

Mössbauer Studies of Double Perovskite $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$

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We investigated the crystallographic and magnetic properties of double perovskite $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$ ($x=0.0, 0.01, 0.03, 0.05, \text{ and } 0.10$). Mössbauer spectra of the $\text{Sr}_2\text{Fe}_{0.9}\text{Cr}_{0.1}\text{MoO}_6$ have been taken at various temperatures ranging from 15 to 415 K. As the temperature increased towards T_C (415 K), the Mössbauer spectra showed line broadening and 1, 6 and 3, 4 line-width differences because of anisotropic hyperfine field fluctuation. The Mössbauer spectra indicated that an anisotropic field fluctuation of $+H$ ($P_+ = 0.85$) was greater than that of $-H$ ($P_- = 0.15$). We also calculated the field fluctuation frequency factors and the temperature dependence of anisotropy energies from its relaxation rate. We interpreted the effect of Cr (f_{2g}^3) doping as a decrease in the anisotropy energy.

Key words : Mössbauer, $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$, Double perovskite

1. Introduction

In the last recent years, spin polarized half-metallic $\text{Sr}_2\text{FeMoO}_6$ oxide has become an important topic of scientific interest in view of its remarkable magneto-resistive properties [1, 2]. So many researchers have reported the lattice constants, magnetization, and resistivity of the double perovskite transition metal oxides, especially for the Fe-based compounds [3-5]. Generally it is known that a ferrimagnetic half metallic state is expected for this ordered perovskite with localized up spin of Fe^{3+} ($3d^5 : t_{2g}^3 e_g^2$) and itinerant down spin electron of Mo^{5+} ($4d^1 : t_{2g}^1$). Recently we have studied a variation of crystallographic and magnetic properties on the small atomic substitution at the B site. Among them, compounds of $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$ are of particular interest since Cr^{3+} ($3d^3 : t_{2g}^3$) ions have a similar electron configuration and ionic radius to Fe^{3+} ions. In this paper, we report the effects of Cr doping on the structural, magnetic, and magnetoresistance properties of $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$ ($x=0.0, 0.01, 0.03, 0.05, \text{ and } 0.10$).

2. Experimental Procedures

The single phases of the polycrystalline $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$

powder samples were prepared by standard solid-state reaction method. Powders of high purity (99.995% or better) of SrCO_3 , Fe_2O_3 , Cr_2O_3 and MoO_3 were mixed, ground, and calcined at 1100°C for 6 h in an atmosphere of 5% H_2 in Ar. The calcined mixtures were pressed into cylindrical bars and sintered at 1200°C for 4 h in the same condition. Color of the final products was blue-black. Chemical composition of the samples was confirmed to be stoichiometric by induction coupled plasma (ICP) and Rutherford backscattering spectrometry (RBS) analysis. The RBS spectra were obtained by oxygen resonance backscattering method using He^{2+} ions with 3.05 MeV and analyzed by computer simulation.

The crystal structure was measured using a x-ray diffractometer with a $\text{CuK}\alpha$ radiation source, and magnetic properties were measured using a vibrating sample magnetometer. Mössbauer spectra were investigated in the temperature range from 15 to 415 K using a conventional spectrometer with a ^{57}Co source in Rh matrix [6].

3. Results and Discussion

Figure 1 shows oxygen resonance Rutherford backscattering spectrum of $\text{Sr}_2\text{Fe}_{0.9}\text{Cr}_{0.1}\text{MoO}_6$. The stoichiometric composition of Fe/Cr ratio was analyzed nearly identical with 0.9/0.1.

Figure 2 shows x-ray diffraction (XRD) patterns for $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$. All samples have only a single phase

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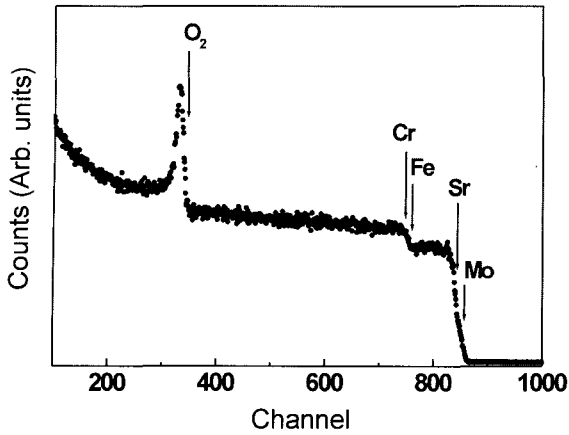


Fig. 1. Oxygen resonance Rutherford backscattering spectrum of $\text{Sr}_2\text{Fe}_{0.9}\text{Cr}_{0.1}\text{MoO}_6$.

