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Interplay between chemical strain, defects and ordering in $Sr_{1-x}La_xFeO_3$ materials

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Different point defect interactions were found to govern the defect chemistry of $SrFeO_{3-\delta}$ and $La_{0.6}Sr_{0.4}FeO_{3-\delta}$. Conventional defect structure model based on two reactions – oxygen release by oxide lattice and the charge disproportionation in Fe-sublattice – can be applied successfully to $La_{0.6}Sr_{0.4}FeO_{3-\delta}$. Successful verification of this model using the available data on the oxygen nonstoichiometry gives virtually zero standard entropy and comparatively high standard enthalpy of iron disproportionation (116.54 ± 1.14 kJ/mol). In turn, the chemical strain of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ was predicted successfully using the simple dimensional model, based on the ionic radii formalism and verified defect structure model. For $SrFeO_{3-\delta}$, a reference set of nonstoichiometry data was chosen from among the multitudinous literature data by comparing the calculated and calorimetrically determined oxide's reduction enthalpies. Some aspects of perovskite – brownmillerite phase transition in $SrFeO_{3-\delta}$ were discussed and the defect structure model for this oxide was proposed and then verified using the chosen data set. Introduction of the vacancy cluster formation in the defect structure model was shown to be necessary since $SrFeO_{3-\delta}$ is highly nonstoichiometric with respect to oxygen and tends to form various ordered structures. As a consequence, chemical expansivity of $SrFeO_{3-\delta}$ with respect to the oxygen nonstoichiometry was found to be much more complex than that of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$. According to our findings, unusually high values and the anomalous character of chemical strain of $SrFeO_{3-\delta}$ are likely to be attributed to the vacancy cluster formation (i.e. short-range ordering) and some degree of long-range vacancy ordering, respectively.

1. Introduction

Undoped and various doped strontium ferrites are widely regarded as promising materials for energy conversion devices such as cathodes for solid oxide fuel cell (SOFC) [1], oxygen permeating membranes [2], catalysts [3] and oxygen sensors [4]. These devices are operated in atmospheres with different oxygen partial pressures (p_{O_2}) or even in the p_{O_2} gradients. It is well known that materials' crystal lattice dimensions depend on their chemical composition. For the oxides with oxygen content depending on p_{O_2} at a given temperature, lattice expansion or contraction is often observed when the p_{O_2} in the gas phase decreases or increases, respectively. This phenomenon is known as a "chemical strain," "chemical expansion" or "defect-induced expansion," highlighting the role of defect equilibria in the origin of this property [5–7]. Investigation of a chemical strain of the state-of-the-art oxide materials is of key importance because uncontrolled defect-induced stresses in the energy conversion devices could be detrimental to their performance. In this respect, it should be noted that the chemical strain of the perovskite-type ferrites $Sr_{1-x}La_xFeO_3$ has not yet been thoroughly studied. For example, there are no high-precision dilatometric data for the parent compound $SrFeO_{3-\delta}$ (SF), whereas available in situ diffraction results at different T and p_{O_2} [8,9] do not allow decoupling chemical and thermal expansion.

Along with the defect structure, a number of factors, such as spin states of magnetic cations, crystal structure, etc., influence the chemical expansion of oxide materials [5,6]. The crystal structure of SF deserves an extended discussion because it is nontrivial and varies significantly depending on T and p_{O_2}.

Phase composition and microstructure of the undoped $SrFeO_{3-\delta}$ have been extensively investigated over the last few decades. At room temperature, a series of phases with general formula

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$SrFeO_{3-1/n}$ ($n = \infty$, 8, 4 and 2) was reported. Crystal structure of disordered cubic perovskite $SrFeO_{3-\delta}$ can be described with either $Pm\bar{3}m$ [8,10] or $Fm3c$ [9] space group. The latter represents doubled primitive perovskite cell and, according to Schmidt and Campbell [9], is more suitable for highly nonstoichiometric SF than $Pm\bar{3}m$, because a large $Fm3c$ unit cell contains an integer number of formula units. The ordered phases comprise tetragonal $SrFeO_{2.875}$ or $Sr_8Fe_8O_{23}$ ($I4/mmm$), orthorhombic $SrFeO_{2.75}$ or $Sr_4Fe_4O_{11}$ ($Cmmm$), and brownmillerite-type $SrFeO_{2.5}$ or $Sr_2Fe_2O_5$ ($Ibm2$) [8–11]. The exact oxygen content in these phases could vary slightly, retaining the crystal structure [10].

As it was shown using X-ray diffraction (XRD) analysis, vacancy-ordered nonstoichiometric strontium ferrites undergo phase transitions upon heating. Space group $I4/mmm$ is characteristic of SF with $\delta < 0.2$ prepared by slow cooling or annealing at low temperatures in air. When heated up to 250–300 °C, this tetragonal SF transforms to the cubic one with $Pm\bar{3}m$ space group [9,10]. In turn, for the orthorhombic $Sr_4Fe_4O_{11}$ (space group $Cmmm$), which requires elaborate annealing techniques for its preparation [10,11], order-disorder transition temperature is 320 °C [10]. Thus, intermediate ordered phases $SrFeO_{3-1/n}$ with $n = 8$ and 4 are present at higher temperatures neither in high (air) nor in low (pure inert gas) p_{O_2} atmosphere.

