Federal State Autonomous Educational Institution of Higher Education «Ural Federal University named after the first President of Russia B.N. Yeltsin»

As a manuscript

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Synthesis, crystal structure and properties of complex oxides with the perovskite structure based on neodymium, alkaline earth and *3d*-transition metals

specialty 02.00.04 – physical chemistry dissertation for the degree of candidate of chemical sciences

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Yekaterinburg - 2019

The work was performed in the Department of Physical and Inorganic Chemistry of the Institute of Natural Sciences and Mathematics of the Ural Federal University named after the first President of Russia B.N. Yeltsin

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INTRODUCTION

<u>The relevance and degree of topic development</u>

The increasing demand on global electrical power consumption, environmental problem and depletion of natural sources stimulate finding a modern and alternative way of renewable energy. Solid oxide fuel cells (SOFC) is one of the reliable alternative sources of renewable energy [1]. The reduction of working temperature down to the intermediate temperature range (600–800 ° C) is one of the main challenges in creating reliable long-term operating devices with improved performance. Various perovskite-type oxides have been studied in order to progress the cathode performance at intermediate temperature [1]. Among these perovskites cobalt based materials attracted much attention due to their high conductivity and good electrochemical properties, however thermal expansion coefficient (TEC) value is too high comparing to the possible electrolytes, like $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM) or $Ce_{0.9}Gd_{0.1}O_{2.8}$ (CGO). Thus, thermomechanical incompatibility, and as a result, short-term stability of the cells with the cobalt-based cathode materials is the main drawback.

The efficiency of standard SOFCs cathode material based on LaMnO₃ can be noticeably enhanced when lanthanum is substituted by neodymium. The moderate TEC value was also detected for the Co-doped materials, as well as Ni-substituted oxides reported as potential cathode materials for the intermediate-temperature solid oxide fuel cells (IT-SOFCs) [2]. Although, there are significant amount of reports available on lanthanum manganites, but limited data presents on A-site substituted neodymium manganite and their iron-, cobalt-, and nickel-doped derivatives.

The aforementioned information confirms the relevance of the present work, which have been performed in the Department of Physical and Inorganic Chemistry, Institute of Natural Science and Mathematics, Ural Federal University named after the first President of Russia B.N. Yeltsin. This work was

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supported by the Act 211 of the Government of the Russian Federation, agreement 02.A03.21.0006.

Goals and Objectives of the Work

The purpose of this work was the systematic study of crystal structure, oxygen nonstoichiometry and transport properties of complex oxides $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) in order to establish the relationship between the chemical composition, structure and functional properties as well as verification of possibility for their use as cathode materials in SOFCs.

Following tasks were set to achieve the aforementioned goal:

- 1. Synthesis of $Nd_{1-x}A_{x}Mn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) complex oxides and their crystal structure refinement.
- 2. Determination of oxygen nonstoichiometry in $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) versus temperature in air following with a comparative study of doping effect.
- 3. Determination of thermal expansion for the studied oxides using HT-XRPD and dilatometry measurements.
- 4. Determination of total conductivity and Seebeck coefficient for the studied oxides versus temperature.
- 5. Examination of chemical compatibility between the studied oxides with moderate TEC and high total conductivity $(Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta})$ and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte.
- 6. Impedance spectroscopic measurements for the $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ cathodes for evaluation of possible application in SOFCs.

Theoretical and practical significance

The experimental results obtained in the work can be treated as basic knowledge which can be used in theoretical calculations and technical design for the best performance as cathode materials in SOFCs. The experimental results on crystal structure, temperature dependent oxygen nonstoichiometry, TEC values, total conductivity and Seebeck coefficient of the studied materials will serve as a basis to establish theoretical links between composition, structure and properties. The calculated values of activation energy in Nd₁. ${}_{x}A_{x}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ provide additional information for understanding of the charge transference mechanism.

Thus, the experimental measurements and theoretical study of Nd₁₋ $_{x}A_{x}Mn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) could support a choice of most optimal material for SOFCs application.

Methodology and research methods

- 1. The synthesis of the studied complex oxides was carried out by citratenitrate method.
- 2. The crystal structure was investigated by X-ray diffraction using a Maxima XRD-7000 and an Equinox 3000 diffractometers. The unit cell parameters were refined using the Le Bail method and structural parameters were refined by the Rietveld method using FullProf software.
- 3. Thermal expansion coefficient was determined using dilatometry and high-temperature X-ray diffraction analysis. Netzsch DIL 402 dilatometer and high-temperature cameras: HTK 1200N (Anton Paar) installed on Maxima XRD-7000 diffractometer were used as instruments.
- 4. Oxygen nonstoichiometry was investigated by thermogravimetric analysis using a Netzsch STA 409 PC instrument. The absolute value of oxygen content at room temperature was calculated from the results of Red-Ox titration with Mohr salt and iodometric titration methods using an automatic titrator Aquilon ATP-02.
- 5. Measurement of total electrical conductivity and thermo-emf was carried out simultaneously using the dc 4-probe method. The oxygen partial

pressure was adjusted and monitored inside the cell of the original design using the Zirconia 318 device.

- 6. Chemical compatibility of complex oxides with respect to electrolyte was studied by contact annealing at a temperature of 1458 K in air.
- 7. Impedance measurements were performed using an Elins Z-2000 instrument.

