Oxidation state and effective pair potential of Fe$^{4+}$ ions in perovskite-type SrFeO$_3$ annealed under high oxygen pressure

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Abstract. The cubic perovskite-type SrFeO$_3$ have been obtained by annealing under high oxygen pressure of 100 MPa at 600K. X-ray absorption fine structure (XAFS) observations on Fe K-edge have been performed from 25 K to 900 K to investigate the temperature variation of the local structure and oxidation state of iron ion in the perovskite-type SrFeO$_3$. The edge features of Fe K-edge XANES spectra and the first differential curves of XANES spectra change gradually and greatly with increasing temperature from 600K to 900K. There is no clear change near the Neel temperature. In the higher temperature region than 600 K, the threshold energy shifted to the low energy side (~2 eV) indicating that Fe$^{4+}$ ion more reduced to Fe$^{3+}$ in air. The temperature dependence of EXAFS Debye-Waller factors was investigated and harmonic effective pair potentials, $V(u)=\alpha u^2/2$, have been evaluated. The potential coefficients $\alpha$ for Fe-O, Fe-Sr and Fe-Fe distances are 6.0, 5.48 and 4.0 eV/A$^2$, respectively.

1. Introduction

The ideal perovskite type structure has a cubic symmetry such as SrTiO$_3$. The cubic perovskite type oxides with the chemical formula Sr$^{2+}$B$^{4+}$O$_3$ (B = Mn, Fe, Co) quench the tetravalent state of the first-row transition metal ion under ambient condition though these transition metal ions are normally in a divalent or trivalent state and a higher valence state is stabilized under strongly oxidizing conditions[1-4]. Annealing and quenching under high oxygen pressure and appropriate temperature is necessary for the stabilization of the tetravalent state of the first-row transition metal ion. The perovskite-type oxides containing transition metal ions in tetravalent state show interesting electrical and magnetic properties [1-4]. SrFeO$_3$ is an antiferromagnet with Neel temperature of 134K [1].

In this study, we have determined the temperature variation of the local structure and oxidation state of iron ion in the perovskite-type SrFeO$_3$ from 25 K to 900K. The analysis of temperature-dependent EXAFS Debye-Waller factor allows us to evaluate the effective pair potentials and the inter-atomic force constants for neighboring atoms [5-7].
2. Experimental and analysis
The starting materials of FeCO3 and SrCO3 (Furuuchi Chem. Co.,Ltd.) in powder form were weighted in the desired ration and milled for 24 hr with acetone. The well-blended mixture of raw materials was pre-fired at 1070 K for 24 hr. They were reground and fired at 1500 K for 24 hr. This firing was repeated three times. As the compounds obtained in this way were oxygen-deficient, they were annealed under pure high oxygen pressure of 100 MPa at 600K for 72 hr. High oxygen pressure was produced by heating an autoclave which had been cooled down to liquid nitrogen temperature and in which oxygen gas had been condensed into liquid [4]. The crystals of SrFeO3 perovskite were identified by X-ray diffraction.

The appropriate amount of fine powder sample and boron nitride powder was mixed and pressed into pellets of <0.2 mm in thickness and 10.0 mm in diameter. All samples had edge-jumps with 0.7 (Δμd), where μ is the linear absorption coefficient and d is the thickness. The measurements of Fe K-edge XAFS spectra were carried out in the transmission mode at beam line BL-12C of the Photon Factory in KEK, Tsukuba (Proposal No. 2006G082). X-ray absorption measurements were made from 300 to 900 K in air. The synchrotron radiation was monochromatized by a Si(111) double crystal monochromator. Mirrors are used to eliminate higher harmonics. Details of the measurement and analysis were given in reference [6,9]

Figure 1. Fourier transforms of the Fe K-edge EXAFS for SrFeO3 perovskite at 300 K. No phase shift corrections are made.

The EXAFS interference function, \( \chi(k) \), was extracted from the measured absorption spectra using the standard procedure [9]. The \( \chi(k) \) was normalized using MacMaster coefficients according to the EXAFS workshop report [10]. Figure 1 shows example of Fourier transforms of the Fe K-edge EXAFS spectra in the ranges of 3.5<k<14.0. In quantitative analyses we carried out the Fourier-filtering technique and a nonlinear least-squares fitting method by comparing the observed \( \chi(k)_{\text{exp}} \) and calculated \( \chi(k)_{\text{calc}} \). We used the EXAFS formula in the single scattering theory with the cumulant expansion up to the fourth order term:

\[
\chi(k) = \frac{1}{T} N_B \sum k^2 R_{AB}^2 \left| f_B(k; \pi) \right| \exp(-2k R_{AB}/(k/\pi)) \exp(-\sigma^2 2k^2 + (2/3)\sigma 4k^4) \\
\times \sin(2k R_{AB} - (2k/R_{AB})(1 + 2R_{AB}/(k/\pi))\sigma 2 - (4/3)\sigma 3k^4 + \psi_{AB}(k))
\]

where \( N_B \) is the coordination number of scattering atoms B at distance \( R_{AB} \) from the absorbing atom A, \( \left| f_B(k; \pi) \right| \) the backscattering amplitude of photoelectrons and \( \psi_{AB}(k) \) the phase shift function. Values of the function \( \left| f_B(k; \pi) \right| \) and \( \psi_{AB}(k) \) were calculated using the FEFF3 program [11]. \( \sigma n \) denotes the nth cumulant. The mean free path \( \lambda(k) \) of the photoelectron is assumed to depend on the wave number, \( \lambda(k)=k/\eta \), where \( \eta \) is a constant. Single-shell fitting was carried out for each nearest-neighbor distance,
where the number of neighboring atoms was fixed at the crystallographic value as N_{B}=6 for the Fe-O distance, N_{B}=8 for the Fe-Sr distance and N_{B}=6 for the Fe-Fe distance. Because the third- and fourth-order terms were negligible, the refinement was performed with harmonic model. The harmonic approximation requires a cumulant up to only second order term. It is known that an anharmonic contribution to the EXAFS Debye-Waller factor appears pronouncedly when the magnitude of $\sigma^2$ is greater than 0.01 Å² [12]. The reliability of fit parameters between the experimental and calculated EXAFS functions was less than 0.036.