In the intermediate-temperature range (300–900 °C) SF exists as either perovskite, brownmillerite, or their mixture, depending on the particular oxygen content (i.e. oxygen partial pressure). At the temperatures higher than 900 °C [8,12], 830 °C [10], or, according to the earlier studies, even 700 °C [13], only the seemingly cubic perovskite phase exists. Such a discrepancy between reported temperatures of brownmillerite-perovskite phase transition is most likely caused by the differences in the p_{O_2} values in gas atmospheres employed for their determination [12].

However, this apparent high-temperature order – disorder transition seems to be more complicated. Taking into account that SF is highly nonstoichiometric and tends to form various vacancy-ordered structures, its microstructure is quite important for discussion of its phase composition. Grenier et al. [14] were the first to assume that the high-temperature microdomain structure of SF is responsible for its vacancy "ordering-disordering" transition. Contrary to the previous studies [13], it was suggested that a complete disordering with sudden redistribution of all oxygen vacancies, which results in cubic perovskite formation, is less likely for SF. Instead, some of the octahedra and tetrahedra of brownmillerite phase should disappear simultaneously, yielding a complex structure with fivefold-coordinated sites and brownmillerite-type domain intergrowths [14]. These domains seem to be small enough, and they are oriented relative to each other in such a way that the overall domain cluster has a cubic shape [15]. As a result, XRD pattern measured on the conventional diffractometer may be typical of the cubic perovskite, while only the synchrotron radiation allows the superstructure reflections to be obtained.

Strong tendency of SF to form coherently packed microdomains was later indicated by Takeda et al. [10] and then confirmed in a number of studies [15–21]. It is remarkable that there are low- and high-temperature experimental evidences favoring the inherent domain structure of SF. For example, both high oxygen mobility at elevated temperatures and unusually high reactivity of SF towards the oxygen intercalation at room temperature could be attributed to the enhanced oxygen diffusion through the extended defects such as domain walls [2,17,20]. Brownmillerite-type microdomains were found using the high-resolution transmission electron microscopy (HRTEM) in either significantly nonstoichiometric or almost fully oxidized SF [18,19], and even in the slightly doped samples annealed at 1200 °C [16], further reinforcing the hypothesis about the inherent nanostructured nature of SF.

It should be mentioned, however, that high-temperature domain structure of SF still remains a subject of controversy in the literature. Challenging the idea of microdomain formation at high temperature, Schmidt and Campbell [12] highlighted the lack of direct evidence supporting the microdomain model. Indeed, the only direct method that could confirm or disprove this model is HRTEM, which, in turn, can only deal with quenched samples. However, their microstructure may be different from that of the in situ high-temperature samples since the former can be formed during quenching [16]. Thus, at the present moment, it is not clear whether the question of microdomain formation in SF at high temperatures could be answered unambiguously.

It is well known that thermodynamic analysis of point defect reactions results in a defect structure model of a particular oxide, which can be verified using the oxygen nonstoichiometry dependencies on T and p_{O_2}. There is a lot of data on the oxygen nonstoichiometry of SF obtained by different means, from conventional thermogravimetry [2,8] and coulometric titration [21–25] to some original experimental techniques [26,27]. However, as seen in Fig. 1, these data suffer from considerable scatter. As it is not obvious which data set is the most reliable, a critical assessment of the existing oxygen nonstoichiometry values is crucial for their further employment, including the defect chemistry analysis.

Along with the oxygen nonstoichiometry, defect structure of SF was also discussed in several papers [21–25]. Either one possible defect reaction equilibrium of oxygen incorporation or two, including the charge disproportionation, were taken into consideration (see eqns. (7) and (8) below). Such models are usually the first choice for the simple case of a transition metal complex oxide with noninteracting, randomly distributed defect species. However, it's not the case for SF because of the high oxygen vacancy concentration and, as described above, its ability to form the ordered structures. The recent ab initio density functional theory (DFT) calculations have predicted that the increase of the Sr content in $La_{1-x}Sr_xFeO_{3-\delta}$ system leads to the increase of the oxygen vacancy interaction [28]. Consequently, a substantial degree of vacancy interaction, closely interrelated with the predisposition to oxygen-vacancy-ordering-induced phase transformations, was found to take place in the endpoint composition – SF – which is in perfect agreement with the empirical observations. Considering all that, it is quite surprising that up to now there were no attempts to factor the expected vacancy ordering into the point defect models.

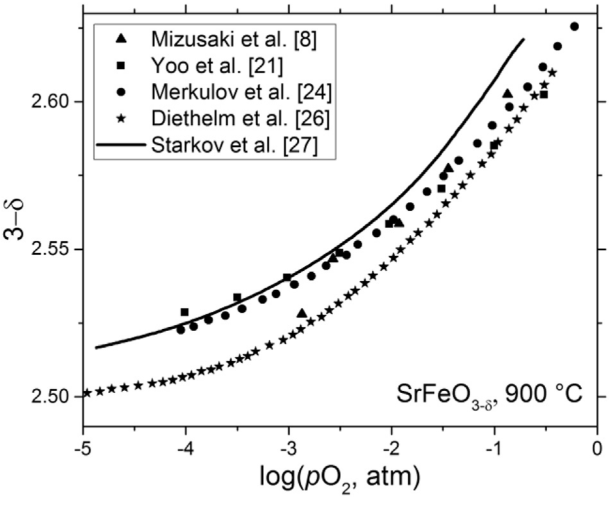

Fig. 1. Available data on oxygen nonstoichiometry of SF at 900 °C [8,21,24,26,27].