<u>Defence items</u>

- 1. The information on synthesis and crystal structure of $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) at room temperature.
- 2. The high temperature structural parameters for $Nd_{1-x}Ba_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (x = 0.25 and 0.5), $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$ and calculated values of thermal expansion.
- 3. Temperature dependencies of oxygen nonstoichiometry for $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) complex oxides in air.
- 4. The values of thermal expansion for the studied complex oxide in air, obtained by high-temperature dilatometry.
- 5. The temperature dependent total conductivity and Seebeck coefficient for $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) in air.
- 6. The results of chemical compatibility test for $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ with $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte and Impedance spectroscopic results.

<u>Reliability of results and approbation of work</u>

The reliability of the results is achieved by an integrated approach using a variety of methods, which are independent and complement each other. The approbation of the work has been made in a form of presentations at the international and Russian conferences and in the journal publications. The main results of the work were presented and discussed at: XXVII Conference "Problems of Theoretical and Experimental Chemistry" (Yekaterinburg, 2017); Sino-Russian ASRTU Conference Alternative Energy: Materials, Technologies, and Devices (Ekaterinburg, 2018); National Seminar on Design Synthesis, Characterization, Reactivity, Theoretical Study and Application of Different Advanced Functional Materials (Barddhaman, India, 2017); II International conference on Modern Synthetic Methodologies for Creating Drugs and Functional Materials (MOSM2018) (Ekaterinburg, 2018).

Publications

Main issues of the thesis are published in 3 articles and 5 abstracts of presentations at All-Russian and international conferences.

Structure and scope of work:

The thesis work consists of introduction, 5 chapters, conclusions and bibliography. The material is presented on 123 pages, the work contains 23 tables, 42 figures, and list of references contains 158 items.

1. LITERATURE REVIEW

The investigations focused on the perovskite-type materials are still under wide current interest in the field of material science due to their various industrial and technological applications [1-4]. Although the number of materials with perovskite structure is huge, some new members of the family appeared recently [5].

The general formula of perovskite is ABX_3 (X = oxygen, halogen, nitrogen, sulfur) where A is large metal cation close-packed in layers with anions and smaller metal ion (B) located in an octahedrally coordinated hole between the close-packed layers. The ideal perovskite-type structure is cubic with *Pm-3m* space group. In this structure, the B cation is 6-fold coordinated and the A cation is 12-fold coordinated with the oxygen anions.

In the ideal perovskite type structure, B-O distance is equal to a/2 (*a* is the cubic unit cell parameter) and the A-O distance is $(a/\sqrt{2})$. From the geometrical point of view following relationship between the ionic radii $r_A + r_0 = \sqrt{2}(r_B + r_0)$ should be satisfied, however some of experimental results showed that the cubic structure was still retained in ABO₃ compounds even though this equation is not exactly followed. Goldschmidt tolerance factor (t) [6], which serves as a measure of deviation from the ideal perovskite structure:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$
(1.1)

can vary within the wide range of 0.75 < t < 1.0. The mineral CaTiO₃ collected from nature supposed to be cubic, but its accurate symmetry was later exposed to be orthorhombic [7].

1.1 Structural studies of $R_{1-x}A_xMnO_{3-\delta}$

A-site substituted rare-earth manganites $R_{1-x}A_xMnO_3$ with perovskite structure were extensively studied due to their interesting properties, which behaviour was depended on oxygen content, synthetic conditions, ordereddisordered phenomenon, and even microstructure (shape and size of particles) [8]. The homogeneity range of $R_{1-x}Ba_xMnO_3$ solid solution was extended using 'two-steps' synthesis mode up to x = 0.60 for the Pr-based samples and x = 0.50for the La-containing manganite [9]. It was reported that $La_{1-x}Ba_xMnO_3$ within the range $0.20 \le x \le 0.40$ possesses rhombohedral structure with *R-3c* space group (sp. gr.) [10].

The crystal structure of $Pr_{1-x}Ba_xMnO_3$ oxides significantly depended on the Ba concentration and temperature: the samples with x < 0.20 at room temperature possessed the orthorhombic structure (sp. gr. *Pbnm*) with double tilting of the MnO₆ octahedra, but oxides with 0.20 < x < 0.40 revealed *Ibmm* sp.gr. with only one tilting of the MnO₆ octahedra [11]. Decreasing of temperature leads to a transition in $Pr_{1-x}Ba_xMnO_3$ (0.20 < x < 0.40) oxides from the orthorhombic to tetragonal structure [11]. At the same time, depending on the preparation condition and Ba-content $Pr_{1-x}Ba_xMnO_3$ ($0.55 \le x \le 0.60$) and $La_{1-x}Ba_xMnO_3$ ($0.45 \le x \le 0.50$) oxides exhibited either cubic disordered simple perovskite-type structure or layered double perovskite supercell $Pr_{1-x}Ba_xMnO_3$ ($0.40 \le x \le 0.50$) and $La_{60}Ba_{40}MnO_3$ [9]. Electron diffraction (ED) patterns of the (La,Pr)_{1-x}Ba_xMnO_3 perovskites are shown in **Fig. 1.1(a,b)** [9].

