

The Enhanced Magnetic Transition Temperature in Double Perovskites A_2FeMoO_6 (A=Ca, Sr and Ba) : Electron Doping Effects

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We have studied effects of the partial substitution of La^{3+} for A^{2+} on the magnetic properties of double perovskites A_2FeMoO_6 (A=Ca, Sr and Ba). Polycrystalline $A_{2-x}La_xFeMoO_6$ ($0 \leq x \leq 0.2$) samples have been prepared by the conventional solid-state reaction in a stream of 5% H_2/Ar gas. The x-ray data indicate that A=Ca is monoclinic with the space group $P2_1/n$, A=Sr is tetragonal with the space group $I4/mmm$, and A=Ba is cubic with the space group $Fm3m$. The substitution of La^{3+} for A^{2+} results in a cell volume increase for A=Ca and a cell volume reduction for A=Ba. The decrease of saturation magnetization with increasing x arises from the reduction of magnetic moment associated with the electron doping and the disorder at the Fe and Mo sites. The partial substitution of magnetic La^{3+} for Ba^{2+} considerably enhances the Curie temperature T_c from 316 K for $x = 0$ to 334 K for $x = 0.2$. This enhancement of T_c with La^{3+} doping originates from electron doping effects in addition to ionic size ones.

Key words : Double perovskite, Magnetization, Magnetic transition temperature

1. Introduction

The double perovskites have been intensively investigated due to the discovery of large low-field room temperature magnetoresistance in Sr_2FeMoO_6 (SFMO) [1]. The magnetic structure of double perovskite SFMO is attributed to the ordered arrangement of Fe^{3+} ($3d^5$, $S=5/2$) and Mo^{5+} ($4d^1$, $S=1/2$) ions arranged alternatively on the B sites in the cubic perovskite ABO_3 [2]. A large anti-ferromagnetic interaction between the $S=5/2$ spins of Fe^{3+} and the $S=1/2$ spins of Mo^{5+} induces a half-metallic ferrimagnetic state with an ideal saturation magnetization (M_s) of $4 \mu_B$ per formula unit (f.u.). However, the observed M_s values are less than the expected one [1]. The reduction of M_s can be ascribed to the mis-site disorder between Fe and Mo ions [1, 3, 4]. Monte-Carlo simulations have predicted a reduction of M_s as a function of the mis-site disorder [3]. In addition to its ordering structure, this compound displays a metallic behavior with the Curie temperature (T_c) of 410-450 K [1, 2, 5].

The early study on A_2FeMoO_6 (AFMO; A=Ca, Sr, and Ba) systems examined the significance of bond distances

on the T_c [2]. By substituting Ca^{2+} or Ba^{2+} for Sr^{2+} in SFMO, the maximum T_c was achieved for SFMO, and the T_c decreased irrelevant to the ionic size of substituting divalent ion (Ca^{2+} or Ba^{2+}) as the amounts of substitution increased [2]. The observed variation in T_c has been investigated in terms of the evolution of the T_c and crystallographic structure as a function of the average ionic radius ($\langle r_A \rangle$) [6]. A remarkable correlation has been found between the T_c and the electronic bandwidth (W), which is controlled by structural parameters, i.e., the maximum T_c value for SFMO corresponds to the compound with a larger estimated W . In AFMO systems, as the $\langle r_A \rangle$ is increased, the symmetry of crystallographic structure evolves from monoclinic (for A=Ca) to tetragonal (Sr) and finally to cubic (Ba).

It has been recently reported that the electron doping in SFMO achieved via the substitution of La^{3+} for Sr^{2+} promotes a rising of the T_c as the doping level increases, while there is a considerable cell expansion [7]. However, Moritomo *et al.* [8] reported that the T_c was nearly independent of the substitution up to the doping level of $x = 0.3$. In this paper, we report the variation of crystal structure and magnetic properties of AFMO by partial substitution of La^{3+} ions into A^{2+} ionic sites resulting in the chemical formula $Ca_{2-x}La_xFeMoO_6$ (CLFMO), Sr_{2-x} -

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$\text{La}_x\text{FeMoO}_6$ (SLFMO), and $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ (BLFMO). The partial substitution of La^{3+} for A^{2+} in AFMO changes (1) the average ionic radius ($\langle r_A \rangle$) without distortion of the crystal symmetry and (2) the valence state of Fe/Mo ions via electron doping.

