STO\_arc | 0.0073 | BTO\_arc | 0.0092 |

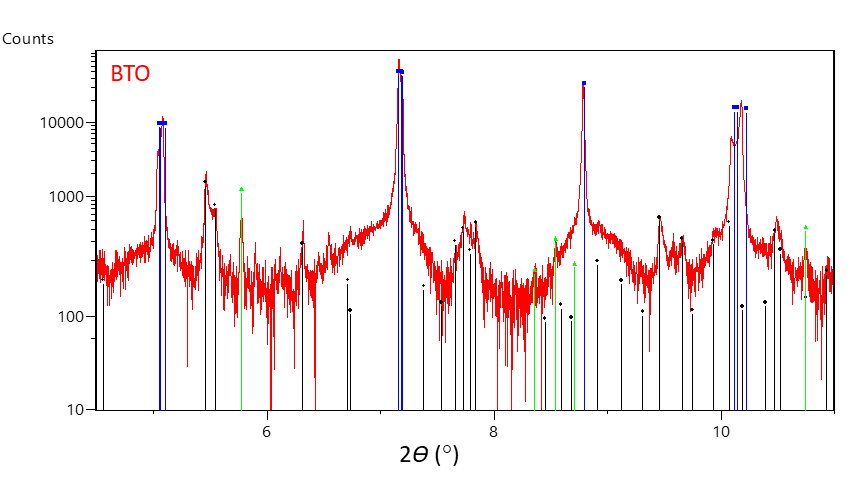
**Supporting information S3. Songhak Yoon *et al.***

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**Supporting information Figure S3. (a)** Intensity is plotted on a logarithmic scale. The main reflections of CTO were indexed as CaTiO3 (blue-colored lines, JCPDS-PDF No. 98-018-3209). The secondary phases were identified to be TiO2 (green-colored lines, JCPDS-PDF No. 98-004-4882) and Ca(OH)2 (magenta-colored lines, JCPDS-PDF No. 98-007-3467).

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**Supporting information Figure S3. (b)** Intensity is plotted on a logarithmic scale. The main reflections of STO were all indexed as SrTiO3 (blue-colored lines, JCPDS-PDF No. 98-007-6186). The secondary phase was identified to be TiO2 (green-colored lines, JCPDS-PDF No. 98-016-8140).

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**Supporting information Figure S3. (c)** Intensity is plotted on a logarithmic scale. The main reflections of BTO were all indexed as BaTiO3 (blue-colored lines, JCPDS-PDF No. 98-006-6482). The secondary phases were identified to be TiO2 (green-colored lines, JCPDS-PDF No. 98-004-4882) and BaCO3 (black-colored lines, JCPDS-PDF No. 98-015-8378).

**Supporting information S4. Songhak Yoon *et al.***







**Supporting information Figure S4.** Powder X-ray diffraction pattern (** = 0.35439 Å) and Rietveld refinement plots of (a) CTO\_arc, (b) STO\_arc, and (c) BTO\_arc obtained at room temperature.

**Supporting information S5. Songhak Yoon *et al.***

**Table S2.** Crystallographic and structural refinement data determined by Rietveld refinements of the synchrotron powder diffraction patterns of arc-melted perovskite titanates.

|  |  |  |  |
| --- | --- | --- | --- |
| Chemical Formula | (a) CTO\_arc | (b) STO\_arc | (c) BTO\_arc |
| Crystal system | orthorhombic | cubic | tetragonal |
| Space group | *Pnma* | *Pmm* | *P*4*mm* |
| *Z* | 4 | 1 | 1 |
| Lattice parameter *a* (Å) | 5.3813(1) | 3.9068(1) | 3.9980(1) |
| Lattice parameter *b* (Å) | 7.6425(1) | – | – |
| Lattice parameter *c* (Å) | 5.4441(1) | – | 4.0238(1) |
| *V*(Å3) | 223.897(1) | 59.628(1) | 64.315(1) |
| *R*p (%) | 8.25 | 7.38 | 9.77 |
| *R*wp (%) | 10.7 | 9.69 | 13.7 |
| *R*exp (%) | 4.43 | 4.07 | 3.65 |
| *χ2* | 5.78 | 5.67 | 14.0 |
| Wavelength (Å) | 0.354388 | 0.354388 | 0.354388 |
| 2*θ* range (deg) | 3–32 | 3–32 | 3–32 |
| 2*θ* step width (deg) | 0.002 | 0.002 | 0.002 |

*R*p, *R*wp, *R*exp, and *χ2* are the reliability factors and goodness-of-fit, respectively.

