



Structural and chemical stability of Sr-, Nb- and Zr-doped calcium manganite as oxygen-storage materials



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ABSTRACT

Perovskites with multivalent transition-metal oxide show interesting properties in oxygen-storage capacity (OSC) due to the structural stability against a large amount of oxygen deficiency. In this study, two series of Mn-containing perovskites with oxygen nonstoichiometry δ , $\text{Sr}_x\text{Ca}_{1-x}\text{Mn}_{0.75}\text{Nb}_{0.25}\text{O}_{3-\delta}$ and $\text{Sr}_x\text{Ca}_{1-x}\text{Mn}_{0.5}\text{Nb}_{0.25}\text{Zr}_{0.25}\text{O}_{3-\delta}$, were synthesized and characterized before and after reduction in Ar-5% H_2 . The doping of Sr on Ca site improves the structural symmetry and stability against reduction and the additional doping of Zr on Mn site decreases the initiating temperature for oxygen loss, which could be related to the increase in lattice parameters. Two of the cubic perovskites, $\text{Sr}_{0.75}\text{Ca}_{0.25}\text{Mn}_{0.75}\text{Nb}_{0.25}\text{O}_{3-\delta}$ and $\text{SrMn}_{0.5}\text{Nb}_{0.25}\text{Zr}_{0.25}\text{O}_{3-\delta}$, were demonstrated to show excellent stability in the course of reduction-oxidation between Ar-5% H_2 and oxygen.

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1. Introduction

Multivalent transition-metal oxide (TMO) has attracted attention for energy conversion devices and catalysis systems due to the possible mixed electronic and ionic conductivity (MIEC) and oxygen deficiency arising from the valence variations [1]. The TMOs can be incorporated into perovskites with a formula of ABO_3 (A: rare earths or alkaline earths, B: transition metals) for the sake of structural stability arising from the 3-dimensional B-O-B framework during the cation valence change and oxygen loss or gain [2,3]. Particularly, perovskites with transition metals on the B site have been used for the electrocatalysts for both low-temperature oxygen reduction reaction in lithium batteries [4,5] and high-temperature solid oxide fuel cells [6,7]. At the same time, it can also be used as three-way catalysts or support of noble-metal catalyst for the conversion of exhaust of automobiles or oxygen-storage materials for separation of oxygen from nitrogen [8–14].

$\text{CaMnO}_{3-\delta}$ (δ is the oxygen nonstoichiometry) is a perovskite with Ca on the A-site and Mn on the B-site, and for a stoichiometric

oxygen content of three, $\delta = 0$, Mn will be tetravalent. Stoichiometric CaMnO_3 is an insulator with low electronic or ionic conductivity. However, the readiness of the reduction of the mixed-valence transition metal cations ($\text{Mn}^{4+}/\text{Mn}^{3+}/\text{Mn}^{2+}$), which could provide high electric conductivity and maintain a large oxygen-vacancy content, contributing to fast oxygen ion diffusion. For example, high electric conductivity of CaMnO_3 -based materials can be achieved by introducing oxygen deficiency [15] or doping higher-valence cations, such as Gd^{3+} or Y^{3+} on A site or $\text{Nb}^{5+}/\text{Mo}^{6+}$ on B site, to achieve a mixed valence of $\text{Mn}^{4+}/\text{Mn}^{3+}$ for thermoelectric materials [16–21]. Poeppelmeier et al. [22] found that CaMnO_3 can be reduced to $\text{CaMnO}_{2.5}$ with Mn^{3+} at 300 °C in H_2 and then to CaMnO_2 with Mn^{2+} at 325 °C, and more oxygen-deficient perovskites with intermediate Mn oxidation states [23,24] between Mn^{3+} and Mn^{4+} have also been obtained by annealing in air or inert gases. The oxygen vacancies ascribed to the oxygen loss can form either mobile point defects or ordered superstructure depending on the δ value [25]. The formation of mixed valences of cations and mobile oxygen defects are crucial to the functionality of CaMnO_3 as oxygen-storage materials in the course of fast oxygen loss/gain without losing the structural stability [13]. In particular, the chemical cycling stability of a perovskite in both air condition and reducing atmosphere is also important for an oxygen-storage catalyst to operate in a condition involving H_2 and hydrocarbon

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at elevated temperatures for an efficient oxygen-storage process.