2. Experimental

Polycrystalline ALFMO samples were prepared by standard solid-state reaction. Powders of high purity (99.99% or better) of ACO_3 , La_2O_3 , Fe_2O_3 , and MoO_3 were mixed, ground, and fired at 900°C in air with several intermediate grindings, followed by firing at 900°C in a stream of 5% H_2/Ar gas for 10~20 hours. The resulting specimens were ground, pressed into pellets, and sintered at 1000°C (CLFMO) and 1100°C (SLFMO and BLFMO) in a stream of 5% H_2/Ar gas. Powder x-ray diffraction patterns were taken with a Phillips diffractometer using $\text{Cu } K_\alpha$ radiation. Magnetization measurements were taken with a commercial vibrating sample magnetometer (Lake Shore, model 7300) and a SQUID magnetometer (Quantum Design).

3. Results and Discussion

Fig. 1 shows powder x-ray diffraction patterns for polycrystalline ALFMO samples. It shows a clean single

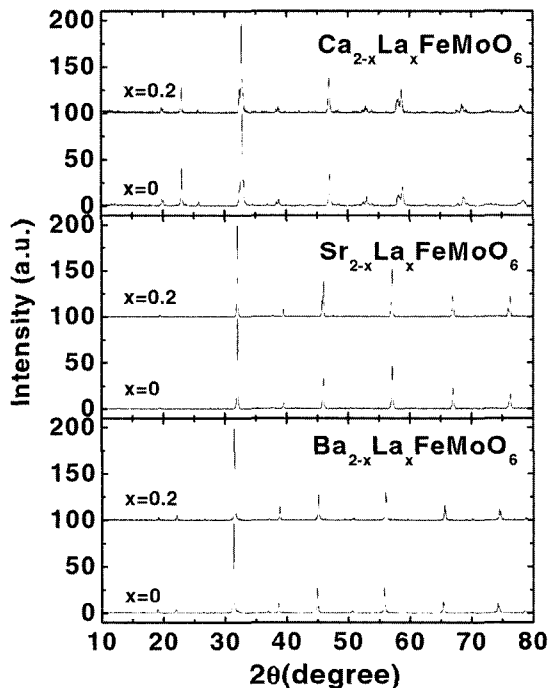


Fig. 1. Powder x-ray diffraction patterns for polycrystalline $\text{Ca}_{2-x}\text{La}_x\text{FeMoO}_6$ (a), $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ (b), and $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ (c) samples.

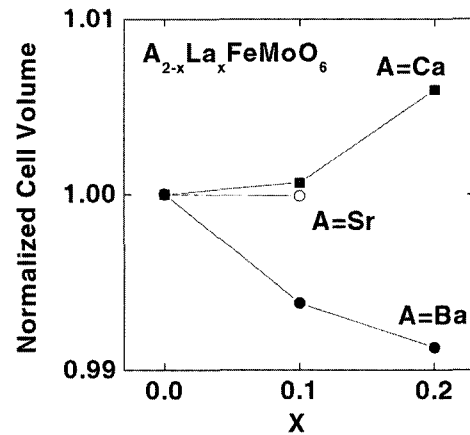


Fig. 2. Normalized cell volumes for $\text{Ca}_{2-x}\text{La}_x\text{FeMoO}_6$, $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$, and $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$.

phase without detectable secondary phases. All peaks in the diffraction patterns can be indexed by monoclinic $P2_1/n$ symmetry for CLFMO, tetragonal $I4/mmm$ symmetry for SLFMO, and cubic $Fm3m$ symmetry for BLFMO.

Fig. 2 shows the normalized cell volumes for $\text{A}=\text{Ca}$, Sr , and Ba with respect to cell volume for $x=0$. In BLFMO the lattice parameter and cell volume decrease monotonically with increasing La content. This is associated with the change of $\langle r_A \rangle$ due to the substitution of smaller La^{3+} ions into the bigger Ba^{2+} ionic sites. However, CLFMO compounds show considerable cell expansion upon La doping due to the substitution of bigger La^{3+} ions for Ca^{2+} ionic sites.

