

Supporting Information for:

A unified view of the substitution-dependent antiferrodistortive phase transition in SrTiO_3

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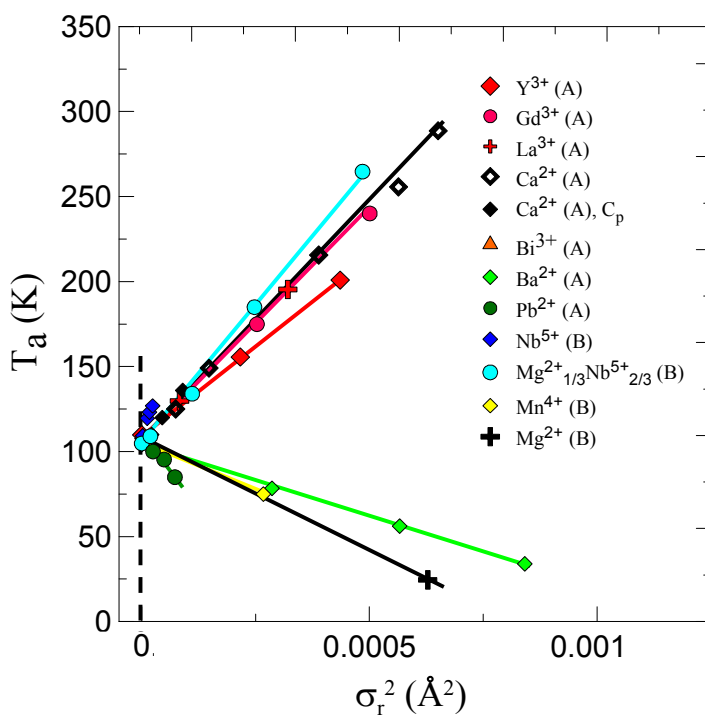


Figure S1: T_a vs. σ_r^2 for all data included in Figure 1c of the main paper. The radius mismatch is calculated only for the site where the substitution is made, and the black dashed line indicates the zero variance obtained for unsubstituted SrTiO_3 .

Extraction of excess heat capacity

As noted in the main text, the choice of a suitable background specific heat to properly extract the excess heat associated with the transition is important. Figure S2a below shows the results of extracting this excess heat capacity for unsubstituted SrTiO_3 using two different backgrounds, consistent with refs. 30 and 31 (black line) and ref. 15 (red line) of the main paper. Both backgrounds involve quadratic functions fit to the data above T_a , where the excess heat capacity is zero. The difference is that the fit using the method of Salje *et al.* (refs. 30,31 of the main paper) constrains the low temperature background to the single green data point shown in Figure S2a (at $0.073 \text{ J mol}^{-1} \text{ K}^{-1}$, 85 K). This point comes from an analysis that determined that the excess entropy associated with the transition varies as the square of the order parameter measured by X-ray diffraction. This allows for the X-ray data and specific heat to be reconciled at some low temperature where the excess heat becomes small, essentially guaranteeing that the extracted entropy saturates in a thermodynamically consistent manner at low temperature. Within this approach the background is only valid for $T > 85 \text{ K}$, and the data below 85 K are thus omitted in Figure 2c. As shown in Table S1 below, the entropy obtained in this manner is indeed very close to that given in ref. 30 of the main text. The alternative method shown in Figure S2a simply subtracts the background from a quadratic fit above the transition temperature. The determination of T_a is largely unaffected, but the excess specific heat quite quickly becomes negative on cooling, which would lead to significant underestimation of the entropy. In order to extract the excess heat capacity for the samples containing Nb, we used the same method as for pure SrTiO_3 , setting the fixed point used below the transition to $0.073 \text{ J mol}^{-1} \text{ K}^{-1}$ at $T = 0.81T_a$. The latter value is simply the same reduced temperature as in the unsubstituted case.