**Supporting information S6. Songhak Yoon *et al.***

**Table S3.** Atomic structural parameters determined by Rietveld refinements of the synchrotron powder diffraction patterns of arc-melted perovskite titanates.Numbers in parentheses are standard deviations.

(a) CTO\_arc

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Atom | *x* | *y* | *z* | *B*iso (Å2) |
| Ca | 0.9931(2) | 0.0369(1) | 1/4 | 0.39(1) |
| Ti | 1/2 | 0 | 0 | 0.05(1) |
| O(1) | 0.0719(4) | 0.4825(4) | 1/4 | 0.36(4) |
| O(2) | 0.7109(3) | 0.2890(3) | 0.0384(2) | 0.26(3) |

(b) STO\_arc

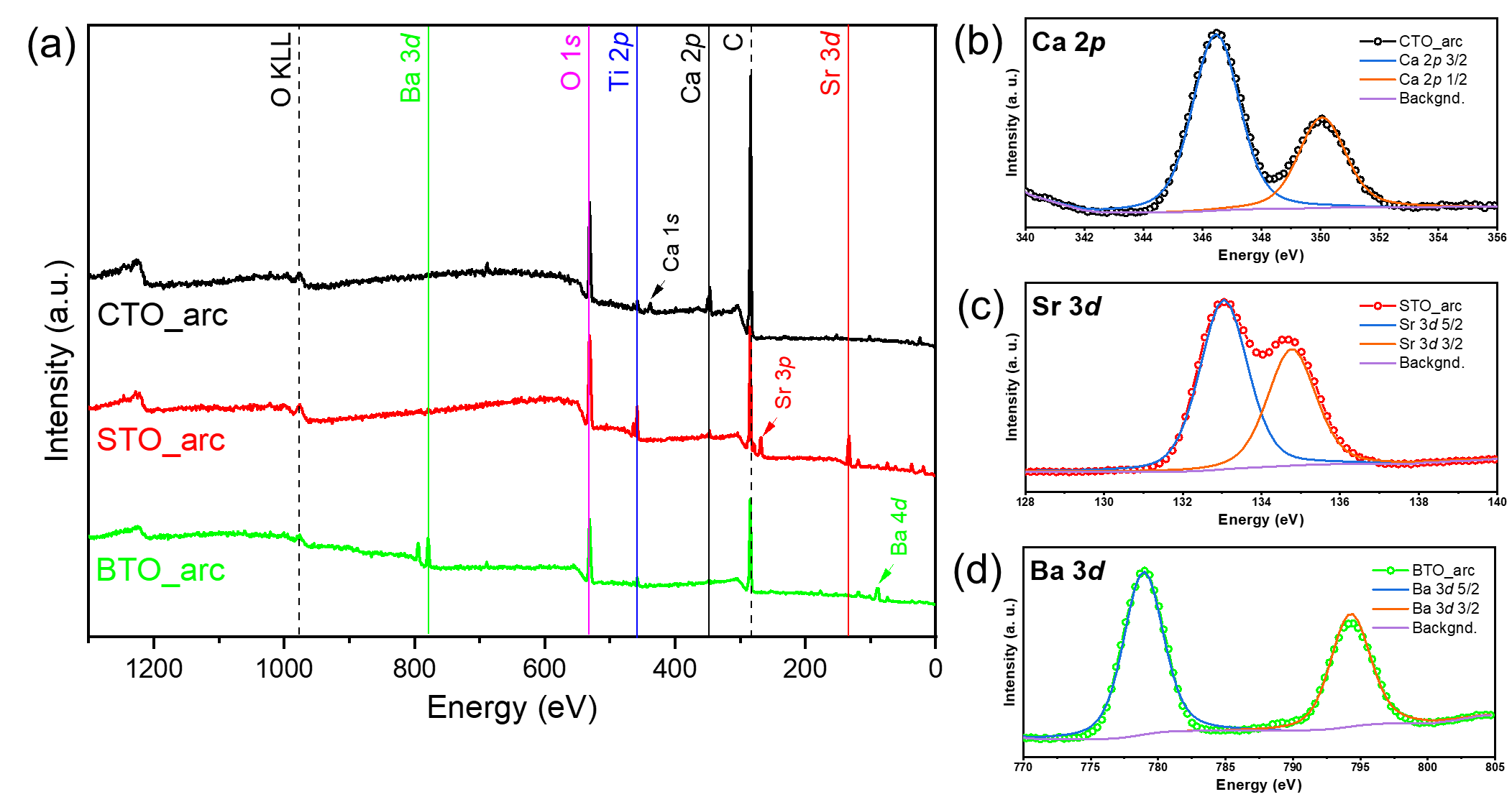
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Atom | *x* | *y* | *z* | *B*iso (Å2) |
| Sr | 0 | 0 | 0 | 0.08(1) |
| Ti | 1/2 | 1/2 | 1/2 | 0.04(2) |
| O | 0 | 1/2 | 1/2 | 0.21(4) |

