Chemical stability of Ca$_{3}$Co$_{4-x}$O$_{9+d}$/CaMnO$_{3-d}$ p–n junction for oxide-based thermoelectric generators

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An all-oxide thermoelectric generator for high-temperature operation depends on a low electrical resistance of the direct p–n junction. Ca$_{3}$Co$_{4-x}$O$_{9+d}$ and CaMnO$_{3-d}$ exhibit p-type and n-type electronic conductivity, respectively, and the interface between these compounds is the material system investigated here. The effect of heat treatment (at 900 °C for 10 h in air) on the phase and element distribution within this p–n junction was characterized using advanced transmission electron microscopy combined with X-ray diffraction. The heat treatment resulted in counter diffusion of Ca, Mn and Co cations across the junction, and subsequent formation of a Ca$_{3}$Co$_{1+y}$Mn$_{1-y}$O$_{6}$ interlayer, in addition to precipitation of Co-oxide, and accompanying diffusion and redistribution of Ca across the junction. The Co/Mn ratio in Ca$_{3}$Co$_{1+y}$Mn$_{1-y}$O$_{6}$ varies and is close to 1 (y = 0) at the Ca$_{3}$Co$_{1+y}$Mn$_{1-y}$O$_{6}$–CaMnO$_{3-d}$ boundary. The existence of a wide homogeneity range of 0 ≤ y ≤ 1 for Ca$_{3}$Co$_{1+y}$Mn$_{1-y}$O$_{6}$ is corroborated with density functional theory (DFT) calculations showing a small negative mixing energy in the whole range.

Introduction

For waste heat harvesting at high temperatures and oxidizing conditions, thermoelectric generators (TEGs) based on oxides represent an interesting technology, enabling increased energy efficiency of any high-temperature process where heat harvesting is viable. Oxide-based thermoelectrics exhibit modest efficiencies compared with state-of-the-art non-oxides, but offer in principle superior stability at high temperatures in air (oxidizing conditions). The stability is however jeopardized by the need for metallic interconnects to form well-conducting contacts between the oxide p- and n-type legs, since the metals are noble (rare and expensive) or they will oxidize over time. Cracking or exfoliation due to differences in coefficients of thermal expansion (CTEs) between ceramic conductors and metal interconnects represent additional challenges. TEGs with direct contact between the p- and n-type legs without metallic interconnects in between have however been proposed. By avoiding the metallic interconnects, manufacturing becomes both simpler and less expensive. Such a direct oxide p–n junction faces however not only challenges in terms of high contact resistances from charge carrier depletion, but also stability issues related to interdiffusion and formation of new phases at the interface region. These stability issues are addressed in the present investigation for the specific case of Ca$_{3}$Co$_{4-x}$O$_{9+d}$/CaMnO$_{3-d}$.

The recently reported all-oxide TEG made of p-type Ca$_{3}$Co$_{4-x}$O$_{9+d}$ and n-type CaMnO$_{3-d}$ introduced a new concept where a new phase with favorable thermoelectric properties is formed in situ at the interface between the p- and n-type conductors. Herein, we further study the materials and present a detailed analysis of the interdiffusion and formation of the secondary phases at the p–n interface in air and typical operating temperature of 900 °C.

According to Woermann et al., Ca$_{3}$Co$_{4-x}$O$_{9+d}$ is stable up to 926 °C in air, at which it decomposes to Ca$_{3}$Co$_{2}$O$_{6}$ and a Co$_{1-x}$Ca$_{x}$O (ss). Ca$_{3}$Co$_{4-x}$O$_{9+d}$ is described with a homogeneity range [Ca$_{3}$Co$_{4-x}$O$_{9+d}$] with x between −0.03 and +0.17 at 900 °C. The homogeneity range increases towards Co-rich compositions with increasing temperatures and becomes narrowly sharp, where it ends at a single point. The stoichiometry of Ca$_{3}$Co$_{4-x}$O$_{9+d}$ in our investigation corresponds to x within the homogeneity range as mentioned above, giving a maximum operating temperature of 900 °C. Ca$_{3}$Co$_{4-x}$O$_{9+d}$ has a superlattice-misfit structure consisting of two monoclinic subsystems: a triple rock salt (RS)-type slab of Ca$_{2}$Co$_{3}$O$_{6}$ and a single CdI$_{2}$-type CoO$_{2}$ slab. The subsystems have
identical $a$, $c$, and $\beta$ parameters, but different $b$ parameters: $a = 4.8376$ Å, $c = 10.833$ Å, $\beta = 98.06$, $b_1 = 4.5565$ Å, and $b_2 = 2.8189$ Å.\(^{10-13}\)