Fig. 3 shows field dependent magnetization of BLFMO samples for $x=0$ and 0.2 measured at 15 K . The magnetization rapidly increases with external fields, and then saturates to a value of M_s . The value of M_s is $3.9\ \mu_B/\text{f.u.}$ for $\text{Ba}_2\text{FeMoO}_6$ (inset of Fig. 3). A large antiferromagnetic interaction between the $S=5/2$ spins of Fe^{3+} and the $S=1/2$ spins of Mo^{5+} induces an ideal saturation magnetization of $4\ \mu_B/\text{f.u.}$ for undoped compounds ($x=0$). The magnitude of M_s systematically decreases with increasing x . This decrease of magnetic moment can be caused by the reduction of moment associated with the electron doping and the mis-site defects. The mis-site defects arise from the misplacement of Fe and Mo ions in the double-perovskite structure (Fe on the Mo site and Mo on the Fe site). Monte-Carlo simulation studies show that the M_s decrease with the increase in the mis-site defect concentration [3]. The rate of decrease is $0.08\ \mu_B/p$ with the mis-site defect concentration p . According to Ogale *et al.* [3], The value of $M_s=3.9\ \mu_B/\text{f.u.}$ ($x=0$) is corresponding to the mis-site-type disorder of 1%, which is in good agreement with the Fe/Mo ordering value (98%) estimated from powder x-ray diffraction refinement. In order to

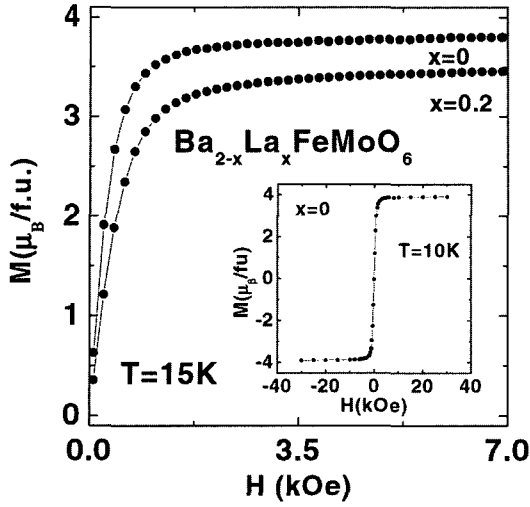


Fig. 3. Magnetization (15 K, 7 kOe) for polycrystalline $\text{Ba}_2\text{FeMoO}_6$.

calculate the degree of Fe/Mo disorder in BLFMO, we apply a simple model which depends on p (Fe on the B'' site and Mo on the B' site) and doping concentration x [7]. In this model, M_s can be written as

$$M_s(x, p) = (1-2p)(4-x). \quad (1)$$

In the absence of mis-site defects ($p = 0$), the ideal M_s decreases at a rate of $0.1 \mu_B/x$ with the increase of doping concentration x . The ideal M_s value with $p = 0$ is $3.8 \mu_B/\text{f.u.}$ for $x = 0.2$. However, the measured moment of $3.5 \mu_B/\text{f.u.}$ is lower than ideal one. The estimated values of p

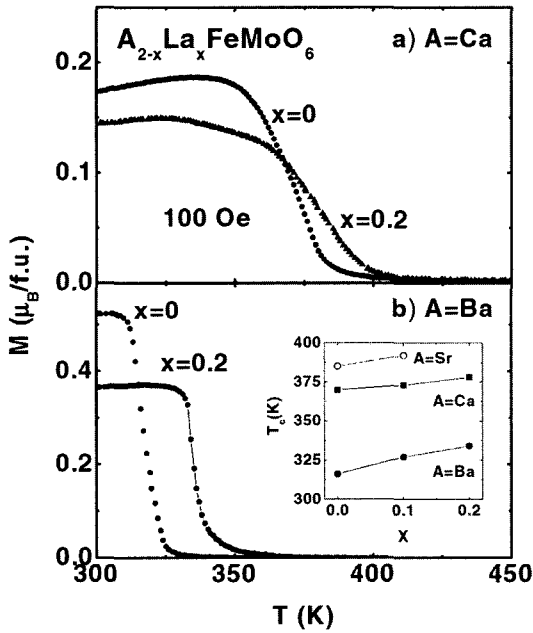


Fig. 4. Magnetization as a function of temperature for $\text{Ca}_{2-x}\text{La}_x\text{FeMoO}_6$ (a) and $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ (b).

from (1) is 3.9% for $x = 0.2$. This indicates that the mis-sites defects reduce the magnetic moments with La doping.

