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RESEARCH HIGHLIGHTS

+ From Caltech's Resnick Fellows

Developing efficient cathode materials
for solid oxide fuel cells



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Developing efficient cathode materials for solid oxide fuel cells

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Global Significance

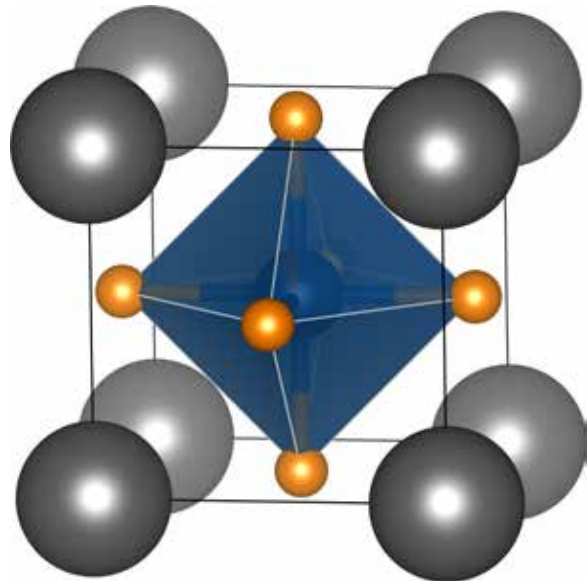
Our society relies heavily on fossil fuels to power our economies. However, limited fossil fuel reserves and the negative environmental impact of fossil fuel combustion calls for the development of sustainable energy resources.

Solid oxide fuel cells offer efficient electrochemical conversion of chemical fuels to electrical energy bypassing the inefficient combustion process. Currently, solid oxide fuel cells typically operate at elevated temperatures of above 1000 °C where ionic and electronic transport properties are fast. However, such harsh operating conditions impose stringent material requirements on solid oxide fuel cell components and demand long start up times.

Lower operating temperatures often lead to losses in efficiencies due to sluggish ionic and electronic transport processes at these moderate temperatures. These losses in efficiency at intermediate temperatures are particularly prominent at the cathodes of solid oxide fuel cells.

Our goal is to develop design strategies for cathode materials with high ionic and electronic conductivity at moderate temperatures.

By understanding the physics of x-ray absorption, local and average coordination chemistry and the materials properties of $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$, we develop general guidelines for improving solid oxide cathode performance at intermediate temperatures.



The cubic crystal structure of $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$. Co/Nb cations are shown in blue, Sr is gray, while oxygen anions are orange. In this structure, $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ exhibits high ionic and electronic conductivity leading to high efficiency solid oxide fuel cell cathode performance at intermediate temperatures.

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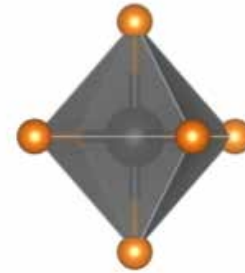
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Project Summary

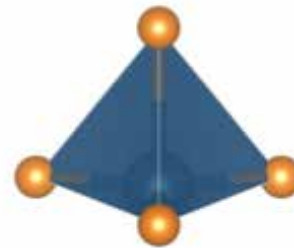
Fast transport of ions and electrons at moderate temperatures is important for high performance solid oxide fuel cell materials. $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ is an ideal material that exhibits fast ionic and electronic transport properties at moderate temperatures. To understand the origin of fast transport properties in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$, we investigate its structure.

One would determine travel speed on land by looking at an aerial map which shows general geographic features such as hills and valleys and in addition consider the specific characteristics of the roads to be used such as road conditions and the number of traffic stops. We use the same approach to determine the origin of the fast transport properties of $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$. We investigate average structure by determining the repeating unit that gives rise to this material using X-ray diffraction. We also take a closer look at the local environment around Co, Nb, and Sr in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ using x-ray absorption studies.

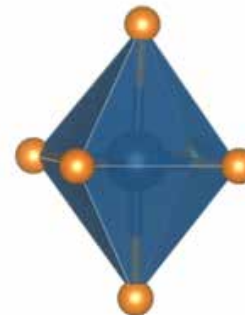
We find that Nb, which is a highly charged cation, retains ideal coordination around it. Despite distortions in the local environment of Co, $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ has a high symmetry cubic structure because of the presence of distributed ideal NbO_6 structural units. Fast transport properties that are observed at high temperatures in $\text{SrCoO}_{3-\delta}$ are preserved at intermediate temperatures in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ because of the presence of Nb. This allows for fast ionic and electronic transport properties at intermediate temperatures in this material.