CaMnO$_{3-\delta}$ has an orthorhombic perovskite type structure, with lattice constants $a = 5.279$ Å, $b = 7.448$ Å and $c = 5.264$ Å at room temperature.\(^4\) Upon heating in air, the oxygen content is reduced and structural phase transitions occur at 893 and 913 °C with resulting tetragonal and cubic structural modifications, respectively.\(^{15}\) However, the phase transition temperatures are strongly dependent on the oxygen stoichiometry.\(^{16}\) According to the CaMnO$_{3-\delta}$ phase diagram the cubic-to-tetragonal and tetragonal-to-orthorhombic transformations occur when $3 - \delta = 2.965$ and 2.98, respectively, at 900 °C.\(^{17}\) Oxygen stoichiometry in air is reported to be 2.94 at 900 °C and hence CaMnO$_{3-\delta}$ should be in the cubic phase domain considering the heat treatment used in this work.

Golovkin et al. have reported phase diagrams of the system Ca-Mn-Co-O.\(^{18}\) Ca$_{1-x}$Co$_x$O$_{1.9}$ exhibits a certain solid solubility of Mn,\(^{19,20}\) and the formation of a quaternary phase Ca$_{2x}$Co$_{1-x}$Mn$_x$O$_{6}$ is described by several authors.\(^{21-23}\) This phase has been reported to have a K$_2$CdCl$_6$ type of structure, the same as the pristine Ca$_2$Co$_3$O$_5$ phase, with space group R3c. Both Hervoches et al.\(^{22}\) and Kanas et al.\(^{24}\) have confirmed a wide homogeneity range for Ca$_{3-x}$Co$_1$Mn$_{1-x}$O$_{4.5}$ extending from $y = 0$ to 1.

To establish all-oxide thermoelectric generators for operation in air at high temperatures, a detailed understanding of the processes taking place at the p-n junction at typical operating temperatures is decisive. In this investigation, we present a comprehensive study of the interdiffusion and formation of secondary phases at the Ca$_{3-x}$Co$_x$O$_{4.9}$/CaMnO$_{3-\delta}$ interface in air at 900 °C.

**Results and discussion**

The SEM cross section view of the specimen in Fig. 1 shows the interface between the relatively dense CaMnO$_{3-\delta}$ and the porous Ca$_{3-x}$Co$_x$O$_{4.9}$ layer after heat treatment at 900 °C for 10 h. The distribution of Co (pink), Mn (blue) and Ca (green) at and in the vicinity of the interface between Ca$_{3-x}$Co$_x$O$_{4.9}$ and CaMnO$_{3-\delta}$ is visualized in the bottom left inset in Fig. 1.

Two distinctly different regions are identified at the junction: “Region (a)” which is a ~10 μm thick porous region at the porous Ca$_{3-x}$Co$_x$O$_{4.9}$ side with a high density of Co-rich grains (pink in Fig. 1, bottom right inset).

“Region (b)” is a ~2 μm thick dense interphase region with a significantly higher Ca/Mn ratio compared to the bulk CaMnO$_{3-\delta}$ (green layer in Fig. 1, bottom right inset). Chemical analysis, topographically performed across the junction (Fig. 2), is in agreement with the observations from Fig. 1. The variations in the concentration of Ca, Mn and Co across the interface are given in Fig. 2b. Mn is seen to diffuse far into the porous Ca$_{3-x}$Co$_x$O$_{4.9}$, while the Mn concentration in Region (b) is lower than in the main bulk phase of CaMnO$_{3-\delta}$. Enhanced level of Ca is observed in Region (b) (interphase region) while a depletion in Ca is obvious in Region (a) (porous region). There is a moderate gradient in the Co concentration all through the Ca$_{3-x}$Co$_x$O$_{4.9}$ layer until we reach the boundary between Region (a) and (b), followed by a steep decrease across Region (b).

