JOURNAL OF
Materials
CHEMISTRY
Communication

Oxygen-holes creating different electronic phases in Fe^{4+}-oxides: successful growth of single crystalline films of $SrFeO_3$ and related perovskites at low oxygen pressure

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Received 11th April 2001, Accepted 20th June 2001
First published as an Advance Article on the web 13th July 2001

We have succeeded for the first time in preparing single crystalline films of $SrFeO_3$, $CaFeO_3$, and Sr_2FeCoO_6, perovskites containing Fe^{4+}, at low oxygen pressure of only 1 kPa, and the dominance of oxygen hole character in transport phenomena was indicated by the positive Hall coefficient of metallic $SrFeO_3$.

Various types of metal–insulator transitions and related phenomena in strongly correlated electron systems like 3d transition metal oxides have been keenly studied.[1] From a chemical viewpoint it is interesting to survey such electronic properties as a function of the number of d electrons, the depth of the d levels relative to O_{2p} levels, and other relevant parameters by changing the valence state of the transition metal ion. In this sense perovskites containing iron in an unusually high valence state of Fe^{4+} (d^4), having deep d levels, are unique and important. Investigations on $SrFeO_3$ (SFO), $CaFeO_3$ (CFO), and others have suggested that their electric and magnetic properties are dominated by oxygen hole character: the realistic electronic configuration of the Fe–O octahedron has been found to be $Fe^{3+}(O_6)^{11-}$ (expressed as $Fe^{3+}\underline{L}$, where $\underline{L}$ stands for a hole in the oxygen octahedron)[2] rather than $Fe^{4+}(O_6)^{12-}$. The dynamics of holes leads to different electronic phases like metallic antiferromagnetism with a screw spin structure for SFO,[3,4] a metal ($T \geqslant 290$ K, orthorhombic) to semiconductor ($T < 290$ K, monoclinic) transition coupled to the breathing phonon mode in such a way as $2Fe^{3+}\underline{L} \rightarrow Fe^{3+}$ (large octahedron) + $Fe^{3+}\underline{L}^2$ (small octahedron) for CFO,[5–8] and metallic ferromagnetism with a relatively high T_C of 340 K and large moments of $4\mu_B$/Fe and $2\mu_B$/Co[9,10] for Sr_2FeCoO_6 (SFCO, containing $Fe^{3+}\underline{L}$ and $Co^{3+}\underline{L}$[11–13]). Moreover, these oxides generally change their electronic properties remarkably under high pressure.[14–16] To further clarify the multi-faceted hole dynamics and thereby open a new research field, sizeable single crystals are needed. However, the use of very high oxygen pressure for synthesis, *e.g.* 2 GPa or more for CFO,[5,17] has made the crystal growth difficult. Here, we report that single crystals of SFO, CFO, SFCO, and also $Sr_2LaFe_3O_9$ (SLFO, SFO doped with electrons) can be obtained in the form of films in a surprisingly low pressure of only 1 kPa O_2.

The film growth was carried out with a pulsed laser deposition method using a KrF excimer laser ($\lambda = 248$ nm). The targets were sintered disks of $SrFeO_{3-\delta}$, $CaFeO_{2.5}$, $Sr_2FeCoO_{6-\delta}$ and $Sr_2LaFe_3O_{9-\delta}$ prepared by a usual ceramic method. Different kinds of substrates including the (001) surfaces of $SrTiO_3$ (STO), $LaAlO_3$ (LAO), $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT), and $LaSrAlO_4$ (LSAO) were tested. STO is a cubic perovskite ($a = 3.905$ Å), whereas LAO is a rhombohedral perovskite with $a = 3.788$ Å and $\alpha = 90.4°$, and LSAT crystallizes in cubic perovskite structure with $a = 7.736$ Å. Hereafter, however, we neglect the slight distortion of LAO and also the doubling of the parameter of LSAT for simplicity and assume cubic structure with $a = 3.788$ and 3.868 Å, respectively. LSAO crystallizes in the K_2NiF_4 structure with an in-plane constant of $a = 3.756$ Å.

During the deposition, the oxygen pressure in the evaporation chamber was kept at 26 Pa and the substrate temperature was maintained at 920 K. The films were grown to a typical thickness of 500 Å at a rate of 0.5 Å s^{-1} and subsequently cooled to room temperature at a rate of 4 K min^{-1} while blowing oxygen containing 10% ozone against the film surface. The total pressure at the film surface was estimated to be roughly 1 kPa.

