Effects of B'-site transition metal on the properties of double perovskites Sr_2FeMO_6 (M=Mo, W): B' 4d–5d system

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Abstract

The crystal structure, magnetic and magnetotransport properties of the variation of B'-site transition metal in Sr_2FeMO_6 (M=Mo, W) with double perovskites structure have been investigated systematically. Measurements of magnetization vs. temperature at $H=5$ T show that $\text{Sr}_2\text{FeMoO}_6$ is a ferromagnet and Sr_2FeWO_6 is an antiferromagnet with $T_N \sim 35$ K. Additionally, the large magnetoresistance ratio (MR) of $\sim 22\%$ ($H=3$ T) at room temperature (RT) was observed in the Sr_2FeWO_6 compound. However, the $\text{Sr}_2\text{FeMoO}_6$ compound did not show any significant MR even at high fields and RT ($\text{MR} \sim 1\%$; $H=3$ T and 300 K). The implications of these findings are supported by band structure calculations to explain the interaction between the 4d(Mo) and 5d(W) orbitals of transition metal ions and oxygen ions.

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1. Introduction

In ordered double perovskites denoted as $\text{A}_2\text{BB}'\text{O}_6$ (where A=alkaline-earth or rare-earth ion), the transition metal sites are occupied alternately by different cations B and B'. It is known that the differences in the valence and size between the B and B' cations in double perovskites type compounds are crucial to controlling the physical properties [1,2]. Among them, $\text{Sr}_2\text{FeMoO}_6$ have been known as

potential magnetoresistance materials, which show large low-field tunneling magnetoresistance (TMR) at room temperature (RT) [3]. On the other hand, recently, the further study to figure out some effects of Fe/Mo disorder on magnetic and electrical properties in $\text{Sr}_2\text{FeMoO}_6$ [4,5]. For ordered state, the Fe^{3+} and Mo^{5+} ions antiferromagnetically coupled and give rise to ferromagnetic metal with saturated magnetization $M_s = 4 \mu_B$. However, most of the experiments data showed a reduced M_s . This fact seems to be related to antisite defects, where some of the Fe and Mo ions interchange their crystallographic positions. 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 [6,7].

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In relation to the electronic configurations of the $\text{Sr}_2\text{FeMoO}_6$, the average valence for Fe was also been found to be intermediate between high spin configurations values of Fe^{2+} and Fe^{3+} from Mössbauer spectroscopy studies [8,9]. This suggests that both electronic configurations with Fe^{2+} and Fe^{3+} must be considered as degenerate, with the final state being a combination of both configurations. Conversely, Sr_2FeWO_6 is known as an antiferromagnetic insulator with T_N of 16–37 K, where Fe^{2+} ions are in the high-spin state ($S=2$) and W^{6+} ion ($5d^0$) is in the non-magnetic state [10–12]. This would give rise to a complete localization of the valence electrons, explaining the decrease in conductivity. Therefore, the fundamental question is why the W case is so different from the Mo case despite the fact that W is 5d analogue of 4d Mo in the row of the Periodic Table?

In this article, we report the synthesis and characterization of the Sr_2FeMO_6 ($M=\text{Mo}, \text{W}$) samples with particular focus on the effect of the variation of B'-site transition metal on the physical properties. We will show that the stronger 2p(O)–4d(Mo) hybridization compared with the 2p(O)–5d(W) hybridization is the main source of the difference between $\text{Sr}_2\text{FeMoO}_6$ and Sr_2FeWO_6 .

2. Experimental

The samples of Sr_2FeMO_6 ($M=\text{Mo}, \text{W}$) were prepared by solid state reaction. Stoichiometric mixtures of high purity oxides SrCO_3 , Fe_2O_3 or MoO_3 and WO_3 were calcined at 800 °C for 12 h in air. The obtained powders were ground and pressed into pellets (15 mm in diameter and 3 mm in thickness). The pellets of $\text{Sr}_2\text{FeMoO}_6$ were then sintered at 1000 °C for 38 h in a 5% H_2/N_2 gas mixture. However, the pellets of Sr_2FeWO_6 were sintered at 1200 °C for 18 h in a 5% H_2/N_2 gas mixture.

X-ray diffraction (XRD) measurements were carried out on a SCINTAG (X1) diffractometer (Cu K_α radiation, $\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA. The GSAS program [13] was used for the Rietveld refinements in order to obtain information on the crystal structures of Sr_2FeMO_6 ($M=\text{Mo}, \text{W}$). The resistivity measurements at zero field [$\rho(T)$] and under a magnetic field [$\rho(H)$] were performed with a quantum design PPMS (physical properties measurements system), using the conventional four-probe technique, under magnetic fields up to 3 T. Magnetization measurements were performed on a SQUID magnetometer from 0 to 350 K.