Co is also seen to diffuse rather far into the CaMnO$_{3-\delta}$ phase. This is in agreement with our recent data on bulk and enhanced grain boundary diffusivity of Co into CaMnO$_{3-\delta}$ where the bulk diffusivity at 900 °C would predict a diffusion length of 0.1 μm, while the enhanced grain boundary diffusion can explain the length closer to 10 μm in Fig. 2b. The faster diffusion of Mn into Ca$_{3-x}$Co$_x$O$_{4.9}$ is most probably related to the porosity promoting enhanced surface diffusion. After careful surface polishing from the Ca$_{3-x}$Co$_x$O$_{4.9}$ side (Fig. 3a), the polished surface was subjected to SEM/EDS analysis.

EDS elemental maps were taken along the surface (4 lowermost sections in Fig. 3b) and quantitative EDS analyses were made at 6 positions (“spots”) according to the numbering given in Fig. 3b (uppermost section). The results of the quantitative analysis are given in Table 1. Figure 3 shows the quantitative EDS analyses made at 6 positions for Ca, Co, Mn, and O at the Ca$_{3-x}$Co$_x$O$_{4.9}$/CaMnO$_{3-\delta}$ interface.
EDS analysis are given in Table 1. The compositions in positions 1 and 5 correspond to CaMnO$_3$ and Ca$_3$Co$_{4-x}$O$_{9+y}$, respectively, while position 6 most probably correspond to mixture of Ca$_3$Co$_{4-x}$O$_{9+y}$ and Co$_3$O$_4$. Position 3 (Region (b)) correspond to the quaternary phase, Ca$_{3}$Co$_{1+y}$Mn$_{1−y}$O$_6$ where the ratio between Ca and the sum of Mn and Co is 1.53 which is close to 1.5 as expected in Ca$_3$Co$_{1+y}$Mn$_{1−y}$O$_6$. We suggest that position 4 is representative for the porous region (Region (a)) due to the ratio Ca/(Mn + Co) is 1.33, which is between Ca$_3$Co$_3$Mn$_{1−y}$O$_6$ and Ca$_3$Co$_{4−y}$O$_{9+y}$. Position 2 shows a cation ratio between CaMnO$_3$ and Ca$_3$Co$_{1+y}$Mn$_{1−y}$O$_6$ and may be a mix of these two phases. It should be emphasized that there are uncertainties related to these calculations, both in the accuracy of the measurement as well as the fact that spot analysis also may include elements from phases below the point of analysis. Besides Ca redistribution, a thin densified reaction layer of Ca$_3$Co$_{1+y}$Mn$_{1−y}$O$_6$ is formed as a result of Co entering into CaMnO$_3$. Variations in the Co/Mn ratio across the Ca$_3$Co$_{1+y}$Mn$_{1−y}$O$_6$ reaction layer is expected as this forms a diffusion barrier for both cations and allows a wide range of mixing ratios, as seen from the steepness of both the Mn- and Co-profiles in Region (b) (Fig. 2).

Besides, a thermopower across the Ca$_3$Co$_{1+y}$Mn$_{1−y}$O$_6$ reaction layer in TEG is directly affected by the Co/Mn ratio in Ca$_3$Co$_{1+y}$Mn$_{1−y}$O$_6$, where the thermopower increases as Co/Mn ratio decreases.$^{24}$

The polished plane view surface was further analyzed by XRD for phase clarification, where the main reflections corresponded to CaMnO$_3$ and Ca$_3$Co$_{4−y}$O$_{9+y}$ (Fig. 4).

With respect to the annealing temperature (900 °C), which is close to the Co$_3$O$_4$/CoO phase transition in air,$^{26}$ Co will definitely be oxidized during cooling and at room temperature to exist as Co$_3$O$_4$. The broad and unsymmetrical set of reflections marked with ‘*’ fits well to the trigonal structure of Ca$_3$Co$_{1+y}$Mn$_{1−y}$O$_6$ with space group $R3c$. These results are in good agreement with our EDS compositional analysis (Fig. 3 and Table 1).

