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Nano-domain states of strontium ferrites $SrFe_{1-y}M_yO_{2.5+x}$ (M=V, Mo; $y \leq 0.1$; $x \leq 0.2$)

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ABSTRACT

Series of the oxygen-deficient strontium ferrites $SrFe_{1-y}M_yO_{2.5+x}$ (M=V, Mo, $y<0.1$; $x<0.2$) substituted with high-charged cations have been investigated by HRTEM and synchrotron radiation XRD. For artificial lowering of x, all the compounds were treated and quenched in vacuum from 950 °C, which led to the formation of the vacancy-ordered brownmillerite phase at local order. Depending on y, the substituted strontium ferrites have three differently disordered nano-domain states. At $y \leq 0.03$ there are twinned lamellar 1D nano-domain structures. At $0.04 \leq y \leq 0.05$ and $0.06 \leq y \leq 0.08$ the intergrown 3D nano-domain structures with two different types of disorder are formed. The higher the y, the lower the domain size. Disordering phenomena of the 3D nano-domain states were examined with local structure simulations followed by the Debye calculation of XRD patterns.

1. Introduction

Under normal ambient conditions, the air-synthesized strontium ferrites $SrFeO_{3-\delta}$ with a perovskite structure are non-stoichiometric with oxygen-deficiency $\delta \sim 0.15$. These compounds exhibit a significant mixed oxygen-ion and electron conductivity at moderately high temperatures, 600–900 °C [1]. Therefore, strontium ferrite is a promising parent compound for the development of mixed conducting materials [2]. However, under the reduced oxygen partial pressure when the temperature is below ~870 °C, the compound transforms, due to a high concentration of defects $\delta \rightarrow 0.5$, to the vacancy-ordered brownmillerite phase [3] with a significantly lower oxygen mobility [4]. Another difficulty in the development of membrane materials on pure or cobalt-doped strontium ferrites is related to an abrupt change in the lattice volume during the phase transition [3,5] that leads to destruction of the material upon heating under the working condition of the membrane reactor [6].

Doping of $SrFe_{1-y}M_yO_{2.5+x}$ with high-charged cations leads to the formation of the system outside the homogeneity region of brownmillerite structure and gives rise to a nano-domain structure [7,8]. The "order–disorder" phase transitions in case of nanostructured oxides do not lead to destruction of the materials. At the same time, despite the presence of high-charged cations, which are obstacles to the motion of vacancies, doping has a weak inhibitory effect on oxygen diffusion [9–11], and in cases of relatively low substitution degree, for example $M=Mo^{6+}$ and $y=0.05$, even improves the diffusion [9].

Many of other non-stoichiometric perovskite-like oxides $ABO_{3-\delta}$ have nano-domain structure for the values of oxygen stoichiometry $3-\delta$ close to the vacancy-ordered brownmillerite phase's $ABO_{2.5}$ [8,12–17]. Nano-domain structures appear as a result of phase separation into the vacancy-ordered phases and are the three-dimensional intergrowth structures of nano-sized brownmillerite domains (perpendicularly oriented to each other) in a matrix of host perovskite lattice. However, due to coherent jointing of differently rotated by 90° orthorhombic domains and regularity of cation sublattice in the system, the nano-domain structure appears in the X-ray diffraction patterns as narrow intense peaks of high-symmetric perovskite structure with weak broadened superstructural reflections [8].

Computer simulation of defective structures and their X-ray diffraction patterns [18] showed that, depending on the arrangement of the nano-domains and on the extended structural defects, the resulting diffraction effects have different features [8]. As a result of simulations, a systematic analysis of the influence of different types of disorder in strongly non-stoichiometric oxides on the diffraction patterns was performed [8].

This work is devoted to the structural investigation of the series of nano-structured oxides based on strontium ferrites $SrFe_{1-y}M_yO_{3-\delta}$ (M=V, Mo; $0<y<0.1$) with a high degree of oxygen non-stoichiometry ($2.5<3-\delta<2.7$).