The Fe L-edge and O K-edge X-ray absorption near edge structure (XANES) measurements were performed at the 6 m high-energy spherical grating monochromatic (HSGM) beamline BL20A. Band structures of tetragonal ($\text{Sr}_2\text{FeMoO}_6$) and orthorhombic (Sr_2FeWO_6) were calculated using the all-electron full-potential theory linear augmented plane wave (FLAPW) method [14]. These calculations were based on first-principles density functional theory (DFT)

with the generalized gradient approximation (GGA) to the exchange-correlation potential.

3. Results and discussion

The powder XRD patterns of the Sr_2FeMO_6 ($M=\text{Mo}, \text{W}$) samples are shown in Fig. 1. Each composition of these samples is of single phase. For the samples with $\text{Sr}_2\text{FeMoO}_6$ and Sr_2FeWO_6 all the peaks in each pattern can be indexed on the basis of a tetragonal (space group: $I4/m$) and orthorhombic unit cell (space group: $Immm$), respectively. Moreover, the concept of the tolerance factor can be adapted to double perovskites as well. In general, for double perovskites, with mixed A-site $\text{AA}'\text{BB}'\text{O}_6$, the tolerance factor (t_{factor}) is defined: [15,16]

$$t = \frac{\frac{r_A + r_{A'}}{2} + r_O}{\sqrt{2} \left(\frac{r_B + r_{B'}}{2} + r_O \right)} \quad (1)$$

In which, r_A , $r_{A'}$, r_B , $r_{B'}$ and r_O are the ionic radii of the respective ions. The $t_{\text{factor}}=1$ for the compound with an ideal cubic perovskite structure. If $t_{\text{factor}} < 1$, the perovskite structure is likely to be unstable. Therefore, the t_{factor} decreased (from 0.990 for $\text{Sr}_2\text{FeMoO}_6$ to 0.988 for Sr_2FeWO_6) giving rise to unstable the structure and induced structure changes from tetragonal to orthorhombic unit cell at RT. The possibility of anti-site disordering due to some Mo or W sites being occupied by Fe atoms and vice versa was taken into account. The atomic parameters derived from typical refinements are given in Table 1. The final structure parameters of Sr_2FeMO_6 ($M=\text{Mo}, \text{W}$) and main bond distances are shown in Table 2. The refined occupancies of the Fe and Mo(W) sites in Table 1 shows that the ratios of Fe/Mo and Fe/W anti-site disorder are around 14 and 0.1%, respectively. Sánchez et al. [7] proposed that the actual degree of order depends mainly on synthesis conditions. Therefore, an increase in order in Sr_2FeWO_6 may be

Fig. 1. XRD patterns of $\text{Sr}_2\text{FeMoO}_6$ indexed in a tetragonal unit cell ($I4/m$) and Sr_2FeWO_6 indexed in an orthorhombic unit cell ($Immm$).

Table 1

Atomic positions, isotropic temperature factors and occupancies for (a) $\text{Sr}_2\text{FeMoO}_6$ and (b) Sr_2FeWO_6

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	Uiso ($\text{\AA}^2$)	Occupancy
(a) $\text{Sr}_2\text{FeMoO}_6$					
Sr	0.5	0	0.25	0.0052(4)	1
Fe1	0	0	0	0.0033(3)	0.857(4)
Mo2	0	0	0.5	0.0033(3)	0.857(4)
Mo1	0	0	0	0.0033(3)	0.143(4)
Fe2	0	0	0.5	0.0033(3)	0.143(4)
O1	0	0	0.2518(3)	0.0156(1)	1
O2	0.2531(1)	0.2531(1)	0.5	0.0156(1)	1
(b) Sr_2FeWO_6					
Sr	0.5	0	0.2508(4)	0.0258(4)	1
Fe1	0.5	0.5	0	0.0179(3)	0.999(2)
W2	0	0	0	0.0179(3)	0.999(2)
W1	0.5	0.5	0	0.0179(3)	0.001(2)
Fe2	0	0	0	0.0179(3)	0.001(2)
O1	0.2400(2)	0.2405(3)	0	0.0577(2)	1
O2	0	0	0.2432(2)	0.0577(2)	1

obtained with increasing the synthesis temperature. The lattice parameters (*a* and *c*) and cell volume of the Sr_2FeWO_6 sample are significantly larger than that of the $\text{Sr}_2\text{FeMoO}_6$ sample which is due to the radius of the W^{5+} ions (0.62 Å) is larger than that of the Mo^{5+} (0.61 Å) ions [17]. Furthermore, the Fe–O distances of Sr_2FeWO_6 (2.059 Å, Table 2) are large than those in $\text{Sr}_2\text{FeMoO}_6$ (1.969 Å, Table 2). Additionally, W–O distance (1.920 Å) is shorter than those in Mo–O distance (1.973 Å). Based on the unit cell data reported by Sánchez et al. [7] the ordered sample FeO_6 octahedral is significantly larger (expanded) than MoO_6 octahedral. This observation is coherent with the large ionic size of Fe^{3+} vs. Mo^{5+} [17]. For the disordered sample the Fe–O and Mo–O bond lengths are more similar, as expected for the high degree of antisite disordering. Our results show the more disordered sample $\text{Sr}_2\text{FeMoO}_6$ (14% anti-site disorder) have similar Fe–O (1.969 Å) and Mo–O

