Band overlap via chemical pressure control in double perovskite $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 2.0$) with TMR effect [☆]

R.S. Liu ^{a,*}, T.S. Chan ^a, S. Mylswamy ^a, G.Y. Guo ^b, J.M. Chen ^c, J.P. Attfield ^d

^a Department of Chemistry and Center for Nano Storage Research, National Taiwan University, Taipei 106, Taiwan

^b Department of Physics, National Taiwan University, Taipei 106, Taiwan

^c National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

^d School of Chemistry, University of Edinburgh, Edinburgh, Scotland EH9 3JJ, UK

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Abstract

The chemical pressure control in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 2.0$) with double perovskite structure has been investigated systematically. We have performed first-principles total energy and electronic structure calculations for $x = 0$ and $x = 2.0$. The increasing Ca content in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ samples increases the magnetic moment close to the theoretical value due to reduction of Fe/Mo anti-site disorder. An increasing Ca content results in increasing $(\text{Fe}^{2+} + \text{Mo}^{6+})/(\text{Fe}^{3+} + \text{Mo}^{5+})$ band overlap rather than bandwidth changes. This is explained from simple ionic size arguments and is supported by X-ray absorption near edge structure (XANES) spectra and band structure calculations.

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1. Introduction

Recently, transition metal oxide materials with rock-salt ordered perovskite structure ($\text{A}_2\text{BB}'\text{O}_6$) have been extensively studied, mainly due to their electric and magnetic properties. $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{FeReO}_6$ materials with this structure have been found to possess large tunneling-type magnetoresistance (TMR) at room temperature [1,2]. The studies of analogues series of A_2FeMoO_6 ($\text{A} = \text{Ca}$ and Ba) also found to display higher TMR and ferrimagnetic properties [3–6]. On the other hand, further study to figure out some effects of Fe/Mo disorder on magnetic and electrical properties in $\text{Sr}_2\text{FeMoO}_6$. For ordered state, the

Fe^{3+} and Mo^{5+} ions antiferromagnetically coupled and give rise to ferromagnetic metal with saturated magnetization (M_s) of $4 \mu_B$. However, most of the experimental data showed a reduced M_s . The fact seems to be related to anti-site defects, where some of the Fe and Mo ions interchange their crystallographic positions [7–9]. The actual degree of Fe/Mo order depends on synthesis conditions. As a rule of thumb, increased order may be obtained with increased synthesis temperature or treatment time [10,11].

Goodenough et al. [12] have first reported the $\text{Sr}_{2-x}\text{Ca}_x\text{FeMoO}_6$ ($0 \leq x \leq 2$) series. They found that ferromagnetic long-range ordered domains are coupled antiferromagnetically across antiphase boundaries; random disorder within domains may be small. In this article we aim to investigate in detail the variation of crystal structure and magnetic properties of the $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 2.0$) samples. Most interestingly, we demonstrate the dramatic changes in the magnetic and transport properties upon tuning the Ca doping amount in Sr site.

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* Corresponding author. Tel.: +886 2 23690152x148; fax: +886 2 23693121.

E-mail address: rsliu@ntu.edu.tw (R.S. Liu).

The polycrystalline samples of the series $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 2.0$) were prepared by using a solid state reaction method. Stoichiometric mixtures of SrCO_3 , CaCO_3 , Fe_2O_3 , and MoO_3 were first calcined in air at 800°C for 12 h. The obtained powders were ground and pressed into pellets. The pellets of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 1.5$) were sintered at 1000°C for 38 h in 5% H_2/N_2 gas mixture, and the pellet with $x = 2.0$ was sintered at 1200°C for 12 h in 5% H_2/N_2 gas mixture.

Synthesised materials were characterized by XRD (X-ray diffraction), SQUID (magnetization measurements) and XANES (X-ray absorption near edge structure). XRD analysis was carried out on a SCINTAG (X1) diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA. Crystal structure information was derived by Rietveld refinement method using GSAS program [13]. Line shape of the diffraction peaks were generated by pseudo-voigt function. In the final run the positional coordinates, isotropic thermal factors, and anti-site disorder of Mo and Fe atoms were refined. XANES studies were performed at Fe L- and Mo M-edges at NSRRC (National Synchrotron Radiation Research Center), Hsinchu, Taiwan with electron beam energy of 1.5 GeV and an average beam current of 200 mA. All measurements were performed at room temperature and spectra were recorded by measuring the sample current.

