

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

J. Kim, H. M. Yang and B. W. Lee\*

Department of Physics, Hankuk University of Foreign Studies, Yongin, Kyungki 449-791, Korea

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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),  $Sr_{2-x}$ -

\*Corresponding author: Tel: +82-31-330-4362,  
Fax: +82-31-333-1696, e-mail: bwlee@hufs.ac.kr

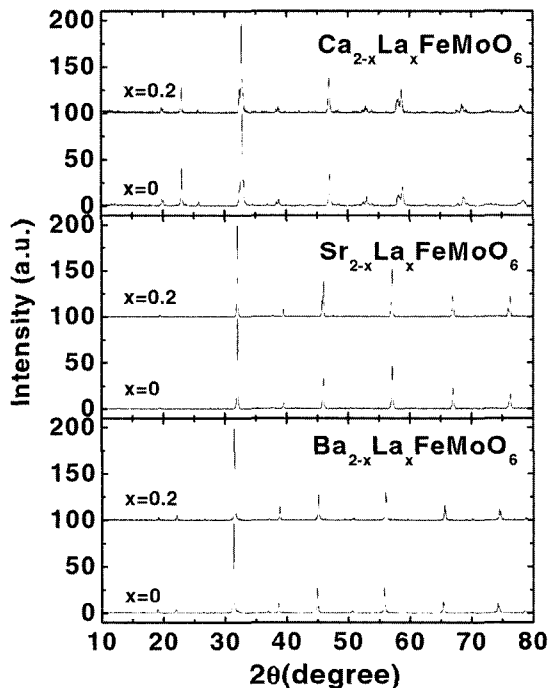
$\text{La}_x\text{FeMoO}_6$  (SLFMO), and  $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$  (BLFMO). The partial substitution of  $\text{La}^{3+}$  for  $\text{A}^{2+}$  in AFMO changes (1) the average ionic radius ( $\langle r_A \rangle$ ) without distortion of the crystal symmetry and (2) the valence state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

## 2. Experimental

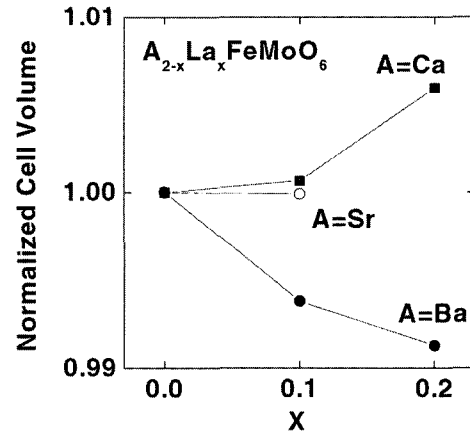
Polycrystalline ALFMO samples were prepared by standard solid-state reaction. Powders of high purity (99.99% or better) of  $\text{ACO}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{MoO}_3$  were mixed, ground, and fired at  $900^\circ\text{C}$  in air with several intermediate grindings, followed by firing at  $900^\circ\text{C}$  in a stream of 5%  $\text{H}_2/\text{Ar}$  gas for 10~20 hours. The resulting specimens were ground, pressed into pellets, and sintered at  $1000^\circ\text{C}$  (CLFMO) and  $1100^\circ\text{C}$  (SLFMO and BLFMO) in a stream of 5%  $\text{H}_2/\text{Ar}$  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 A=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  $\text{La}^{3+}$  ions into the bigger  $\text{Ba}^{2+}$  ionic sites. However, CLFMO compounds show considerable cell expansion upon La doping due to the substitution of bigger  $\text{La}^{3+}$  ions for  $\text{Ca}^{2+}$  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  $\text{Fe}^{3+}$  and the  $S=1/2$  spins of  $\text{Mo}^{5+}$  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