(b) BTO\_arc

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Atom | *x* | *y* | *z* | *B*iso (Å2) |
| Ba | 0 | 0 | -0.0095 | 0.26(1) |
| Ti | 1/2 | 1/2 | 0.4968 | 0.20(2) |
| O(1) | 1/2 | 1/2 | 0.0144 | 0.19(5) [a] |
| O(2) | 1/2 | 0 | 0.4934 | 0.19(5) [a] |

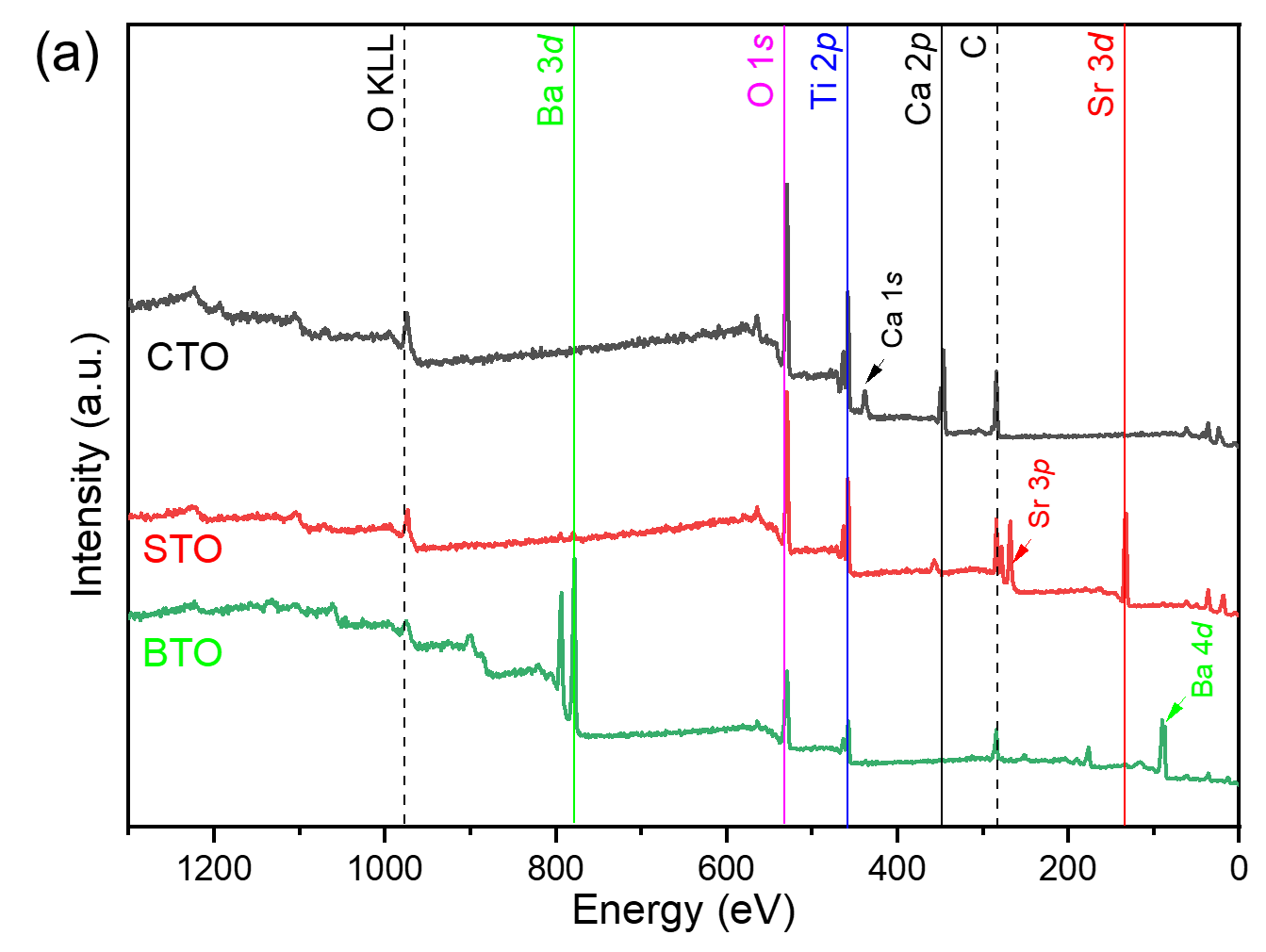
An anisotropic strain model was applied. Thermal factors (*B*iso) for O(1) and O(2) are constrained during the refinements otherwise a negative thermal factor was obtained after refinements.[a]

