Supporting Information for

An insight into the effects of transition metals on the thermal expansion of complex perovskite compounds: Experimental and density functional theory investigation

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Experimental details:

The obtained perovskite powder was die-molded into a rectangular bar of 5×5×10mm and then Cold Isostatic Pressed (CIPed) at 100MPa. The ceramics were then fired at 850 °C for 4h with a heating rate of 10 °C /min. The fired ceramics were then used for the measurement of the TEC. The CTE was measured using a dilatometer (DiL 402PC, NETZCH, Germany) equipped with an Al_2O_3 pushrod and sample holder at a heating rate of 5 °C /min in the temperature range of 20–727 °C under the constant applied load of 30N. Prior to actual measurements, a calibration measurement with an alumina standard was conducted to obtain a calibration curve, which was later automatically used by the system-contained software to correct the shrinkage data.

Rietveld refinement results:

Table S1 is the summery of the results of Rietveld refinement. Figure S1-S4 show the Rietveld profiles refinement of the samples which are characterized as single phase by X-ray diffraction (XRD) pattern comparison. The best Rietveld fit profiles and the difference curve between the observed and the calculated profiles are shown.

Table S1 Cell parameters obtained from Rietveld refinement [#]

Compounds	2θ range (°)	Step width (°)	Rietveld refinement information			
			a (Å)	c (Å)	Rp (%)	Rwp (%)
$LaCoO_3$	4-120	0.01	5.443	13.095	4.72	5.95
$LaCo_{0.5}Fe_{0.5}O_3$			5.490	13.236	4.97	6.64
$LaCo_{0.5}Ni_{0.5}O_3$			5.463	13.131	3.91	5.08
$LaCo_{0.5}Mn_{0.5}O_3$			5.502	13.388	5.94	7.45

[#] XRD tests details: 293 K (temperature), Cu-Kα (radiation), 0.1540598 nm (wavelength), 2θ (scan mode).

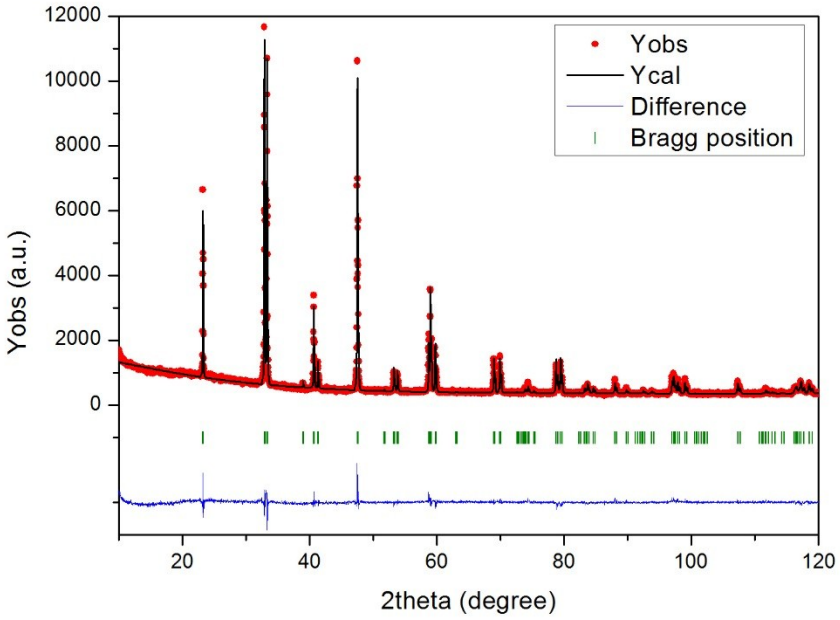

Figure S1. Rietveld refinement plots of $LaCoO_3$.