FLAPW (full-potential augmented plane wave) method [14] was used to determine the band structure of tetragonal ($x = 0$) and monoclinic ($x = 2.0$) in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ samples based on first-principles density functional theory (DFT) with the generalized gradient approximation (GGA) to the exchange-correlation potential. The wave function, charge densities, and potentials were expanded in terms of the spherical harmonics inside the muffin-tin spheres with $L_{\text{max}} = 10, 6, 6$, respectively. The number of k -points in irreducible Brillouin zone wedge used in the tetrahedron integration method is 288 for the tetragonal structure and 130 for the monoclinic structure.

2. Results and discussion

The powder XRD patterns of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 2.0$) samples are shown in Fig. 1. All compositions of the series are in single phase. Sample with $x < 1.0$ can be indexed on the basis of a tetragonal unit cell (space group: $I4/m$) where as sample with $x > 1.5$ is indexed based on monoclinic (space group: $P2_1/n$). Substitution of smaller Ca^{2+} ions ($1.34 \text{ \AA}$) in place of larger Sr^{2+} ($1.44 \text{ \AA}$) ions results in reduction in lattice parameters [15]. Hence the lattice parameters (a and c) decrease with increasing Ca content as shown in Fig. 2. The ideal crystal structures of $x < 1.0$ with tetragonal cell and $x > 1.5$ with monoclinic cell are also shown in the inset.

The magnetization isotherms of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ are typically ferromagnetic with negligible remanence and coercivity as illustrated in Fig. 3. The saturation magnetizations at 5 K for all the studied compounds are listed in

Fig. 1. Powder X-ray diffraction patterns of the series samples of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 2.0$).

Fig. 2. Lattice constants (a and c) as a function of x in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 2.0$).

Fig. 3. Magnetization isotherms of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 2.0$) at 5 K.

Table 1. For the $x \geq 1.5$ samples, the obtained values are consistent with a ferromagnetic state near the expected $4 \mu_B \text{ fu}^{-1}$ for a nominal ionic configuration Fe^{3+} ($S = 5/2$)/ Mo^{5+} ($S = 1/2$). However, for $x < 1.5$ samples, the observed total magnetic moment is smaller than the expected value. This variation can be attributed to the effect of anti-site disorder at the octahedral Fe and Mo cation sublattices [6,16]. The anti-site cation occupancy, p , ideally reduces the net moment to $4-2p \mu_B \text{ fu}^{-1}$,

Table 1
Fe/Mo anti-site occupancy and saturation magnetization (μ_B) for $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($0 \leq x \leq 2.0$)

Samples	Fe/Mo anti-site (%)	μ_B
$x = 0$	15.1	2.56
$x = 0.5$	11.1	3.23
$x = 1.0$	13.4	3.03
$x = 1.5$	11.4	3.82
$x = 2.0$	7.7	3.99

however, the local magnetic disorder caused by the anti-site defects reduces the ordered moment still further.

Fe L-edge XANES spectra of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($x = 0, 0.5, 1.0$ and 1.5) are shown in Fig. 4a. Even though the Fe profile changes systematically with Ca content from

Fig. 4. (a) Fe L-edge XANES spectra of FeO , Fe_3O_4 , Fe_2O_3 and $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($x = 0, 0.5, 1.0$ and 1.5). (b) Mo M-edge XANES spectra of MoO_2 , MoO_3 and $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($x = 0, 0.5, 1.0$ and 1.5).