In order to achieve high-efficiency oxygen storage promoters, the TMOs are generally partially stabilized during the oxidation-reduction process [26]. The structure and chemical stability of CaMnO_3 can be tuned by either alio-valent or iso-valent doping on A- or B- site. Taguchi et al. [27] studied the structure of $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x \leq 0.5$) with different amount of iso-valent Sr doping on Ca site, and found that the doping increased the angle of Mn–O–Mn bonds. The $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ showed a transition between a hexagonal crystal at $x = 1$ to an orthorhombic one at $x = 0$ for the oxygen-stoichiometric sample [28]. Iso-valent doping of Si on Mn site in $\text{CaMnO}_{3-\delta}$ has also been studied and the small Si^{4+} preferring occupying the tetragonal sites was reported to reduce the oxygen content and increase conductivity of the perovskite [29]. The doping on Mn^{4+} site with lower-valence ions, such as Al^{3+} , would induce the formation of brownmillerites ($\text{Ca}_2\text{AlMnO}_{5+\delta}$) which can be used for oxygen enrichment during the heating and cooling process [11,30]. The high-valence $\text{Nb}^{5+}/\text{Mo}^{6+}$ doping on Mn^{4+} does not induce the change of structure type but it causes the oxygen-content and Mn-valence variation. $\text{CaMn}_{1-x}\text{Nb}_x\text{O}_3$ ($0 \leq x \leq 0.6$) contains a mixed valence of $\text{Mn}^{4+}/\text{Mn}^{3+}$ or $\text{Mn}^{3+/2+}$ depending of the content of dopants, but it suffers from phase segregation during the reduction in a H_2 -containing atmosphere at temperature below 900°C to produce CaMnO_2 [31,32]. On the contrary, $\text{SrMn}_{0.5}\text{Nb}_{0.5}\text{O}_{3-\delta}$ with a cubic crystal structure showed high stability against Ar-5% H_2 reduction up to 950°C without losing the perovskite structure [33]. Though beneficial to the stability of the structure against reduction, the incorporation of large amounts of heavy elements, such as Sr and Nb would induce the decrease of oxygen-storage capacity (OSC) of CaMnO_3 , and a balance should be stroke between the chemical stability and the OSC. In this study, two series of $\text{CaMn}_{0.75}\text{Nb}_{0.25}\text{O}_{3-\delta}$ or $\text{CaMn}_{0.5}\text{Nb}_{0.25}\text{Zr}_{0.25}\text{O}_{3-\delta}$ perovskites were doped with incremental iso-valent Sr on the A site to check the OSC of these perovskite and the stability against reducing atmosphere up to 900°C in Ar-5% H_2 and to further assess the impact of B-site doping on the chemical stability of perovskite. This work could benefit the selection of manganese-based perovskite as oxygen-storage materials for oxidation of hydrocarbon in terms of a balance between the OSC and structural stability.

2. Experimental

Stoichiometric powders of SrCO_3 (99.99%, Alfa Aesar, metal basis), CaCO_3 (99%, Alfa Aesar), MnO_2 (98%, Alfa Aesar, metal basis), ZrO_2 (Puratronic, 99.978%) and Nb_2O_5 (99.9985%, Alfa Aesar, metal basis) were weighed and mixed with a pestle in an agate mortar for 30 min. The admixture was transferred into an alumina crucible for a preliminary calcination at 1000°C for 2 h. Monophasic materials

were obtained by a final sintering of the pelletized material at $1350\text{--}1420^\circ\text{C}$ for 5 h with slow cooling ($1^\circ\text{C}/\text{minute}$) for the recovery of oxygen content. The formulae and notations of the compounds are listed in Table 1. Thermogravimetric analysis (TGA) was carried out on a NETZSCH 49C thermogravimeter at a heating and cooling rate of 5°C min^{-1} between room temperature and 900°C in flowing Ar-5% H_2 . Reduction-re-oxidation (redox) property of the selected samples was assessed by first reducing the sample to 900°C in Ar-5% H_2 and then oxidizing the reduced sample in pure oxygen from room temperature to 900°C . The dwelling times at 900°C was set to be 5 min. Room temperature X-ray diffractions (XRDs) were performed on powdered samples using a PANalytical Empyrean diffractometer operated in reflection mode using $\text{Cu-K}\alpha_1$ (wavelength: 1.5406 \AA) radiation for the analysis of unit cells and structure. Rietveld refinements of the XRD data were performed on a Gsas program [34] to obtain the structure and cell parameters. Scanning electron microscopy (SEM) of the as-prepared and tested samples was taken on a Jeol 6700F microscope.