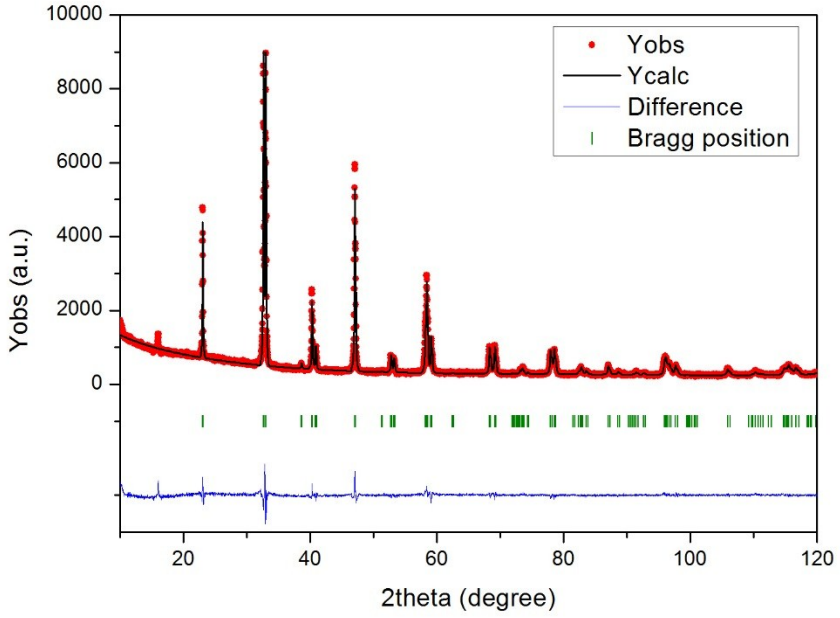

Figure S2. Rietveld refinement plots of $LaCo_{0.5}Fe_{0.5}O_3$.

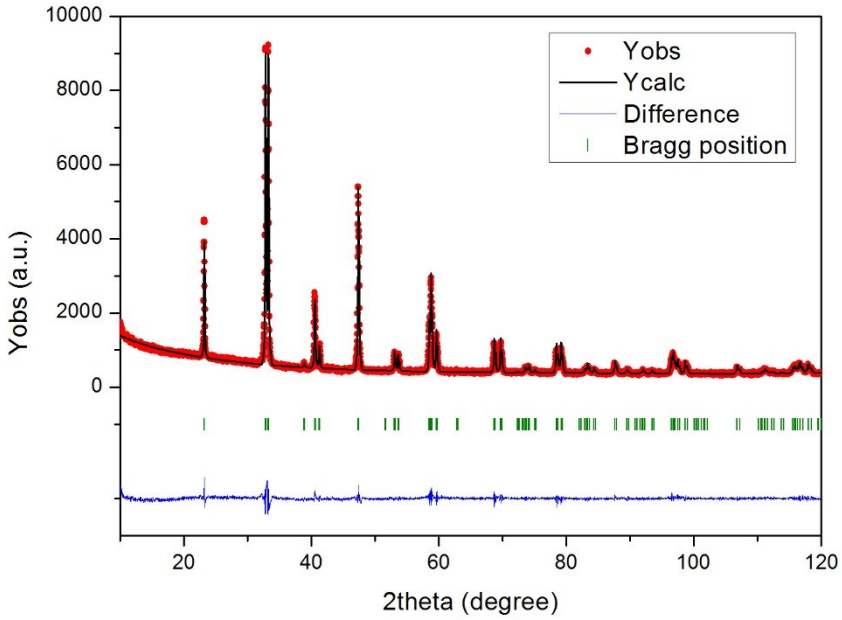

Figure S3. Rietveld refinement plots of $LaCo_{0.5}Ni_{0.5}O_3$.

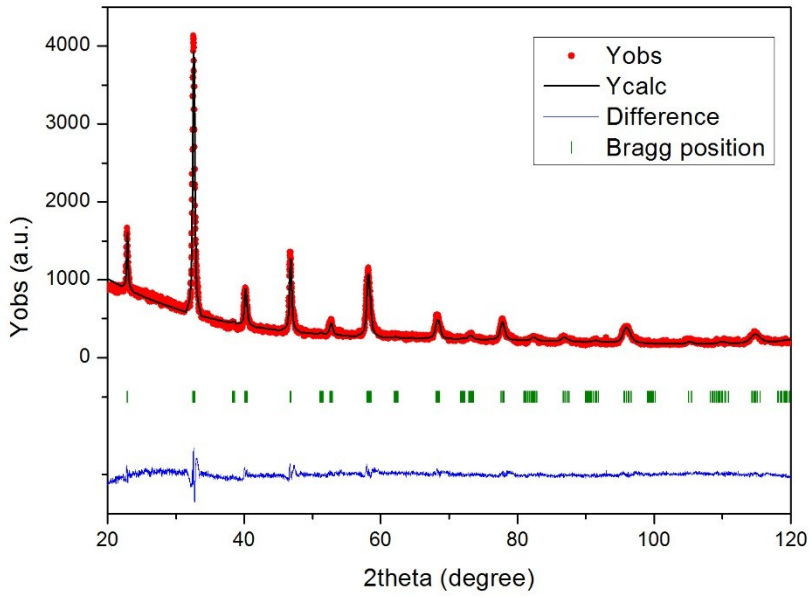

Figure S4. Rietveld refinement plots of $LaCo_{0.5}Mn_{0.5}O_3$.

