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J. Am. Chem. Soc., **2008**, 130 (12), 3764-3765 • DOI: 10.1021/ja800415d

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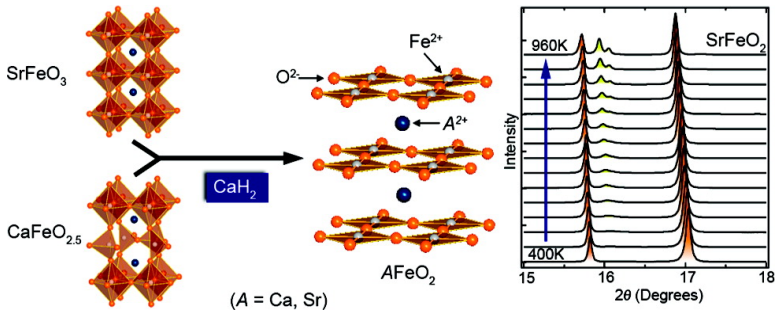

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Published on Web 03/04/2008

Stability of the Infinite Layer Structure with Iron Square Planar Coordination

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The iron perovskites (Sr,Ca)FeO_{3-y} ($0 \leq y \leq 0.5$) have been a subject of intensive studies for many years because of a variety of interesting fundamental aspects, ranging from charge disproportionation ($2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$), vacancy ordered structures, screw spin structure, giant magnetoresistance, to high-spin-to-low-spin transition.[1] Furthermore, they show fast oxygen transport properties observed at moderate temperatures, making them appealing for low-cost industrial applications as gas sensors, electrodes for solid oxide fuel cells, membranes for oxygen separation, and electrocatalysis.[2]

A reduction of transition metal oxides by metal hydride at low temperatures has become a useful tool to generate greater oxygen deficiencies (or lower valence) than could be achieved by standard methods, leading to unprecedented frameworks with less coordination numbers.[3] Applying the new method to $SrFeO_3$ (Figure 1a), we have recently obtained a new compound $SrFeO_2$ ($y = 1$) bearing an unusual square-planar coordination around iron (Figure 1c).[4] It is isostructural with the undoped high-T_c superconductor $SrCuO_2$, the "infinite-layer" (IL) compound.[5] Doubled oxygen deficit with respect to the brownmillerite phase $SrFeO_{2.5}$ ($y = 0.5$) (Figure 1b), once thought as the terminal phase, and considerably low-temperature reoxidation (starting at ~400 K) may further enhance the potentials for aforementioned applications.

The question, which is of fundamental and practical importance, is how stable the IL structure is against external parameters (temperature T, pressure P, substitution, etc.). It has been theoretically demonstrated, for example, for an isolated d^6 system that a square-planar coordination occurs only when the metal is in the triplet ($S = 1$) ground state and is bonded with π-donor ligands.[6] This is in marked contrast to the case of $SrFeO_2$ (quintet ($S = 2$) ground state and σ-donor ligands), where the tetrahedral geometry should have been stabilized. Given that $SrFeO_2$ is a metastable phase only obtainable through the low-T route, one might suspect that it would easily be destroyed upon being heated. Furthermore, the bond valence sum (BVS) calculations giving nearly ideal values of +2 for both Sr and Fe might indicate that the formation of $SrFeO_2$ was fortunate, i.e., a perfect match in the ionic radii of Sr^{2+}, Fe^{2+}, and O^{2-}.[4] Here, we will report on the successful synthesis of the complete solid solution of $Sr_{1-x}Ca_xFeO_2$ together with their thermal stability measured by in situ X-ray diffraction (XRD). The robust nature of the IL structure against both x and T allows extensive tuning of the physical properties to meet industrial demands.

The precursors $Sr_{1-x}Ca_xFeO_{3-y}$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) were prepared in air by using high-T ceramic reactions. In the ambient atmosphere, the oxygen deficiency y increases with x and becomes $y = 0.5$ for $x = 1$. Subsequently, the reaction with CaH_2 was performed at 553 K in an evacuated Pyrex tube. A longer reaction time is required with greater x. For example, $SrFeO_2$ was readily formed by a 1-day reaction at 553 K, but $CaFeO_2$ was formed by a 1-week reaction at the same temperature.

