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A-site substitution effect on crystal structure and properties of $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A=Ca, Sr, Ba; x = 0, 0.25)

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ABSTRACT

The effect of A-site substitution by alkaline earth metals (A=Ba, Sr, Ca) on the crystal structure and properties of the $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (x = 0, 0.25) perovskite-like oxides were studied in the temperature range of 25–1000 °C in air. The $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ samples were synthesized by the citrate-nitrate combustion technique. X-ray powder diffraction (XRPD) patterns were refined by the Rietveld method using orthorhombic unit cell for $NdMn_{0.5}Fe_{0.5}O_{3-\delta}$ and $Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (sp. gr. *Pnma*); and monoclinic unit cell for $Nd_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ and $Nd_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (sp. gr. $P2_1/n$). The refinement results for the single-phase samples revealed that the unit cell volume decreased while decreasing the size of A-dopant in $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$. Oxygen content and oxidation state of Mn in $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ increased in the row: $Nd_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_{2.81}$, $Nd_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_{2.85}$, $Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{2.93}$ at all temperature studied. Oxygen non-stoichiometry of the $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ samples was almost independent of temperature even at high temperatures except for $NdMn_{0.5}Fe_{0.5}O_{3-\delta}$. The thermal expansion coefficient (TEC) for $Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ was found to be $10.1 \times 10^{-6} K^{-1}$ in the range of 25–800 °C. Temperature dependencies of total conductivity possessed semiconductor-type behavior and were interpreted within the small polaron hopping mechanism. The maximum value of conductivity (25 S/cm) was obtained for $Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ at 1000 °C in air. The Seebeck coefficient values decreased with temperature from positive to negative values indicating that both electrons and electron holes may contribute to the electric conductivity of the oxides.

1. Introduction

Undoped rare earth manganites ($LnMnO_3$, Ln = rare earth element) and partially A- and B-site substituted oxides were extensively studied in respect of their physical and chemical properties [1–6]. These materials attract significant interest from theoretical and practical point of view due to their colossal magnetoresistance (CMR) properties [7], charge ordering [8], orbital ordering, phase separation scenario, order-disorder transition [9], etc. The materials with CMR properties can be used for multipurpose applications in memory storage devices [9], read-write heads, spintronic devices and infrared sensors [10]. Electrochemical devices such as Solid Oxide Fuel Cells (SOFCs) are another area of application for manganites. $(La,Sr)MnO_3$ is currently used as SOFC cathode by numerous companies for commercial production of electrolyte- and anode-supported planar SOFCs [11]. Recently, N. Hou et al. reported the electrical conductivities of $Sm_{0.5}Ba_{0.5}MnO_{3-\delta}$ sample equal to 1.15 and 0.10 S/cm in air and H_2, respectively, applying it as anode for SOFC with H_2 and CH_3OH fuel [12].

The performance of standard $(La,Sr)MnO_3$ cathode can be noticeably improved when lanthanum is replaced by praseodymium or neodymium [13]. Indeed, $Pr_{0.6}Sr_{0.4}MnO_3$ and $Nd_{0.6}Sr_{0.4}MnO_3$ showed lower cathodic overpotential and higher values of total conductivity compared with that for $La_{0.6}Sr_{0.4}MnO_3$ [13]. Although $Pr_{0.6}Sr_{0.4}MnO_3$ showed slightly better characteristics than $Nd_{0.6}Sr_{0.4}MnO_3$, in this work a smaller size neodymium was chosen as a rare-earth element to partially compensate the increase in linear thermal expansion coefficient (LTEC) due to iron doping [14–16].

Although a significant amount of reports concerning lanthanum manganites are available in literature, little information was reported for the mixed neodymium manganites and ferrites, $NdFe_{1-x}Mn_xO_3$ [17–20]. Crystal and magnetic structures of $NdMn_{0.5}Fe_{0.5}O_3$ were reported earlier [17,18,20]. The single phase $NdMn_{0.5}Fe_{0.5}O_3$ was shown to adopt the orthorhombic structure (sp. gr. *Pbnm*). Neutron diffraction refinement using $P2_1/n$ sp. gr. indicated an absence of Mn and Fe ordering. The orthorhombic crystal structure (sp. gr. *Pnma*) remained unchanged in the whole concentration range for $NdFe_{1-x}Mn_xO_3$ as

