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Proposal number: [2010A1593]

Beamline used: BL02B2

Research Summary:

Low and High Temperature Structural Investigation of $\text{YBa}_2\text{Fe}_3\text{O}_7$

Introduction

Perovskites $A\text{FeO}_{3-z}$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) were long believed to be reducible until $z = 0.5$. Using a low temperature synthesis we have been able to overcome this limit and reach iron square planar coordination in SrFeO_2 which is isostructural to the infinite layer structure of the undoped high-Tc superconductor SrCuO_2 [1]. Oxygen square planar coordination around iron is rare because iron atoms are normally three-dimensionally coordinated: FeO_6 octahedra, FeO_5 pyramids, and FeO_4 tetrahedra. In order to develop this coordination we synthesized the solid solution $(\text{Sr}_{1-x}\text{Ca}_x)\text{FeO}_2$ ($0 \leq x \leq 1$) [2]. As a result, a phase transition to a new CaFeO_2 structure type is observable around $x = 0.8$ exhibiting tetrahedrally distorted FeO_4 square planes that rotate along the c-axis, resulting in a $\sqrt{2}a \times \sqrt{2}a \times c$ superstructure. A similar study performed by substituting strontium by barium shows a phase transition around 30 % Ba-substitution, leading to a new BaFeO_2 -type structure containing three types of iron sites with different coordination geometries: FeO_4 square planes, FeO_3 plane (i.e. rhombus and triangular coordination), and FeO_6 octahedron with substantial oxygen deficiency.[3] These polyhedra are arranged in an ordered manner, resulting in a $2a \times 2a \times c$ superstructure. The three new phases SrFeO_2 , CaFeO_2 and BaFeO_2 demonstrate how the coordination of iron can be flexible and that oxide reducibility limits can be further expanded therefore providing new chemical and physical properties. For instance, SrFeO_2 exhibits a pressure induced intermediate spin transition from $S = 2$ to $S = 1$ accompanied by an antiferromagnetic insulator to ferromagnetic half-metal transition [4].

We have recently focused our attention on the substitution of the A site by trivalent cation in order to create mixed valence materials and possibly obtain new physical properties: charge ordering (CO), metal insulator transitions, etc... Our study started with $\text{YBa}_2\text{Fe}_3\text{O}_8$ which has an A-site ordered structure along the c axis with corner sharing octahedral sandwiched between FeO5 pyramids Using CaH_2 as a powerful reductant, we successfully synthesized $\text{YBa}_2\text{Fe}_3\text{O}_7$ (Fig. 1) which may, from laboratory-XRD study, be the only copper-free isostructural phase with $\text{YBa}_2\text{Cu}_3\text{O}_7$. The original tetragonal structure distorts into an orthorhombic one, changing the lattice parameters from $a = 3.91729 \text{ \AA}$, $c = 11.8274 \text{ \AA}$ to $a = 3.96915 \text{ \AA}$, $b = 3.88431 \text{ \AA}$ and $c = 11.7348 \text{ \AA}$ (Fig. 1). Mossbauer spectroscopy indicates that this material is magnetically ordered at room temperature with three equally present iron sites, one of which is seemingly ascribed with Fe^{2+} in high spin state ($S = 2$) with a square planar coordination.

Electronic, magnetic, and structural phase transitions in mixed-valence transition-metal oxides have for a long time been a source of interest to chemists and physicists. One of the most interesting example from the literature is the Verwey transition ($T_v = 124 \text{ K}$) in Fe_3O_4 . The low temperature charge ordered phase remains unknown therefore preventing a complete understanding of this phenomenon. The low and high temperature study of our new material could be of great interest in reason of its structural features as well as electronic features which could add clues on CO transitions and the impact of the square planar coordination over such phenomena.

Experimental

$\text{YBa}_2\text{Fe}_3\text{O}_7$ powders were inserted in a 0.1 mm diameter capillary and installed in the BL02B2 diffractometer. The capillary was cooled down using N_2 gas and the sample was exposed to the beam for 20 minutes from 100 K to 300 K with 20 degree steps.

The crystal structure and cell parameters were refined using both synchrotron X-ray diffraction data at room temperature. The Rietveld method, implemented in the computer program RIETAN-2000, was used. The peak shape model used was a modified split-pseudo-Voigt function. The agreement indices are R -weighted pattern, $R_{\text{wp}} = [\sum w_i (y_{\text{io}} - y_{\text{ic}})^2 / \sum w_i (y_{\text{io}})^2]^{1/2}$, R -pattern, $R_p = \sum |y_{\text{io}} - y_{\text{ic}}| / \sum (y_{\text{io}})$, R -Bragg factor, $R_1 = \sum |I_o(h_k) - I(h_k)| / \sum I_o(h_k)$ and goodness of fit (GOF), $\chi^2 = [R_{\text{wp}} / R_{\text{exp}}]^2$, where $R_{\text{exp}} = [(N - P) / \sum w_i y_{\text{io}}^2]^{1/2}$, y_{io} and y_{ic} are the observed and calculated intensities, w_i is the weighting factor, $I_o(h_k)$ and $I(h_k)$ are the observed and calculated integrated intensities, N is the total number of y_{io} data when the background is refined,

and P is the number of adjusted parameters.