![Figure 2. Experimental Fe K-edge XANES spectra and the first differential curves of XANES spectra in SrFeO₃ perovskite.](image)

3. Results and discussion

3.1. Oxidation state and local structure changes in SrFeO₃ perovskite.

X-ray absorption near-edge structure (XANES) spectra are quite sensitive to the oxidation states of X-ray absorbing atom and three-dimensional atomic configuration around the atom. XANES spectra are useful for determining the oxidation state of Fe ions in SrFeO₃ perovskite. Temperature dependences of Fe K-edge XANES spectra and the first differential curves of XANES spectra in SrFeO₃ perovskite are shown in Figures 2a and 2b. The edge features change gradually and greatly with increasing temperature from 600K to 900K. From the detailed comparison of the spectra patterns, it observed that the threshold energy shifts gradually to the low energy side (~2 eV) in the higher temperature region than 600 K indicating that Fe⁴⁺ ion more reduced to Fe³⁺ in air. There is no clear change near the Neel temperature of 134K.

3.2. EXAFS Debye-Waller factors and potential coefficients for Fe-O, Fe-Sr and Fe-Fe distances

Obtained local bond distances agreed with those by X-ray diffraction analysis. The temperature dependence of $\sigma^2$ for the Fe-O distances (1.935(5) Å at 300 K), Fe-Sr distance (3.33(1) Å) and Fe-Fe distance (3.84(1)) Å in SrFeO₃ perovskite are shown in Figure 3. The Debye-Waller type factor $\sigma^2$ includes the effects of static and dynamic disorders. The static disorder is the configuration disorder, while the dynamic disorder arises from the thermal vibration of atoms. The contribution of the thermal
vibration, $\sigma_{\text{thermal}}$, can be estimated under the assumption of classical statistical dynamics by the temperature dependence of $\sigma^2$ [5]. A steep slope in the figure represents a weak bonding. The gradient for the experimental $\sigma^2$ is equal to $k_B/\alpha$, if we evaluate the anharmonic effective pair potential $V(u) = \alpha u^2/2$ from the contribution to the thermal vibration, where $k_B$ is the Boltzmann constant, $\alpha$ is the potential coefficients and $u$ is the deviation of the bond distance from the location of the potential minimum. The potential coefficients $\alpha$ for Fe-O, Fe-Sr and Fe-Fe distances are 6.04 eV/A$^2$, 5.48 eV/A$^2$ and 4.0 eV/A$^2$, respectively. The potential coefficient decreases as a result of the increase in the distance. The potential coefficient $\alpha$ of Fe$^{4+}$-O (6.04 eV/A$^2$) is comparable to those of Ti$^{4+}$-O (6.9 eV/A$^2$) in CaTiO$_3$ and of Ge-O (9.8 eV/A$^2$) in CaGeO$_3$[13]. The potential coefficient $\alpha$ of Fe$^{4+}$-Fe$^{4+}$ (4.0 eV/A$^2$) is relatively smaller than those of Ti-Ti (8.0 eV/A$^2$) in CaTiO$_3$ and of Ge-Ge (7.4 eV/A$^2$) in CaGeO$_3$ [13]. The short-range correlation of the atomic motion between Fe$^{4+}$-Fe$^{4+}$ is relatively smaller than other perovskite type compounds.

Figure 4. Temperature dependence of $\sigma^2$ for the Fe-O, Fe-Sr and Fe-Fe distances in SrFeO$_3$ perovskite

References
[1] Takeda T, Yamaguch Y and Watanabe H 1972 J. Phys. Soc.Japan 33 967
[2] Takeda T and Ohara O 1974 J. Phys. Soc.Japan 37 275
[3] Takeda Y, Naka S, Takano M, Shinjyo T, Takeda T and Shimada M 1978 Mater. Res. Bull. 13 61
[4] Yoshiasa A, Inoue Y, Kanamaru F and Koto K 1990 J. Solid State Chem. 86 75
[5] Yoshiasa A, Nagai T, Murai K, Yamanaka T, Kamishima O and Shimomura O 1998 Jpn. J. Appl. Phys. 37 728
[6] Yoshiasa A and Maeda H Solid State Ionics 1999 121 175
[7] Yoshiasa A, Murai K, Nagai T and Katayama Y 2001 Jpn. J. Appl. Phys. 40 2395
[8] Yoshiasa A, Okube M, Ohtaka O, Kamishima O and Katayama Y 2000 Jpn. J. Appl. Phys. 39 6747
[9] Maeda H 1987 J. Phys. Soc.Japan 56 2777
[10] Lytle F W, Sayers D E and Stern E A 1989 Physica, B 158 701
[11] Rehr JJ, Mustre de Leon J, Zabinski SI and Albers RC 1991 Am. Chem. Soc. 113 5135
[12] Yoshiasa A, Koto K, Maeda H and Ishii T 1997 Jpn. J. Appl. Phys. 36 781
[13] Yoshiasa A, Nakajima K, Murai K and IOkube M 2001 J. Synchrotron Rad. 8 940