

## Rational Design of Iron Oxides with Square Planar Coordination

The coordination number in ionically bonded structures is governed by the relative size of oppositely charged ions, which, to a first approximation, may be regarded as charged rigid spheres. Each ion tries to surround itself symmetrically with the largest possible number of oppositely charged neighbors. Unusual coordination beyond the constraint of the ionic model may occur in association with highly directional covalent bonding, as realized, for example, in many silicates and sulfides. A successful approach for exploring unusual coordinations in molecular compounds is the use of organic ligands with specific sterical constraints. This cannot be applied, however, to nonmolecular inorganic solids.

Iron, one of the most abundant elements in the earth, forms an uncountable number of oxides, some of which have been widely used in industry as low-cost ferrite magnets and pigments. In almost all of them, the iron ions are tetrahedrally or octahedrally coordinated. However, we recently succeeded in a low-temperature synthesis of  $\text{SrFeO}_2$ , a new compound bearing an unprecedented square-planar

oxygen coordination around  $\text{Fe}^{2+}$  (Fig. 1(b)) [1].  $\text{SrFeO}_2$  is isostructural with “infinite layer” cupric superconducting oxides, and exhibits a magnetic order far above room temperature in spite of the two-dimensional structure.

The target compound was obtained by the reductive reaction using  $\text{CaH}_2$  as a reducing agent of a well-known perovskite  $\text{SrFeO}_3$  (Fig. 1(a)). The synchrotron powder X-ray diffraction (XRD) experiment was carried out with a large Debye-Scherrer camera installed at beamline **BL02B2**, using an imaging plate as a detector. The synchrotron XRD patterns of the sample were indexed assuming the tetragonal unit cell with  $a=3.99107(3)$  Å and  $c=3.47481(5)$  Å. The Rietveld refinement from the synchrotron data assuming the space group of  $P4/mmm$  converged to  $R_{\text{wp}} = 6.04\%$  and  $\chi^2 = 4.41$  (see Fig. 2).

$\text{SrFeO}_2$  transforms back up to  $\text{SrFeO}_{3-y}$  upon heating in 0.1 MPa oxygen atmosphere. The oxygen uptake proceeds via the brownmillerite-type intermediate  $\text{SrFeO}_{2.5}$ , which is already formed below 390 K, increasing the potential for its application in low-cost catalysis, oxygen ion conduction or oxygen

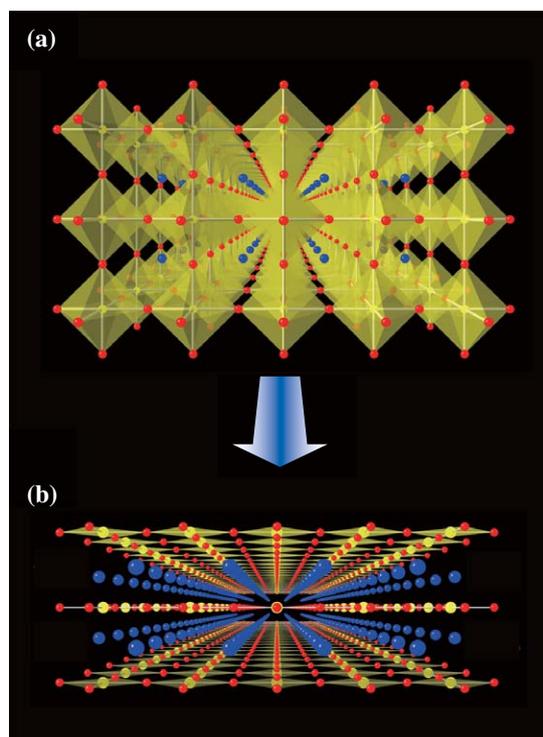


Fig. 1. Structural transformation from (a) cubic perovskite  $\text{SrFeO}_3$  to (b) infinite-layer  $\text{SrFeO}_2$  via topotactic route. Iron, strontium and oxygen atoms are represented as blue, green and yellow spheres, respectively.

gas absorption at reduced working temperatures.

Subsequently, we reported the synthesis of the complete solid solution of  $\text{Sr}_{1-x}\text{Ca}_x\text{FeO}_2$ , together with its thermal stability measured by *in situ* XRD [2]. The robust nature of the square-planar coordination against both chemical substitution and temperature allows extensive tuning of the physical properties to meet industrial demands. Furthermore, we showed the synthesis of a spin-ladder  $\text{Sr}_3\text{Fe}_2\text{O}_5$  through reactions of the double-layered perovskite  $\text{Sr}_3\text{Fe}_2\text{O}_7$  with  $\text{CaH}_2$  (see Fig. 3) [3]. Together with  $\text{SrFeO}_2$ , this finding establishes new avenues for the solid-state chemistry of ferrous oxides with the square-planar coordination potentially including a serial ladder system  $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{2n+1}$  ( $n$ =integer), and for the solid-state physics of multiple-spin ladders.  $\text{Sr}_3\text{Fe}_2\text{O}_5$  exhibits an antiferromagnetic order owing to interladder coupling, but at a significantly reduced temperature compared with  $\text{SrFeO}_2$ , reflecting dimensional reduction.