A detailed TEM/EDS analysis of the interface between CaMnO$_3$ and Region (b) is presented in Fig. 5, where (a) to (d) are STEM-image and EDS analysis, while (e) and (f) are TEM-image and SAD zone axis patterns, respectively. The most striking feature is the sharp boundary between CaMnO$_3$ and Region (b) shown by the yellow line in Fig. 5(e). Above the yellow line, the Ca$_3$Co$_{1+y}$Mn$_{1−y}$O$_6$ phase is confirmed by the SAD $[121]$ zone axis patterns shown in (f), and further supported by the EDS analysis in (b)–(d) showing the presence of Ca, Co and Mn. The absence of Co and presence of Ca and Mn below the yellow line ((b)–(d)) confirm the presence of only CaMnO$_3$ in this region. Although we expect some diffusion of Co into the

### Table 1

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<td>21</td>
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Fig. 3 (a) A schematic illustration of the polished sample prior to SEM/EDS analysis. The figure is not drawn to scale, and Regions (a) and (b) are extended for the sake of clarity. (b) Plane view of back scattered electron image (uppermost section) followed by corresponding EDS maps of Ca (green), Co (pink), Mn (blue) and O (red). The assessment of the chemical composition was supplemented by spot EDS analysis according to the positions numbered from 1 to 6 in the uppermost section, and the results are given in Table 1.
CaMnO₃₋₅ phase (Fig. 2), the concentration is below the detection limit in (d).

The CaMnO₃₋₅ grains are identified as the low temperature (LT) orthorhombic CaMnO₃₋₅ phase (Fig. 4) and the appearance of the CaMnO₃₋₅ grains in Fig. 5(e) indicate high defect concentration appearing as a line pattern.

The high defect concentration is probably due to tensile stresses in CaMnO₃₋₅ originating from the phase transition between the high temperature cubic phase (HT) to the LT phase, which is followed by a significant volume contraction.

A detailed TEM/EDS analysis of Region (a) is given in Fig. 6. The EDS analysis in Fig. 6(c) confirms the formation of a Co-oxide rich phase, however connected to a phase containing Ca, Co and Mn. SAD [12–1] zone axis patterns identified this phase to be Ca₃Co₁₋ₓMn₁₋ₓO₆ (Fig. 6(d)) showing that Ca₃Co₁₋ₓMn₁₋ₓO₆ also may be formed quite far from the initial interface between Ca₃Co₄₋ₓO₉₋₅ and CaMnO₃₋₅. The reason for the formation of Ca₃Co₁₋ₓMn₁₋ₓO₆ far into Region (a) is a combination of Co depletion of the Ca₃Co₄₋ₓO₉₋₅ phase, due to diffusion of Co towards CaMnO₃₋₅ and counter diffusion of Mn into the Ca₃Co₄₋ₓO₉₋₅ phase (some solid solubility). At some critical composition, Ca₃Co₄₋ₓO₉₋₅ will decompose and form Ca₃Co₁₋ₓMn₁₋ₓO₆ and a Co-oxide rich phase. The depletion of Ca in Region (a) (Fig. 2b) suggests that Ca diffuses towards Region (b), which is intuitively surprising since diffusion seemingly takes place against its concentration gradient.

However, assuming that the thermodynamic activity (chemical potential) of calcium in the Ca₃Co₄₋ₓO₉₋₅ phase is much higher than in the Ca₃Co₁₋ₓMn₁₋ₓO₆ phase there will be a thermodynamic driving force for Ca-diffusion from Region (a) to Region (b). This explains the enhanced Ca concentration in Region (b) and Ca depletion in Region (a) (Fig. 2b). However, the formation of Ca₃Co₁₋ₓMn₁₋ₓO₆ depends on diffusion of Mn through the increasing layer of dense Ca₃Co₁₋ₓMn₁₋ₓO₆ which is expected to follow the parabolic law. Hence, the formation of Ca₃Co₁₋ₓMn₁₋ₓO₆ will virtually stop with time, corresponding to a fixed thickness of the Ca₃Co₁₋ₓMn₁₋ₓO₆ layer. The effect of counter diffusion and the formation of Ca₃Co₁₋ₓMn₁₋ₓO₆ on TEG performance is thoroughly elaborated in a previous paper by Kanas et al.⁶ Ca₃Co₁₋ₓMn₁₋ₓO₆ forms together with Ca₃Co₁₋ₓO₉₋₅ and CaMnO₃₋₅ a p–p–n junction which exhibits ohmic behavior and a transverse thermoelectric effect, boosting the open-circuit voltage of the module. Furthermore, the electron energy levels of Ca₃Co₁₋ₓMn₁₋ₓO₆ are located intermediate of those of Ca₃Co₄₋ₓO₉₋₅ and CaMnO₃₋₅, which reduces the depletion of charge carriers at the Ca₃Co₄₋ₓO₉₋₅–Ca₃Co₁₋ₓMn₁₋ₓO₆ and Ca₃Co₁₋ₓMn₁₋ₓO₆–CaMnO₃₋₅ interfaces, as compared to initial Ca₃Co₁₋ₓO₉₋₅–CaMnO₃₋₅ p–n interface.⁶