The film structure was investigated with cross-section transmission electron microscopy (TEM, Hitachi HD-2000) and four-circle X-ray diffraction (XRD, Rigaku RU300, CuKα radiation). Resistivity and the Hall effect were measured over a temperature range of *ca.* 5–280 K (Quantum Design, PPMS). Mössbauer spectroscopy was conducted in back scattering geometry at room temperature with a ^{57}Co/Rh source. The source velocity was calibrated using pure iron as a control sample. Reported below are the most representative experimental data.

Fig. 1(a) shows an equi-intensity contour map of the X-ray scattering around the (203) point for the SFO film grown on LSAT (SFO/LSAT). The Kα_1- and Kα_2-peaks of the film are clearly split from each other and their widths are as narrow as those of the substrate, certifying that the sample is an epitaxially grown single crystal of excellent crystallinity. The film structure is tetragonal with $a_{SFO} = 3.865$ Å (in-plane) and $c_{SFO} = 3.837$ Å (out-of-plane). This slight distortion from the cubic structure of a free crystal ($a = 3.850$ Å[3]) is due to an elastic strain caused by the in-plane lattice matching with the substrate. Consistent with this, the TEM image of the same sample viewed along [100] showed smooth connection of the film and the substrate without any misfit dislocations in the interface region. An EDX measurement on the cross-section found that the atomic Fe : Sr ratio was equal to 1 : 1 within experimental error. On the other hand, the XRD peaks of the SFO/STO film were much broader than those of the SFO/LSAT film. The mismatch of 1.43% for this combination seems to have been too large to be compensated for by a homogeneous strain of the film.

The Mössbauer spectra of the SFO/LSAT film (back scattering geometry) and a powdered sample prepared using a high-pressure technique[10] (absorption geometry) are compared in Fig. 1(b). The solid lines represent the single Lorentzian functions fitted to the experimental data. The parameter values deduced are given in the figure. We considered it possible that the film spectrum was split into a quadrupole doublet because of the tetragonal distortion, but

DOI: 10.1039/b103259n

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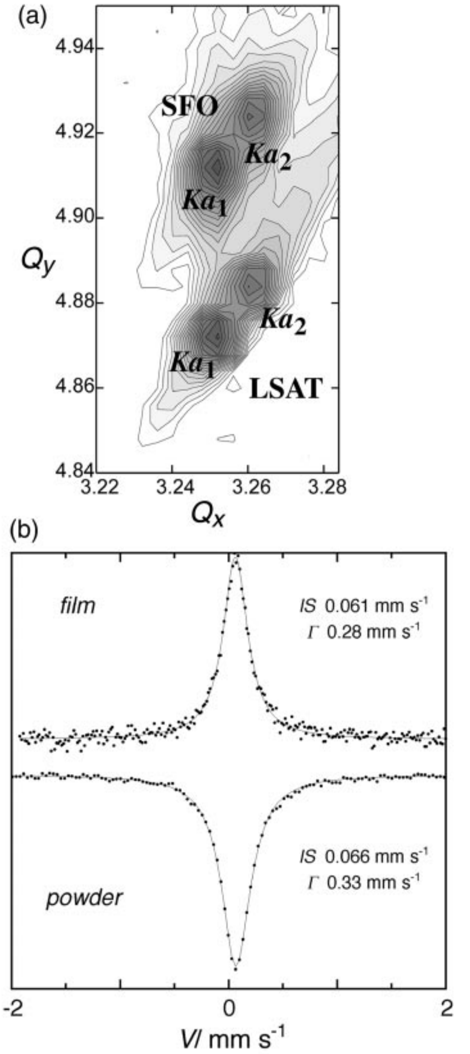

Fig. 1 (a) Reciprocal mapping around the (203) point measured by X-ray scattering. The upper peaks are from the $SrFeO_3$ film, and the lower ones are from the LSAT substrate. (b) Mössbauer spectra of the same $SrFeO_3$/LSAT film (back scattering geometry) and a powdered sample prepared using a high-pressure technique (absorption geometry) measured at room temperature. The solid lines represent the single Lorentzian functions fitted to the experimental data. *IS* and Γ stand for isomer shift relative to α-Fe and the peak width at half maximum, respectively.

the use of double Lorentzian functions did not lead to any significant improvement in fitting. The isomer shifts of these two samples were identical within experimental error, and the peak widths were near the instrumental resolution limit, again indicating good homogeneity of the film. We should emphasize here that there is no sign of ferric ions appearing in oxygen-deficient samples.[18,19] The film was fully oxidized in the deposition chamber, without any post-annealing at high oxygen pressure.