Ideal NbO_6



Distorted CoO_4



Distorted CoO_6

An illustration of the local environments of Nb and Co in cubic $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$. Nb occupies perfect octahedral (NbO_6) coordination as shown in gray while Co occupies two distorted sites shown in blue, an octahedral (CoO_6) and a tetrahedral site (CoO_4). Despite the local distortions of Co, on average $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ retains cubic average symmetry where high ionic and electronic conductivity can be achieved due to the presence of distributed ideal NbO_6 octahedral units.

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Potential Impact

The fundamental study of the origin of high conductivity at moderate temperatures in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ has far reaching effects that will ultimately lead to the development of other high performance cathode materials at intermediate temperatures.

What sets this research apart is the fundamental approach which yields important lessons in solid oxide fuel cell cathode design. We merge numerous techniques, combining x-ray diffraction and x-ray absorption, and ultimately show that a microscopic understanding of structure is crucial to unraveling the origin of improved conductivity in this material.

Ultimately, this research will enable the design of efficient solid oxide fuel cells that operate at intermediate temperature mitigating costs and stringent materials requirements associated with conventional solid oxide fuels that operate at high temperatures.

So far, solid oxide fuel cells have found applications in remote areas such as in space probes and in stand alone power supplies for data centers. Improvements such as lower operating temperatures and higher efficiencies will bring this technology to our door steps.

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The Science

Substitution of highly charged cations such as Nb^{5+} in place of Co in $\text{SrCoOO}_{3-\delta}$ stabilize the cubic structure to low temperatures allowing for high ionic and electronic conductivity in this material at moderate temperatures. We prepare an array of materials $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ where $0.21 \leq \delta \leq 0.49$. These systems have an average cubic structure as shown by room temperature x-ray diffraction. X-ray absorption studies of the Nb, Sr, and Co K-edge reveal fixed Sr^{2+} and Nb^{5+} oxidation states despite changes in δ , while the Co oxidation state varies between $\text{Co}^{2.67+}$ and Co^{3+} to accommodate the changes in oxygen content. In cubic $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$, symmetry requires that both Nb and Co occupy ideal octahedral coordination. However, local structure studies reveal ideal octahedral coordination around Nb^{5+} but distorted octahedral and tetrahedral sites around Co cations. The distribution of ideal NbO_6 octahedral units in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ inhibits vacancy ordering thus allowing for high ionic and electronic conductivity. High conductivity of oxygen anions and electrons at moderate temperatures makes $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ an ideal cathode material for intermediate temperature solid oxide fuel cells.