DFT results for the mixing energy of Ca₃Co₁₋ₓMn₁₋ₓO₆ depicted in Fig. 7 show small negative values for the entire composition range, with a shallow minimum at y = 0.25, corresponding to a mixing energy of −5 meV per formula unit. According to the DFT calculations the most stable Ca₃Co₁₋ₓMn₁₋ₓO₆ composition should be in the vicinity of y ~ 0.25, corresponding to a [Co]/[Mn] ratio of ~1.67.

Nevertheless, the negative mixing energy obtained in the entire range from y = 0.1 to 0.9 supports the existence of solid solubility in the whole range from y = 0 to 1, as confirmed by Hervoches et al.²² and Kanas et al.²⁴ A small mixing energy is reasonable given that Co and Mn have similar atom sizes, and the DFT result serves to confirm that the nature of chemical bonding is not greatly affected by the substitution. At finite temperature the free energy would clearly show a broad minimum dominated by the entropy term which was not considered in these 0 K calculations.

All in all, the comprehensive structural analysis of the Ca₃Co₄₋ₓO₉₋₅/CaMnO₃₋₅ p–n junction gives an important overview of the complexity, described by counter diffusion and formation of several reaction products at the interface. In high-

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**Fig. 4** XRD diffractogram of the polished top view surface at the interface between CaMnO₃₋₅ and Ca₃Co₄₋ₓO₉₋₅. The reflections marked with ‘+’ and ‘−’ are due to the presence of Ca₃Co₁₋ₓMn₁₋ₓO₆ and Ca₃Co₄₋ₓO₉₋₅, respectively. CaMnO₃₋₅ is identified as the low temperature (LT) orthorhombic phase while Ca₃Co₁₋ₓMn₁₋ₓO₆ fits well with a trigonal structure with space group R3c. CaMnO₃₋₅ and Ca₃Co₄₋ₓO₉₋₅ are marked as (CMO) (CCO), respectively.

**Fig. 5** (a) STEM and (e) TEM images of Region (b) connected to CaMnO₃₋₅ with the corresponding EDS maps of (b) Ca, (c) Mn and (d) Co. The yellow line in (e) marks the interface between CaMnO₃₋₅ (lower part) and Ca₃Co₁₋ₓMn₁₋ₓO₆ (upper part). SAD [12–1] zone axis patterns of regions above the yellow line (grain A and B) confirm the presence of Ca₃Co₁₋ₓMn₁₋ₓO₆ and an example is shown in (f).
temperature applications the hot side of this TEG boosts the overall performance through a high open circuit voltage which occurs due to counter diffusion of cations resulting in formation of $\text{Ca}_3\text{Co}_{1+y}\text{Mn}_{1-y}\text{O}_6$ with a high thermopower.\(^5,\text{34}\)

**Conclusions**

The $\text{Ca}_3\text{Co}_{4-x}\text{Mn}_x\text{O}_{9+y}/\text{CaMnO}_3$ $\text{P-n}$ junction is not stable at 900 °C as a new $\text{Ca}_3\text{Co}_{1+y}\text{Mn}_{1-y}\text{O}_6$ intermediate phase forms through counter diffusion of Ca, Co and Mn. On the $\text{CaMnO}_3$ side, a thin dense layer of $\text{Ca}_3\text{Co}_{1+y}\text{Mn}_{1-y}\text{O}_6$ with variable composition forms, in which further in-diffusion of Co is slow. On the $\text{Ca}_3\text{Co}_{4-x}\text{Mn}_x\text{O}_{9+y}$ side, Mn diffusion into $\text{Ca}_3\text{Co}_{1+y}\text{Mn}_{1-y}\text{O}_6$ together with Co deficiency gives decomposition into $\text{Ca}_3\text{Co}_{1+y}\text{Mn}_{1-y}\text{O}_6$ and Co-oxide. The diffusion profiles are in qualitative agreement with our recently published data on Co diffusion in $\text{CaMnO}_3$. DFT calculations and experimental evidence support the wider homogeneity range ($0 \leq y \leq 1$) of $\text{Ca}_3\text{Co}_{1+y}\text{Mn}_{1-y}\text{O}_6$.