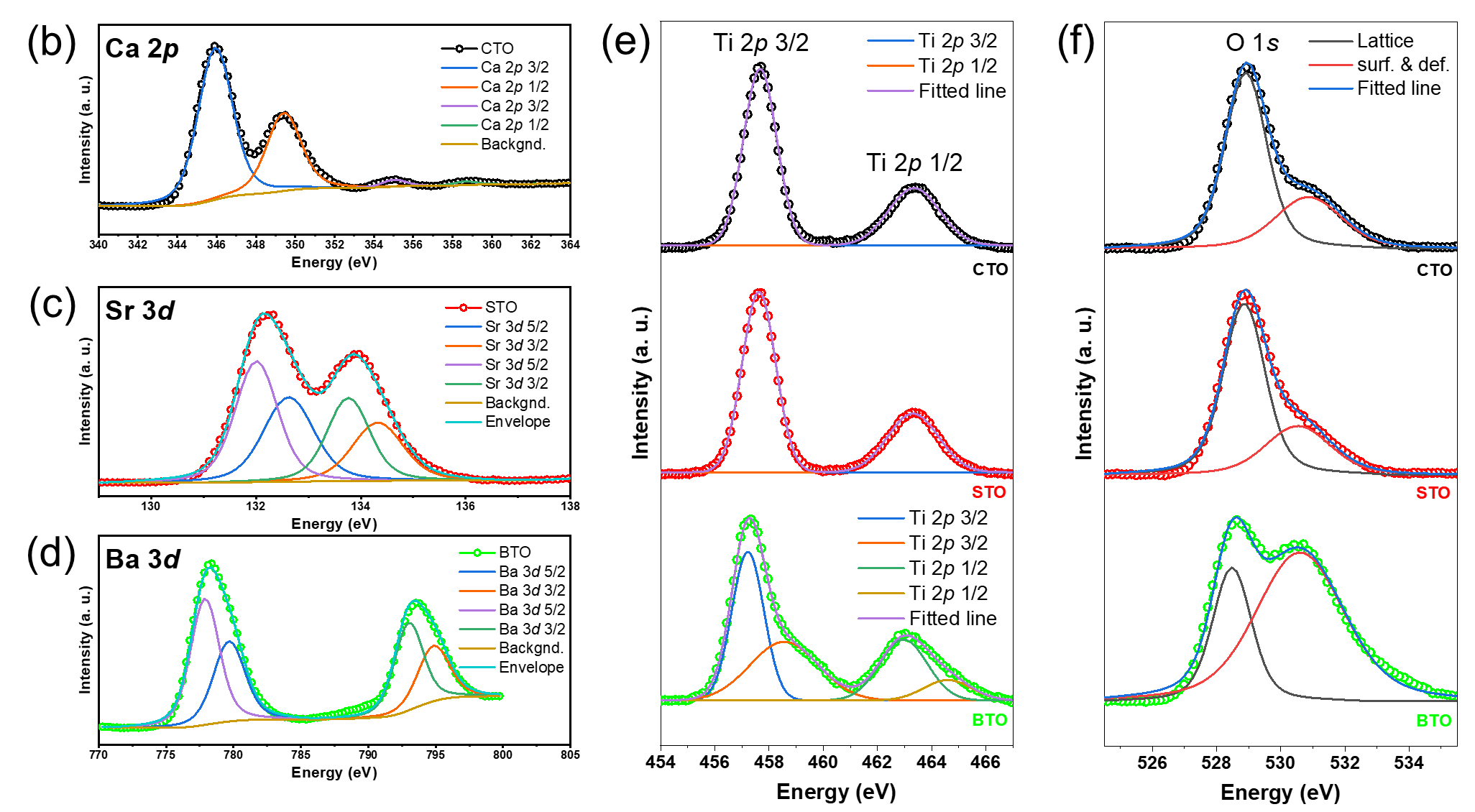
**Supporting information S7. Songhak Yoon *et al.***

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**Supporting information Figure S5.** X-ray photoelectron spectroscopy (XPS) data for CTO\_arc, STO\_arc, and BTO\_arc. (a) Survey spectra, (b) Ca 2*p* of CTO\_arc, (c) Sr 3*d* of STO\_arc, and (d) Ba 3*d* of BTO\_arc.