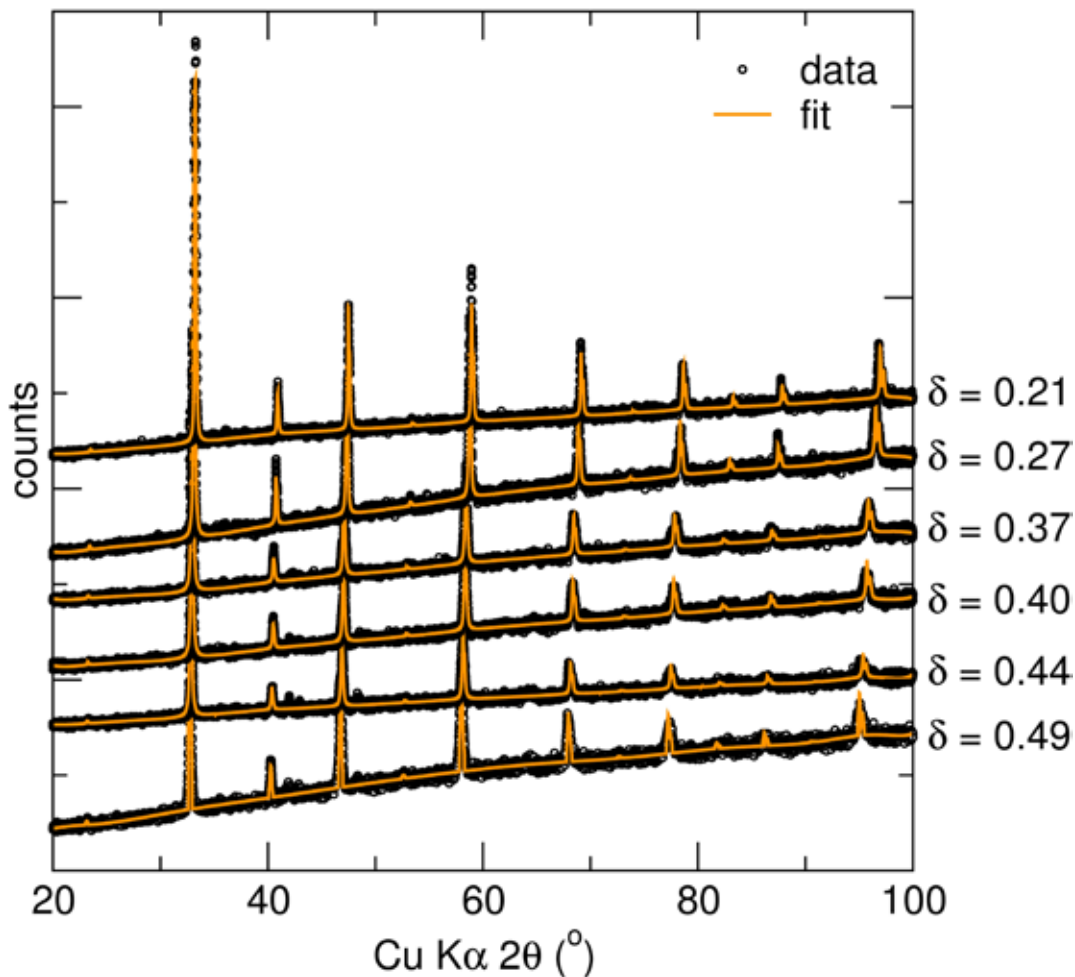
Key Results

Highly charged Nb^{5+} cation centers in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ preserve ideal local octahedral coordination while local Co environments show significant under-coordination and distortion with a range of Co bond lengths. Despite the distortions around Co cations, the distribution of ideal NbO_6 octahedral units in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ inhibits vacancy ordering stabilizing cubic symmetry in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ and ultimately ensuring high ionic and electronic conductivity. Our work suggests that the substitution of highly charged cations can help stabilize high symmetry structures in transition metal oxides and thus help improve ion and electron conductivity.

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Key Results

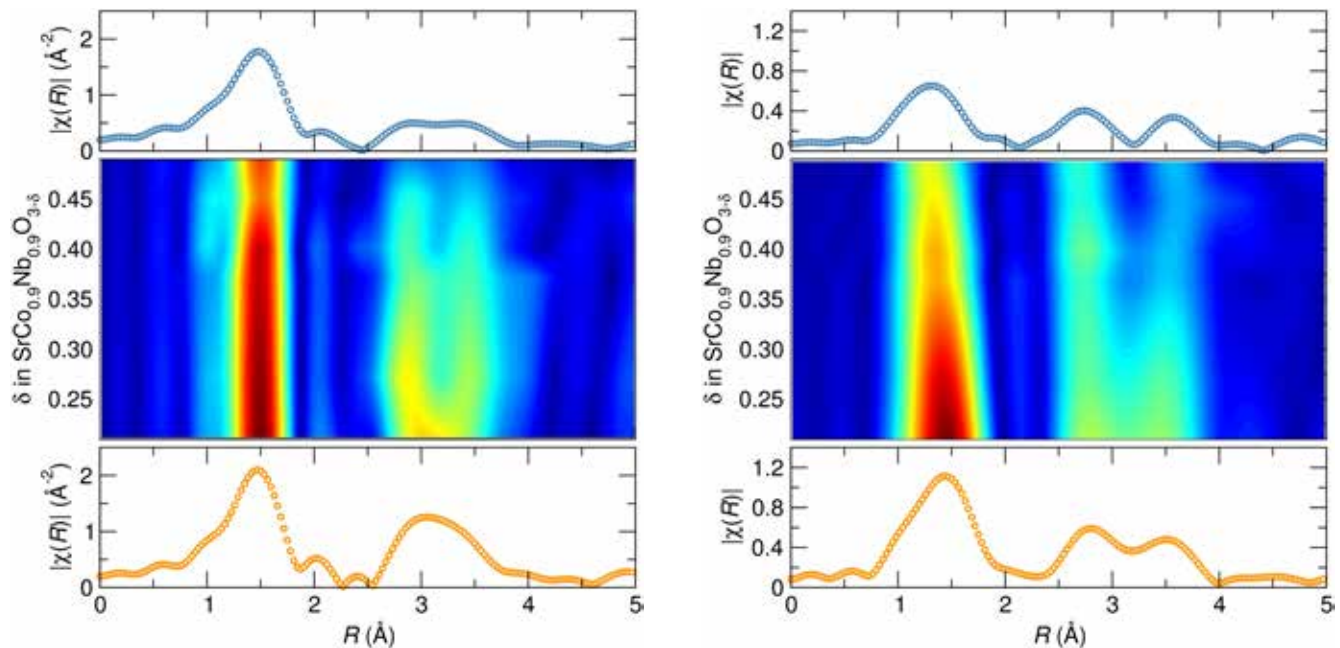


Room temperature x-ray diffraction patterns (black) of $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ are well modeled by the cubic structure shown in the inset. The cubic structural model is shown in orange. Nb substitution in place of Co stabilizes the cubic phase where ideal ionic and electronic conductive properties can be attained at moderate temperatures.