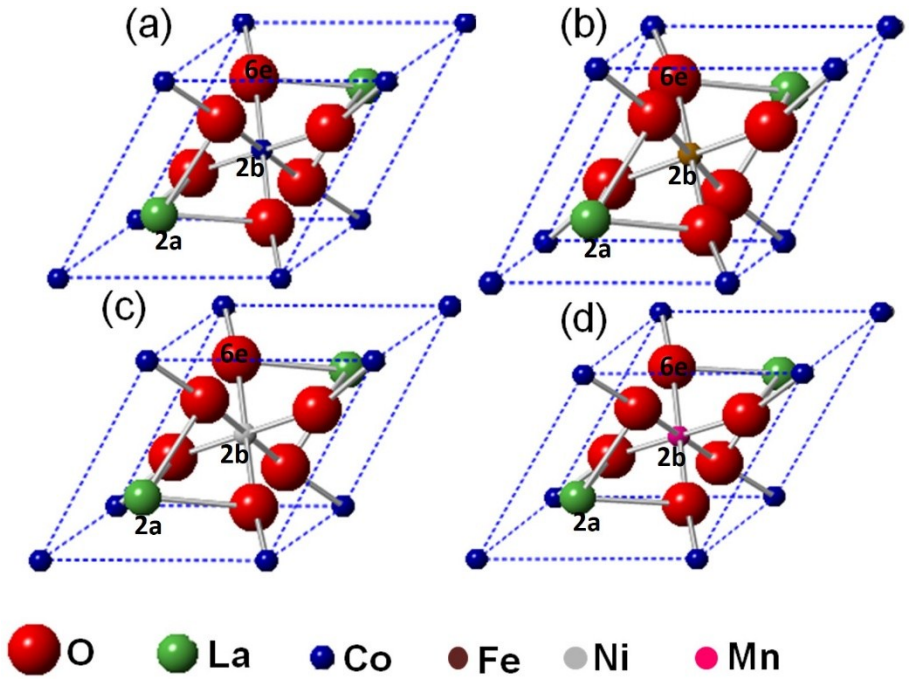

Figure S5. The cell structure of (a)$LaCoO_3$, (b) $LaCo_{0.5}Fe_{0.5}O_3$, (c) $LaCo_{0.5}Ni_{0.5}O_3$, (d) $LaCo_{0.5}Mn_{0.5}O_3$.