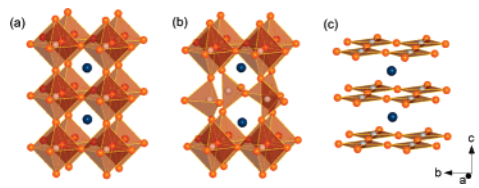

Figure 1. Idealized structures of $AFeO_3$ (A = Sr, Ca) (a), $AFeO_{2.5}$ (b), $AFeO_2$ (c). Blue, gray, and orange spheres are A, iron, and oxygen.

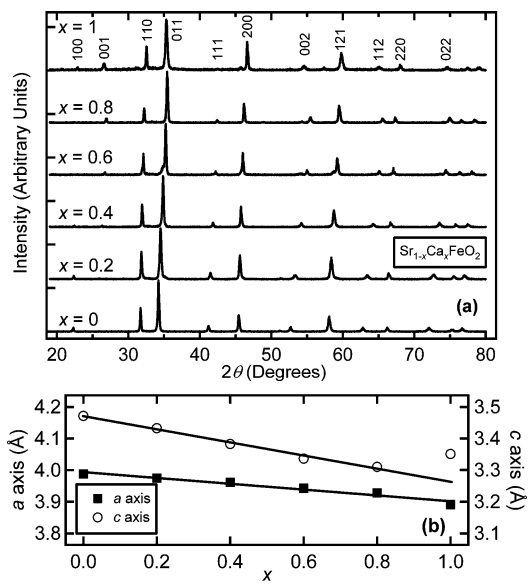

Figure 2. (a) XRD patterns of $Sr_{1-x}Ca_xFeO_2$ and (b) the cell constants.

As shown in Figure 2a, the powder XRD patterns of the final products for $0.2 \leq x \leq 1.0$ were very similar to those for $x = 0$, where all peaks are indexable in the tetragonal lattice. Rietveld structural refinements were performed using the synchrotron XRD data taken at SPring-8. We assumed the IL structure of $SrFeO_2$, $P4/mmm$ space group with $A = (Sr_{1-x}Ca_x)$ on 1d (0.5, 0.5, 0.5), Fe on 1a (0, 0, 0), and O on 2f (0.5, 0, 0). The fits readily converged to give $R_{wp} = 4.20\%$, $\chi^2 = 0.21$ for $x = 0.2$, $R_{wp} = 3.86\%$, $\chi^2 = 0.24$ for $x = 0.4$, $R_{wp} = 3.35\%$ and $\chi^2 = 0.48$ for $x = 0.8$. Site occupancy was confirmed as 100% for all sites. Both the a and c parameters decrease linearly with x up to $x = 0.8$, in consistency with the reduced ionic radius for Ca (vs Sr).

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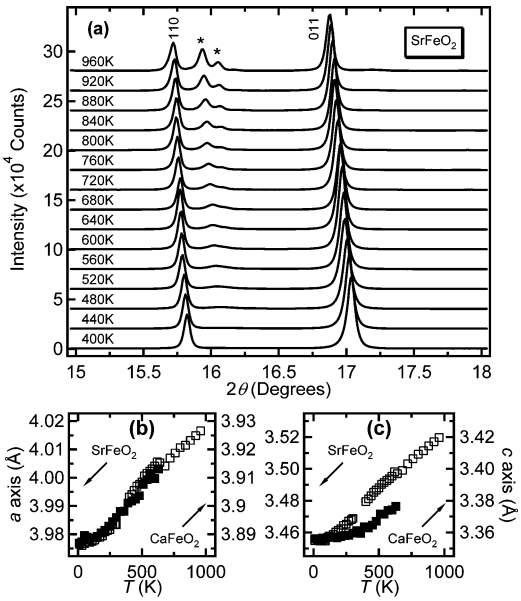

Figure 3. (a) XRD patterns of $SrFeO_2$ at high T, The $SrFeO_{2.5}$ peaks are indicated with *; (b) and (c) evolution of the lattice parameters of $SrFeO_2$ (open) and $CaFeO_2$ (solid).