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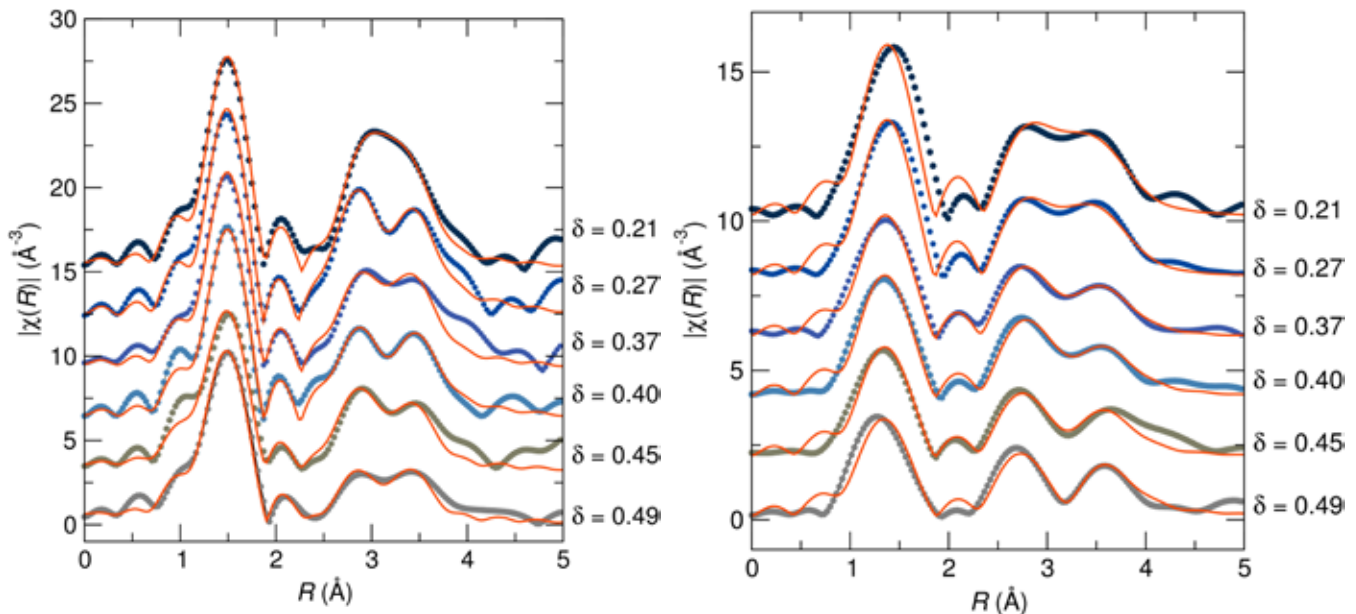


The extended x-ray absorption fine structure (EXAFS) of Nb (left) and Co (right) in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ where $0.21 \leq \delta \leq 0.49$. The data shows the local environment around Nb (left) and Co (right). The various peaks correspond to different coordination shells around Nb and Co. The peak at the shortest distance (R) corresponds to Nb(Co)-O bond lengths, the intermediate distance peak is from Nb(Co)-Sr coordination shells while the farthest shell is due to Nb(Co)-Co coordination. While the Nb-O (left) bond length shows modest changes in intensity and minimal shifts with increase in δ , there is a drastic decrease in intensity and a shift to left of the Co-O (right) bond length with δ . This suggests that increase in oxygen deficiency leads to lower coordination and local distortions around Co while Nb preserves ideal octahedral coordination. Beyond the nearest neighbor coordination shell, the further neighbor coordination shells of both Nb and Co show a marked decrease in intensity with increase in δ .