Using hydrothermal method Jeffrey *et al* [12] prepared single-crystalline nanocubes of La_{1-x}Ba_xMnO₃ (x = 0.3, 0.5, and 0.6) as pseudo-cubic phase with particle sizes of 50-100 nm depending on doping level [12]. The transmission electron microscopy (TEM) and high-resolution TEM images for La_{0.5}Ba_{0.5}MnO₃ and 30-nm La_{0.7}Ba_{0.3}MnO₃ nanocube samples are shown in **Fig. 1.1 (c, d),** respectively. [12]. Raveau *et al* [13] synthesized La_{1-x}Ba_xMnO₃ (0.4 $\leq x \leq 0.9$) series in air and found two sets of characteristic peaks corresponded to the hexagonal and cubic perovskites. Another research group synthesized La₁₋ $_{x}Ba_{x}MnO_{3}$ nanoparticles with 40 to 70 nm diameter using an ionic liquid route where LaMnO₃ was indexed to the cubic (*Pm3m*) phase and the mixed composition samples were indexed to the rhombohedral (*R3cH*) phase in a hexagonal setting [14].



Figure 1.1 – ED patterns of the perovskite $R_{1-x}BaxMnO_3$. (a) Coexistence of the P-type double perovskite for $Pr_{1-x}BaxMnO_3$ and *Imma* (x = 0.40). (b) ED patterns for $La_{0.6}Ba_{0.4}MnO_3$ with $R\overline{3}c$ and P-type double-cell [9]. (c) TEM image of 20 to 500 nm diameter content $La_{0.5}Ba_{0.5}MnO_3$ nanocubes. (d) High-resolution TEM image of a 30-nm $La_{0.7}Ba_{0.3}MnO_3$ nanocube along with a selected area diffraction pattern (inset) [12].

 $Nd_{1-x}Ba_xMnO_3$ (0 < x < 0.1) exhibits O'-orthorhombic distortions due to the cooperative Jahn-Teller effect, although oxide with x = 0.1 does not show any distortions and increase of the barium content leads to the gradual decreasing of the orthorhombic distortions in the crystal structure [15]. The distortion arises from the mismatch between ionic sizes of different ions. The reported oxidized and reduced samples of $Nd_{1-x}Ba_xMnO_{3-y}$ (x > 0.2, y < 0.25) were described as pseudocubic perovskite structure. The unit cell volume increases markedly with increasing of oxygen vacancy concentration which is accompanied with conversion of small Mn^{4+} ions into large Mn^{3+} ions [15]. On the other hand, $Sm_{1-x}Ba_xMnO_3$ samples exhibit larger unit cell distortions in comparison with the Nd series. However, the crystal structure distortions for the $Sm_{1-x}Ba_xMnO_3$ (x > 0.3) samples prepared in air become very small similar to the Nd-based series [15].

The Sr doped $R_{1-x}Sr_xMnO_3$ ($0 \le x \le 0.5$) system was reported by Y. Sakaki *et al.* [16]. The solid solutions were synthesized using a conventional ceramic technique and a thermal decomposition of nitrate mixture method. In contrast to $La_{1-x}Sr_xMnO_3$ with x = 0.2-0.3, which possesses the rhombohedrally distorted perovskite structure, the Pr-, Nd-, Sm- and Gd-containing $R_{1-x}Sr_xMnO_3$ solid solutions with x>0.3 were orthorhombically distorted [16]. The degree of orthorhombicity (a/b ratio) has been found to increase from La to Gd and to decrease with increasing the Sr content [16]. At the same time nanoparticles of $La_{1-x}Sr_xMnO_3$ ($0.25 \le x \le 0.47$) prepared via molten salt synthesis exhibited rhombohedral structure with the $R\bar{3}c$ symmetry [17].

Shlapa *et al* [18] prepared La_{1-x}Sr_xMnO₃ series through different methods such as sol-gel method, precipitation from non-aqueous solution and precipitation from reversal microemulsions. They claimed that the use of organic precursors and non-aqueous media permitted to decrease the crystallization temperature of nanoparticles significantly and single-phase crystalline product could be prepared in one stage [18]. The reported Sm₁₋ _xSr_xMnO₃ ($0.2 \le x \le 0.5$) [19], nanocrystalline Pr-deficient Pr_{1-x}Sr_xMnO_{3- δ} [20],

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 $Gd_{1-x}Sr_{x}MnO_{3}$ (0.2 $\leq x \leq 0.5$) [21] $Eu_{1-x}SrxMnO_{3}$ (0.2 $\leq x \leq 0.5$) [22] manganites were described as orthorhombic phases with sp. gr. *Pbnm*.

Nanocrystalline $La_{1-x}Ca_xMnO_3$ (0.0 $\leq x \leq 0.5$) prepared by a low temperature self-propagating combustion method [23] was reported as cubic phase, but depending on oxygen content it can crystallize in orthorhombic structure [24]. $La_{1-x}Ca_xMnO_3$ (0.7 $\leq x \leq 1$) with high concentration of Ca, reported as orthorhombic phase [25, 26]. Gonzalez-Calbet *et al* [27] studied several samples of $La_{0.5}Ca_{0.5}MnO_{3-\delta}$ with various δ values, using ED and highresolution electron microscopy (**Fig. 1.2**). The ordering of the oxygen vacancies in a frame of orthorhombic structure for the oxygen content $\delta = 0.25$, and $\delta =$ 0.5 isostructural to Sr₂FeO₅ with sp. gr. *Ibm2* has been detected [27].