3. Results and discussions

3.1. Crystallographic analysis of XRD for samples before and after reduction

Fig. 1 shows the XRDs of the as-prepared samples with variable Sr content from 0 to 100%. The angular range of $36^\circ < 2\theta < 43^\circ$ is emphasized with a rectangle since this region includes superlattice reflections sensitive to the orthorhombic or tetragonal structure and its related tilting system [35]. It can be seen that with the increase of strontium content, the main XRD peak shifts to the low angle direction, indicating the increase of equivalent cell volume due to the larger ionic size of Sr than that of Ca. The Nb-doped CaMnO_3 perovskites ($\text{CaMn}_{1-x}\text{Mn}_x\text{O}_3$) were reported to be orthorhombic perovskite with GdFeO_3 structure. When the Nb content is higher than 0.5, the Ca–O–Nb bonds will percolate to form a framework that can effectively vary the oxygen content by inhibiting the formation of Mn^{3+} in a distorted octahedra due to the intrinsic Jahn-Teller effect [36]. The XRDs for CMN and S25C75MN show that they preserved the pristine structure of CaMnO_3 and crystallized in $Pnma$ symmetry while those for $\text{S}_{75}\text{C}_{25}\text{MN}$ and SMN were getting close to cubic perovskites. The relationship between orthorhombic and cubic crystal structures can be defined as follows: $a_0 \approx c_0 \approx \sqrt{2}a_c$ and $b_0 \approx 2a_c$, where information related to the orthorhombic and cubic structures are labeled with “o” and “c” subscripts, respectively. The detailed Rietveld refinements revealed that $\text{S}_{75}\text{C}_{25}\text{MN}$ and SMN could be fitted well into a cubic structure, as shown in Fig. 2. The symmetry of $Pm\text{-}3m$ for $\text{S}_{75}\text{C}_{25}\text{MN}$ and SMN was utilized following the structure of $\text{SrMn}_{0.5}\text{Nb}_{0.5}\text{O}_3$ [33]. As the

Table 1
Unit-cell parameters of $(\text{Sr,Ca})\text{Mn}_{0.75}\text{Nb}_{0.25}\text{O}_{3-\delta}$ and $(\text{Sr,Ca})\text{Mn}_{0.50}\text{Nb}_{0.25}\text{Zr}_{0.25}\text{O}_{3-\delta}$ before and after reduction in Ar-5% H_2 at 900°C .

	Symmetry	As-prepared				Reduced at 900°C	
		a/ \AA	b/ \AA	c/ \AA	V/ \AA^3	a/ \AA	V/ \AA^3
$\text{CaMn}_{0.75}\text{Nb}_{0.25}\text{O}_{3-\delta}$	CMN	$Pnma$	5.3998 (2)	7.5711 (3)	5.3572 (2)	219.02 (1)	Decompose
$\text{Sr}_{0.25}\text{Ca}_{0.75}\text{Mn}_{0.75}\text{Nb}_{0.25}\text{O}_{3-\delta}$	S25CMN	$Pnma$	5.4069 (2)	7.6637 (3)	5.3974 (2)	223.65 (2)	Decompose
$\text{Sr}_{0.75}\text{Ca}_{0.25}\text{Mn}_{0.75}\text{Nb}_{0.25}\text{O}_{3-\delta}$	S75CMN	$Pm\text{-}3m$	3.8752 (2)			232.78 (1) ^b	3.8750 (3) ^a
$\text{SrMn}_{0.75}\text{Nb}_{0.25}\text{O}_{3-\delta}$	SMN	$Pm\text{-}3m$	3.8944 (3)			236.25 (1)	3.9391 (2)
$\text{CaMn}_{0.50}\text{Nb}_{0.25}\text{Zr}_{0.25}\text{O}_{3-\delta}$	CMNZ	$Pnma$	5.4433 (2)	7.7312 (4)	5.5275 (3)	232.61 (3)	Decompose
$\text{Sr}_{0.25}\text{Ca}_{0.75}\text{Mn}_{0.50}\text{Nb}_{0.25}\text{Zr}_{0.25}\text{O}_{3-\delta}$	S25CMNZ	$Pnma$	5.5199 (3)	7.7675 (1)	5.5053 (2)	236.05 (4)	Decompose
$\text{Sr}_{50}\text{Ca}_{50}\text{Mn}_{0.50}\text{Nb}_{0.25}\text{Zr}_{0.25}\text{O}_{3-\delta}$	S50CMNZ	$Pnma$	5.5633 (3)	7.8632 (7)	5.5551 (3)	243.01 (2)	3.9706 (1)
$\text{Sr}_{0.75}\text{Ca}_{0.25}\text{Mn}_{0.50}\text{Nb}_{0.25}\text{Zr}_{0.25}\text{O}_{3-\delta}$	S75CMNZ	$Pm\text{-}3m$	3.9542 (1)			247.31 (1)	3.9864 (1)
$\text{SrMn}_{0.50}\text{Nb}_{0.25}\text{Zr}_{0.25}\text{O}_{3-\delta}$	SMNZ	$Pm\text{-}3m$	3.9718 (3)			250.64 (1) ^b	3.9961 (1)

^a Reoxidised after reduction at 900°C .

^b Volumes of cubic cells were multiplied by 4.

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