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Evolution of the A-site Coordination of Sr_{1-x}Ca_xFeO₂ (x = 0, 0.8 and 1)Cédric Tassel,^a Masaichiro Mizumaki,^b Saburo Hosokawa,^a Yoji Kobayashi,^a Hiroshi Kageyama^a^a Kyoto University, ^b Japan Synchrotron Radiation Research Institute**Abstract**

In this report, we have investigated the local coordination of strontium and calcium in Sr_{1-x}Ca_xFeO₂ (x = 0, 0.8 and 1) via extended x-ray absorption fine structure at room temperature. We observe the different local coordinations in the infinite layer phases (x = 0, 0.8) and distorted infinite layer structure CaFeO₂.

Keywords: Infinite Layer, Square-Planar Coordination, Perovskite

Background and Purpose

Iron oxides are well known in solid state chemistry to yield mainly octahedral, tetrahedral and pyramidal coordination around iron. A decade ago, we have discovered a rare case of square planar coordination around iron via low temperature topochemical reduction of SrFeO₃, which is a perovskite that contains corner-shared octahedra (Fig. 1a)[1]. SrFeO₂ exhibits a structure known as an “infinite layer” that was previously observed in SrCuO₂ (P4/mmm) and LaNiO₂. In SrFeO₂, the layers are separated by strontium (A-site) in an eight-fold coordination. Expansion of the low temperature strategy allowed for the discovery of more materials containing square planar FeO₄ units such as Sr₂FeO₃ and Sr₃Fe₂O₅, which were obtained from the reduction of the Ruddlesden-Popper phases Sr₂FeO₄ and Sr₃Fe₂O₇ [2,3]. Further expansion of this family was obtained via chemical substitution of the A site Sr_{1-x}A_xFeO₂ (A = Ca, Ba, Nd, Sm, Ho) [4-8] and B site SrFe_{1-x}B_xO₂ (B = Ru, Co, Mn) [9,10].

The Sr_{1-x}Ca_xFeO₂ solid solution is unique, since while the infinite layer structure remains up to x = 0.8, at higher calcium contents, CaFeO₂ exhibits a distorted structure (P-421m) where calcium shifts out of the median plane and the square planes of iron distort tetrahedrally and rotate within the layers (Fig. 1b). Out-of-plane distortions of square planes towards tetrahedra are rare⁷ but here occur because Ca, smaller than Sr, would rather prefer a six-fold coordination.

In this report, we have investigated the local structural changes occurring in the Sr_{1-x}Ca_xFeO₂ solid solution before and after the structural transition at room temperature (x > 0.8). The goal of this research was to investigate the possible coordination differences between calcium and strontium in SrFeO₂, Sr_{0.2}Ca_{0.8}FeO₂ and CaFeO₂. The use of extended X-ray absorption spectroscopy (EXAFS) allows for local structural observations that cannot be obtained in diffraction data which provides averaged structural information.

Experimental Summary

The materials were prepared using methods reported in ref. 6. EXAFS data were obtained from the absorption spectroscopy data studied at the Sr K-edge (16.11 keV) and Ca K-edge (4.04 keV) in transmission mode measured at the BL01B1 beamline at SPRING-8 (Japan). The k-weight and range were k³ and 2–14 Å⁻¹ for the calculation of the Fourier transform. The k³χ(k) spectra of Ca in CaFeO₂ and Sr_{0.2}Ca_{0.8}FeO₂, Sr in SrFeO₂ and in Sr_{0.2}Ca_{0.8}FeO₂ are shown in Figure 2.