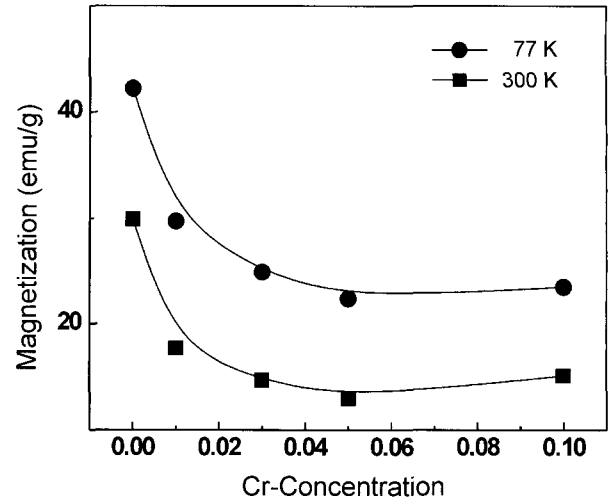


Fig. 3. Cr concentration dependence of magnetization for $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$.

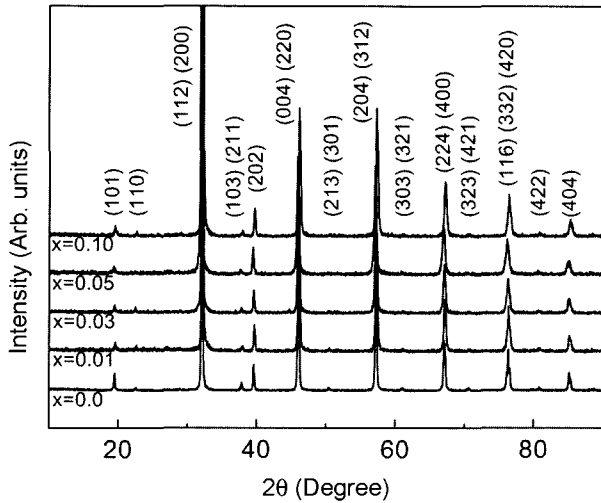


Fig. 2. X-ray diffraction patterns of $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$ ($x=0.0, 0.01, 0.03, 0.05, \text{ and } 0.10$).

and exhibit a series of superstructure reflections due to cation order of Fe (or Cr) and Mo on alternate B-sites of the perovskite structure [7]. The XRD patterns were indexed on the tetragonal ($I4/mmm$; $z=2$) structure. The structural parameters are listed in Table 1. The unit cell parameters decrease linearly with increasing the Cr concentration. This result follows Vegards law [8], approximately. It can be expected in view of the fact that the ionic radius of the Cr^{3+} ion (0.65 \AA) is smaller than that of the Fe^{3+} ion (0.67 \AA) [9].

Figure 3 shows the dependence of magnetization upon the concentration of Cr under the maximum applied of 1 T at 77 and 300 K. The saturation magnetization value of $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$ decreases as the Cr content increases. It is explained that the substitution of the Cr^{3+} ($3d^3 : t^3_{2g}$) for Fe^{3+} ($3d^5 : t^3_{2g} e^2_g$) at the Fe-O-Mo bond structure decreases net spin moment. The $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$ samples exhibit negative magnetoresistance (MR), with

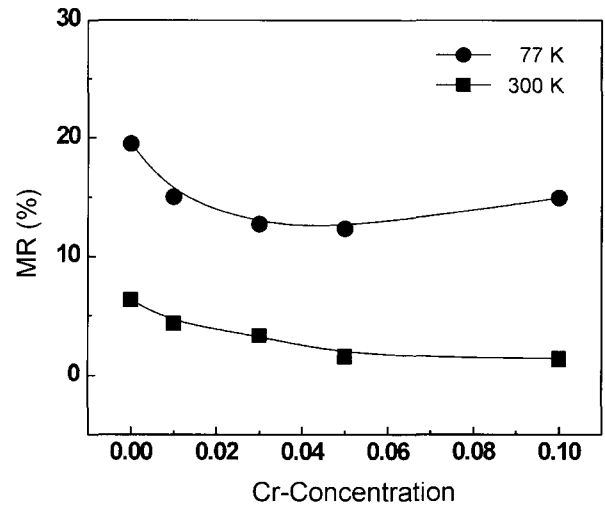


Fig. 4. Cr concentration dependence of magnetoresistance for $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$.