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reported in [14,19]. However, Chakraborty et al. [20] observed formation of O-orthorhombic (for $0 \le x \le 0.8$) and $O^{'}-$orthorhombic (for $0.8 \le x \le 1$) phases as a result of Jahn-Teller distortion. The $NdMn_{0.5}Fe_{0.5}O_3$ composition possesses G-type antiferromagnetic structure with onset of magnetic ordering slightly above room temperature (RT) [17]. The total conductivity of $NdFe_{1-x}Mn_xO_3$ exponentially increases with Mn content owing to the hopping of charge carriers among Mn^{3+}–O–Mn^{4+} clusters [20]. The hopping is hindered by the Fe^{3+} cations and oxides with $x \le 0.2$ exhibited very high resistivity [20,21]. The small polaron hopping mechanism of conduction was suggested; activation energies for $NdFe_{1-x}Mn_xO_3$ varied from ~0.35 eV for $x = 0.2$ to ~0.18 eV for $x = 1$ [20].

Phase equilibria, crystal structure and thermal expansion studies for the $Nd_{1-x}Ba_xMn_{1-y}Fe_yO_3$ system were reported in [14]. $Nd_{0.9}Ba_{0.1}Mn_{1-y}Fe_yO_3$ ($0 \le y \le 0.7$) and $Nd_{0.8}Ba_{0.2}Mn_{1-y}Fe_yO_3$ ($0 \le y \le 0.5$) were single-phase at 1100 °C with the orthorhombic structure (sp. gr. *Pnma*) [14]. The LTEC value increased with Fe content in the series $Nd_{0.8}Ba_{0.2}Mn_{1-y}Fe_yO_3$ ($y = 0.1$, 0.3, 0.5). The average LTEC value for $Nd_{0.8}Ba_{0.2}Mn_{0.5}Fe_{0.5}O_3$ was equal to $11.10 \pm 0.20 \times 10^{-6}\,K^{-1}$ in the temperature range of 303–1573 K [14]. This value was noticeably lower compared with that for $La_{0.78}Ba_{0.22}Mn_{0.6}Fe_{0.4}O_3$ (LTEC = $12.7 \times 10^{-6}\,K^{-1}$ in the range of 293–1370 K) [16]. No other high-temperature data were found for $Nd_{1-x}A_xMn_{1-y}Fe_yO_3$ (A═Ca, Sr, Ba) in literature. Some properties for the similar $La_{1-x}Sr_xMn_{0.5}Fe_{0.5}O_3$ system [22] were reported by Kato et al. $La_{1-x}Sr_xMn_{0.5}Fe_{0.5}O_3$ with $x = 0$–0.5 were indexed in the orthorhombic symmetry (sp. gr. *Pbnm*). $LaFe_{0.5}Mn_{0.5}O_{3.03}$ and $La_{0.7}Sr_{0.3}Fe_{0.5}Mn_{0.5}O_{3.02}$ were shown to be over-stoichiometric in respect to oxygen content, which was almost independent from temperature [22]. The samples with $x = 0$, 0.3, 0.5 exhibited semiconductor behavior in the temperature range of 20–450 °C in air with a small decrease in total conductivity above 450 °C; the values of total conductivity were about ~0.4 S/cm at 1000 °C for $x = 0$, 0.3, 0.5 [22]. The charge transfer in $La_{0.7}Sr_{0.3}Mn_{1-y}Fe_yO_3$ ($0.03 \le y \le 0.25$) was described by the hopping mechanism [23].

The aim of this work was to study the effect of alkaline earth metal substitution for Nd on the crystal structure and properties of $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A═Ba, Sr, Ca). Here we reported the synthetic procedure as well as crystal structure, average oxidation state of 3*d*-metals, thermal expansion, temperature dependences of oxygen content, total conductivity and the Seebeck coefficient for $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ in air.

2. Experimental

$NdMn_{0.5}Fe_{0.5}O_{3-\delta}$, $Nd_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$, $Nd_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ and $Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ were synthesized by citrate-nitrate combustion technique. Nd_2O_3 (Lanhit, 99.99%), Mn $(CH_3COO)_2 \times 4H_2O$ (Merck, ≥99%), $FeC_2O_4 \times 2H_2O$ (Vekton, ≥99.9%), $BaCO_3$ (Lanhit, 99.99%), $SrCO_3$ (Aldrich, ≥99.9%) and $CaCO_3$ (Khimreaktivsnab, > 99%) were used as precursor materials. Before the synthesis $CaCO_3$, $SrCO_3$ and $BaCO_3$ were annealed at 500 °C for 12 h in air to eliminate moisture and absorbed gases. The starting materials were weighed and mixed in an appropriate molar ratio followed by an addition of distilled water, an excess of nitric acid (≈20 mol of nitric acid per formula unit of $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_3$) and crystalline citric acid monohydrate $C_6H_8O_7 \times H_2O$ (Vekton, 99%). The amount of $C_6H_8O_7 \times H_2O$ was taken in 1:1 ratio to the final mass of oxide. The as-prepared solution was evaporated on a hot plate forming viscous gel until self-combustion occurred. The obtained powders were grounded with C_2H_5OH and calcined at 1100 °C in air for 24 h three times with intermediate grindings. Finally, the powder samples were uniaxially pressed into pellets at 40 bar and sintered at 1350 °C for 15 h in air. For total conductivity and the Seebeck coefficient measurements the $NdMn_{0.5}Fe_{0.5}O_{3-\delta}$ and $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A═Ca, Sr, Ba) samples were sintered as rectangular-shaped bars at the same conditions yielding relative density > 92%.