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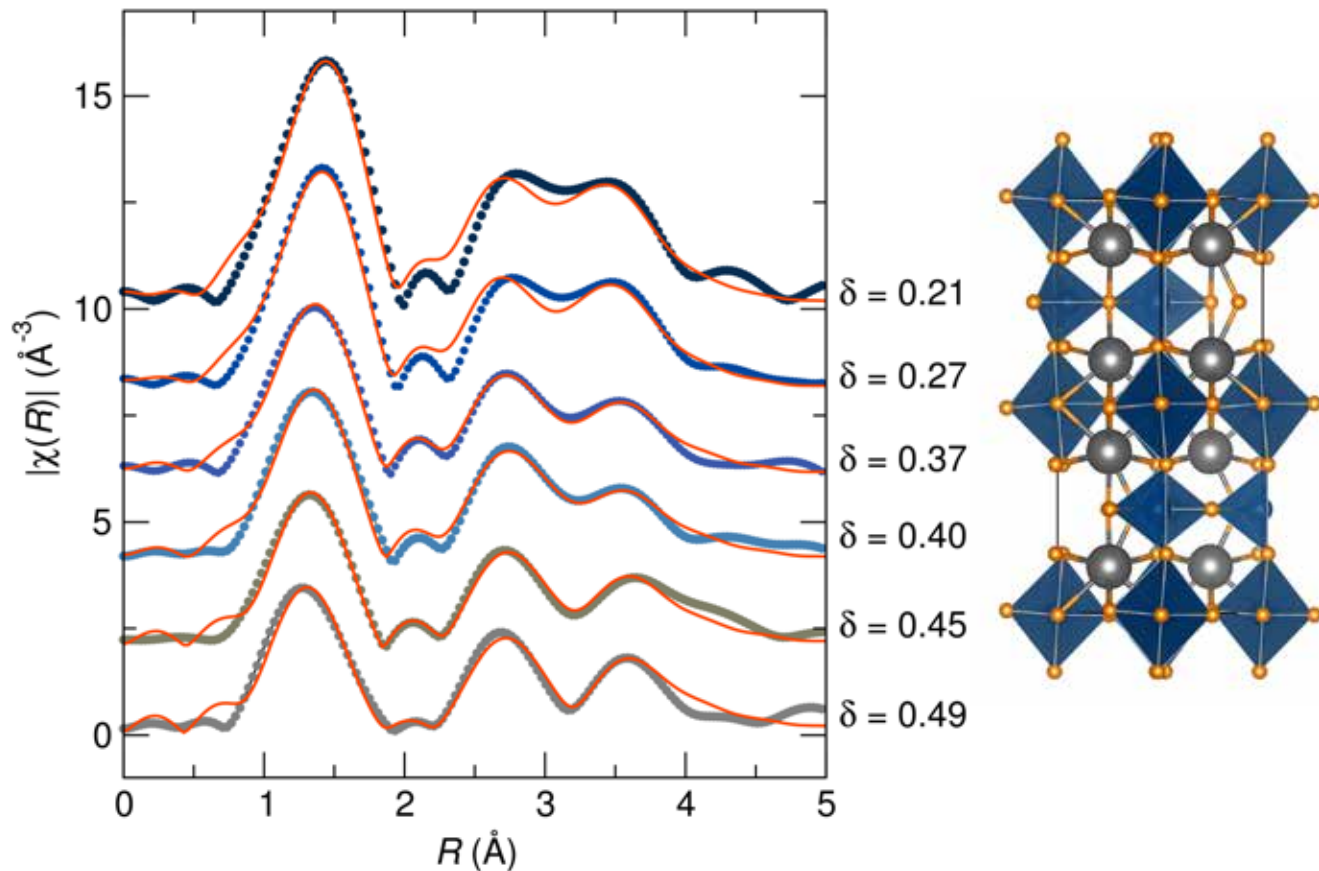


The extended x-ray absorption fine structure of Nb (left) and Co (right) in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ as modeled by the cubic structure of $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$. The local structure model is shown in orange. Nb occupies ideal octahedral coordination environments in the series $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ as evidenced by the great agreement between the data and the cubic model as illustrated in the left figure. The Co local structure is distorted from ideal octahedral symmetry as shown by discrepancies between the data and the cubic fit for the nearest neighbor Co-O bond length in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$.

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Key Results



The local structure of Co in $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ modeled to the orthorhombic structure of $\text{SrCoO}_{3-\delta}$ which is shown on the right. Better agreement between the orthorhombic model (orange) and the data especially for the nearest neighbor Co-O coordination shell shows that the environment around Co consists of distorted CoO_6 octahedral and CoO_4 tetrahedral units.

Future Steps

We show material design strategies to achieve high conductivity phases at intermediate temperatures through substitution of highly charged cations in transition metal oxides. This finding opens opportunities for further material design to identify new highly conductive compositions at intermediate temperature for applications in solid oxide fuel cells. We also show the importance of understanding both local and average structure in order to understand structure-property relations in functional materials encouraging the use of local (x-ray absorption) and average (diffraction) probes in material studies.