However, we could not obtain a sufficient fit to the data for $x = 1$ ($R_{wp} = 6.20\%$ and $\chi^2 = 18.38$). In addition, a deviation from the linear dependence (the Vegard's law) is seen for the c-axis (Figure 2b), though the linear dependence for the a-axis is kept up to $x = 1$. These results suggest the existence of some structural defects such us corrugation of the layers and/or stacking faults in $CaFeO_2$. The destabilization of the IL structure with increasing x is rationalized by calculating valences of A and Fe, both of which deviate more from +2 (see for Supporting Information). However, we would like to emphasize more strongly that its solubility range is considerably wide, in fact much wider than that of the IL cuprates $Sr_{1-x}Ca_xCuO_2$ ($0.13 < x < 0.17$) at ambient pressure.[8] It is noteworthy that the application of high pressure widens the solubility range of the cuprates from $x = 0$ to $x \approx 1$.[9]

Shown in Figure 3a and Figure 6S are evolutions of the in situ synchrotron XRD profiles of $SrFeO_2$ and $CaFeO_2$, where the sample was sealed in a silica capillary tube with an inner diameter of 0.3 mm. Each scan was performed for 5 min after a time of interval of 2 min between scans. The brownmillerite phase appeared and grew upon heating due to the oxidation of the IL phase. It means that the oxygen uptake occurs through O_2 gas left in a tiny inner space of capillary and even through the capillary itself. Nevertheless, what is remarkable here is the observation that the IL phase persists at least up to the highest temperature measured in this study, 960 K for $SrFeO_2$ and 630 K for $CaFeO_2$. These temperatures are much higher than the temperature at which the reducing reaction with CaH_2 was conducted. Furthermore, the Debye temperatures Θ_D calculated from the Debye−Grüneisen model are 395 K for $SrFeO_2$ and 733 K for $CaFeO_2$, which are comparable with those for stable phases, e.g., 525.5 K ($SrRuO_3$), 542 K ($CaRuO_3$), 612 K ($SrVO_{2.5}$) and 337 K ($TbFeO_3$),[10] indicating that the IL structure, *once it is formed*, could be as structurally rigid as thermodynamically stable phases. The lower thermal stability of $CaFeO_2$ with respect to $SrFeO_2$ would be linked to the low rate of reduction and the presence of defects in $CaFeO_2$. The higher Θ_D for $CaFeO_2$ in turn would be due to the shorter c-axis, leading to reinforced interlayer coupling. In fact, the c-axis variation for $SrFeO_2$ as a function of T is approximately twice that for $CaFeO_2$ (Figure 3b and 3c).

In conclusion, we have demonstrated that the IL iron oxide is amazingly robust against substitution as well as temperature. These stabilities should be attributed to the extremely strong hybridization between Fe $d_{x^2-y^2}$ and O p, as evidenced by the surprisingly low isomer shift in the ^{57}Fe Mössbauer spectroscopy of $SrFeO_2$ and $CaFeO_2$ (see Supporting Information and ref 4). We strongly believe that this is a genuine and universal feature for structures with a square-planar coordinated iron. Thus, using the hydride reduction to other iron oxides, we will be able to access new materials with square-planar coordinated irons that have potential future applications working even at high temperatures.

Acknowledgment. We acknowledge T. Saito, M. Azuma, and K. Kato for help in the synchrotron radiation experiments at Spring-8 and M. Isobe and Y. Ueda for the XRD experiments at ISSP. The authors express their thanks to the MEXT, Japan, for Grants-in-Aid Nos. 19052004, 17684018, 17105002, and 16076210 and to the GCOE program, Kyoto University.

Supporting Information Available: Experimental details and characterization data for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA800415D