Fe and Cr K-edges EXAFS Study of Double Perovskite \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\) \((0 \leq x \leq 2.0)\) and \(\text{Sr}_2\text{CrMO}_6\) \((\text{M} = \text{Mo}, \text{W})\) Systems

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The local structure of the double perovskite \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\) \((0 \leq x \leq 2.0)\) and \(\text{Sr}_2\text{CrMO}_6\) \((\text{M} = \text{Mo}, \text{W})\) systems have been probed by extended X-ray absorption fine structure (EXAFS) spectroscopy at the Fe and Cr K-edges. We found Fe-O (ave) distance apparently decreases from 1.999 Å \((x = 0)\) to 1.991 Å \((x = 1.0)\) in \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\) (tetragonal structure). When \(x\) is increased further from 1.5 to 2.0, the Fe-O bond distance decreased from 2.034 Å to 2.012 Å (monoclinic structure). In addition, Cr-O, Sr-Cr, and Cr-Mo bond distances in \(\text{Sr}_2\text{CrWO}_6\) are all slightly larger than the bond distances of \(\text{Sr}_2\text{CrMoO}_6\), which is due to the ionic radius of the \(\text{W}^{5+}\) (0.62 Å) which is larger than the ionic radius of \(\text{Mo}^{5+}\) (0.61 Å). The results are consistent with our XRD refinements data.

Keywords: Double perovskites; X-ray absorption spectroscopy; EXAFS.

INTRODUCTION

In ordered double perovskites, denoted as \(\text{A}_2\text{BB'}\text{O}_6\) (where \(\text{A} = \) alkaline-earth or rare-earth ion), the transition metal sites are occupied alternately by different cations \(\text{B}\) and \(\text{B'}\). It is well known that the differences in the valence and size between \(\text{B}\) and \(\text{B'}\) cations in double perovskite type compounds are crucial in controlling physical properties.\(^1\)\(^-\)\(^2\) Recently, Kobayashi et al. have reported a high spin polarization for an oxide material with a double-perovskite structure, \(\text{Sr}_2\text{FeMoO}_6\), which also has a high Curie temperature, \((T_C = 420 \text{ K})\).\(^3\) Other Fe-based ordered double perovskites \(\text{A}_2\text{FeMO}_6\) \((\text{A} = \text{Ba}, \text{Sr}, \text{Ca}; \text{M} = \text{Mo}, \text{Re})\) have also been reported having a tunneling magnetoresistance (TMR) nature and a high \(T_C\).\(^4\)\(^-\)\(^5\)

In a recent report, Goodenough et al. have first reported the series of samples \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\) \((0 \leq x \leq 2)\).\(^10\) They found that ferromagnetic long-range ordered domains are coupled antiferromagnetically across antiphase boundaries; random disorder within domains may be small. On the other hand, tunneling-type magnetoresistance has also been reported on Cr-based double perovskites \(\text{A}_2\text{CrMO}_6\) \((\text{A} = \text{Sr}, \text{Ca}; \text{M} = \text{Mo}, \text{W}, \text{Re})\).\(^11\)\(^-\)\(^13\) The major difference between Fe-based and Cr-based double perovskites is that in the Cr compound, there can be no valence degeneracy between the Cr and the Mo or W ions, since Cr can only be in the 3+ state \((3d^3)\). Anyway, at this stage a very little research clarified the local structure by extended X-ray absorption fine structure (EXAFS).

This article, we report for the first time the Fe and Cr EXAFS spectra to investigate the local structure of \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\) \((0 \leq x \leq 2)\) and \(\text{Sr}_2\text{CrMO}_6\) \((\text{M} = \text{Mo}, \text{W})\) compounds.

EXPERIMENTAL SECTION

The synthesis of polycrystalline samples of \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\) \((0 \leq x \leq 2.0)\) and \(\text{Sr}_2\text{CrMO}_6\) \((\text{M} = \text{Mo}, \text{W})\) were reported elsewhere by our group.\(^14\)\(^,\)\(^15\) X-ray absorption experiments were carried out at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. All data were collected at room temperature. Fe and Cr K-edge data were recorded in transmission mode for synthesized powder mounted on scotch tape, at the BL 17C Wiggler beam line using a double-crystal Si (111) monochromator. The X-ray harmonic was rejected by mirrors. The spectra were scanned from 5.8 to 7.5 keV using a gas-ionization detector. The ion chambers used for measuring the incident \((I_0)\) and transmitted \((I)\) beam intensities were filled with a mixture of \(\text{N}_2\) and \(\text{H}_2\) gases and a mixture of \(\text{N}_2\) and Ar gases, respectively. The en-
ergy scales were calibrated by monitoring with Fe and Cr foils. The data analysis of the experimental EXAFS spectra was performed using the UWXAFS package.\textsuperscript{16-17} The AUTOBK code was used for background subtraction.\textsuperscript{18} The resulting EXAFS spectra were $k^2$-weighted and Fourier transformed in the range of $4 \leq k \leq 14$ Å\textsuperscript{-1} with a Hanning apodization function. A nonlinear least-square curve fitting procedure in the FEFFIT code was carried out in the range of $1.8 \leq k \leq 4.1$ Å\textsuperscript{-1}, corresponding to the first shell of M-O, where M was Fe or Cr.\textsuperscript{19} Based on the plane wave single scattering, the general EXAFS formula can be expressed as a summation of over all shells $i$ by the following equation:\textsuperscript{20}