The temperature dependences of resistivity and the Hall coefficient of the same film are shown in Fig. 2. The metallic behavior down to low temperatures also indicates full oxidation of the film because even a 1% oxygen deficiency is known to lead to semiconductivity.[3] The Hall coefficient was found to be nearly independent of both temperature and external magnetic field (up to 9 T) above 110 K, and this simplicity allows us to conclude that its positive sign is consistent with the aforementioned hole-carrier picture. The carrier number is 1.5 holes per chemical unit, which is considerably larger than a naïve estimation of one hole per chemical unit. To explain this discrepancy a detailed band structure calculation is needed. Around 110 K both the resistivity and the Hall coefficient exhibit anomalous behavior. The T-dependence of the resistivity is hysteretic, indicating the occurrence of a first order transition, and $d^2\rho/dT^2$ changes its sign from negative to positive as the temperature decreases. The Hall coefficient first decreases slightly but subsequently increases rapidly below 100 K. These trends most likely reflect changes in the hole scattering due to magnetic ordering. However, we should not take these as indicating a T_N of 107 K, lower by 27 K than that for a free crystal, because stoichiometric sintered pellets also show a resistive anomaly at 110 K,[20] not at the T_N of 134 K. Thus, there seems to be room for a reinvestigation of the antiferromagnetic transition of SFO. A complicated situation was suggested by the coexistence of magnetically ordered and disordered components in the Mössbauer spectra for $107\ K \leqslant T \leqslant 134\ K$.[18,21] We note here that the measurement of the Hall effect reported here is the first one ever done on 'Fe^{4+}'-oxides.

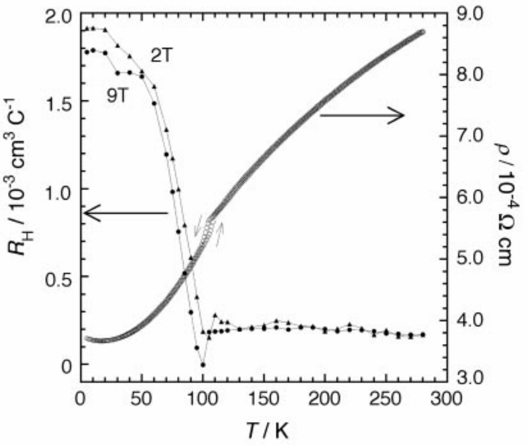

Fig. 2 Temperature dependences of resistivity and the Hall coefficient of the $SrFeO_3$/LSAT film.

Concerning the film growth process, an SFO/LSAT film deposited at $pO_2 = 26$ Pa as above and cooled subsequently in the same atmosphere indicated a nearly 1 : 1 mixture of $SrFeO_{2.75}$ and $SrFeO_{2.5}$ in its Mössbauer spectrum. These are the most oxygen-deficient members of a series of phases, $SrFeO_{3-1/n}$ ($n = \infty$, 8, 4, 2).[18,19] The driving force for the further oxidation to the $n = \infty$ phase is likely the good lattice matching with LSAT. The unit volume of $SrFeO_{3-1/n}$ is known to increase as oxygen deficiency, *i.e.* $1/n$, increases, making the compensation of mismatch by elastic deformation less and less feasible.

Shown in Fig. 3 are the metal–semiconductor transitions in

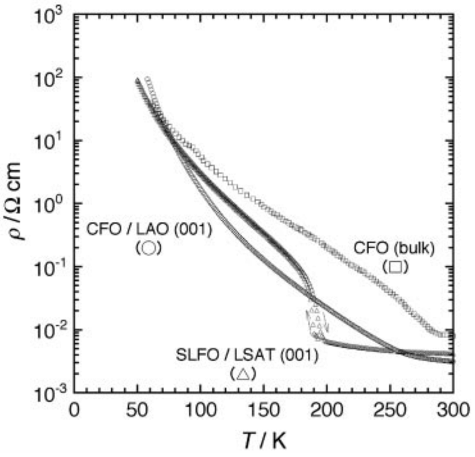

Fig. 3 Metal–semiconductor transitions of the $CaFeO_3$/LAO and $Sr_2LaFe_3O_9$/LSAT films. The data for a sintered $CaFeO_3$ pellet are also included for comparison.

