Charge Transfer in Half-metallic $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ System

R. S. Liu, T. S. Chan, S. Mylswamy, J. M. Chen, and J. P. Attfield

$^1$Department of Chemistry and Center for Nano Storage Research, National Taiwan University, Taipei 106, Taiwan
$^2$National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan
$^3$School of Chemistry, University of Edinburgh, Edinburgh, Scotland EH9 3JJ, UK

Structural transformation from tetragonal to monoclinic resulting from chemical pressure effect due to substitution of $\text{Sr}^{2+}$ by a smaller $\text{Ca}^{2+}$ in the double-perovskite $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ has been investigated. A detailed analysis of XRD (X-Ray diffraction) and XANES (X-ray absorption near-edge structure) data are presented to supplement the structural transformation and charge transfer of Fe and Mo ions in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$.

PACS numbers: 61.66.Fn, 74.25.Jb, 74.62.Dh

I. INTRODUCTION

Characterization of a material as half-metallic specifies one spin channel is metallic while the other one is insulating [1]. These compounds are largely studied in recent literature because of their potential applications in spintronics. $\text{Sr}_2\text{FeMoO}_6$ has been considered as half-metallic ferrimagnetic with double-perovskite structure [2]. Due to its high Curie temperature ($\sim 420\text{K}$) and large tunneling magnetoresistance (TMR) effect at room temperature this material attracted attentions of many scientists [3, 4]. Further studies on other members of this double-perovskite family with a general formula of $\text{A}_2\text{BB'}\text{O}_6$ ($\text{A}$=alkaline-earth or rare earth ion and $\text{B}=\text{B'}$=transition metal ion) revealed that the occurrence of TMR property is a more common feature [5–8].

Goodenough and Doss found that long range ordered domains are coupled antiferromagnetically across antiphase boundaries in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ series [9]. In the present investigation we report the transformation of crystal structure (tetragonal to monoclinic) of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ due to the substitution of smaller $\text{Ca}^{2+}$ in place of bigger $\text{Sr}^{2+}$ cations which causes an internal chemical pressure. Due to internal chemical pressure in the structure, charge transfer may take place between Fe and Mo. XANES (X-ray absorption near-edge structure) is a powerful tool to investigate the valence state of metals. We have applied this technique to record Fe K-edge and Mo M-edge spectra to understand the charge transfer from Mo to Fe.
II. EXPERIMENTAL

The polycrystalline samples of \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\) \((0 \leq x \leq 1.5)\) were synthesized by solid state reaction. High purity powders of SrCO\(_3\), CaCO\(_3\), Fe\(_2\)O\(_3\) and MoO\(_3\) were mixed in stoichiometric quantity and ground well. Mixtures were calcined in air at 800\(^\circ\)C for 12h. and resulted powders were ground and pressed into pellets of 15mm in diameter and 3mm in thickness. Pellets of \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\) \((0 \leq x \leq 1.5)\) were sintered at 1000\(^\circ\)C for 38h in 5\% H\(_2\)/N\(_2\) gas mixture.

Powder X-ray diffraction (XRD) data were collected at room temperature with a SCINTAG (X1) diffractometer (Cu K\(_\alpha\) radiation, \(\lambda = 1.5406 \text{ Å}\)) at 40 kV and 30 mA. Lattice constants and cell volume were refined by Rietveld analysis with the program GSAS \([10]\). XANES measurements at Fe-K and Mo-M edges were performed at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan with electron beam energy of 1.5 GeV and a maximum stored current of 240 mA. The spectra were recorded by measuring the sample current. The incident photon flux \((I_0)\) was monitored simultaneously by using a Ni mesh located after the exit slit of the monochromatic beam. All the measurements were performed at room temperature. The reproducibility of the adsorption spectra of the same sample in different experimental runs was found to be extremely good.

III. RESULTS AND DISCUSSION

Powder XRD results show that all the \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\) \((0 \leq x \leq 1.5)\) samples are of single phase. Samples with \(x = 0.5\) and \(x = 1.5\) are indexed based on tetragonal unit cell (space group: \(I4/m\)) and monoclinic (space group: \(P2_1/n\)), respectively which are shown
FIG. 2: Cell volume as a function of $x$ in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 1.5$).

FIG. 3: Fe K-edge X-ray absorption near-edge structure spectra of FeO ($\text{Fe}^{2+}$), $\text{Fe}_3\text{O}_4$ ($\text{Fe}^{2+} \text{Fe}^{3+}$), $\text{Fe}_2\text{O}_3$ ($\text{Fe}^{3+}$) and $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$.

in Fig. 1. Structural transformation in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ is observed from tetragonal to monoclinic in the region of $x = 1$–1.5 at room temperature.