Figure 1.2 - Structural projections of $La_{0.5}Ca_{0.5}MnO_{2.5}$ along (a) [100] and (b) [101] orientation [27].

Jirak *et al* described the crystal structure of $Pr_{1-x}Ca_xMnO_3$ ($0.1 \le x \le 0.9$) at room temperature where orthorhombic distortion was observed in the range of $0.1 \le x \le 0.5$ [28]. At low temperature $Pr_{1-x}Ca_xMnO_3$ showed four regions of different symmetry: orthorhombic ($0.1 \le x \le 0.3$), pseudo-tetragonal compressed ($0.3 \le x \le 0.75$), pseudo-tetragonal elongated ($0.75 \le x \le 0.9$) and pseudo-cubic ($0.9 \le x \le 1$) [28]. The reported $Pr_{0.5}Ca_{0.5}MnO_3$ nanoparticles were also described as orthorhombic structure [29]. Similar crystal structure (of GdFeO₃-type) for bulk and nanocrystalline Nd_{1-x}Ca_xMnO₃ ($0 \le x \le 0.6$) at room temperature was reported by several authors [30, 31, 32, 33] although monoclinic symmetry was found for x = 0.3 and 0.4 at low-temperature [33]. Gd_{1-x}Ca_xMnO₃ and Eu_{1-x}Ca_xMnO₃ ($0.1 \le x \le 0.5$) were also described as orthorhombic for x = 0.3 and 0.4 at low-temperature [33].

1.2 Structural studies of $RMn_{0.5}B_{0.5}O_{3-\delta}$

The structural behavior of $\text{RMn}_{0.5}\text{B}_{0.5}\text{O}_{3-\delta}$ is quite complex due to multiple oxidation state of manganese ions. The magnetic properties of $\text{LaMn}_{0.5}\text{B}_{0.5}\text{O}_{3-\delta}$ (B = Cr, Co, Ni etc) were analyzed earlier in terms of structural description of these oxides as simple disordered perovskites ($\text{LaMn}_{0.5}\text{B}_{0.5}\text{O}_3$) or double perovskites (La_2MnBO_6) in order to understand the actual nature of the magnetic exchange interactions. Nanocrystalline $\text{LaMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ powder prepared by a polyvinyl alcohol-based sol-gel synthesis was reported as orthorhombic disordered type perovskite structure [36], however Yoshimatsu *et al.* described same composition in the form of film grown by pulsed-laser deposition as double perovskites $\text{RMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (R = La, Pr, Nd, Sm and Gd) decreases with the reducing of lanthanide size [36]. The reported XRD data claimed that NdMn_{0.5}\text{Fe}_{0.5}\text{O}_3 possessed an orthorhombic structure with sp. gr. *Pbnm* and refined neutron diffraction data using monoclinic sp. gr. *P2*₁/n found

an absence of Mn and Fe ordering [38]. However, Chakraborty *et al.* [39] observed the formation of O-orthorhombic (for $0 \le x \le 0.8$) and O'-orthorhombic (for $0.8 \le x \le 1$) phases because of Jahn-Teller distortion.

The high-resolution diffraction and small angle scattering neutron investigation of LaCo_{0.5}Mn_{0.5}O_{3+ δ} (δ = -0.03, 0 and 0.05) synthesized by a conventional solid-state reaction technique revealed that the samples possessed monoclinic crystal structure with sp.gr. *P2₁/n* at 2K and 300K [40]. La₂CoMnO₆ synthesized at comparatively low temperature had monoclinic structure with charge ordering at low temperatures which transformed to a rhombohedral structure at higher temperature without loss of charge ordering [41]. Aruna et al claimed that LaMn_{1-x}Co_xO₃ (0.2 \leq x \leq 0.5) had a pseudocubic structure isomorphous to LaCrO₃ [42]. Similar reports on RMn_{0.5}Co_{0.5}O₃ (R = La, Pr, Nd, Nd_{0.5}Sm_{0.5}, Sm, Eu, Tb Gd and Ho) are available in literature where authors have claimed the cation-disordered orthorhombic structure (*Pnma*) [43–46].

The sample with 50% substitution of Mn by Ni in LaMnO₃ was biphasic. The obtained rhombohedral phase has transformed to either monoclinic or orthorhombic phase at low temperature [47]. The described lower symmetry phase is due to the ordering of Ni/Mn at B-site sublattice. The crystallization of LaMn_{0.5}Ni_{0.5}O₃ perovskite structure in rhombohedral (*R-3c*) and orthorhombic (*Pbnm*) phase denoted a random distribution of Ni and Mn over the octahedral sites while the ordering of Ni and Mn into a distinguishable site can be seen in rhombohedral (*R-3* or *R-3m*) and monoclinic (*P2*₁/*n*) phases. Generally, the B-site ordering in perovskite materials is stabilized when B and B' cations differ significantly in charge and/or ionic size [48]. In case of La₂NiMnO₆, the complete B-site ordering could be achieved only when fixed Ni²⁺ and Mn⁴⁺ charge difference will maintain. Several reports claimed that well-ordered La₂NiMnO₆ shows either monoclinic or rhombohedral symmetry with Ni²⁺ and Mn⁴⁺ cations while disordered phase shows orthorhombic symmetry with a random distribution of Ni³⁺ and Mn³⁺. The synthesized La₂NiMnO₆ at 1100°C