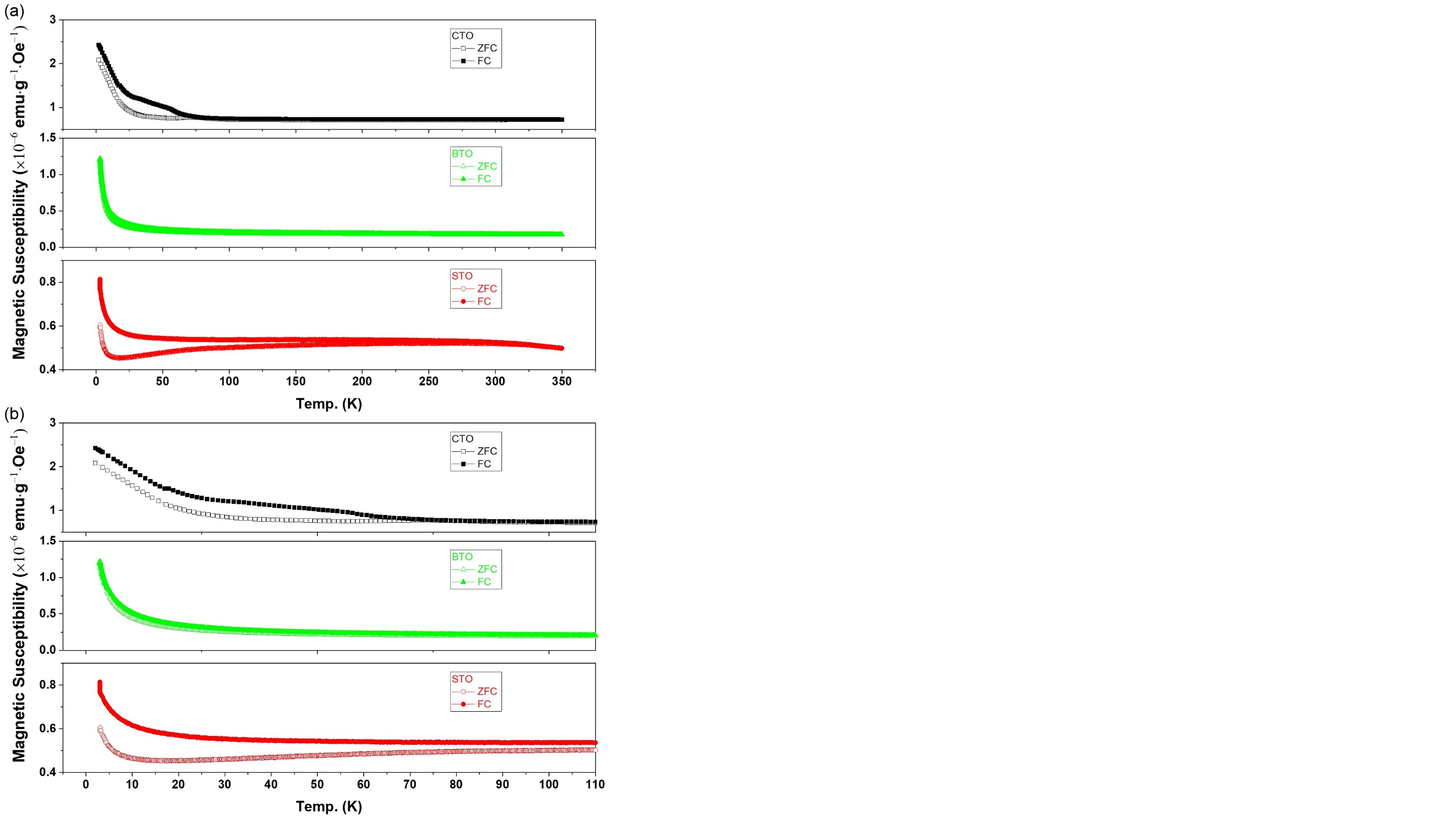
**Supporting information S8. Songhak Yoon *et al.***