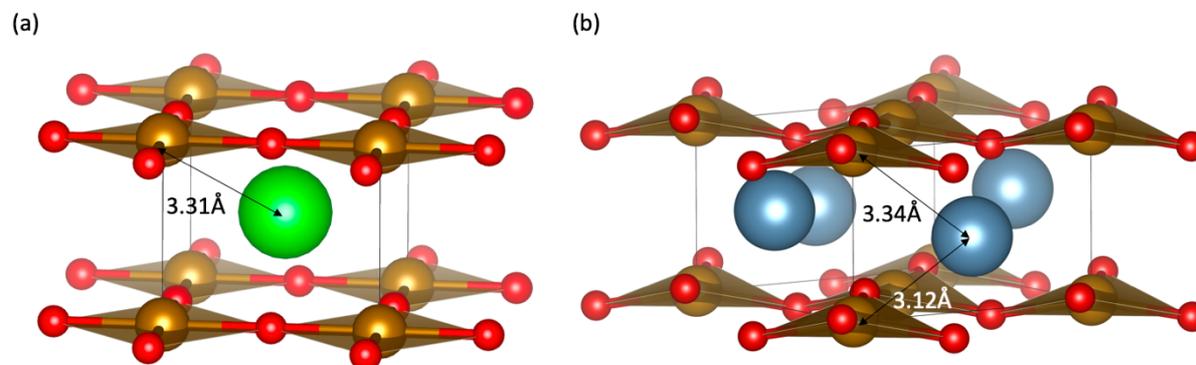


Fig. 1. (a) Crystal structure of SrFeO₂. The red, orange and green spheres represent, oxygen, iron and strontium, respectively. (b) Crystal structure of CaFeO₂. The blue spheres represent calcium.

