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SCIENCE DIRECT

Journal of Solid State Chemistry 179 (2006) 111–116

JOURNAL OF SOLID STATE CHEMISTRY

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Electron-doping through La^{III}-for-Sr^{II} substitution in $(Sr_{1-x}La_x)_2FeTaO_6$: Effects on the valences and ordering of the *B*-site cations, Fe and Ta

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Received 18 August 2005; received in revised form 4 October 2005; accepted 5 October 2005
Available online 11 November 2005

Abstract

We have employed aliovalent *A*-site cation substitution, La^{III}-for-Sr^{II}, to dope the $Sr(Fe_{0.5}Ta_{0.5})O_3$ perovskite oxide with electrons. Essentially single-phase samples of $(Sr_{1-x}La_x)(Fe_{0.5}Ta_{0.5})O_3$ were successfully synthesized up to $x \approx 0.3$ in a vacuum furnace at 1400 °C. The samples were found to crystallize (rather than with orthorhombic symmetry) in monoclinic space group $P2_1/n$ that accounts for the partial ordering of the *B*-site cations, Fe and Ta. With increasing La-substitution level, x, the degree of Fe/Ta order was found to increase such that the La-richest compositions are best described by the *B*-site ordered double-perovskite formula, $(Sr,La)_2FeTaO_6$. From Fe L_3 and Ta L_3 XANES spectra it was revealed that upon electron doping the two *B*-site cations, Fe^{III} and Ta^{V}, are both prone to reduction. Magnetic susceptibility measurements showed spin-glass type behaviour for all the samples with a transition temperature slightly increasing with increasing x.

Keywords: Double perovskite; Cation ordering; Valence states; XANES spectroscopy

1. Introduction

The *B*-site ordered double-perovskite (DP) structure of the compounds, $A_2B'B''O_6$, is derived from that of the single-perovskite (SP) compounds, ABO_3, upon co-occupation of the octahedral cation site with two different metal species, B' and B'', in an ordered manner, such that each $B'O_6$ octahedron is surrounded by six corner-sharing $B''O_6$ octahedra, and vice versa. The ideal face-centred cubic unit cell of a *B*-site ordered DP is $2 \times 2 \times 2 = 8$ times larger than the primitive cubic cell of the SP that corresponds to the disordered case. The DP compound family has been intensively revisited since the discovery of room-temperature half-metallicity and tunnelling-type magnetoresistance effect in Sr_2FeMoO_6 [1], Sr_2FeReO_6 [2] and many other ferri/ferromagnetic $A_2Fe(Mo,Re)O_6$ ($A =$ Ca, Sr, Ba) compounds. As a common crystal-chemical feature, these compounds have been found to possess not only (i) high degree of order, but also (ii) valence mixing between the *B*-site cations, Fe and Mo/Re [3–9].

The high degree of order in $A_2B'B''O_6$ is achieved only if the charge difference between the *B* cations is large enough [10]. Accordingly only the $A_2B'^{I}B''^{VII}O_6$ and $A_2B'^{II}B''^{VI}O_6$-type compounds are usually perfectly ordered, whereas among the $A_2B'^{III}B''^{V}O_6$ compounds various levels of ordering are observed. For the latter case, the degree of order is known to strongly depend on the synthesis conditions [10,11], but it also depends on the particular A, B' and B'' cations. Empirically for many of the known systems the degree of order of the *B* cations increases when the size of the *A* cation decreases [10].

The valence mixing between the B' and B'' cations depends also on multiple factors. In the prototype DP

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0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.10.004

half-metal, Sr_2FeMoO_6, the itinerant *d* electron of formally pentavalent Mo ($4d^1$) transfers part of its charge and spin to formally trivalent Fe ($3d^5$), and as a consequence the mixed-valence states, $Fe^{II/III}$ and $Mo^{V/VI}$, are realized. The precise charge balance between Fe and Mo is then controlled by, e.g. the choice (= average size) of the *A*-site cation constituent [9,12–14]. In partially disordered samples the valence mixing is hindered: the misplaced Fe (and Mo) atoms with Fe (Mo) rather than Mo (Fe) atoms as nearest-neighbour *B* cations possess integer rather than mixed valence value, as probably most directly revealed from ^{57}Fe Mossbauer spectra for such samples [3,5,9,15]. Hence it seems that the degree of order and the valence mixing (and thereby even the metallicity/half-metallicity) are strongly linked characteristics for the $A_2Fe(Mo,Re)O_6$-type compounds.

