Structural, electrical and magnetic characterization of the double perovskites Sr_2CrMO_6 ($\text{M} = \text{Mo}, \text{W}$): B' 4d–5d system

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Abstract

We report on the preparation and characterization of the variation of B' -site transition metal in Sr_2CrMO_6 ($\text{M} = \text{Mo}, \text{W}$) with double perovskites structure. The magnetic susceptibility shows that $\text{Sr}_2\text{CrMoO}_6$ and Sr_2CrWO_6 are antiferromagnets with $T_N = 40$ and 30 K at $H = 1$ T, respectively. In addition, a large magnetoresistance ratio (MR) of $\sim 38\%$ ($H = 3$ T) at 5 K was observed in the Sr_2CrWO_6 compound. However, the $\text{Sr}_2\text{CrMoO}_6$ compound does not show any significant MR even at high fields (MR $\sim 4\%$; $H = 3$ T and 5 K). The measured O K-edge X-ray absorption is in agreement with the calculated O p -density of states for both compounds.

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1. Introduction

Recently, $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{FeReO}_6$ have been known as prospective magnetoresistance compounds, which show an appreciable intrinsic tunneling-type magnetoresistance (TMR) at room temperature (RT) in the polycrystalline form [1–3]. These features are due to their half-metallic nature and a relatively high Curie temperature (T_C). In a simple picture, FeO_6 and MoO_6 octahedral alternate arrangement in the crystal structure of $\text{Sr}_2\text{FeMoO}_6$; the ferrimagnetic

structure can be described as an ordered arrangement of parallel Fe^{3+} ($3d^5$, $S = 5/2$) magnetic moments, antiferromagnetically coupled with Mo^{5+} ($4d^1$, $S = 1/2$) spins. Thus a saturation magnetization of $M_s = 4 \mu_B$ is predicted. Indeed, the M_s values of bulk materials reported so far are systematically much smaller than the predicted $4 \mu_B$. This fact seems to be related to anti-site effects resulting from partial disorder of Fe and Mo ions among the B/B' sublattices [4–7].

In relation to the electronic configurations of the $\text{Sr}_2\text{FeMoO}_6$, the average valence for Fe was also 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. On the

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other hand, TMR have also been reported on Cr-based double perovskites A_2CrMO_6 ($A = Sr, Ca$; $M = Mo, W, Re$) compounds [10–12]. The major difference between Fe-based and Cr-based double perovskites oxides is that in the Cr compound, there can be no valence compensation between the Cr and the Mo, W ions, since Cr can only be in the $3 +$ state ($3d^3$). Anyway, at this stage a very little research has been clarified on their physical measurements of X-ray absorption spectroscopy and band structure calculations. In this study, we report the synthesis and characterization of the Sr_2CrMO_6 ($M = Mo, W$) samples with a particular focus on the effect of the variation of B'-site transition metal on the physical properties. The measured O (oxygen) K-edge X-ray absorption is in agreement with the calculated O p -density of states for both the compounds.

2. Experimental

The samples of Sr_2CrMO_6 ($M = Mo, W$) were prepared by solid state reaction. The stoichiometric mixtures of high purity oxides $SrCO_3$, Cr_2O_3 and MoO_3 or WO_3 were calcined at 800 °C for 12 h in air. The obtained powders

were ground and pressed into pellets. The pellets of Sr_2CrMoO_6 were then sintered at 1500 °C for 10 h in a 5% H_2/N_2 gas mixture. However, the pellets of Sr_2CrWO_6 were sintered at 1550 °C for 12 h in a 5% H_2/N_2 gas mixture.

X-ray diffraction (XRD) measurements were carried out on a SCINTAG (X1) diffractometer (Cu $K\alpha$ 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_2CrMO_6 ($M = Mo, W$). Electron diffraction (ED) and high resolution transmission electron microscopy (HRTEM) were carried out using a JEOL 4000EX electron microscope operated at 400 kV. Image simulation was made using CaRIne software. The resistivity measurements were performed with a Quantum Design PPMS, using the conventional four-probe technique. Magnetization measurements were performed on a SQUID magnetometer from 0 to 350 K. The Cr K-edge X-ray absorption near edge structure (XANES) measurements were performed in transmission mode at the S-5B/W20 X-ray Wiggler beamline. The O K-edge XANES measurements were performed at a 6-m high-energy spherical grating monochromator (HSGM) beamline. Band structures of cubic Sr_2CrMO_6 ($M = Mo, W$) were calculated using the all-electron full-potential theory linear augmented plane wave (FLAPW) method [14]. The 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 Fig. 1(a) and (b) display the observed and calculated XRD patterns at 300 K for Sr_2CrMO_6 ($M = Mo, W$) samples. All the observed peaks can be fitted with the