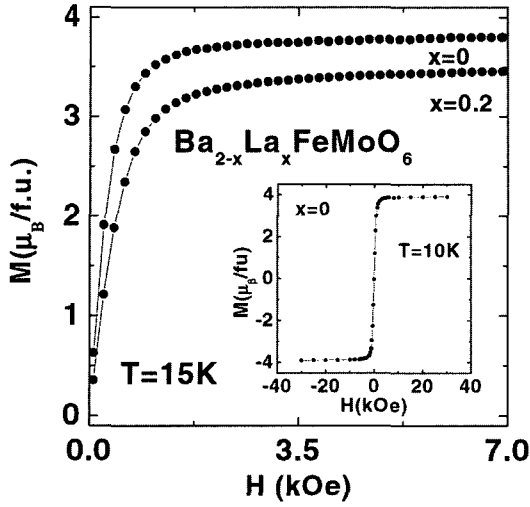


Fig. 3. Magnetization (15 K, 7 kOe) for polycrystalline  $\text{Ba}_2\text{FeMoO}_6$ .

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  $p$

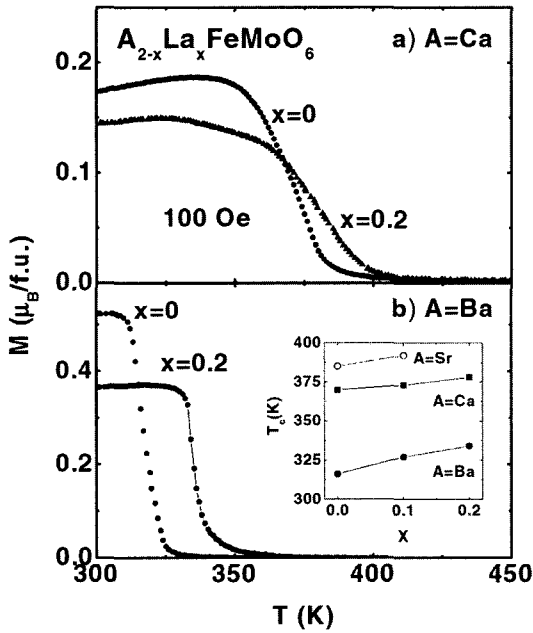


Fig. 4. Magnetization as a function of temperature for  $\text{Ca}_{2-x}\text{La}_x\text{FeMoO}_6$  (a) and  $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$  (b).

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  $\text{La}^{3+}$  for  $\text{A}^{2+}$  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  $\text{La}^{3+}$  for  $\text{A}^{2+}$  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  $\text{La}^{3+}$  ion ( $1.36 \text{ \AA}$ ) is smaller than that of  $\text{Ba}^{2+}$  ion ( $1.61 \text{ \AA}$ ), we expect the enhancement of  $T_c$  for BLFMO with increasing  $x$ . Contrast to BLFMO system, the ionic radius of  $\text{La}^{3+}$  ion is slightly larger than that of  $\text{Ca}^{2+}$  ion ( $1.34 \text{ \AA}$ ). 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  $\text{La}^{3+}$  for  $\text{A}^{2+}$ , the doped electrons are considered to occupy mainly the down-spin Mo  $4d$  band in AFMO [8], which changes the valence state of

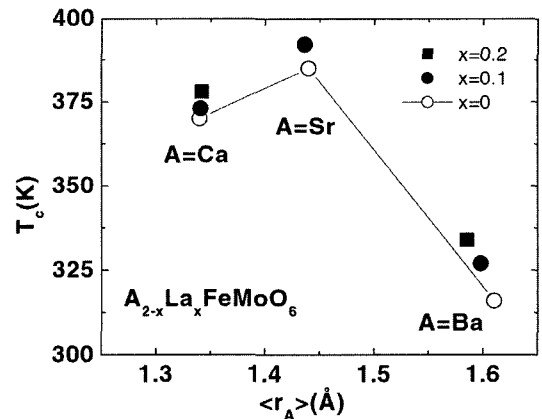


Fig. 5.  $T_c$  vs.  $\langle r_A \rangle$  for  $\text{A}_2\text{FeMoO}_6$ .

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  $\text{La}^{3+}$  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  $\text{La}^{3+}$  for  $\text{A}^{2+}$  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  $\text{La}^{3+}$  doping is associated with electron doping effects in addition to ionic size ones.

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