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2. Experimental

The samples of $SrFe_{1-y}M_yO_{2.5+x}$, where $M=V^{5+}$, Mo^{6+}; $y=0–0.08$, $x=0–0.2$, were prepared using the solid state reactions as described in [8]. For artificial lowering of x, all the compounds were treated for several hours and quenched in a ~10 mbar vacuum from 950 °C to the room temperature. The oxygen content in the samples was measured by means of iodometric titration [19] and Mössbauer spectroscopy (from the ratio of octa- and tetra-iron positions).

The XRD experiments were performed at synchrotron radiation (SR) of the VEPP-3 storage ring, Siberian Synchrotron and Terahertz Radiation Center (the Budker Institute of Nuclear Physics, Novosibirsk, Russia) on the 2nd and 4th beamlines [20].

The full-profile Rietveld analysis of XRD patterns was carried out with the use of TOPAS software. Monte Carlo simulation of the particles having a nano-domain structure and Debye calculation of the diffracted intensities on the generated particles were made with the use of DISCUS program package [18].

HRTEM images were obtained on a JEM-400EX (Jeol) microscope at the Rzhanov Institute of Semiconductor Physics, Novosibirsk, Russia.

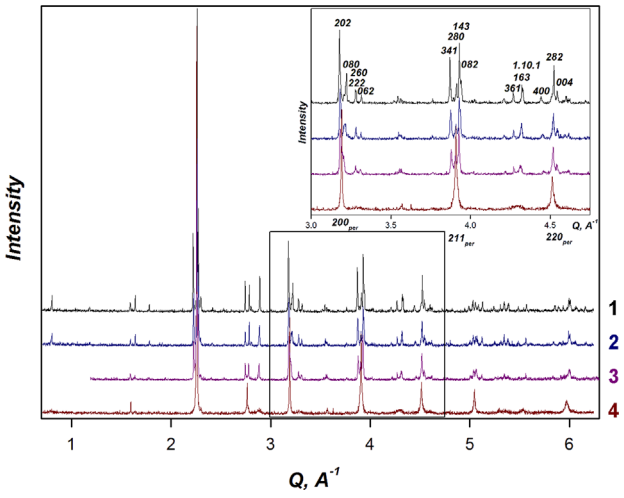

Fig. 2. High-angular resolution X-Ray diffraction patterns of nanostructured $SrFe_{1-y}V_yO_{2.5+x}$, $\lambda \sim 1.54$ Å: (1) $SrFe_{0.99}V_{0.01}O_{2.5+x}$; (2) $SrFe_{0.98}V_{0.02}O_{2.5+x}$; (3) $SrFe_{0.97}V_{0.03}O_{2.5+x}$; and (4) $SrFe_{0.96}V_{0.04}O_{2.5+x}$; $x \approx 0.04–0.2$.

3. Results and discussion

According to the synchrotron radiation diffraction data, strontium ferrites substituted with high-charged cations $SrFe_{1-y}V_yO_{3-\delta}$ and $SrFe_{1-y}Mo_yO_{3-\delta}$ slowly cooled at normal pressure pO_2 (in air) keep the cubic perovskite structure with the oxygen stoichiometry $3-\delta=2.8–2.9$. At artificial lowering of the oxygen stoichiometry by keeping and quenching in vacuum, the X-ray diffraction patterns show that the cubic structure is not preserved in $SrFe^{3+}_{1-y}V^{5+}_yO_{2.5+x}$ (Figs. 1 and 2) and $SrFe^{3+}_{1-y}Mo^{6+}_yO_{2.5+x}$ (Fig. 3), here their oxygen stoichiometry is $3-\delta=2.5+x=2.5–2.7$. Up to a substitution degree of $y=0.03$, a deformated brownmillerite structure is formed. One can see (Fig. 2) that an increase in y from 0 to 0.03 decreases the degree of orthorhombic splitting and increases broadening of the Bragg maxima (that appear due to microstrains). At a further increase in the substitution degree, the orthorhombic splitting completely disappears and intensive narrow perovskite peaks appear accompanied by additional weak broadened reflections. Superstructure reflections are more intensive at a lower substitution degree y and can be indexed in a doubled cubic perovskite cell $a_{per} \times 2a_{per} \times a_{per}$.