showed orthorhombic crystal symmetry with slight monoclinic distortion [49], while the sample synthesized at 1300°C crystallized in monoclinic structure. [47]. The neutron diffraction data for La₂NiMnO₆ at ambient temperature showed 85% of B-site Ni-Mn ordering [41]. Similar results were obtained by Sanchez-Benitez et al who reported 88.14% degree of long-range ordering between Ni and Mn sites at 210K for NdNi_{0.5}Mn_{0.5}O₃ [50], as well as other rare earth perovskites, such as Pr₂NiMnO₆ [51], La₂Ni_{1-x}Mn_{1+x}O₆ [52], Gd₂NiMnO₆ [53], Ho₂NiMnO₆ [54] were also reported as monoclinic phases with sp. gr. $P2_1/n$.

It was found that A-site cation ordering expressively affects physical properties of perovskite manganites [55, 56]. This A-site layer-type ordering phenomenon also noticed in RBaCo₂O_{5-δ} [57, 58]. D. Muñoz-Gil et. al. reported the preparation process of disordered cubic Gd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-δ} perovskite and corresponding A-cation ordered GdBaMnFeO_{$6-\delta$} perovskites by annealing at 675 °C in H₂/N₂ flow for 4 hours [59]. Nakajima et al described the crystal structure of A-site disordered R_{0.5}Ba_{0.5}MnO₃ cubic perovskite cell and compared with corresponding RBaMn₂O₆ ordered perovskite [56]. The representation of the most significant structural feature of RBaMn₂O₆ (Fig. 1.3a, 1.3b) is that two types of rock-salt layers (RO and BaO) make the sandwich with the MnO₂ square sublattice. Therefore, the MnO₆ octahedron itself is distorted in a noncentrosymmetric manner that both Mn and oxygen atoms in the MnO₂ plane are displaced toward the RO layer (Fig. 1.3c), in contrast to the rigid MnO_6 octahedron in the A-site disordered manganite [56]. According to this explanation, it is easy to say that the structural and physical properties of RBaMn₂O₆ can be no longer explained in terms of the basic structural distortion as tolerance factor (t) for R_{0.5}B_{0.5}MnO₃ [60]. Fig. 1.3d and Fig. 1.3e show the structural data of Pr containing compounds synthesized at different synthetic

conditions and synthesized by procedure of ordered-disordered manganite perovskite, respectively [56].



Figure 1.3 - (a) Crystal structure and (b) structural concept of the A-site ordered manganite $RBaMn_2O_6$, and (c) an illustration of the distorted MnO_6 octahedron, (d) Structural parameters at room temperature plotted as a function of the degree of the A-site order (%) for Pr-compounds, (e) A scheme of sample preparation [56].

1.3 Oxygen non-stoichiometry

Currently, several reports available regarding defect models describing the oxygen excess in rare-earth manganites using cation vacancies in the metal sub-lattice [61, 62]. Cherepanov et al determined the maximum (NdMnO_{3.071}) and minimum (NdMnO_{3.01}) δ -value for neodymium manganite in air at 1100 °C and 1500 °C respectively [63]. The process of oxygen incorporation into ideal RMnO₃ accompanied with disordering in cation sub-lattice can be written using Kröger-Vink notation as follow [61-64]:

$$\frac{3}{2}O_2 = 3O_0^{\times} + V_R^{\prime\prime\prime} + V_{Mn}^{\prime\prime\prime} + 6h^{\cdot}$$
(1.2)

The replacement of rare-earth metal by a divalent metal ion A (Ba, Sr, Ca) promotes the increase in oxidation state of Mn from +3 to +4 in order to compensate the charge differences:

$$AO \xrightarrow{RMnO_3} A'_R + O_O^{\times} + Mn'_{Mn}$$
(1.3)

Here Mn^{3+} transformed into Mn^{4+} by the capturing of electron holes. In undoped rare-earth manganites a tendency of Mn^{3+} to raise its oxidation state in air condition is a driving force for the appearance of oxygen excess. Together with atomic disordering, the process of partial charge disproportionation is acknowledged in RMnO₃ oxides [61-64]:

$$2Mn_{Mn}^{\times} = Mn_{Mn}^{\bullet} + Mn_{Mn}^{\prime} \tag{1.4}$$

where Mn_{Mn}^{\bullet} , Mn_{Mn}^{\times} and Mn_{Mn}^{\prime} denote Mn⁴⁺, Mn³⁺ and Mn²⁺, respectively.

The oxygen non-stoichiometry at room temperature can be varied depending on heat treatment prehistory. Rørmark et al [64] reported the undoped and doped LaMnO_{3±δ} which was synthesized at different experimental condition. The synthesis conditions, crystal structure and oxygen content for LaMnO_{3±δ} and related materials are listed in **Table 1.1**.