Cell volume change with respect to $x$ value in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ is shown in Fig. 2. An increase in Ca content decreases the cell volume. This may be due to substitution of smaller Ca$^{2+}$ ions in place of larger Sr$^{2+}$ ions [11]. From the Fig. 2, it is interesting to note that structural transformation is smooth and continuous from tetragonal to monoclinic as the $x$ value increases from 0 to 1.5.

The Fe K-edge and Mo M-edge spectra of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ are presented in Fig. 3.
FIG. 4: Mo M-edge X-ray absorption near-edge structure spectra of MoO$_2$ (Mo$^{4+}$), MoO$_3$(Mo$^{6+}$) and (Sr$_{2-x}$Ca$_x$)FeMoO$_6$.

and Fig. 4, along with standards for comparison (FeO, Fe$_2$O$_3$ and Fe$_3$O$_4$ for Fe and MoO$_2$ and MoO$_3$ for Mo), respectively. It is well established that the effective ionic valence of the compounds can be measured from the chemical shift of the core-level x-ray photoemission [12–14]. The Fe preedge peak around 7112 eV and edge jump peak around 7125 eV represent $1s$ to $3d$ (dipole forbidden process) and $1s$ to $4p$ transitions, respectively [15]. In Fe K-edge spectra we have considered the relative intensity of 0.5 to deduce the Fe valence change upon Ca substitution. When Ca content increases from 0 to 1.5, clear positive energy shift was observed which indicates the increase of Fe valence from 2+ towards 3+. Based on standard FeO (Fe$^{2+}$) and Fe$_3$O$_4$(Fe$^{3+}$) spectra (Fig. 3), valence states of Ca doped samples are much higher than 2+ and lower than 3+.

In Fig. 4 the intense peaks at the Mo M-edge onset involve 3$d$-core to 4$d$ final-state transitions. These peaks provide useful information on 4$d$ states, core-hole interaction and multiple effects [16]. Two strong peaks were observed in MoO$_3$ standard at Mo M-edge, the low energy peak (A), due to $3p$ to $4d_{2g}$ excitations and high energy peak (B), due to $3p$ to $4d$ $e_g$ excitations. The clear decrease of strength of peak B with increasing Ca content indicates the reduction of Mo valence.

Based on the above Fe K-edge and Mo M-edge data it is understood that the fraction of charge ($y$) is transferred from Mo to Fe as Ca content ($x$) increases in [(Sr$_{2-x}$Ca$_x$)Fe$^{2+y}$Mo$^{6-y}$O$_6$]. A simple prediction for the change in $y$ is given to compare the sums of ionic radii for the extremes of $y$. For $y = 0$, $r$(Fe$^{2+}$) = 0.78 Å and $r$(Mo$^{6+}$) = 0.59 Å and their sum is 1.37 Å; at $y = 1$, $r$(Fe$^{3+}$) = 0.645 Å and $r$(Mo$^{5+}$) = 0.61 Å, giving a
sum of 1.255 Å. Moreover, based on the chemical formula \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\), assuming oxygen stoichiometry, if the valence of Fe is \(2 + y\), then Mo should formally be in the \(6 - y\) state and not in \(5 - y\) state. Therefore, we deduce that an increase in Ca content (an increase in chemical pressure) will tend to shift the charge balance towards \(\text{Fe}^{3+}\cdot\text{Mo}^{5+}\) and not \(\text{Fe}^{3+}\cdot\text{Mo}^{4+}\).

IV. CONCLUSIONS

The XRD result shows that all the \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6(x = 0\) to 1.5) samples are of single phase. It is observed that the cell volume decreases as the Ca content increases. This is due to the substitution of smaller \(\text{Ca}^{2+}\) ions in place of larger \(\text{Sr}^{2+}\) ions which causes internal chemical pressure. Fe K-edge and Mo M-edge XANES studies prove that the fraction of charge \((y)\) is transferred from Mo to Fe with increasing Ca content in \((\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6\).

Acknowledgments

We thank financial supports from the National Science Council of Taiwan under the grant number 92-2113-M-002-036 and the Ministry Economic Affairs of Taiwan under the grand number 92-EC-17-A-08-S1-0006.

References

* Electronic address: rsliu@ntu.edu.tw