The aim of the present work was to find new potential candidates for half-metallic DP oxides. The SP oxide, $Sr(Fe_{0.5}Ta_{0.5})O_3$ with trivalent Fe ($3d^5$) and pentavalent Ta ($5d^0$) [7,8], was selected for the target system. The strategy was set so as to dope the system through aliovalent La^{III}-for-Sr^{II} substitution with additional electrons, which then might be shared by the two *B*-site cations, Fe and Ta, to facilitate mixed-valence states for both of them. X-ray absorption near-edge structure (XANES) spectroscopy and X-ray diffraction (XRD) techniques were utilized for sample characterization in terms of the valence states and ordering of Fe and Ta, respectively. Magnetic properties were evaluated on the basis of SQUID (superconducting quantum interference device) measurements.

2. Experimental

A series of samples of the $(Sr_{1-x}La_x)_2FeTaO_6$ system was synthesized by means of solid-state reaction from stoichiometric mixtures of high-purity (99.9%) powders of $SrCO_3$, La_2O_3, Fe_2O_3 and Ta_2O_5. The La_2O_3 powder was fired in air at 1000 °C for 24 h and checked for phase purity before accurate weighing. The powder mixture was calcined in air at 1000 °C for 24 h. The calcined powder was pelletized and sintered in a high-temperature vacuum furnace in alumina crucibles at 1400 °C for 20–30 h. The time required for successful synthesis was found to increase with increasing La substitution level, *x*. The phase purity of the samples was confirmed by X-ray powder diffraction (Rigaku RINT-2500 V equipped with a rotating anode; Cu K_α radiation). The lattice parameters and the fractional occupancies of Fe and Ta at the two *B*-cation sites (of the DP structure) were determined from the XRD data by means of Rietveld refinement using the refinement software, RIETAN 2000 [16]. The data for the refinements were collected using a large-window sample holder (200 mm × 170 mm) in the range of $15^\circ \leqslant 2\theta \leqslant 120^\circ$ with a measurement step of 0.02° and counting for 1 s at each step.

Oxygen content was determined cerimetrically for two representative samples, $x = 0.0$ and 0.2. A precisely weighed specimen of 15–20 mg of sample powder was dissolved in 120 ml of 9 M HCl solution in a beaker under Ar flow aided by stirring and heating. After the sample was completely dissolved, the solution was rapidly cooled back to room temperature and the titration of the possibly existing reduced species of Fe^{2+} and/or Ta^{4+} was performed (after adding 15 ml of concentrated phosphoric acid to act as a complexant for Fe^{3+}) with 0.008 M $Ce(SO_4)_2$ solution (standardized against Mohr's salt) using ferroin as an indicator. Blank experiments were found essentially important to be able to take into account the unfavorable but unavoidable redox reaction between Cl^- and Fe^{3+} in concentrated HCl solutions; these experiments were carried out using Fe_2O_3 as a source of Fe^{3+} and following exactly the same sample solution and titration procedure as used in the actual titration experiments. Each titration experiment was repeated three times in minimum with a good reproducibility (better than ± 0.005 for the final oxygen content).

Changes in the valence states of the two *B* cations, Fe and Ta, upon electron doping were probed by Fe L_3- and Ta L_3-edge XANES spectroscopy experiments carried out at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan, with an electron beam energy of 1.5 GeV and a maximum stored current of 240 mA [8,13]. All the measurements were performed at room temperature. The Ta L_3-edge XANES spectra were recorded in transmission mode using gas-filled ionization chambers at the multipole Wiggler beamline BL17C. The ion chambers used for measuring the incident (I_0) and the transmitted beam intensities were filled with a mixture of N_2 and H_2 gases and a mixture of N_2 and Ar gases, respectively. The sample was ground to pass through a 400-mesh sieve to fulfill the requirement that the size of the particles is smaller than the absorption length in the material, i.e. $\mu d < 1$, where *d* is the particle size and μ is the total absorption coefficient. The resultant fine powder was rubbed homogeneously onto Scotch tape. Then the thickness of the sample was carefully adjusted by folding the Scotch tape several times to achieve $\Delta\mu x \approx 1$, where $\Delta\mu x$ is the edge step. The Fe L_3-edge spectra were recorded by measuring the sample drain current in an ultrahigh vacuum chamber (10^{-9} Torr) at the 6-m high-energy spherical grating monochromator (HSGM) beamline BL20A. The incident photon flux (I_0) was monitored simultaneously by using a Ni mesh located after the exit slit of the monochromatic beam. All the absorption measurements were normalized to I_0.

Magnetization measurements were performed both in zero-field-cooled (ZFC) and field-cooled (FC) modes (10 Oe; 5–400 K) using a SQUID magnetometer (Quantum Design MPMSR-5S).

3. Results and discussion

The $(Sr_{1-x}La_x)_2FeTaO_6$ samples were found to be of single phase up to the La-substitution level of $x = 0.3$. For