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Oxygen nonstoichiometry and high-temperature transport in $SrFe_{1-x}W_xO_{3-\delta}$

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Abstract

The complex oxides in the series $SrFe_{1-x}W_xO_{3-\delta}$ were synthesized and attested to have cubic structure. The oxygen content was measured by coulometric titration technique, and electrical conductivity was measured by four-probe d.c. method in the oxygen partial pressure range 10^{-18}–0.5 atm and at temperatures 650–950 °C. Thermal expansion tests were performed in air within temperature interval 20–1000 °C. The partial molar thermodynamic functions of labile oxygen ions were calculated using coulometric titration data. Conductivity analysis was utilized to separate partial contributions from oxygen ions, n-and p-type electron charge carriers. The concentration and mobility of p-type charge carriers were calculated by combining data from oxygen content and conductivity measurements. It is shown that partial replacement of iron for tungsten results in a strong disordering of the oxygen sub-lattice that renders the perovskite to brownmillerite phase transition suppressed. The observed ion conductivity level in the sample $x=0.1$ at $T<850$ °C occurs somewhat higher than in the undoped ferrite while electron contribution remains nearly the same. The increase in the concentration of the dopant results in filling of oxygen vacancies and in respective decrease of the oxygen ion conductivity level. The thermal expansion coefficient is observed to monotonously decrease with the increase in tungsten content.

Keywords: Strontium ferrite; Perovskite; Brownmillerite; Oxygen nonstoichiometry; Vacancy disordering; Ion conductivity; Hole mobility

1. Introduction

Perovskite-like strontium ferrite $SrFeO_{3-\delta}$, where δ is about 0.15 at synthesis in air, exhibits significant oxygen-ion conductivity on the background of dominant electron conductivity [1,2]. However, heating in reducing conditions results in increase of oxygen deficiency, $\delta \rightarrow 0.5$, and at temperatures below 870 °C the oxygen depleted ferrite $SrFeO_{2.5}$ acquires brownmillerite type structure with ordering of oxygen vacancies [3,4]. The ordering is very undesirable because of the deleterious influence on transport properties. The tendency for the vacancies to order can be suppressed by doping the iron sublattice. This possibility has been successfully demonstrated in works [5–7] where substitutions were used of Ti, Al and Sc for Fe. It has been shown that moderate doping does not influence substantially the ion conductivity level in the doped derivatives. At the same time, the electron contribution exhibits rather strong a decline. Recently the data appeared on the synthesis and structure of the solid solutions $SrFe_{1-x}M_xO_{3-\delta}$, where M = Mo or W and $0.1 \le x \le 0.3$ [8]. The present work is aimed at studying transport properties and thermo-mechanical characteristics in the ferrite doped with tungsten.

2. Experimental

The samples of $SrFe_{1-x}W_xO_{3-\delta}$, where $x=0.1$ and 0.2 were prepared using solid state reactions. The X-ray powder diffraction was employed for phase purity verification and structural characterization. The electrical conductivity was measured by 4-probe d.c. technique. The rectangular ceramic sample was wired with Pt current leads and potential probes,

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Table 1
Perovskite unit cell parameters and activation energies for the n-type electron conductivity* (E_n), p-type electron conductivity** (E_p), hole mobility*** (E_μ), and ion conductivity (E_i) in perovskite-type $SrFe_{1-x}W_xO_{3-\delta}$

	x	
	0.1	0.2
a (Å) in as-prepared $SrFe_{1-x}W_xO_{3-\delta}$	3.890(1)	3.905(1)
a (Å) in reduced $SrFe_{1-x}W_xO_{2.5}$	3.922(1)	3.928(2)
E_i, eV	0.63	0.65/0.98
E_n, eV	2.3	2.1
E_p, eV	−0.34	−0.22
E_μ, eV	0.22	0.27
ΔH_{ox}, eV/kJ mol^{-1}	−1.1/−106	−1.0/−96
ΔH_{red}, eV/kJ mol^{-1}	4.1/395	3.7/357
E_g, eV	1.5	1.4

* The E_n values are given at $pO_2 = 10^{-16}$ atm.
** The E_p values are given at $pO_2 = 10^{-2}$ atm.
*** The E_μ values correspond to a fixed oxygen contents 2.73 and 2.85 oxygen atoms per unit formula for $x = 0.1$ and $x = 0.2$ respectively.

and mounted in the holder connected to a measuring circuit. The holder was covered with the electrochemical cell of yttria-stabilized zirconia (YSZ). Two pairs of Pt electrodes were deposited upon the cell, which served as an oxygen pump and a sensor, thus enabling one to independently change and measure the partial pressure of oxygen over the sample. Conductivity measurements were carried out in isothermal runs. The oxygen content variations at changes of oxygen partial pressure and temperature with respect to a reference point were measured by means of the coulometric titration technique of the powdered samples. The electrical parameters were measured using a high-precise voltmeter Solartron 7081. The oxygen pump current was supplied by a Yokogawa 7651 current source. The electrical measurements are described in detail elsewhere [9,10]. Thermal expansion was studied with the using of a Linseis L75V dilatometer.