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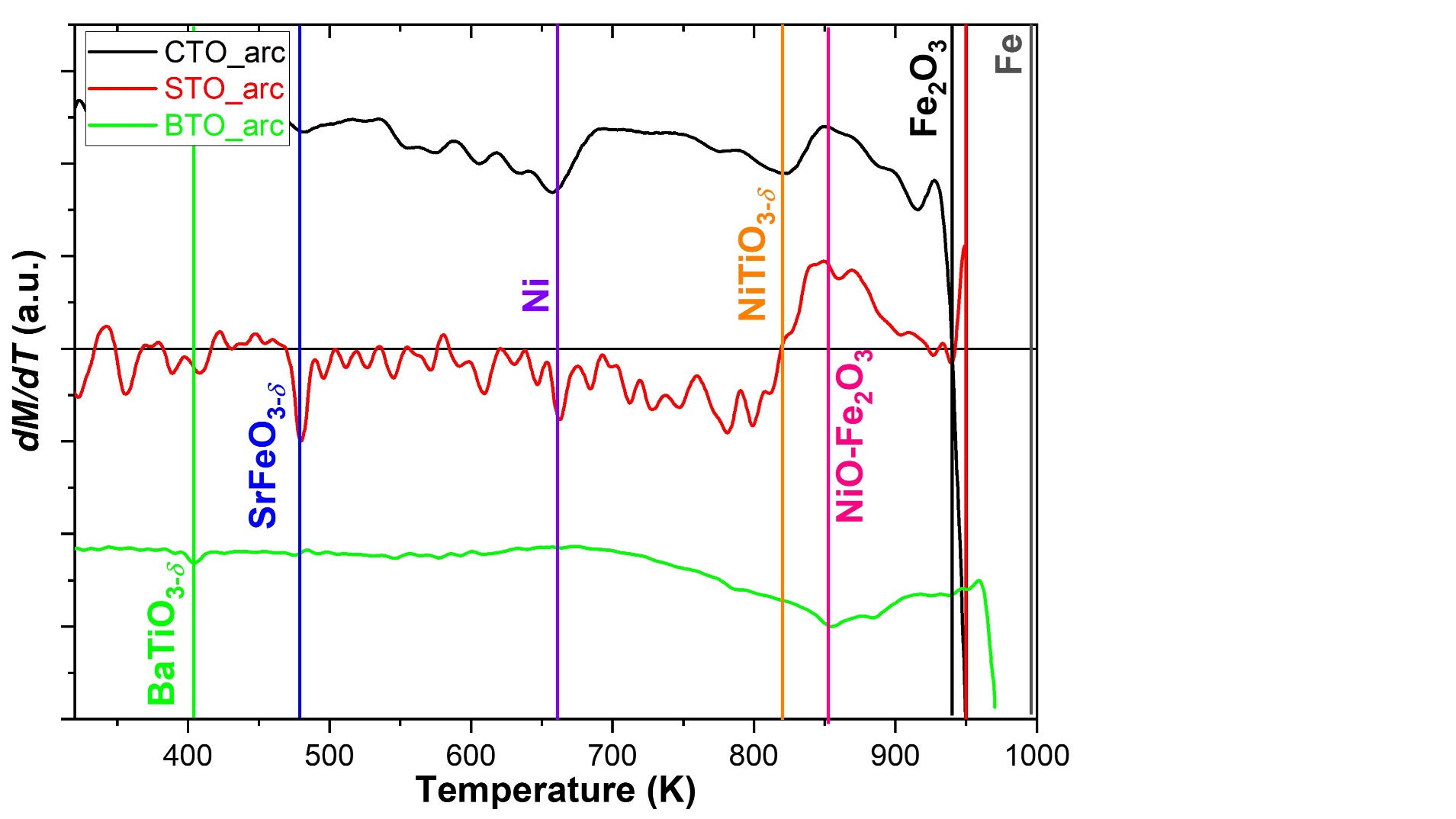


**Supporting information Figure S6.** XPS spectra of pristine CTO, STO, and BTO. (a) Survey spectra, (b) Ca 2*p* of CTO, (c) Sr 3*d* of STO, and (d) Ba 3*d* of BTO. (e) Ti 2*p* (f) O 1*s*.

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**Supporting information Figure S7.** Magnetic susceptibility curves for pristine CTO, STO, and BTO in comparison to arc-melted samples in Fig. 4 a) full range of 3 K –350 K, b) enlarged low-temperature region of a).

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**Supporting information Figure S8.** Derivative magnetization of arc-melted samples, CTO\_arc (black), STO\_arc (red), and BTO\_arc (green). The critical temperatures, i.e., Curie or Néel temperatures, are given with corresponding compounds. The respective values are listed in Table S11.