It was reported that the substitution of Fe and Co for Mn and alkaline metal for R in RMnO₃ decreased the oxygen content since they served as acceptor-type dopants [62, 64, 65, 66]. The variation of oxygen nonstoichiometry versus temperature for similar types of perovskite oxide materials is shown in **Fig. 1.4** [66]. The substitution in both A- and B-sites of rare-earth element and Mn/Fe by Sr and Co respectively enhance the oxygen losses since they act as acceptor-type dopants (Sr'_{Nd}) and (Co'_{Fe}) . However, Sr-substitution in A-site (**Fig. 1.4a**) revealed a stronger effect on the oxygen content in comparison to B-site substitution. **Fig. 1.4b** describes the substitution effect of Fe by Co which leads to the decrease in oxygen content due to its electronegative nature in comparison with iron ($\chi_{Co} = 1.70$ and $\chi_{Fe} = 1.64$ in the Allred and Rochow scale) [67] and thus, formation of acceptor-type negatively Co'_{Fe} charged defect, which is compensated by the appearance of positive oxygen vacancies V_0 .



Figure 1.4 – Temperature dependencies of oxygen non-stoichiometry in $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ solid solutions in air: y = 0.3 (a) and x = 0.7 (b). (b)in air [66].

Table	1.1	—	The	crystal	structure,	synthesis	conditions	and	oxygen	non-
stoichi	ome	try	for va	arious m	anganites [[64].				

Materials	Structure	Annealing	Atmosphere	Delta(δ)
LaMnO _{3+δ}	Hexagonal/	1000 °C/96h +	Air	0.16
	Rhombohedral	1100 °C/5h		
$La_{0.8}Ca_{0.2}MnO_{3+\delta}$	Orthorhombic	1000 °C/96h	Air	0.07
$La_{0.6}Ca_{0.4}MnO_{3+\delta}$	Orthorhombic	1000 °C/96h	Air	0
$La_{0.4}Ca_{0.6}MnO_{3+\delta}$	Orthorhombic	1000 °C/96h	Air	0
$La_{0.2}Ca_{0.8}MnO_{3+\delta}$	Orthorhombic	1000 °C/96h	Air	0
CaMnO _{3+δ}	Orthorhombic	1100 °C/72h +	Air	0
		1200 °C/96h		
$La_{0.8}Sr_{0.2}MnO_{3+\delta}$	Hexagonal/	1150 °C/120 h	Air	0.06
	Rhombohedral			
$La_{0.6}Sr_{0.4}MnO_{3+\delta}$	Hexagonal/	1150 °C/60 h	Air	0
	Rhombohedral			
$La_{0.4}Sr_{0.6}MnO_{3+\delta}$	Tetragonal	1400 °C/24 h	Air	0
$La_{0.2}Sr_{0.8}MnO_{3+\delta}$	Cubic	1400 °C/24 h	Air	0
SrMnO _{3+δ}	Cubic	1100 °C/72 h	Air	0
SrMnO _{3-δ}	Cubic	1525 °C/2 h	Air	0.02

1.4 Thermal expansion coefficient (TEC)

The use of perovskite oxide materials at high temperature in fuel cells requires closely match TEC value between them and electrolyte materials [68]. Mixed electronic and ionic conductor such as $La_{1-x}Sr_xCoO_3$ is not only undergoes thermal expansion but expand due to chemical reduction of the transition-metal cation [69]. In case of perovskite oxide, the increasing temperature leads to the formation of oxygen vacancies and the decrease in average oxidation state of 3*d*-transition metals [70]. The change of oxidation state affects not only crystal structure, but also lattice volume due to the increase in metal-oxygen bond length.

The thermal expansion of lanthanum manganite and related materials has been studied using dilatometry and high-temperature XRPD [71, 72, 73]. **Fig. 1.5** shows the dilatometric behaviour of $La_{1-x}Sr_xMnO_{3-\delta}$ (0 < x < 0.5) and $La_{0.75}Sr_{0.25}Cu_{0.5-x}Co_xMn_{0.5}O_{3-\delta}$ (x = 0, 0.25, and 0.5) series [71, 72].



Figure 1.5 – Relative thermal expansion for (a) $La_{0.75}Sr_{0.25}Cu_{0.5-x}Co_xMn_{0.5}O_{3-\delta}$ (x = 0, 0.25, and 0.5) and (b) $La_{1-x}Sr_xMnO_3$ series versus temperature [71, 72].

Fig. 1.5b illustrates the relative thermal expansion of various Srsubstituted lanthanum manganites along with yttria stabilized zirconia (YSZ) [71]. As can be seen $\Delta L/L_0$ monotonically increases over the whole studied temperature range for x > 0.19. Small bend on temperature dependencies was observed at 750 and 800 °C for x = 0.1 and x = 0 samples respectively. This behaviour was due to structural transition which was confirmed using room temperature X-ray analysis of several quenched samples.

Table 1.2 shows the TEC values for $LaMnO_{3-\delta}$ and related materials as well as electrolytes materials.

Table 1.2 - Thermal expansion coefficients of various oxides in the temperature range of 25 - 1000 $^{\circ}$ C.