$$\chi(k) = S_0^2 \sum_{i} N_i F_i(k) \frac{\sin(2kR_i + \delta_i(k))e^{-2k/\lambda}}{kR_i^2}$$

where $F_i(k)$ is the backscattering amplitude from each of the $N_i$ atoms in the shell $i$ at distance $R_i$, with Debye-Waller factor $\sigma_i^2$, $S_0$ is the amplitude reduction factor, $\delta_i(k)$ is the total phase shift, and $\lambda(k)$ is the photoelectron mean free path. The $F_i(k)$, $\sigma_i$, and $\lambda(k)$ were theoretically calculated by a curved wave \textit{ab initio} procedure in the code FEFF7.\textsuperscript{21} The refinements were based on the minimization $R$ factor,\textsuperscript{22} which is defined as follows:

$$R = \frac{\sum_{i} \left\{ [\text{Re}(\tilde{f}_i)]^2 + [\text{Im}(\tilde{f}_i)]^2 \right\}}{\sum_{i} \left\{ [\text{Re}(\tilde{F}_i)]^2 + [\text{Im}(\tilde{F}_i)]^2 \right\}}$$

where $f_i = \tilde{F}_i - \tilde{F}_{\text{mod}}$, $\tilde{F}$ is the function to be minimized, $\tilde{F}$ is the function weighted by $k^2$, and $N$ is the number of function evaluation. When fitting in $R$-space, $N = 2(R_{\text{max}} - R_{\text{min}})/\delta R$, where $\delta R$ is the grid spacing in $R$-space.

In the fitting procedure, the interatomic distance ($R_i$), Debye-Waller factor ($\sigma_i^2$), and threshold energy difference ($\Delta E$) were set as variables, and the coordination number for the first shell of oxygen atoms was fixed to the crystallographic value of 6 for all the samples.

RESULTS AND DISCUSSION

XRD measurement of samples was performed by using Cu $K\alpha$ radiation and it is confirmed by the Rietveld refinement method to demonstrate the samples are phase pure and in single phase.\textsuperscript{14,15} Experimental $k^2$-weighted Fe $K$-edge EXAFS spectra of (Sr$_{2-x}$Ca$_x$)FeMoO$_6$ (0 $\leq x \leq 2.0$) are shown in Fig. 1, and the Fourier transforms $F(R)$ are shown in Fig. 2. The data range taken for transformation is from 4 to 14 Å\textsuperscript{-1}. Structural parameters were obtained from fitting in $r$-space in the interval of 1.8-2.3 Å\textsuperscript{-1}. The solid lines and empty circles represent the fitted and experimental data, respectively. The first prominent peak in the Fourier transform is assigned to the Fe-O contribution. The bond length between atoms, Debye-Waller factor, and EXAFS fitting parameter of (Sr$_{2-x}$Ca$_x$)FeMoO$_6$ (0 $\leq x \leq 2.0$) samples are listed in Table 1. Our research interest is on the variation of local structure of FeO$_6$ octahedron arrangement, and we therefore discuss the fitting on the first peak in order to obtain the Fe-O bond distances which are indicating a higher degree of regularity of
the FeO₆ octahedron in the double perovskite framework. Table 1 presents the EXAFS refinement results for all the samples. When x increased from 0 to 1.0, the Fe-O bond distance decreases steadily from 1.999 to 1.991. At the same time, above 1.0 the structure is transformed into monoclinic and shows a higher Fe-O bond distance (2.034) and it reduces to 2.012 when x becomes 2.0. The results are consistent with our XRD refinement data. Debye-Waller factors for x=0 (σ² = 0.045) and x=2.0 (σ² = 0.092) are also reported in Table 1. It is noted that the Debye-Waller factor for x=0 is notably smaller than those of x=2, which is indicating a higher degree of regularity of the FeO₆ octahedron in the double perovskite tetragonal frameworks.