the CFO/LAO and SLFO/LSAT films taking place at 270 and 190 K, respectively. The measured out-of-plane lattice constants were 3.763 and 3.904 Å, respectively. In comparison with the behavior of a free CFO crystal,[20] the transition of the CFO/LAO film is more gradual and the transition temperature is lower by about 20 K. We do not attribute these changes to oxygen deficiency because the resistivity in the high temperature region is considerably smaller than that of a sintered pellet prepared at high pressure and near that of the SFO/LSAT film (Fig. 2), but instead attribute them to elastic interactions with the substrate. The fact that the transition in a free CFO crystal is accompanied by a structural change ($Pnma \rightarrow P2_1/n$)[6–8] should be remembered. In the low temperature structure, two kinds of Fe–O octahedra, both almost regular in shape but different in size from each other, are ordered in a rock salt manner, and the holes are confined in the smaller ones. Elastic substrate–film interactions should tend to suppress any type of distortion of the film. The low temperature phase of the film may differ from that of a free crystal. Low temperature Mössbauer spectroscopic measurements are in progress.

SLFO with a formal valence of $Fe^{11/3+}$ may be considered as SFO doped with electrons. The doping creates a new ground state. Although the O_{2p} holes remain delocalized in SFO, those in SLFO become confined by the following mechanism: $3(Fe^{3+}\underline{L}^{2/3})$ (metal, $T \geqslant 200$ K)$\rightarrow 2Fe^{3+} + Fe^{3+}\underline{L}^2$ (semiconductor, $T < 200$ K).[22–25] An accompanying structural change is known to be much smaller[23,26] than for CFO. Likely because of this inherent weak coupling of the hole dynamics to the lattice system, the SLFO/LSAT film exhibited a transition quite similar to that of a free crystal. The sharpness and the presence of a small hysteresis are both signs of a first order transition.

The temperature dependences of resistivity and magnetization of the SFCO/LAO film are shown in Fig. 4. The film is no doubt a metallic ferromagnet with a T_C of about 340 K, which is close to that of a free crystal.[9,10] The saturation moment was estimated from the magnetization (M) *vs.* field (H) curve measured at 5 K (inset) to be *ca.* $4.2\mu_B$/(Fe + Co), about 70% of the bulk value,[9,10] although the mixing of a large diamagnetic contribution by the substrate crystal might have led to an underestimation. The film is a soft ferromagnet with a small coercive force of 0.1 T.[10]

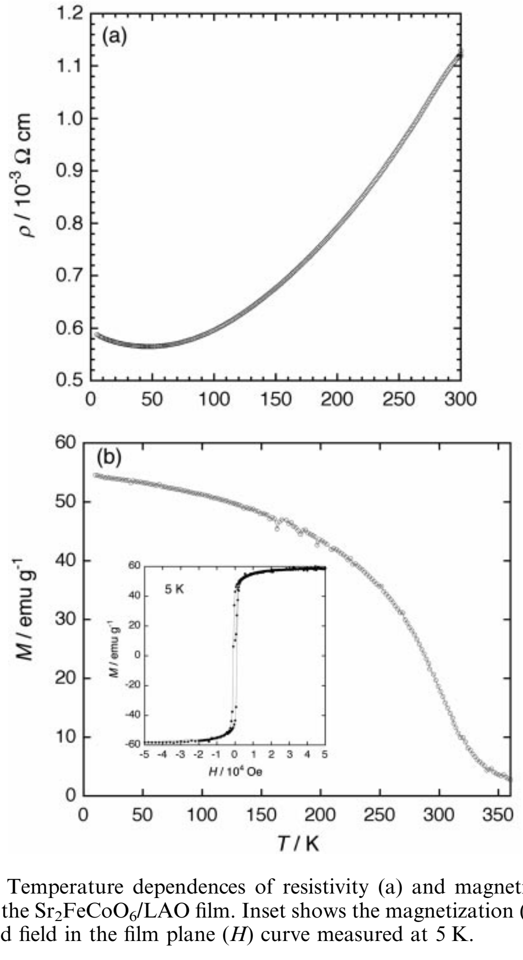

Fig. 4 Temperature dependences of resistivity (a) and magnetization (b) of the Sr_2FeCoO_6/LAO film. Inset shows the magnetization (M) *vs.* applied field in the film plane (H) curve measured at 5 K.

The present success in the growth of single crystalline films at a low pressure is a breakthrough in the physics and chemistry of oxygen holes in 'Fe^{4+}'-oxides.