Results

The Rietveld refinement was performed using two phases: reduced (85%) and precursor compounds (15%). The agreement values are acceptable with $R_{wp} \approx 5.2\%$. Confirming that the structure is similar with $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Table 1).

The evolution of the lattice parameters do not reveal phase transition against temperature (Fig. 2). However, it is clearly observable on figure 2 that the a axis is stable or slightly decreasing against temperature while the b and c axis expand.

The structure of this material can be compared to the bivalent YBaFe_2O_5 which has similar pyramids. In this material, iron is in both divalent and trivalent state and a Verwey transition can be observed at low temperatures. A possible reason to the absence of phase transition in our compound lies in the presence of square planes which could block this phenomenon. $\text{YBa}_2\text{Fe}_3\text{O}_7$ is supposed to be isostructural with $\text{YBa}_2\text{Cu}_3\text{O}_7$. However the lattice parameters of the superconductor exhibit positive thermal expansion. The decrease of the a axis against temperature indicates that our compound might show distortions against temperature.

Conclusion

Using synchrotron x-ray diffraction we have shown that despite of the structural similarities of our new material with known compounds $\text{YBa}_2\text{Fe}_3\text{O}_7$ exhibit an original behavior. Further analysis using Rietveld refinement and Mossbauer spectroscopy have to be performed to completely understand this phenomenon.

References

- [1] Tsujimoto, Y. et al., Nature 450, 1062 (2007).
- [2] Tassel, C. et al. J. Am. Chem. Soc. 2008, 130 (12), 3764-3765 ; Tassel, C. et al. J. Am. Chem. Soc., 2009, 131 (1), 221–229.
- [3] Yamamoto, T. et al., in preparation.
- [4] Kawakami, T. et al., Nature Chemistry 1, 371-376 (2009)

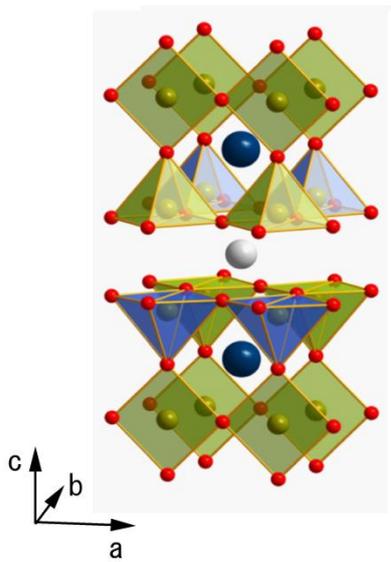


Figure 1. Structure of $\text{YBa}_2\text{Fe}_3\text{O}_7$

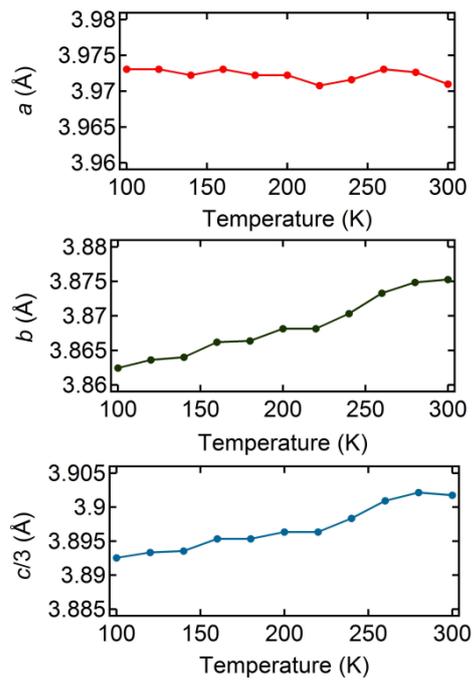


Figure 2. In-situ SXRD of $\text{Sr}_{0.2}\text{Ba}_{0.8}\text{FeO}_3$ with CaH_2 at 350°C .

Atom	site	<i>sof</i>	<i>x</i>	<i>Y</i>	<i>z</i>	$100B_{\text{iso}}$ (\AA^2)
Y	<i>1h</i>	1	0.5	0.5	0.5	0.71(7)
Ba	<i>2t</i>	1	0.5	0.5	0.1719(6)	0.35(8)
Fe	<i>1a</i>	1	0	0	0	0.543718
Fe	<i>2q</i>	1	0	0	0.3463(9)	0.543718
O	<i>1b</i>	1	0.5	0	0	1
O	<i>2q</i>	1	0	0	0.1799(5)	1
O	<i>2s</i>	1	0.5	0	0.3944(6)	1
O	<i>2r</i>	1	0	0.5	0.6094(3)	1

Pmmm, $a = 3.9747151(8) \text{ \AA}$, $b = 3.8711(8) \text{ \AA}$, $c = 11.7266(1) \text{ \AA}$, $R_{\text{wp}} = 5.19 \%$,
 $R_{\text{p}} = 3.39 \%$, and $\chi^2 = 5.61$.

Table 1. Rietveld refinements parameters of $\text{YBa}_2\text{Fe}_3\text{O}_7$.