**Experimental**

Phase-pure $\text{CaMnO}_3$ powder was synthesized by solid-state reaction using a stoichiometric ratio of $\text{CaCO}_3$ (Inframat Advanced Materials, >99% purity) and $\text{MnO}_2$ (Sigma Aldrich, >99% purity) precursors, mixed and heated twice at 1200 °C for 14 h in air with grinding in between. A dense $\text{CaMnO}_3$ pellet (diameter 12 mm, thickness 4 mm) was formed by cold isostatic pressing (CIP) at 200 MPa followed by sintering at 1300 °C for 14 h in air using a heating rate of 200 K h\(^{-1}\) and cooling rate of 100 K h\(^{-1}\). The dense $\text{CaMnO}_3$ pellet was ground and polished with SiC papers and diamond paste to 1 μm. $\text{Ca}_3\text{Co}_{4-x}\text{Mn}_x\text{O}_{9+y}$ powder, with the nominal stoichiometry $\text{Ca}_3\text{Co}_{1+y}\text{Mn}_{1-y}\text{O}_6$, was prepared by spray pyrolysis (CerPoTech AS, Norway), and a $\text{Ca}_3\text{Co}_{4-x}\text{Mn}_x\text{O}_{9+y}$ layer was produced by tape casting according to ref. 6. The tape was cast, laminated, and attached onto the polished $\text{CaMnO}_3$ surface by pressing at 10 MPa and 80 °C for 3 min. The sample was then calcined at 450 °C for 1 h in air to remove organics and further heated at 900 °C for 10 h. Firm adhesion between $\text{Ca}_3\text{Co}_{4-x}\text{Mn}_x\text{O}_{9+y}$ and $\text{CaMnO}_3$ was obtained after the heat treatment.

The sample was subsequently embedded in epoxy and divided in pieces for both cross section and plane view examinations. The specimens were ground with SiC paper, and final polishing was done with colloidal $\text{Al}_2\text{O}_3$ (0.05 μm). For the plane view examination, the specimen was polished down stepwise from the $\text{Ca}_3\text{Co}_{4-x}\text{Mn}_x\text{O}_{9+y}$ side. The exposed area was analyzed by scanning electron microscopy (SEM) with energy dispersive X-ray energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) in between each polishing step. Cross section specimens were examined by a combination of SEM and transmission electron microscopy (TEM) enabling structural studies at both micro- and nanoscale. The TEM specimen, covering a ∼15 μm long region across the $\text{CaMnO}_3$/$\text{Ca}_3\text{Co}_{4-x}\text{Mn}_x\text{O}_{9+y}$ interface, was cut out by use of a focused ion beam (FIB) and thinned down to about 100 nm. EDS was conducted to map and quantify the elemental composition globally and locally by SEM and TEM, respectively. To improve statistics, line scan data sets were added after aligning the onset of the dense interface region.

A Rigaku MiniFlex600 system using Cu Kα radiation and florescence correction was used for the XRD investigation, while a Hitachi TM3000 SEM, a JEOL2010F TEM operated at 200 kV and a Cs probe corrected FEI Titan G2 60-300 TEM operated at 300 kV were used for the SEM and TEM studies.
The mixing energy of Ca$_3$Co$_{1+y}$Mn$_{1-z}$O$_{6}$ was calculated within the spin-polarized density functional theory (DFT) utilizing the projector-augmented-plane wave method as implemented in VASP$^{27,28}$ and choosing the generalized-gradient approximation functional PBE$^{29}$ A supercell consisting of $2 \times 2 \times 2$ primitive unit cells was used to emulate the solid solution, which was set up by randomly replacing 2, 4, 6, 8, 10, 12, and 14 of the 16 Mn atoms with Co atoms in the Ca$_3$Co$_{1+y}$Mn$_{1-z}$O$_6$ supercell. To obtain an estimate of the mixing energy, we rely on a ferromagnetic ordering with spin aligned in intra-chain (111) direction. The plane-wave energy cutoff was set to 520 eV with a $2 \times 2 \times 2$ Monkhorst-Pack $k$-point sampling of the Brillouin zone. Atomic coordinates and unit cell were relaxed until the total energy varied by less than 0.03 meV per formula unit.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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