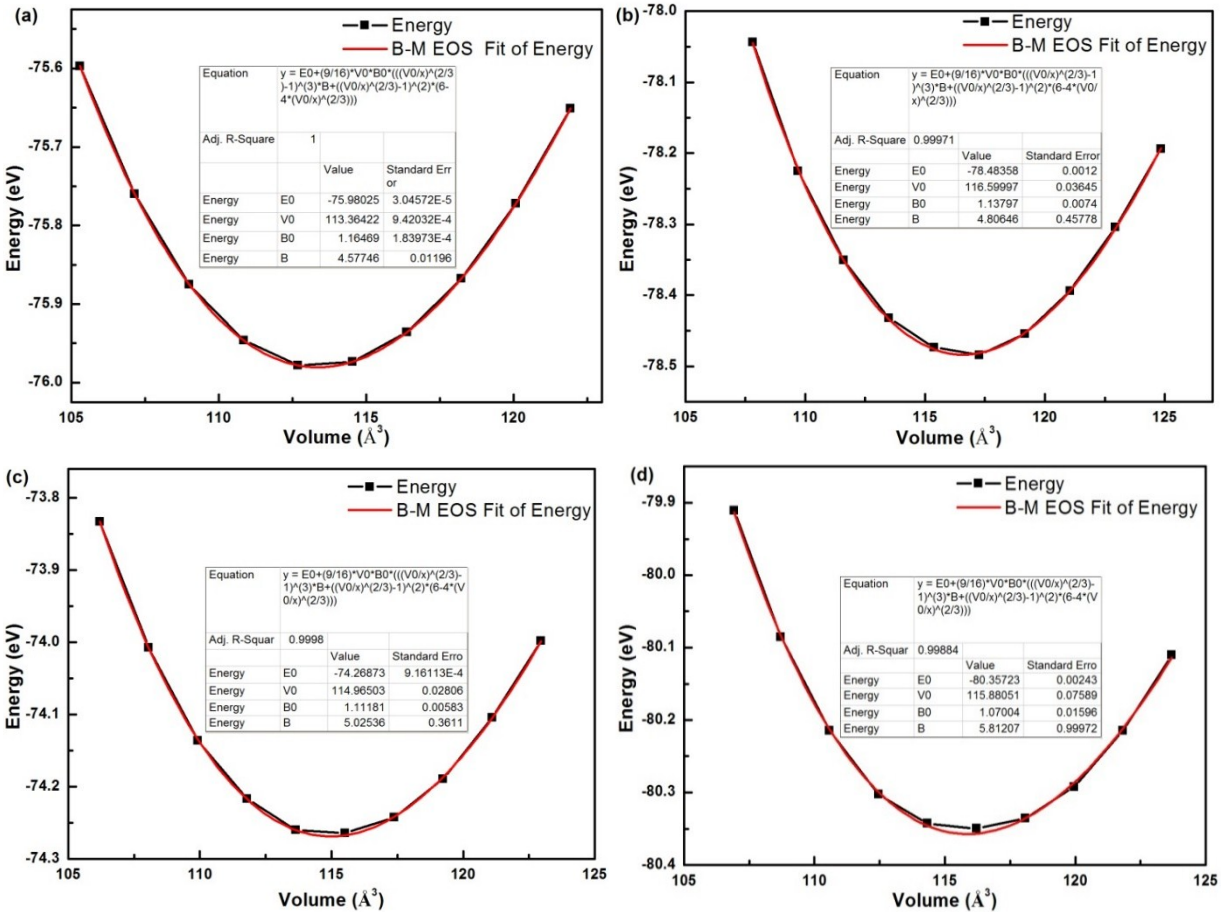

Figure S6. Total energy versus cell volume for (a) $LaCoO_3$(b) $LaCo_{0.5}Fe_{0.5}O_3$, (c)$LaCo_{0.5}Ni_{0.5}O_3$, and $LaCo_{0.5}Mn_{0.5}O_3$.

The ten different volumes of compounds obtained by QHA method also reflect the change of temperature, providing a good groundwork for the study of various thermodynamic properties. The energy versus the cell volume curves of four different compounds were shown in Fig. S6, as obtained through VASP and Phonopy. As we can clearly observe, the energy first showed a trend of decreasing with the increase of volume, reaching the lowest point of energy, which is the most stable point of the material structure, and then showed an upward trend. The relationship of energy vs. volume was fitted with 3-order Birch-Murnaghan equation of state to obtain the most stable structur. And the results of equilibrium volume, energy and standard error were shown in Figure S6 inset tables.

Table S2 Charge transfer (electron) for $LaCo_{0.5}X_{0.5}O_3$ (X = Co, Fe, Ni and Mn,) compounds.

Compounds	Charge transfer (Valence charge-Bader charge)			
	La	Co	X	O
$LaCoO_3$	2.08=11-8.92	1.44=9-7.56	1.44=9-7.56	-1.16=6-7.16
$LaCo_{0.5}Fe_{0.5}O_3$	2.07=11-8.93	1.42=9-7.58	1.65=8-6.35	-1.19=6-7.19
$LaCo_{0.5}Ni_{0.5}O_3$	2.10=11-8.90	1.48=9-7.52	1.4=10-8.60	-1.17=6-7.17
$LaCo_{0.5}Mn_{0.5}O_3$	2.10=11-8.90	1.38=9-7.62	1.98=7-5.02	-1.25=6-7.25

Table S3 Average bond length of $LaCo_{0.5}X_{0.5}O_3$ (X = Co, Fe, Ni and Mn,) compounds obtained from geometry optimization.

Compounds	Bond length (Å)		
	La-O	Co-O	X-O
$LaCoO_3$	2.701	1.937	1.937
$LaCo_{0.5}Fe_{0.5}O_3$	2.607	1.921	1.973
$LaCo_{0.5}Ni_{0.5}O_3$	2.588	1.922	1.958
$LaCo_{0.5}Mn_{0.5}O_3$	2.602	1.947	1.932