Table 1. The structural parameters of $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$.

		$x = 0.00$	$x = 0.01$	$x = 0.03$	$x = 0.05$	$x = 0.10$
Tolerance factor		0.9179	0.9180	0.9181	0.9182	0.9184
Lattice constants (\AA)	(a_0)	5.5729	5.5679	5.5649	5.5646	5.5644
	(c_0)	7.9077	7.9027	7.9019	7.8990	7.8991

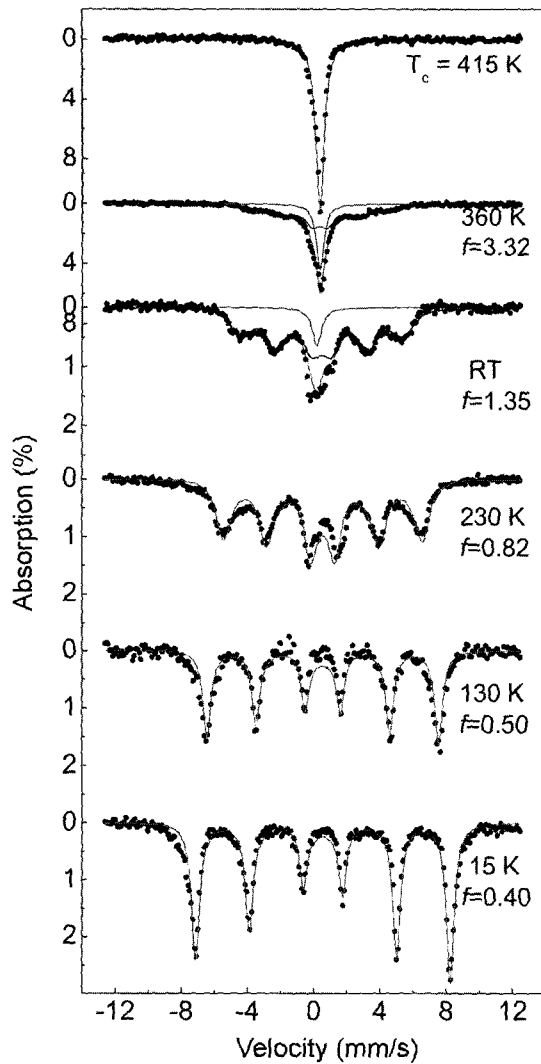


Fig. 5. Mössbauer spectra of $\text{Sr}_2\text{Fe}_{0.9}\text{Cr}_{0.1}\text{MoO}_6$ at various temperatures. The relaxation frequency f is in units of Γ/\hbar .

the MR defined as $\text{MR}(T,H) = [R(H) - R(0)]/R(0)$. In $\text{Sr}_2\text{Fe}_{0.9}\text{Cr}_{0.1}\text{MoO}_6$, the observed MR is 14.9% at 77 K and 1.4% at 300 K under 1 T applied magnetic field. As shown in Fig. 4, the MR ratio decreases with increasing the Cr content, which is similar to the result obtained for magnetization trend.

Figure 5 shows that the Mössbauer spectra of $\text{Sr}_2\text{Fe}_{0.9}\text{Cr}_{0.1}\text{MoO}_6$ at various temperatures. Mössbauer absorption lines are six Lorentzian lines and are sharp at 15 K. The observed Mössbauer parameters show hyperfine field $H_{\text{hf}} = 479.9$ kOe, isomer shift $\delta = 0.56$ mm/s, and quadrupole splitting $\Delta E_Q = -0.05$ mm/s at 15 K. The absorption lines become broader with increasing temperature and paramagnetic phase starts to coexist near the room temperature. We determined Curie temperature $T_c = 415$ K for $\text{Sr}_2\text{Fe}_{0.9}\text{Cr}_{0.1}\text{MoO}_6$, however the temperature dependence

of Mössbauer absorption line-width shows asymmetrical line broadening. That is, the Mössbauer spectra of 1, 6 and 3, 4 lines have different line broadening ratio. In order to explain the line broadening of Mössbauer spectra and the difference between 1, 6 and 3, 4 line-width, we used the following expression derived by Blume and Tjon [10], for the line shape of the Mössbauer absorption spectra in the presence of a fluctuating magnetic field, which jumps between the values $+H$ and $-H$ along the z -axis with a frequency f :