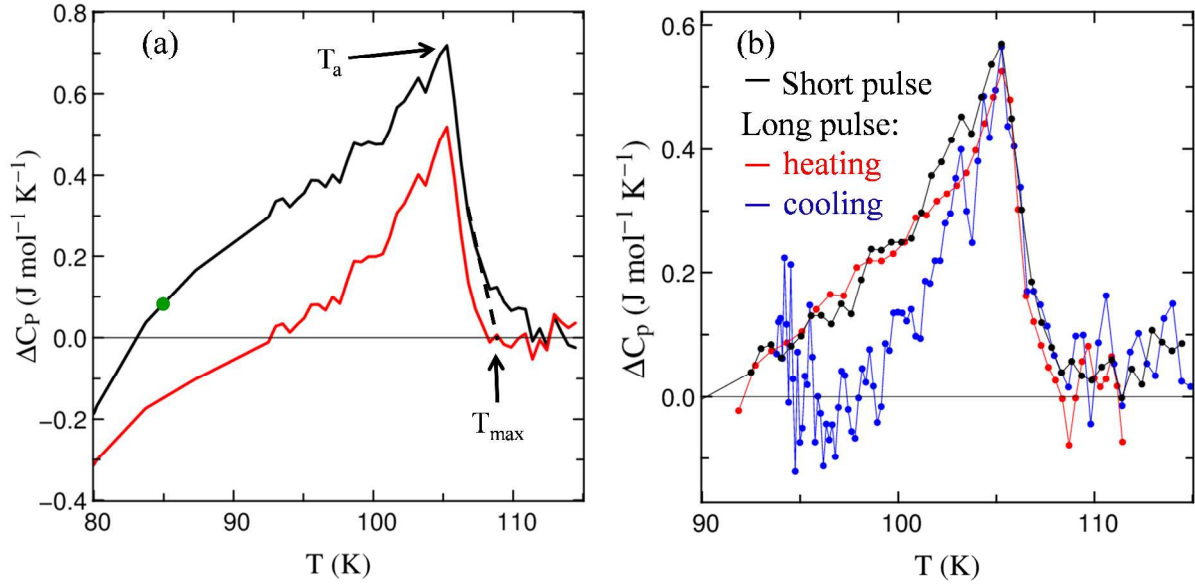


Figure S2: Excess specific heat results for unsubstituted SrTiO_3 . (a) ΔC_p obtained with two different backgrounds, comparable to that performed in refs. 30 and 31 (black), and 15 (red) of the main paper. The green dot is the special point in the analysis of Salje *et al.* The black dashed line illustrates the extrapolation used to obtain $T_{\max}$. (b) ΔC_p obtained in both the relaxation (short pulse) and scanning (long pulse) modes. The background used in (b) is that used to produce the red curve in (a), though it should be evident that the similarities between the three curves in (b) will be unaffected by the choice of background. The fact that the amplitude of ΔC_p is identical for both long and short pulses is consistent with the fact that the antiferrodistortive phase transition is second order, as discussed in the text. Heating and cooling results also reveal no thermal hysteresis.

Table S1: Summary of parameters extracted from the specific heat data on $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$. T_a and $T_{\max}$ are defined in Figure S2, while FWHM is the full-width-at-half-maximum obtained from ΔC_p vs. T , and ΔS is the change in entropy across the transition (between $T = 0.81 T_a$ and $T_{\max}$, see above). Errors are shown in parentheses under the variable.

x (at. %)	T_a (± 0.5 K)	$T_{\max}$ (± 0.5 K)	FWHM (± 0.7 K)	ΔS (J/mol/K)
0.0	105.0	111.6	11.1	0.088(4)
0.2	109.4	114.8	16.1	0.090(4)
1.0	119.7	132.3	14.6	0.114(6)
1.4	123.0	134.7	11.8	0.108(5)
2.0	126.9	136.2	16.3	0.117(6)

Table S2: Bond lengths in the tetragonal phase for the relatively highly distorted SrTiO_3 structure obtained from ref 23 used for the bond valence calculations. For reference, in the cubic phase at 300 K this same material has A-O distances of 2.774 Å and B-O distances of 1.962 Å.

Metal site	M-O distance (Å)	Number
A	2.687	4
A	2.770	4
A	2.853	4
B	1.958	2
B	1.962	4