Materials	Temperature °C	Atmosphere	TEC×10 ⁻⁶ K ⁻¹	Ref		
LaMnO ₃	25-960	Air	10.7	71		
$La_{0.7}Sr_{0.3}MnO_{3-\delta}$	25-960	Air	11.7	71		
$La_{0.5}Sr_{0.5}MnO_{3-\delta}$	25-960	Air	12.5	71		
$La_{0.7}Ca_{0.3}MnO_{3-\delta}$	25-900	Air	12.28	74		
$La_{0.}Ca_{0.5}MnO_{3-\delta}$	25-900	Air	11.19	74		
LaFeO _{3-δ}	30-1000	Air	10.8	75		
La _{0.8} Fe _{0.2} O _{3-δ}	30-1000	Air	11.7	75		
LaCoO _{3-δ}	100-1050	Air	22.5	73		
La _{0.5} Ca _{0.5} CoO _{3-δ}	30-700	Air	18.2	76		
$La_{0.5}Sr_{0.5}CoO_{3-\delta}$	30-450	Air	16	76		
LaNiO _{3-δ}	30-1000	Air	13.2	77		
LaNi _{0.5} Fe _{0.5} O _{3-δ}	30-1000	Air	11	77		
LaSrMnCoO _{5+δ}	30-1000	Air	15.8	78		
SOFCs electrolytes						
YSZ	30-1000	Air	9.73	79		
LSGM	30-1000	Air	10.1	79		
$Ce_{0.8}Sm_{0.2}O_{2-\delta}$	30-1000	Air	12.32	80		
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	100-400	Argon	11.5	81		
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	100-400	Air	11.5	81		

1.5 Conductivity (σ) and Seebeck coefficient (S)

The electronic conductivity of manganites and their derivatives with the perovskite structure have been widely studied earlier. It was shown that electronic conductivity of RMnO₃ significantly varies with partial doping by various cations in A or B sub-lattices [82].

Fig. 1.6 shows the variation of conductivity with temperature and nature of dopants in both A and B-sites. The experimental data on electrical conductivity for La_{1-x}Sr_xMnO₃ series, which reveal highest conductivity for La_{0.33}Sr_{0.67}MnO₃ between 423 and 1073 K, are shown in **Fig. 1.6a** and **1.6b** [83]. At the lower temperature range (300–423 K) the La_{0.60}Sr_{0.40}MnO₃ sample exhibited the largest conductivity value. The temperature dependencies of conductivity for most of the samples demonstrate semiconductor-type behaviour over the studied temperature range. The metallic behaviour (the conductivity decreases with increasing temperature) was noticed in the high-temperature region for the samples with x = 0.33, 0.40 and 0.50.

Fig. 1.6c shows the temperature dependencies of dc-conductivity for La_{0.75}Sr_{0.25}Cu_{0.5-x}Co_xMn_{0.5}O_{3- $\delta}$} (x = 0, 0.25, and 0.5) where σ significantly increases with temperature and doping level (x) [72]. The highest conductivity for La_{0.75}Sr_{0.25}Cu_{0.5-x}Co_xMn_{0.5}O_{3- $\delta}$} at 850 °C was measured as 36.5, 90.5 and 173.7 S cm⁻¹ for x = 0.0, 0.25 and 0.5, respectively. Introduction of Co ions into B-site as a rule increases the conductivity value because of its mixed oxidation states. It was noticed that highest conductivity is correlated with strong hybridization between 3*d* orbital of transition metals and 2*p* orbital of oxygen. **Fig. 1.6d** represented the conductivity of La_{1-x}Sr_xCo_{1-y}Mn_yO₃ (0.00 ≤ x ≤ 0.10, 0.00 ≤ y ≤ 0.10) which increased with temperature. The increase of Sr concentration leads to higher conductivity and, in contrast, it decreases with increasing Mn concentration [84]. The conductivity values of doped and undoped oxides with the perovskite structure are listed in **Table 1.3**.



Figure 1.6 – (a) Temperature dependencies of electrical conductivity for (a) La_{1-x}Sr_xMnO₃ ($0 \le x \le 1.0$), and (b) enlarged view with a linear scale for $\sigma \le 1000$ S cm⁻¹ [83]. (c) Temperature dependence of dc-conductivity of La_{0.75}Sr_{0.25}Cu_{0.5-x}Co_xMn_{0.5}O_{3- δ} (x = 0, 0.25, and 0.5) series in air [72]. (d) Electrical conductivity (σ) plotted as a function of temperature in La_{1-x}Sr_xCo_{1-y}Mn_yO₃ (0.00 $\le x \le 0.10$, 0.00 $\le y \le 0.10$) [84].

The Seebeck coefficient (S) of $La_{1-x}Sr_xMnO_3$ ($0 \le x \le 1.0$) gradually decreases with the concentration of Sr and temperature and is found to change the sign from positive to negative as shown in **Fig. 1.7a** and **1.7b** [83]. The S value was negative in entire temperature range for $x \ge 0.33$, indicating that electrons are the main charge carriers. The maximum and minimum value of S at low temperature were found for x = 0 and x = 1, respectively.