$$W(k) = \frac{2}{\Gamma} \text{Re} \sum_{m_0, m_1} \frac{1}{4} |\langle I_0 m_0 | H^{(+)} | I_1 m_1 \rangle|^2 \times \sum_{i,j} \frac{1}{2} \langle j | (P - W - i\alpha f)^{-1} | i \rangle, \quad (1)$$

where

$$P = -i(\omega - \omega_0) + \frac{1}{2}\Gamma, \quad \alpha = (g_0 m_0 - g_1 m_1)\mu H, \\ W = \begin{pmatrix} -f & f \\ f & -f \end{pmatrix}, \quad F = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Here $H^{(+)}$ is the operator for emission of gamma ray by the nucleus. Γ is the natural line-width, ω and k are the frequency and wave vector of gamma photon. $|I_0 m_0\rangle$ and $|I_1 m_1\rangle$ ($m_0 = \pm 1/2, m_1 = \pm 1/2, \pm 3/2$) represent the ground and the first excited states of ^{57}Fe , respectively. g_0 and g_1 are the g factors of the ground and the first excited states of ^{57}Fe , μ is the magneton, and ω_0 is the frequency of the unsplit line for ^{57}Fe . Since the earlier expression shows only the absorption probability, it is necessary to carry out the integration

$$a(v) = \int_{-\infty}^{\infty} W(\omega) F[\omega - \omega_0 - (\omega_0/c)v] d\omega \quad (2)$$

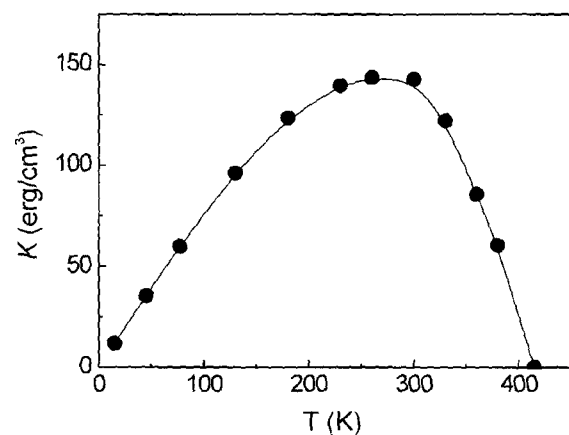


Fig. 6. Temperature dependence of anisotropy energy K for $\text{Sr}_2\text{Fe}_{0.9}\text{Cr}_{0.1}\text{MoO}_6$.

in order to fit the theoretical curve to the Mössbauer spectra. $F(x)$ is a single line source spectrum, c is velocity of light, and v is the Doppler velocity of the source. The line shape function $a(v)$ was calculated for each Doppler velocity v and the results are shown as solid lines through the data point in Fig. 5 with corresponding value f . The Mössbauer spectra indicated that an anisotropic field fluctuation of $+H$ ($P_+ = 0.85$) was greater than that of $-H$ ($P_- = 0.15$). The relaxation rate f increases rapidly as the temperature approaches T_C . J. Blasco *et al.* [11], reported the relaxation effect in the Cr substituted compound using micro-spin resonance (ZF- μ SR) method.

Now, the anisotropy energy can be estimated from the f values using the following expression [12],

$$f = f_0 \exp(-KV/k_B T), \quad (2)$$

where f_0 is a frequency factor, K is the effective anisotropy energy per unit volume, and V is the particle volume. The volume V of the average particle was measured to be $5.24 \times 10^{-16} \text{ cm}^3$, and frequency factor f_0 was obtained the extrapolated rate of $8.2 \text{ } \Gamma/\hbar$ at T_C . Figure 6 shows temperature dependence of the anisotropy energy for $\text{Sr}_2\text{Fe}_{0.9}\text{Cr}_{0.1}\text{MoO}_6$. The calculated the maximum anisotropy energy was 143.5 erg/cm^3 for 260 K, which is associated with the large Mössbauer line broadening. This value is slightly smaller than 149.6 erg/cm^3 at 260 K for $\text{Sr}_2\text{FeMoO}_6$ [13].

In conclusion, the hyperfine field fluctuation phenomenon in double perovskite $\text{Sr}_2\text{Fe}_{1-x}\text{Cr}_x\text{MoO}_6$ system was observed by Mössbauer spectroscopy and the anisotropy energy decreases according to the substitution of Cr.

Acknowledgments

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