This work was partly supported by the Grant-in-Aids for COE Research on Elements Science, No. 12CE2005 (the Ministry of Education, Culture, Sports, Science and Technology of Japan). This work was partly supported by the Grant-in-Aid for Scientific Research on Priority Areas (B) No. 751 from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The authors are grateful to Professor K. Mibu for his support in the measurement of the four-circle X-ray diffraction.

Notes and references

1 M. Imada, A. Fujimori and Y. Tokura, *Rev. Mod. Phys.*, 1998, **70**, 1039.
2 A. E. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, S. Suga, N. Kimizuka, Y. Takeda and M. Takano, *Phys. Rev. B*, 1992, **45**, 1561.
3 J. B. MacChesney, R. C. Sherwood and J. F. Potter, *J. Chem. Phys.*, 1965, **43**, 1907.
4 Y. Takeda, Y. Yamaguchi and H. Watanabe, *J. Phys. Soc. Jpn.*, 1972, **33**, 967.
5 M. Takano, N. Nakanishi, Y. Takeda, S. Naka and T. Takada, *Mater. Res. Bull.*, 1977, **12**, 923.
6 S. Morimoto, T. Yamanaka and M. Tanaka, *Physica B*, 1997, **66–67**, 237.
7 P. M. Woodward, D. E. Cox, E. Moshopoulou, A. W. Sleight and S. Morimoto, *Phys. Rev. B*, 2000, **62**, 844.
8 T. Takeda, R. Kanno, Y. Kawamoto, M. Takano, S. Kawasaki, T. Kamiyama and F. Izumi, *Solid State Sci.*, 2001, **2**, 673.
9 P. Bezdicka, L. Fournes, A. Wattiaux, J. C. Grenier and M. Pouchard, *Solid State Commun.*, 1994, **91**, 501.
10 S. Kawasaki, M. Takano and Y. Takeda, *J. Solid State Chem.*, 1996, **121**, 174.
11 R. H. Potze, G. A. Sawatzky and M. Abbate, *Phys. Rev. B*, 1995, **51**, 11 501.
12 T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda and M. Takano, *Phys. Rev. B*, 1997, **56**, 1290.
13 J. Okamoto, H. Miyauchi, T. Sekine, T. Shidara, T. Koide, K. Amemiya, A. Fujimori, T. Saitoh, A. Tanaka, Y. Takeda and M. Takano, *Phys. Rev. B*, 1997, **62**, 4455.
14 M. Takano, S. Nasu, T. Abe, K. Yamamoto, S. Endo, Y. Takeda and J. B. Goodenough, *Phys. Rev. Lett.*, 1991, **67**, 3267.
15 S. Nasu, T. Abe, K. Yamamoto and S. Endo, *Hyperfine Interact.*, 1991, **67**, 527.
16 G. Kh. Rosenberg, A. P. Milner, M. P. Pasternak, G. R. Hearne and R. D. Taylor, *Phys. Rev. B*, 1998, **58**, 10 283.
17 Y. Takeda, S. Naka, M. Takano, T. Shinjo, T. Takada and M. Shimada, *Mater. Res. Bull.*, 1978, **13**, 61.
18 Y. Takeda, K. Kanno, T. Takeda, O. Yamamoto, M. Takano, N. Nakayama and Y. Bando, *J. Solid State Chem.*, 1986, **63**, 237.
19 M. Takano, T. Okita, N. Nakayama, Y. Bando, Y. Takeda, O. Yamamoto and J. B. Goodenough, *J. Solid State Chem.*, 1988, **73**, 140.
20 S. Kawasaki, M. Takano, R. Kanno, T. Takeda and A. Fujimori, *J. Phys. Soc. Jpn.*, 1998, **67**, 1529.
21 S. Kawasaki and M. Takano, unpublished results.
22 M. Takano, J. Kawachi, N. Nakanishi and Y. Takeda, *J. Solid State Chem.*, 1981, **39**, 75.
23 P. D. Battle, T. C. Gibb and P. Lightfoot, *J. Solid State Chem.*, 1990, **84**, 271.
24 T. Ishikawa, S. K. Park, T. Katsufuji, T. Arima and Y. Tokura, *Phys. Rev. B*, 1998, **58**, R13326.
25 J. Matsuno, T. Mizokawa, A. Fujimori, K. Mamiya, Y. Takeda, S. Kawasaki and M. Takano, *Phys. Rev. B*, 1999, **60**, 4605.
26 J. Q. Li, Y. Matsui, S. K. Park and Y. Tokura, *Phys. Rev. Lett.*, 1997, **79**, 297.