Fig. 4 shows the temperature dependence of magnetization $M(T)$ for ALFMO measured at 100 Oe. The magnetic transition temperature T_c is defined as the minimum value of temperature in the dM/dT vs T curve. In BLFMO, the T_c increases from 316 K for $x = 0$ to 334 K for $x = 0.2$ at a rate of 1.8 K/% with La doping. The T_c of CLFMO increases slightly with increasing x from 370 K for $x = 0$ to 378 K for $x = 0.2$. The change of T_c due to the partial substitution of La^{3+} for A^{2+} in AFMO can be explained in terms of the three competing factors: mis-site defects, ionic size effect, and carrier doping. The presence of Fe/Mo disorder due to mis-site defects destroys the half-metallic ferromagnetic state, and leads to the decrease of T_c [3]. In BLFMO system, the mis-site defect concentration increases from 1% for $x = 0$ to 3.9% for $x = 0.2$ with La doping, this should lead to the decrease of T_c . However, the T_c increases with increasing La concentration. The partial substitution of La^{3+} for A^{2+} in AFMO changes the $\langle r_A \rangle$ and the valence state of Fe/Mo ions via electron doping. The substitution of the smaller ion into the bigger ionic site reduces the $\langle r_A \rangle$ and broadens the W and so enhances the T_c [6]. Since the ionic radius of La^{3+} ion (1.36 \AA) is smaller than that of Ba^{2+} ion (1.61 \AA), we expect the enhancement of T_c for BLFMO with increasing x . Contrast to BLFMO system, the ionic radius of La^{3+} ion is slightly larger than that of Ca^{2+} ion (1.34 \AA). Considering ionic size effect, we cannot expect any enhancement of T_c in CLFMO with increasing x . However, the T_c of CLFMO increases slightly with increasing x from 370 K for $x = 0$ to 378 K for $x = 0.2$.

With substitution of La^{3+} for A^{2+} , the doped electrons are considered to occupy mainly the down-spin Mo $4d$ band in AFMO [8], which changes the valence state of

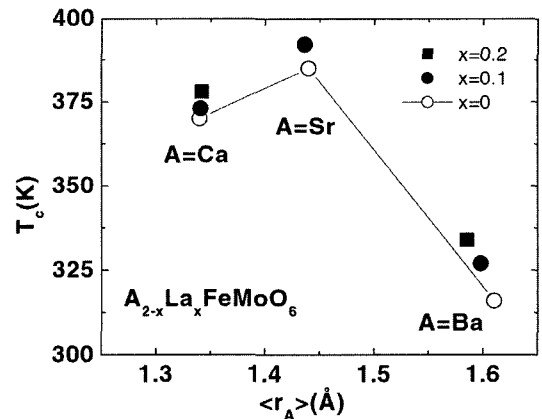


Fig. 5. T_c vs. $\langle r_A \rangle$ for A_2FeMoO_6 .

Fe/Mo ions. A plot of the T_c vs. $\langle r_A \rangle$ is shown in Fig. 5. Open symbols represent data for $x = 0$ and filled symbols correspond to data for $x \neq 0$. The variation of T_c for $x \neq 0$ is not found to follow the line for $x = 0$ (solid line in the figure). This indicates that the enhancement of T_c with La^{3+} doping in these oxides originates from electron doping effects in addition to ionic size ones in the small doping concentration regions.

4. Conclusion

We have examined some effects of the partial substitution of La^{3+} for A^{2+} on magnetic properties of AFMO. With increasing x in $\text{A}_{2-x}\text{La}_x\text{FeMoO}_6$, the Fe/Mo disordering increases and the magnitude of M_s decreases systematically. The T_c of BLFMO increases from 316 K for $x = 0$ to 334 K for $x = 0.2$, however, the T_c of CLFMO is not enhanced significantly with increasing x . The enhancement of T_c with La^{3+} doping is associated with electron doping effects in addition to ionic size ones.

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