Crystal structures and magnetic properties of the double perovskite $(Ca_{2-2x}Sr_{2x})FeMoO_6$

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Abstract

Chemical size effect on structural and magnetic properties in $(Ca_{2-2x}Sr_{2x})FeMoO_6$ has been examined. The compounds crystallize in the monoclinic system for $0.0 \leq x < 0.2$, the orthorhombic for $0.2 \leq x < 0.4$ and the tetragonal for $0.4 \leq x$. The Curie temperature T_C increases with increasing x from 318 K (x=0.0) to 393 K (x=1.0). At 82 K, the saturation magnetization of all samples remains $M_S \leq 3.5\mu_B$/formula unit compared to a theoretical spin-only moment $4\mu_B$/formula unit for a perfectly ordered compound. This discrepancy is probably due to a slight disorder and valence-fluctuation between the Fe and Mo atoms.

Key words: crystal; magnetic; double perovskite

Tunneling-type magnetoresistance (TMR) in perovskite-type transition-metal oxide has recently been investigated extensively [1–3]. Those compounds have attracted recent attention because they may be half metals with high magnetic transition temperature and have spin-dependent transport properties which may be useful in magnetic devices. It is of extrinsic nature, and gives rise to a large magnetoresistance in the ferromagnetic phase. This mechanism has been proposed as originated by spin-dependent electron tunneling through the grain boundaries [4]. This feature made these systems very interesting for the application in the magnetoresistance tunnel junctions. Here we investigated crystal structures and magnetic properties of the series of $(Ca_{2-2x}Sr_{2x})FeMoO_6$ ($0.0 \leq x \leq 1.0$).

The synthesis were performed from powders of $SrCO_3$, $CaCO_3$, Fe_2O_3, and MoO_3 ground together in stoichiometric ratios and calcined at 900^{o}C in a stream of 2% H_2/Ar for 3 hours. The products were ground, pelletized and then annealed in a flowing mixture of 2% H_2/Ar at the temperatures of 1150^{o}C. All samples were then cooled in this atmosphere to room temperature at a rate of 150^{o}C/h. X-ray diffraction powder patterns were obtained on a Shimadzu XRD6000. The data were collected in steps of 0.02^o over the range $5^o \leq 2\theta \leq 120^o$. Lattice constants and crystal structures were refined by a Riqus system (Materials Data Inc. software) with the extent of disordering between the Fe and Mo sites. Riqus is a PC program for Rietveld structure refinement and whole-pattern fitting of powder diffraction patterns made with X-ray.

X-ray powder diffraction data indicates that single-phase materials can be made for the entire series. As been previously reported, the X-ray diffraction pattern of pure Ca_2FeMoO_6 was indexed on the monoclinic structure. The compounds are orthorhombic for $0.2 \leq x \leq 0.3$ and reflections were indexed in the space group Pbnm. The structure change in $(Ca_{2-2x}Sr_{2x})FeMoO_6$ system can clearly be seem orthorhombic structure of

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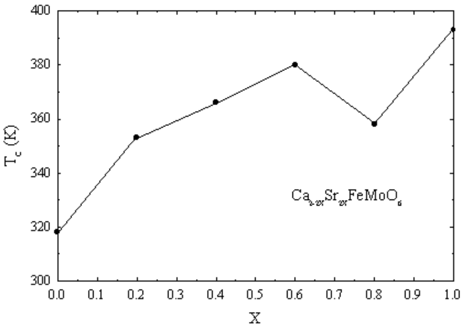

Fig. 1. Curie temperatures T_C for the $(Ca_{2-2x}Sr_{2x})FeMoO_6$.

Table 1
Lattice parameters and cell volume for $(Ca_{2-2x}Sr_{2x})FeMoO_6$.

x	0.0	0.3	0.6	0.8	1.0
Space group	$P2_1/n$	Pbnm	I4/m	I4/m	I4/mmm
a (Å)	5.048	5.503	5.553	5.581	5.586
b (Å)	5.524	5.503	5.553	5.581	5.586
b (Å)	7.705	7.783	7.866	7.918	7.914
V (Å^3)	230.2	235.8	242.6	246.7	247.0

the $x \leq 0.3$ composition changes to tetragonal when $x > 0.3$. Table 1 shows plots of cell volume and lattice parameter versus composition $(0.0 \leq x \leq 1.0)$, respectively. In fact, we have refined the structures of $(Ca_{2-2x}Sr_{2x})FeMoO_6$ from powder XRD data using the Rietveld program Riqas. The refined atomic positions, an isotropic temperature factors B for all atoms, together with reliability factor, are listed in Table 2.

In order to obtain the information on the magnetic properties for all the compounds, the magnetization (M) measurements have been done under 0.2 T. The data yielding the Curie point of each sample were obtained and plotted in Fig. 1. Magnetic hysteresis loops with field up to 0.8 T have been measured at 82 K in this series. All samples show virtually the similarly magnetic behavior, each exhibiting saturation magnetization and a small coercive field. These values of saturation magnetization displayed as saturation moment per formula unit M_S and shown in Fig. 2. Saturation magnetization for Ca_2FeMoO_6 was 3.1 μB and slight below the values of 4 μB expected on the basis of spin only value for Fe^{3+} (high spin $3d^5$) and Mo^{5+} ($4d^1$) with the antiferromagnetic configuration. A ferromagnetic interaction would give moments too high. Upon further Sr doping, the M_S decreases to $\sim$ 2.4 μB for Sr_2FeMoO_6. Those experimentally observed magnetization values M_S always are lower than the expected value of 4 μB which should be ascribed to the effect of the order degree and valence fuctuation.

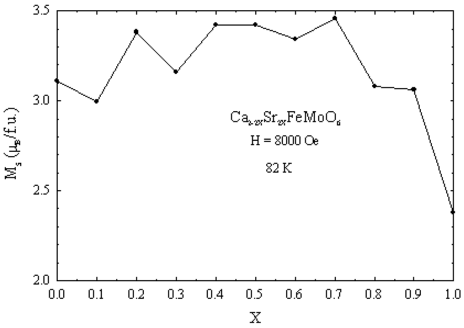

Fig. 2. The variation of the saturation magnetization M_S with x at 82 K for the system $(Ca_{2-2x}Sr_{2x})FeMoO_6$.

Table 2
Atomic positions, isotropic temperature B factors and occupancy N for $(Ca_{2-2x}Sr_{2x})FeMoO_6$ with x=0.0. The R_{wp} (%) of the refinement is 4.1662%.

atom	X	Y	Z	N	B (Å^2)
Ca	0.5161	0.5499	0.2486	1	1.4717
Fe1	0	0.5	0	0.7202	1.2296
Mo1	0	0.5	0	0.2798	1.2296
Fe2	0.5	0	0	0.2798	0.1789
Mo2	0.5	0	0	0.7202	0.1789
O1	0.2157	0.2104	-0.0527	1	0.5897
O2	0.3076	0.7462	-0.0333	1	1.6814
O3	0.4128	-0.0116	0.2244	1	0.1288

In conclusion, we have shown that the double perovskite alloy system $(Ca_{2-2x}Sr_{2x})FeMoO_6$ forms a solid solution throughout $0.0 \leq x \leq 1.0$. Powder X-ray Rietveld analysis indicates that due to substitution of Ca by Sr, four structure symmetry transitions were observed. The drop in the magnetic moment is due to a slight disorder and valence-fluctuation between the Fe and Mo atoms.

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