**Supporting information S11. Songhak Yoon *et al.***

**Table S4.** Summary of critical temperatures of representative perovskites and further magnetic materials**.**

|  |  |  |  |
| --- | --- | --- | --- |
| Materials | Critical Temperature (K) | Critical Temperature (K)  (From experimental results) | Ref. |
| NiTiO3 | 820 | 820 (CTO\_arc)  819 (STO\_arc) | [⁠1](#_CTVL001f871ba82deca4ac08f98e2c18210e13b) |
| CaFeO3 | *T*N: 120 | – | [⁠2](#_CTVL001983c48337b2b440c9e2ac87e5848e18f) |
| SrFeO3 | *T*N: 473 | 479 (STO\_arc) | [⁠3](#_CTVL001ecd90965125f482aab4b50f592d4a46b) |
| BaFeO3 | *T*N: 250 | – | [⁠4](#_CTVL001d3cb2e803fa040738a9ad5b1325a5a27) |
| (Ca,Sr) TiO3 | – | – |  |
| BaTiO3 | 396 | 400 (BTO\_arc) | [⁠5](#_CTVL0011ac796bab4f4419587882ce7ca364530) |
| Fe | 1043 | – |  |
| Ni | 627 | 656 (CTO\_arc)  661 (STO\_arc) |  |
| Fe2O3 | 948 | 950 (CTO\_arc)  949 (STO\_arc)  946 (BTO\_arc) |  |
| NiO-Fe2O3 | 858 | 848 (CTO\_arc)  850 (STO\_arc)  853 (BTO\_arc) |  |

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**Supporting information Figure S9.** *M*-*H* curves at various temperatures for pristine CTO, STO, and BTO samples with paramagnetic correction.

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**Supporting information Figure S10.** *M*-*H* curves at (a) RT and (b) 3 K of CTO\_arc, STO\_arc, and BTO\_arc without paramagnetic correction.

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**Supporting information Figure S11.** Normalized experimental and simulated X-ray absorption spectra (XAS) at the *L*2 *e*g peak for the CTO\_arc, STO\_arc, and BTO\_arc. Lines are expremental spectra and dots are simulation results; green for Ti4+, black for Ti3+ with charge transfer, and red for Ti3+ without charge transfer, respectively.[⁠6](#_CTVL001f0190d6b4ddc40caab41cd64a2aadd2b)

**Supporting information S15. Songhak Yoon *et al.***

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**Supporting information Figure S12.** Sum rules for the Ti *L*-edges XAS and X-ray magnetic circular dichroism (XMCD) spectra of the CTO\_arc, STO\_arc, and BTO\_arc. The blue lines are the integrated area of the spectra.

From XMCD in total electron yield, we obtained spin magnetic moments using sum rules. The orbital magnetic moment is quenched due to random direction in bulk samples. The equation of is used for the sum rule, where *nh* is the number of holes in *d* shells (*nh* = 9 for Ti).[⁠7](#_CTVL001d6cb42e645464c03983c6e3f555ad7cb) The *p* and *q* are the integrated areas of the XMCD signal at the *L*3 edge and *L*2,3 edges, respectively. The *r* is the integrated area of the corrected XAS by the subtraction of a baseline at *L*2,3 edges. The obtained spin magnetic moment values by XMCD sum rule analysis were 0.016 µB/Ti, 0.021 µB/Ti, and 0.027 µB/Ti for CTO\_arc, STO\_arc, and BTO\_arc, respectively. The obtained magnetic moment values are negligible compared to the contribution of transition metal impurities.

**Supporting information S16. Songhak Yoon *et al.***

The elements like Fe, Co, and Ni were quantitatively analyzed by ICP-OES (inductively coupled plasma-optical emission spectrometry, Spectro Ciros CCD ICP-OES) in solutions. The oxygen and hydrogen contents were determined by the hot-gas extraction method using an ELTRA ONH 2000 analyzer. Each sample was measured three times and the obtained oxygen and hydrogen amounts were averaged.

**Table S5**. Elemental analysis of 3*d* impurities by ICP-OES (parts per million in weight) and oxygen deficiency (*δ*) estimated by the oxygen contents obtained by the hot-gas extraction technique.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | Fe | Co | Ni | *δ* |
| CTO | 90 | 80 | 100 | 0.03 ± 0.03 |
| CTO\_arc | 70 | 80 | 100 | 0.06 ± 0.03 |
| STO | 60 | 80 | 100 | 0.03 ± 0.03 |
| STO\_arc | 60 | 70 | 100 | 0.11 ± 0.03 |
| BTO | 90 | 100 | 100 | 0.17 ± 0.03 |
| BTO\_arc | 100 | 80 | 100 | 0.25 ± 0.03 |

**References**

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