$x = 0$ to $x = 1.5$, the chemical shift does not vary significantly. Additionally, from Fig. 4a it is deduced that Fe valence is much higher than $2+$ and less than $3+$ over the range of Ca substitution, which is based on the variation of relative intensity ratio of the energy at 710 and 708 eV. Mössbauer spectroscopy [4,17] also confirms the mixed-valence state of Fe. 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. In Fig. 4b show the Mo M-edge XANES spectra of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($x = 0, 0.5, 1.0$ and 1.5). Two strong spectral features were observed in the MoO_3 standard. The low energy peak (A), due to the $3p$ to $4d$ t_{2g} excitations; and the high-energy peak (B), due to $3p$ to $4d_{eg}$ excitations. The intense peaks at the Mo M-edge onset involve $3p$ -core to $4d$ final-state transitions. These features can provide a probe of the $4d$ states, albeit modified by transition matrix element, core-hole-interaction and multiplet effects [18]. From the Fig. 4b, it is observed that the increasing Ca content show a clear decrease in the relative strength of peak (B), which is the strong support for the Mo valence reduction.

Fig. 5a ($x = 0$) and 5b ($x = 2.0$) shows the density of states of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ calculated by FLAPW method. These are calculated based on Rietveld refined models with tetragonal unit cell (where $x = 0$) and monoclinic unit cell (where $x = 2.0$). In the present study it is predicted that at the Fermi level (E_F), the density of states is non-zero only in spin down band where as the occupied spin-up band just below E_F mainly consists of Fe $3d$ electrons which forms localized spins on the sites. In contrast, the spin down band around E_F is hybridized Fe $3d$ t_{2g} and Mo $4d$ t_{2g} state. These predicted electronic features are similar to the calculations made by Kobayashi et al. [1] and Fang et al. [19].

Considerable change in spin-down band is observed in the case of $\text{Ca}_2\text{FeMoO}_6$ compared to $\text{Sr}_2\text{FeMoO}_6$ where as only minor change is observed in spin-up band. Also splitting of hybridized Fe $3d$ t_{2g} and Mo $4d$ t_{2g} bands is observed which may be due to the decrease in structural symmetry. The density of states of the $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ ($x = 2.0$) sample in the spin-down band has a local peak at E_{F-} and so it strongly enhanced (about 1.5 times) compared to that of $x = 0$ sample.

The influence of Ca content on the charge transfer y in $(\text{Sr}_{2-x}\text{Ca}_x)\text{Fe}^{2+y}\text{Mo}^{6-y}\text{O}_6$ is an important factor. To predict the change in y , sums of ionic radii of Fe and Mo are calculated at two extremes of y . For $y = 0$, sum of radii is $1.37 \text{ \AA}$ [$r(\text{Fe}^{2+}) = 0.78 \text{ \AA}$ and $r(\text{Mo}^{6+}) = 0.59 \text{ \AA}$] and for $y = 1$ sum is $1.255 \text{ \AA}$ [$r(\text{Fe}^{3+}) = 0.645 \text{ \AA}$ and $r(\text{Mo}^{5+}) = 0.61 \text{ \AA}$] which indicates an increase in Ca content will tend to shift the charge balance towards $\text{Fe}^{3+} + \text{Mo}^{5+}$. As this allows the transition metal oxide framework to contract, y increases with x . This increase in band overlap is supported by our XANES and band calculation results. Recently, Viola et al. [20] speculate that a mixed $\text{Mo}^{6+} - \text{Mo}^{5+}$ valence in reduced $\text{Sr}_2\text{CoMoO}_{6-\delta}$ samples

Fig. 5. The total and site-decomposed density of states (D.O.S.) of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ (a) $x = 0$ and (b) $x = 2.0$.

(where Co has a valence of $2+$) leads to a dramatic enhancement of the electronic conductivity, as compared to that of the pure Mo^{6+} sample. This finding is similar to our results, which is due to a decrease in Mo valence giving a better band overlap.

3. Summary

The variations of crystal structure and magnetization resulting from chemical pressure effects of substituting Sr^{2+} by the smaller Ca^{2+} in the double perovskite $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeMoO}_6$ have been investigated. We conclude that the chemical pressure effects of doping Ca in Sr site is an important factor in controlling the charge transfer and hence the electrical and magnetic properties of the magnetoresistive $\text{Sr}_2\text{FeMoO}_6$ type materials.

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