Phase composition of the samples was analyzed at RT by X-ray powder diffraction (XRPD) using XRD-7000 Maxima instrument (Shimadzu) with Cu-Kα radiation (FWHM ~0.01° at 2θ). High-temperature XRPD (HT-XRPD) was performed in air within the 30–1000 °C temperature range using HTK 1200 N (Anton Paar) HT-chamber. XRPD patterns were refined by the Rietveld method using FullProf program [24].

Temperature dependencies of oxygen non-stoichiometry were determined by thermo-gravimetric analysis (TGA) using the Netzsch STA 409 PC instrument. A powder oxide sample was placed in the alumina crucible annealed at 1000 °C. Equilibrium mass changes of the oxide sample were measured in the temperature range of 25–1100 °C on cooling with steps of 100 °C in air flow (50 ml/min) using the empty alumina crucible as a reference material. The absolute values of oxygen content at RT were calculated from the results of dichromate titration and iodometric titration described in details in Ref. [25] and Ref. [26], respectively. Automatic titration apparatus Akvilon (ATP-02) was used. The total conductivity and Seebeck coefficient measurements were carried out simultaneously using the standard 4-probe DC technique with Pt wire leads. The data were collected in the temperature range of 25–1000 °C on cooling with steps of 50 °C. The measurements were performed at a given temperature until constant values of both electrical resistivity and thermo-emf were gained.

3. Result and discussion

3.1. Crystal structure of $Nd_xA_{1-x}Mn_{0.5}Fe_{0.5}O_{3-\delta}$

Similarly to previously reported data for related oxides, which are crystallized either in the orthorhombic structure $NdMnO_{3+y}$ (*Pbnm*) [27], $NdFeO_3$ (*Pbnm*) [28], $NdMn_{0.5}Fe_{0.5}O_3$ (*Pbnm*) [17], $Nd_{0.70}Ba_{0.30}MnO_3$ (*Imma*) [29], $Nd_{0.70}Sr_{0.30}MnO_3$ (*Pbnm*) [30], $Nd_{0.70}Ca_{0.30}MnO_3$ (*Pbnm* [31] and *Pnma* [32]) or in the cubic structure $LaMn_{0.5}Fe_{0.5}O_3$, $La_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_3$, $La_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_3$ [33], the obtained single-phase $Nd_xA_{1-x}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ revealed the perovskite-like structure.

Since $NdMn_{0.5}Fe_{0.5}O_{3-\delta}$ was previously reported as orthorhombic phase with *Pnma* or *Pbnm* setting of space group No. 62 [14,17,19,20] the initial refinements for the prepared $NdMn_{0.5}Fe_{0.5}O_{3-\delta}$ and $Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ were performed using the structural model reported in [17]. The refinement results are presented in Table 1. Similarly, $Nd_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ and $Nd_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ were first indexed to the orthorhombic structure with sp.gr. *Pnma* (Table 1). A closer

Table 1
The unit cell parameters refined by the Rietveld method and *R*-factors for the $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A═Ca, Sr and Ba) solid solutions.

Sample name	*sp.gr.*	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3	R_B, %	R_f, %	χ^2
$NdMn_{0.5}Fe_{0.5}O_{3-\delta}$	*Pnma*	5.673	7.679	5.431	236.56	4.82	4.80	2.32
$Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	*Pnma*	5.503	7.776	5.511	235.89	7.67	7.67	1.96
$Nd_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	$P2_1/n$	5.462	5.480	7.723	231.24	5.16	7.32	1.78
	Pnma	5.464	7.723	5.479	231.19	8.80	12.7	2.70
$Nd_{0.75}Ca_{.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	$P2_1/n$	5.418	5.488	7.684	228.53	5.74	8.43	1.48
	Pnma	5.489	7.685	5.419	228.59	6.12	8.92	1.71