(1.973 Å) bond lengths. Moreover, the more ordered sample Sr_2FeWO_6 (0.1% anti-site disorder) have significantly larger FeO_6 octahedral more than WO_6 octahedral. The results were consistent with the published results [7].

The temperature dependence of high-field ($H=5$ T) magnetization of Sr_2FeMO_6 ($M=\text{Mo}, \text{W}$) was shown in Fig. 2(a). Measurements of magnetization vs. temperature at $H=5$ T show that $\text{Sr}_2\text{FeMoO}_6$ is a ferromagnet and Sr_2FeWO_6 is an antiferromagnet with $T_N \sim 35$ K. Fig. 2(b) shows magnetic hysteretic curves recorded of Sr_2FeMO_6 ($M=\text{Mo}, \text{W}$) at $T=5$ K. For the reason clarity, we only display the region of $1 \text{ T} \geq H \geq -1 \text{ T}$. The magnetization curves measured at 5 K show no appreciable hysteresis for Sr_2FeWO_6 . Moreover, it also shows the hysteresis loop below 1 T for $\text{Sr}_2\text{FeMoO}_6$ in Fig. 2(b), consistent with the ferromagnetic behavior mentioned above.

The transport properties of Sr_2FeMO_6 ($M=\text{Mo}, \text{W}$)

Table 2

Structure parameters, Fe/Mo and Fe/W anti-site occupancy and selective bond distances (Å) for (a) $\text{Sr}_2\text{FeMoO}_6$ and (b) Sr_2FeWO_6 . Reliability factors after the Rietveld refinement are also given

(a) Sr ₂ FeMoO ₆							
<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>R</i> _p (%)	<i>R</i> _{wp} (%)	χ ²	Fe/Mo anti-site
5.5686(3)	5.5686(3)	7.8985(4)	244.93(2)	7.73	11.82	1.44	15%
Bond distances (Å)							
<i>d</i> Fe ₁ –O ₁ × 2	<i>d</i> Fe ₁ –O ₂ × 4	⟨Fe ₁ –O⟩	<i>d</i> Mo ₂ –O ₁ × 2	<i>d</i> Mo ₂ –O ₂ × 4	⟨Mo ₂ –O⟩		
1.968(1)	1.969(1)	1.969(1)	1.982(2)	1.969(1)	1.973(1)		
(b) Sr ₂ FeWO ₆							
<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>R</i> _p (%)	<i>R</i> _{wp} (%)	χ ²	Fe/W anti-site
5.6135(3)	5.6509(3)	7.9407(4)	251.88(2)	7.36	10.14	2.14	0.1%
Bond distances (Å)							
<i>d</i> Fe ₁ –O ₁ × 2	<i>d</i> Fe ₁ –O ₂ × 4	⟨Fe ₁ –O⟩	<i>d</i> W ₂ –O ₁ × 2	<i>d</i> W ₂ –O ₂ × 4	⟨W ₂ –O⟩		
2.039(2)	2.069(1)	2.059(1)	1.931(2)	1.914(1)	1.920(1)

Fig. 2. (a) Temperature dependence of high-field ($H=5$ T) magnetization of Sr₂FeMoO₆ ($M=Mo, W$). (b) The magnetization hysteresis curves (M vs. H) recorded at $T=5$ K of Sr₂FeMoO₆ ($M=Mo, W$).

samples are illustrated in Fig. 3. Both $\rho(H=0$ T), $\rho(H=1$ T) and $\rho(H=3$ T) show a half-metallic behavior over the whole temperature range down to 5 K for Sr₂FeMoO₆ and an insulator behavior over the whole temperature range down to around 170 K for Sr₂FeWO₆. Plots of magnetoresistance (MR) against temperature for Sr₂FeMoO₆ ($M=Mo, W$) are also given in the inset of Fig. 3. The MR ratio is defined by $MR(T, H) = [\rho(T, H=0) - \rho(T, H=3 \text{ T})] / \rho(T, H=3 \text{ T})$ where H denotes the external field. The large MR ratio of $\sim 22\%$ ($H=3$ T) at room temperature (RT) was observed in the Sr₂FeWO₆ compound. However, the Sr₂FeMoO₆ compound did not show any significant MR even at high fields and RT ($MR \sim 1\%$; $H=3$ T and 300 K).