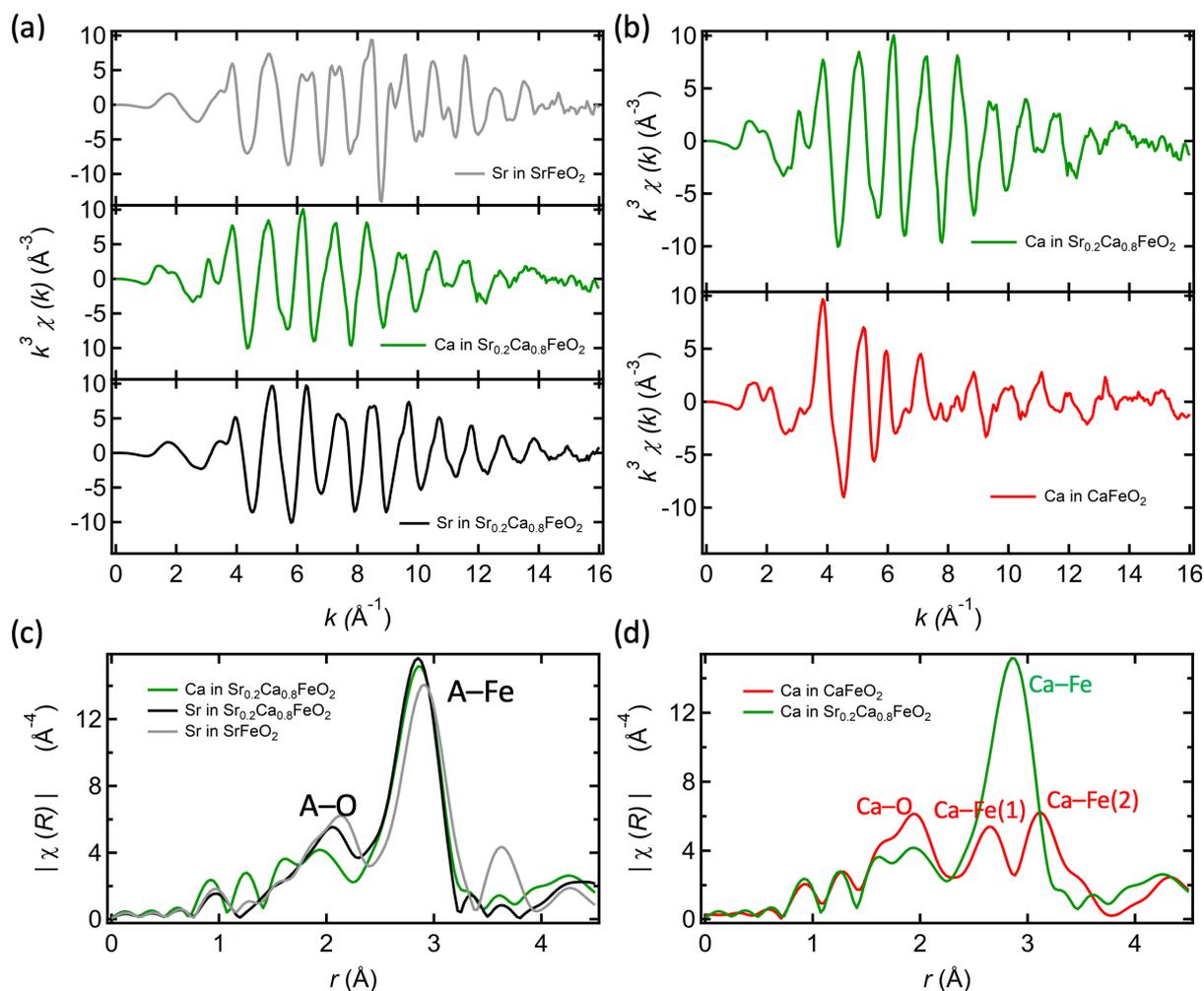


Fig. 2. (a) $k^3\chi(k)$ spectra of Ca in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$, Sr in SrFeO_2 and Sr in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$. (b) $k^3\chi(k)$ spectra of Ca in CaFeO_2 and Ca in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$. (c) Comparison of extended x-ray absorption spectroscopy of Sr in SrFeO_2 , Sr in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$ and Ca in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$. (d) EXAFS of calcium in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$ compared to the EXAFS spectrum of CaFeO_2 .

Results and Discussion

Figure 2c shows the radial distribution function obtained from EXAFS data of the Sr K-edge in SrFeO_2 which exhibits two main peaks. As seen in figure 1a, in the SrFeO_2 structure, the local environment of strontium consists of eight oxygen in the first coordination sphere with a distance of 2.65 Å. This distance can be assigned to the peak 1 (labeled “A-O”) located at 2.15 Å. This value is smaller than expected from the diffraction data, due to the backscattering phase term of the EXAFS equation. Peak 2 (labeled “A-Fe”), the largest peak at around 2.91 Å, can be assigned to the Sr–Fe and the out-of-plane Sr–Sr distances, at 3.31 Å and 3.47 Å, respectively.

Next, we compare the Sr- and Ca-centered radial distribution functions of the Ca-substituted structure ($x = 0.8$). Looking at peak 1 (A-O) of figure 2c, the Ca-O length (light green) is naturally the shortest (~1.96 Å), while the Sr-O distance in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$ (black) is longer, and closer to that in SrFeO_2 (grey). However, peak 2 (A-Fe), which reflects the second coordination shell and hence longer-range order, shows a different story. Here, the Sr-Fe and Ca-Fe lengths (black and light green) in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$ are indistinguishable and equally shorter than in SrFeO_2 . Within $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$, Sr and Ca occupy crystallographically equivalent sites, but these differences between peaks 1 and 2 suggest that there is more local distortion around Ca rather than Sr, based on the different A-O distance. This is not observed using diffraction data, which tends to average atomic positions and makes it difficult to characterize local structure. This observation should however be taken with care owing to the difficulties inherent with EXAFS concerning distances and the presence of a

“ghost peak” on the left shoulder of peak **1** in figure 2c.

In figure 2d, the structure of $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$ and the distorted infinite layer CaFeO_2 are compared in terms of Ca-centered radial distribution functions. The first peak assigned to Ca–O is located at a similar position for both CaFeO_2 and $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$ (red and green), which suggests that the Ca–O environment should be similar in the two phases. The main change between the infinite layer structure and the distorted infinite layer can be witnessed by the two peaks observed at 2.64 Å and 3.13 Å. The former can be assigned to the bond lengths obtained from diffraction (figure 1b), the short Ca–Fe(1) distance 3.12 Å and the longer Ca–Fe(2) distance 3.34 Å and out-of-plane 3.35 Å Ca–Ca distance. This observation confirms the displacement of the Ca atoms from the median plane of the lattice in agreement with the diffraction data. The distances are different however from the diffraction determined one with a 0.49 Å difference measured with EXAFS between Ca–Fe(1) and Ca–Fe(2) and 0.22 Å measured by diffraction. This may therefore indicate that more complex distortions occur within the material.

Challenges

The difficulty of this study lies in the quantitative investigation of the local structure around the *A* site. In this study we have observed that in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{FeO}_2$, strontium and calcium sit in similar environments. EXAFS of the different atoms suggest however shorter Ca–O bonds than Sr–O. Precise determination of the local structure of Ca in this structure is however difficult using this sole technique. Although here, we observed a qualitative difference between Ca and Sr, it is difficult to represent the genuine overall structure of the material and subtle changes of coordinations of iron as a function of the different atoms in its vicinity. To solve this, only a combination of different techniques (pair-distribution function, EXAFS and X-ray/neutron diffraction) could lead to the complete understanding of the anionic and cationic distribution of the structure.

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