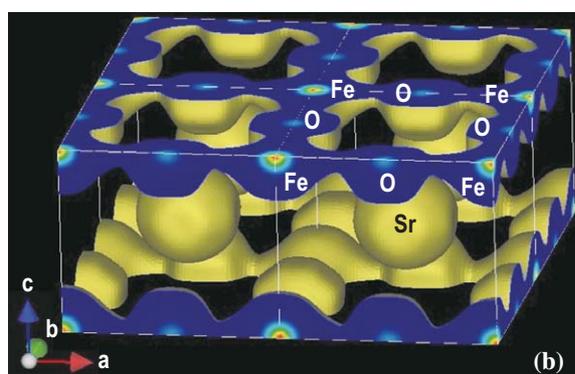
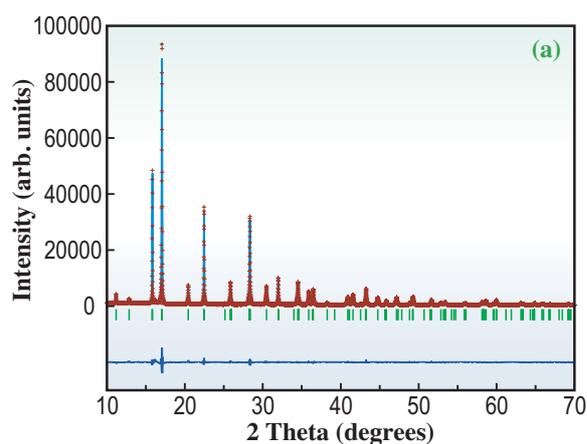


Fig. 2. (a) Structural characterization of  $\text{SrFeO}_2$  by Rietveld refinement of high- $q$ -resolution synchrotron X-ray diffraction at room temperature measured at BL02B2. The wavelength was 0.77747 Å. The solid lines and the overlying crosses and bars indicate the calculated intensities, the observed intensities and the positions of calculated Bragg reflections. The difference between the observed and calculated profiles is plotted at the bottom. (b) The electron density in  $\text{SrFeO}_2$  obtained by the maximum entropy method (MEM).

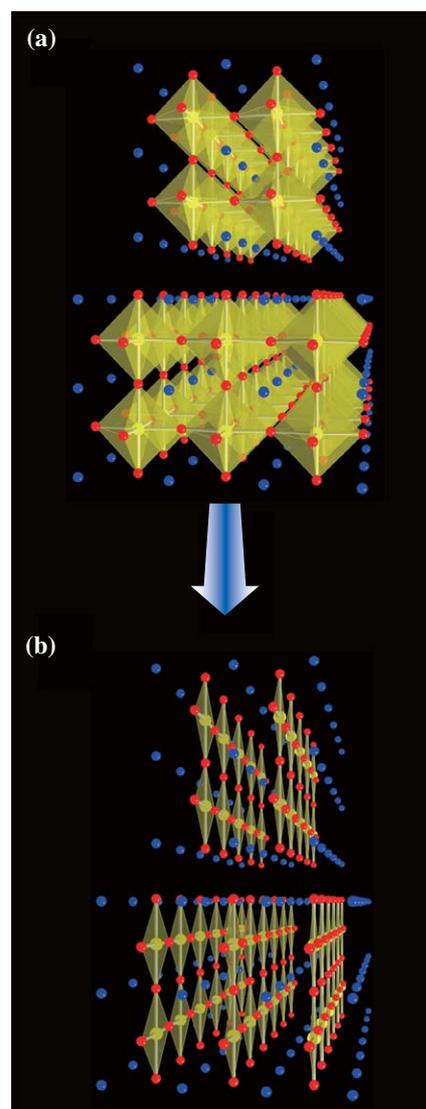


Fig. 3. Structural transformation from (a) cubic perovskite  $\text{Sr}_3\text{Fe}_2\text{O}_7$  to (b) infinite-layer  $\text{Sr}_3\text{Fe}_2\text{O}_5$ . Iron, strontium and oxygen atoms are represented as blue, green and yellow spheres, respectively.

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## References

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