Fig. 1. Rietveld fits for powder XRD data of Sr_2CrMO_6 ($M = Mo, W$) with (a) Sr_2CrMoO_6 and (b) Sr_2CrWO_6 space group $Fm3m$, at 300 K. Observed (crosses) and calculated (solid line) intensities are shown with the difference at the bottom.

Table 1

Atomic positions, isotropic temperature factors and occupancies for (a) Sr_2CrMoO_6 and (b) Sr_2CrWO_6

Atoms	x	y	z	uiso ($\text{\AA}^2$)	Occupancy
(a) Sr_2CrMoO_6					
Sr	0.25	0.25	0.25	0.0019(3)	1
Cr1	0	0	0	0.0030(3)	0.567(9)
Mo2	0.5	0.5	0.5	0.0030(3)	0.567(9)
Mo1	0	0	0	0.0030(3)	0.433(4)
Cr2	0.5	0.5	0.5	0.0030(3)	0.433(4)
O1	0.2483(2)	0	0	0.0085(7)	1
(b) Sr_2CrWO_6					
Sr	0.25	0.25	0.25	0.0163(5)	1
Cr1	0	0	0	0.0207(3)	0.806(3)
W2	0.5	0.5	0.5	0.0207(3)	0.806(3)
W1	0	0	0	0.0207(3)	0.194(3)
Cr2	0.5	0.5	0.5	0.0207(3)	0.194(3)
O1	0.2484(1)	0	0	0.0262(2)	1

reflection conditions of the space group $Fm\bar{3}m$ for Sr_2CrMO_6 ($M = \text{Mo}, \text{W}$). The possibility of anti-site disordering due to some Mo or W sites being occupied by Cr atoms and vice versa was taken into account. The atomic parameters derived from typical refinements are given in Table 1. The refined occupancies of the Cr and Mo(W) sites in Table 1 shows that the ratios of Cr/Mo and Cr/W anti-site disorder are around 43 and 19%, respectively. Sánchez et al. [15] proposed that the actual degree of order depends mainly on synthesis conditions. Therefore, an increase in order in Sr_2CrWO_6 may be obtained by increasing the synthesis temperature.

Fig. 2(a) and (b) show a typical ED pattern and HRTEM lattice image, recorded along the $[110]$ zone-axis direction of Sr_2CrWO_6 . The simulated pattern along zone axis $[110]$

Fig. 2. (a) ED pattern and (b) HRTEM lattice image along the $[110]$ direction of Sr_2CrWO_6 sample. (c) Simulated pattern along the zone axis $[110]$.

is shown in Fig. 2(c). The lattice image is belonging to a cubic cell with $a = b = c = 7.8\text{\AA}$. The cell symmetry obtained by ED was identified by the observation only of hkl reflections indicating F -centering of the unit cell which is consistent with the XRD refinement result.

The plot magnetic susceptibility (χ) vs. temperature (T) (as shown in Fig. 3) indicates that (a) $\text{Sr}_2\text{CrMoO}_6$ and (b) Sr_2CrWO_6 is an antiferromagnet with $T_N = 40$ and 30 K at $H = 1\text{ T}$, respectively. As shown in Fig. 3(a) and (b), the Curie–Weiss plot for Sr_2CrMO_6 ($M = \text{Mo}, \text{W}$) reasonably well for $T > 150\text{ K}$ give positive Weiss temperature $\theta \sim 83$ and 18 K at $H = 1\text{ T}$, respectively. These data suggest that although there exists both ferro- and antiferromagnetic interactions, the ferromagnetic interaction dominates over the antiferromagnetic one. The transport properties of Sr_2CrMO_6 ($M = \text{Mo}, \text{W}$) samples are shown in Fig. 4. Both $\rho(H = 0\text{ T})$ and $\rho(H = 3\text{ T})$ show a semiconductor-like behavior over the whole temperature range up to 5 K . The resistivities (ρ) of Sr_2CrWO_6 sample (about $10^3\text{ }\Omega\text{cm}$) is higher than $\text{Sr}_2\text{CrMoO}_6$ (about $10^2\text{ }\Omega\text{cm}$). The plots of magnetoresistance against temperature for Sr_2CrMO_6 ($M = \text{Mo}, \text{W}$) are also given in the inset of Fig. 4. The magnetoresistance ratio (MR) is defined by $\text{MR}(T, H) = [\rho(T, H = 0) - \rho(T, H = 3\text{ T})] / \rho(T, H = 3\text{ T})$ where H denotes the external field. The large MR ratio of