Table 1. The bond length between atoms, Debye-Waller factor, and EXAFS fitting parameter of the (Sr₂₋ₓCaₓ)FeMoO₆ (0 ≤ x ≤ 2.0) samples

<table>
<thead>
<tr>
<th></th>
<th>x = 0</th>
<th>x = 0.5</th>
<th>x = 1.0</th>
<th>x = 1.5</th>
<th>x = 2.0</th>
</tr>
</thead>
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<tr>
<td>EXAFS Fe-O(Å) (average)</td>
<td>1.999</td>
<td>1.996</td>
<td>1.991</td>
<td>2.034</td>
<td>2.012</td>
</tr>
<tr>
<td>EXAFS Fe-O(1) (equatorial)</td>
<td>1.982</td>
<td>1.980</td>
<td>1.976</td>
<td>2.001</td>
<td>1.991</td>
</tr>
<tr>
<td>EXAFS Fe-O(2) (axial)</td>
<td>2.032</td>
<td>2.029</td>
<td>2.021</td>
<td>2.099</td>
<td>2.055</td>
</tr>
<tr>
<td>σ² (Å²)</td>
<td>0.0045</td>
<td>0.0038</td>
<td>0.0047</td>
<td>0.074</td>
<td>0.092</td>
</tr>
<tr>
<td>R (Å)</td>
<td>[1.8, 2.3]</td>
<td>[1.8, 2.3]</td>
<td>[1.8, 2.3]</td>
<td>[1.8, 2.3]</td>
<td>[1.8, 2.3]</td>
</tr>
<tr>
<td>K (Å⁻¹)</td>
<td>[4, 14]</td>
<td>[4, 14]</td>
<td>[4, 14]</td>
<td>[4.5, 14]</td>
<td>[4.5, 14]</td>
</tr>
<tr>
<td>θl</td>
<td>3.8 × 10⁻⁴</td>
<td>5.9 × 10⁻⁴</td>
<td>2.7 × 10⁻³</td>
<td>7.8 × 10⁻³</td>
<td>9.2 × 10⁻³</td>
</tr>
</tbody>
</table>

Fig. 3 shows the Fourier transformed F(R) EXAFS data recorded for Sr₂CrMo₆ (M = Mo, W) samples at the Cr K-edge. The first prominent peak in the Fourier transform is assigned to Cr-O contribution and is followed by the second peak corresponding to Sr-Cr distances. The third prominent peak is assigned to the Cr-Mo (Cr-W) distance. The bond length between atoms, Debye-Waller factor, and EXAFS fitting parameter of Sr₂CrMo₆ (M = Mo, W) samples are listed in Table 2. It is noted that the first peak of Cr-O, second peak of Sr-Cr and third peak of Cr-Mo bond distance in Sr₂CrWO₆ are all slightly larger than Sr₂CrMoO₆, which is due to the larger ionic radius of the W⁵⁺ (0.62 Å) compared to that of Mo⁵⁺ (0.61 Å).

Table 2. The bond length between atoms, Debye-Waller factor, and EXAFS fitting parameter of the Sr₂CrMo₆ (M = Mo, W) samples

<table>
<thead>
<tr>
<th></th>
<th>Sr₂CrMoO₆</th>
<th>Sr₂CrWO₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXAFS Cr-O (Å)</td>
<td>1.985</td>
<td>1.989</td>
</tr>
<tr>
<td>σ² (Å²)</td>
<td>0.051</td>
<td>0.083</td>
</tr>
<tr>
<td>R (Å)</td>
<td>[1.8, 4.1]</td>
<td>[1.8, 4.1]</td>
</tr>
<tr>
<td>K (Å⁻¹)</td>
<td>[4.4, 14]</td>
<td>[4.4, 14]</td>
</tr>
<tr>
<td>EXAFS Sr-Cr (Å)</td>
<td>3.399</td>
<td>3.405</td>
</tr>
<tr>
<td>EXAFS Cr-Mo(W) (Å)</td>
<td>3.981</td>
<td>4.086</td>
</tr>
</tbody>
</table>

CONCLUSIONS

We have carried out the Fe and Cr K-edge EXAFS analysis to study the local structure of (Sr₂₋ₓCaₓ)FeMoO₆ (0 ≤ x ≤ 2.0) and Sr₂CrMo₆ (M = Mo, W) systems. The data show that the structure is transformed from a high symmetry tetragonal (x = 0) to a low symmetry monoclinic unit cell (x = 2.0). Understanding the effect of Ca²⁺ substitution on the local struc-
ture of the (Sr$_{2-x}$Ca$_x$)FeMoO$_6$ system provides important insights into how the structure of these materials can be tailored to give optimum chemical and electronic properties. Moreover, in the Sr$_2$CrMO$_6$ (M = Mo, W) system our interest is focused on double perovskite compounds having the general formula A$_2$(BB’/c)O$_6$, since various B’ metal ions can be stabilized by adequately controlling structure and synthesis conditions. The EXAFS curve-fitting analysis allows us to distinguish the difference in Cr-O bond lengths for different substitutions of B’ metal ions, which supports the long-range structure presented by Rietveld refinement.

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REFERENCES