3. Results and discussion

The as-prepared and reduced $SrFe_{1-x}W_xO_{3-\delta}$ samples are invariably found to have a cubic elementary cell. The cell parameters for different specimens are collected in Table 1. Following the charge neutrality requirement one can expect that replacement of iron for tungsten should result in disappearance of Fe^{4+} and in simultaneous increase in the concentration of Fe^{3+} cations. The average size of Fe^{4+} and W^{6+} is smaller that the size of Fe^{3+} cations. Hence, the lattice parameter in $SrFe_{1-x}W_xO_{3-\delta}$ must increase with tungsten content, and, indeed, it is seen from the obtained data. High-temperature treatment of samples in vacuum results in loss of oxygen that, in turn, also favors the concentration increase of Fe^{3+} cations and crystal lattice expansion.

The thermal expansion data collected in air are shown in Fig. 1. It is seen that incorporation of tungsten is accompanied with the substantial decrease in geometrical sizes of the doped samples at heating. It is important to notice that thermal expansion in isobaric conditions is related not only with the response to the temperature rise but also reflects oxygen depletion from the crystal lattice. The relevant expansion is sometimes called "chemical expansion". The combined, thermal and chemical expansion smaller in tungsten substituted samples than in the parent ferrite owing to lower deficiency of anion sublattice.

The disordering state of the anion sub-lattice makes rather direct impact upon transport properties. It is interesting, therefore, to analyze partial thermodynamic functions in the obtained solid

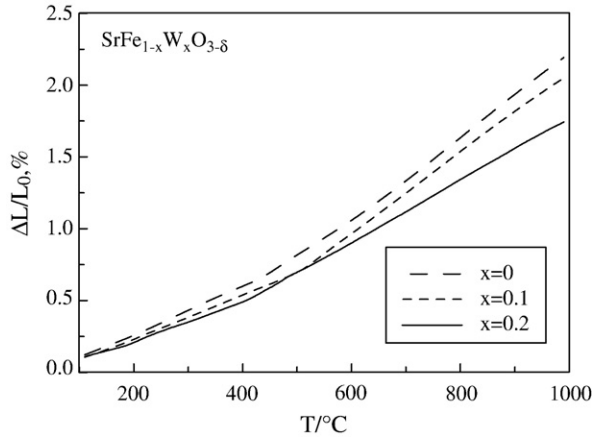

Fig. 1. Dilatometric curves for $SrFe_{1-x}W_xO_{3-\delta}$ ceramic samples in air.

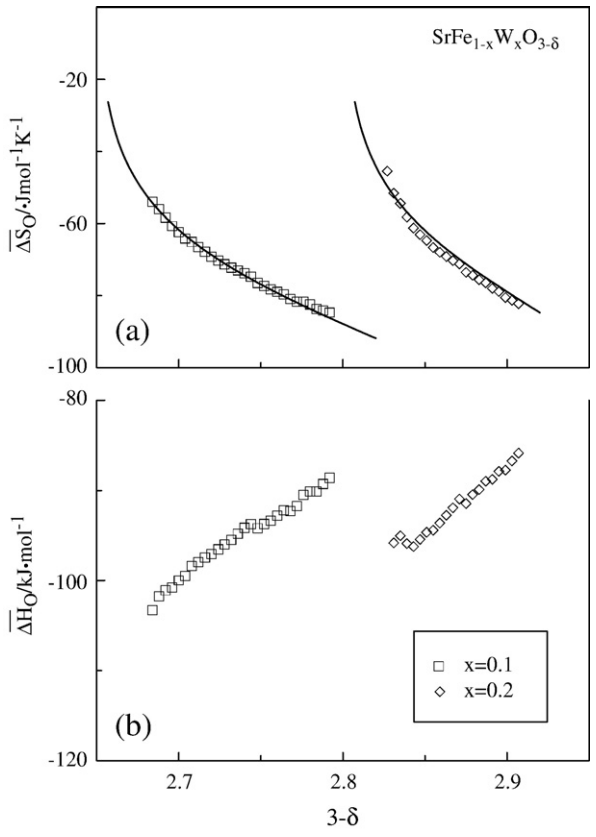

Fig. 2. Partial molar entropy (a) and enthalpy (b) of mobile oxygen in $SrFe_{1-x}W_xO_{3-\delta}$. Solid lines illustrate results of calculations according to (3).