Fig. 3. Temperature dependence of magnetic susceptibility (χ) and Curie–Weiss plot for (a) $\text{Sr}_2\text{CrMoO}_6$ and (b) Sr_2CrWO_6 in the temperature from 5 to 350 K .

Fig. 4. Temperature dependence of resistivity at a magnetic field of 0 and 3 T of $\text{Sr}_2\text{CrMoO}_6$ ($M = \text{Mo}, \text{W}$) with (a) $\text{Sr}_2\text{CrMoO}_6$ and (b) Sr_2CrWO_6 . (b) Plot of MR% against temperature of $\text{Sr}_2\text{CrMoO}_6$ ($M = \text{Mo}, \text{W}$) is also given in the inset.

~38% ($H = 3 \text{ T}$) at 5 K was observed in the Sr_2CrWO_6 compound. However, the $\text{Sr}_2\text{CrMoO}_6$ compound did not show any significant MR even at high fields (MR ~4%; $H = 3 \text{ T}$ and 5 K). In Fig. 5(a) we show the Cr K-edge XANES spectrum of $\text{Sr}_2\text{CrMoO}_6$ ($M = \text{Mo}, \text{W}$), the spectra of Cr^{3+} in standard Cr_2O_3 , and the Cr^{4+} in standard CrO_2 are also plotted. In Fig. 5(a), pre-edge features of A and B result from transitions to bound the final states in the 3d orbital. Moreover, there is a relatively intense and symmetric resonance above the absorption edge (C), and a broader structure to high energy (D). The rising part of the $\text{Sr}_2\text{CrMoO}_6$ ($M = \text{Mo}, \text{W}$) main edge can be seen to have a chemical shift identical to that of the Cr^{3+} standard and well separated from that of the Cr^{4+} standard. To obtain detailed information on the electronic and geometric structures around the Cr ion, the pre-edge features of the Cr K-edge XANES spectrum is shown in Fig. 5(b). Moreover, the $\text{Sr}_2\text{CrMoO}_6$ ($M = \text{Mo}, \text{W}$) pre-edge manifests a three-features (k1, k2 and k3) structures, similar to the Cr^{3+} standard, whereas the Cr^{4+} standard has a quite separate bimodal-feature structure. Among the Cr^{4+} materials the sharp low energy k1-feature is particularly distinctive with

Fig. 5. (a) Cr K-edge XANES spectrum of $\text{Sr}_2\text{CrMoO}_6$ ($M = \text{Mo}, \text{W}$), the spectra of Cr^{3+} in the standard Cr_2O_3 , and the Cr^{4+} in the standard CrO_2 are plotted. (b) Cr K-edge XANES pre-edge spectra of $\text{Sr}_2\text{CrMoO}_6$ ($M = \text{Mo}, \text{W}$) with manifests a three-features (k1, k2 and k3) structures.

the intensities and positions of the k2 and k3 features which is varying between compounds. Therefore, the structure of the pre-edge further supports the assignment of a Cr^{3+} state in $\text{Sr}_2\text{CrMoO}_6$ ($M = \text{Mo}, \text{W}$).

We also performed X-ray absorption spectroscopic (XAS) measurements at O K-edge. The spectra were recorded by measuring the X-ray fluorescence yield technique at RT. The experimental XAS spectra are displayed in Fig. 6 together with the calculated O p -DOS

Fig. 6. O K-edge X-ray absorption spectrum (XAS) and O *p*-decomposed DOS of Sr_2CrMO_6 ($M = \text{Mo}, \text{W}$).

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 for the Cr-based double perovskites is rather adequate.

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