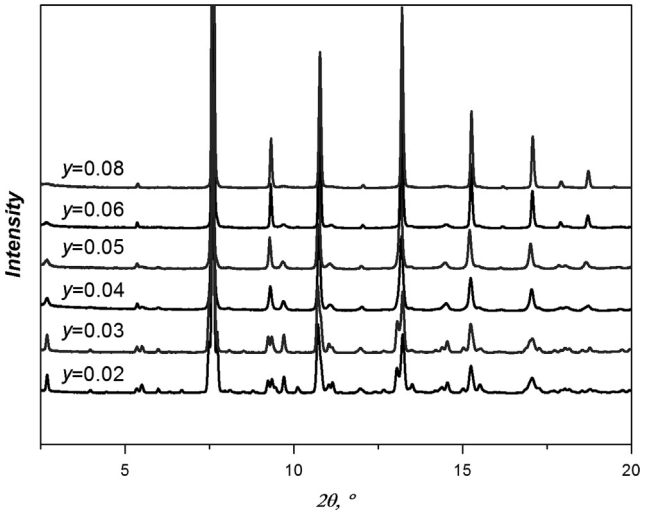

Fig. 3. X-Ray diffraction patterns of nanostructured $SrFe_{1-y}Mo_yO_{2.5+x}$, $\lambda=0.3685$ Å.

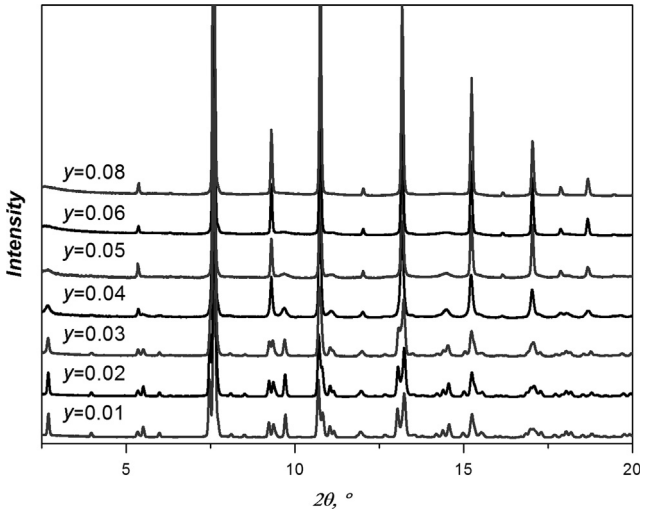

Fig. 1. X-Ray diffraction patterns of nanostructured $SrFe_{1-y}V_yO_{2.5+x}$, $\lambda=0.3685$ Å.

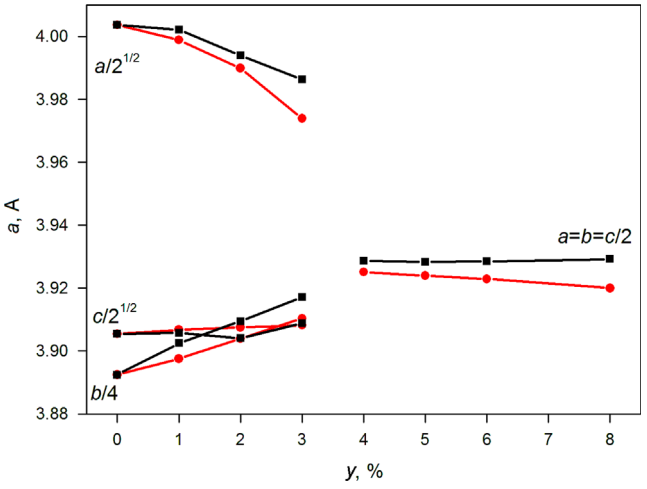

Fig. 4. The dependence of reduced lattice constants on y in $SrFe_{1-y}M_yO_{2.5+x}$ according to full-profile Rietveld analysis, where M=V (■) and M=Mo (●).