Information about the effective oxidation states of Fe and the local structural distortions around these ions is provided by X-ray absorption spectroscopic (XAS) investigations. Fig. 4 shows the Fe L_{2,3}-edge XANES spectra of Sr₂FeMoO₆ and Sr₂FeWO₆ along with the FeO, Fe₃O₄ and Fe₂O₃ standards. The main spectral features of the L_{2,3} edge of Fe originate from dipole transitions from the core Fe 2p level to the empty Fe 3d states [18,19]. The spectra show two broad multiplet structures separated by spin-orbit splitting of Fe 2p_{3/2} (L₃ edge; 705–715 eV) and Fe 2p_{1/2} (L₂ edge; 715–725 eV). Both the edges, L₃ and L₂, are further divided into two peaks. The splitting and intensity

Fig. 3. Temperature dependence of resistivity at a magnetic field of 0, 1 and 3 T of Sr₂FeMoO₆ ($M=Mo, W$) with (a) Sr₂FeMoO₆ and (b) Sr₂FeWO₆. (b) Plot of MR% against temperature of Sr₂FeMoO₆ ($M=Mo, W$) is also given in the inset.

ratio between the two peaks is determined by the interplay of crystal-field effects and electronic interactions. The L₃ absorption edge of Fe^{II} species in an octahedral crystal field typically exhibits a main peak at a lower energy (~ 708 eV), followed by a weaker peak or a shoulder at a higher energy (~ 710 eV). Based on the chemical shift, both the Sr₂FeMoO₆ and Sr₂FeWO₆ of Fe valence is much greater than 2+ but less than 3+. The average valence for Fe has also been found to be intermediate between high-spin configurations values of Fe²⁺ and Fe³⁺ from Mössbauer spectroscopy studies [20,21].

To discuss the different transport properties between the Sr₂FeMoO₆ ($M=Mo, W$) samples, we use the full-potential augmented plane-wave (FLAPW) method to do the band structure calculations. The calculations were based on the Rietveld refined models of Sr₂FeMoO₆ with the tetragonal unit cell and Sr₂FeWO₆ with the orthorhombic unit cell. The density of states obtained by this calculation is shown in Fig. 5(a) for Sr₂FeMoO₆ and (b) for Sr₂FeWO₆. The predicted electronic features for Sr₂FeMoO₆ and Sr₂FeWO₆ resembles those calculated by Kobayashi et al. [1] and Fang et al. [22]. Based on the above descriptions, the fundamental question is why the W case so different from the Mo case despite the fact that W is 5d analogue of Mo in

Fig. 4. Fe 2p-edge X-ray absorption near edge structure (XANES) spectra of $\text{Sr}_2\text{FeMoO}_6$ and Sr_2FeWO_6 along with of three standards, FeO , Fe_3O_4 and Fe_2O_3 .

the row of the Periodic Table? Fang et al. [22] proposed that the p–d hybridization between oxygen and M (Mo, W) to be the main source of this difference. Because the 5d orbital of W is more extended than the 4d orbital of Mo, the stronger $2p(\text{O})$ – $5d(\text{W})$ hybridization pushes the 5d band, which is the p–d antibonding state, higher in energy. Therefore, the Sr_2FeWO_6 band gap opens up and the electron transfer will not occur. Our band structure calculations as shown in Fig. 5 are consistent with the published results and show that the p–d bonding counterpart in the energy position of the spin-up t_{2g} bands is clearly deeper for Sr_2FeWO_6 than that of $\text{Sr}_2\text{FeMoO}_6$.

The experimental XAS spectra are displayed in Fig. 6 together with the calculated O p-DOS spectra. Clearly, there is a good agreement between XAS and O p-DOS over the whole energy range studied, indicating that the present theoretical description of the electronic structure of the Fe-based double perovskites is rather adequate. Three peaks, labelled A, B and C, are clearly seen in the Fig. 6(a). The peak A corresponds to transitions into the unoccupied Mo t_{2g} majority-spin and Fe–Mo t_{2g} minority-spin bands, the peak B corresponds to transitions into the Fe e_g minority-spin band and the peak C corresponds to transitions into the Mo e_g bands. The calculated DOS for the FM $\text{Sr}_2\text{FeMoO}_6$ is in agreement with previous calculations [23].

Fig. 5. The density of states (DOS) of (a) $\text{Sr}_2\text{FeMoO}_6$ and (b) Sr_2FeWO_6 .

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Fig. 6. O K-edge X-ray absorption (XAS) and O p-decomposed DOS of (a) $\text{Sr}_2\text{FeMoO}_6$ and (b) Sr_2FeWO_6 .

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