Materials	Temperature, °C	σ, S/cm	Ref
LaMnO _{3-δ}	1000	80	86
$La_{0.7}Sr_{0.3}MnO_{3-\delta}$	1000	125	16
$Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$	1000	251	16
$Gd_{0.7}Sr_{0.3}MnO_{3-\delta}$	1000	92	16
$La_{0.5}Sr_{0.5}MnO_{3-\delta}$	1000	395	83
LaFeO _{3-δ}	800	0.10	77
$La_{0.7}Sr_{0.3}FeO_{3-\delta}$	700	120	87
LaCoO _{3-δ}	800	1000	88
La _{0.7} Co _{0.3} O _{3-δ}	800	1650	89
LaNiO _{3-δ}	800	40	77
LaNi _{0.5} Fe _{0.5} O _{3-δ}	800	190	77
$La_{0.75}Sr_{0.25}Co_{0.5}Mn_{0.5}O_{3-\delta}$	850	175	72
$La_{0.75}Sr_{0.25}Cu_{0.5}Mn_{0.5}O_{3-\delta}$	850	38	72

Table 1.3 - Total electrical conductivity of $\text{RMO}_{3-\delta}$ and related doped oxides in air.

Temperature dependencies of the Seebeck coefficient (S) for La₁. _xCa_xMnO_{3+ δ} ($0 \le x \le 1$) are shown in **Fig. 1.7c** [86]. With increasing of Ca concentration there was no change in the sign of S; it becomes more negative at higher concentration of Ca and almost temperature independent above 600 °C. Undoped LaMnO_{3+ δ} exhibits negative values of S, which absolute values decreasing with temperature while doped samples reveal positive values at low temperature and negative above 500 °C. Such behaviour proved coexistence of two different types of charge carriers in the oxides. The positive S value at low temperature indicates the electron holes as main charge carriers while electrons are the main charge carriers above 500 °C. For partially Ca-substituted lanthanum manganite it was shown that the decrease of temperature reduces carrier mobility, which leads to the increase of thermopower value [90]. The Seebeck coefficient for Ba-substituted lanthanum manganites La_{1-x}Ba_xMnO₃ exhibits similar behaviour like undoped LaMnO_{3+ δ} [91].

The Seebeck coefficient (S) versus temperature is plotted in **Fig. 1.7d** for $La_{1-x}Sr_xCo_{1-y}Mn_yO_3$ ($0.00 \le x \le 0.10$, $0.00 \le y \le 0.10$) [84]. The authors found positive S value for all samples in the whole temperature range studied. At low temperature, highest Seebeck coefficient (S) was found about 336 μ V/K, 220

 μ V/K and 258 μ V/K for LaCoO₃, La_{0.95}Sr_{0.05}CoO₃ and La_{0.95}Sr_{0.05}Co_{0.95}Mn_{0.05}O₃ respectively. These results indicate that simultaneous substitution of Sr and Mn at La and Co site respectively improved the Seebeck coefficient compared to Mn-free oxide. This phenomenon probably correlated with the 3*d* electron configuration and characteristic spin degeneracy of cobalt ions [92].



Figure 1.7 – (a) Temperature dependence of the Seebeck coefficient, S, for La_{1-x}Sr_xMnO₃ ($0 \le x \le 1.0$), and (b) enlarged view between $-100 \le S \le 50 \ \mu V \ K^{-1}$ [83]. (c) La_{1-x}Ca_xMnO_{3+ δ} ($0.0 \le x \le 1.0$) [86]. (d) La_{1-x}Sr_xCo_{1-y}Mn_yO₃ ($0.00 \le x \le 0.10, 0.00 \le y \le 0.10$) in air, [84].

1.6 Thermodynamic stability of lanthanum manganite and its chemical compatibility with electrolytes

The chemical compatibility of electrodes with electrolytes is very important in fuel cell industry. Several authors found that LaMnO₃, can react with yttria stabilized zirconia (YSZ) which is the main reason of SOFC

degradation [93, 94]. The product of chemical interaction $La_2Zr_2O_7$ forms at the interface between ZrO_2 -based solid electrolyte and the LaMnO₃-based cathode [93, 94]. The specific electrical resistivity of $La_2Zr_2O_7$ was three times larger than that for LaMnO₃ which significantly enhanced internal resistivity losses.

Numerous studies on the reaction between LaMnO₃ and YSZ have been reported earlier [93, 95, 96]. The reaction between film type electrodes and YSZ substrates also investigated where exchange with the atmosphere might play a significant role [93, 97]. **Fig. 1.8a** and **1.8b** show the microstructure of LaMnO₃ thick film electrodes on YSZ annealed for 2h and 100 h at 1450°C [95]. The 2 h annealed contact between the electrode and YSZ substrate was not so critical, however the duration of 100 h leads to obvious interaction (**Fig. 1.8b**). Due to application as electrode materials in SOFCs, LaMnO₃ and its derivatives were broadly studied for chemical compatibility with different electrolytes [98-107].



Figure 1.8 – Microstructure of LaMnO₃ thick film electrodes on YSZ annealed at 1450°C for (a) 2h. (b) 100h; LM = LaMnO₃, YSZ = yttria stabilized zirconia, $LZ = La_2Zr_2O_7$ [95].

1.7 The task setting and research overview

A literature review highlighted that $LaMnO_{3-\delta}$ and its derivatives have already been studied quite well in terms of phase stability, crystalline and defect structure, oxygen non-stoichiometry, conductivity, and other physicochemical properties.

To date, there is significant amount of reports available for lanthanum manganites but not much for neodymium manganite, as well as, iron- and cobalt-containing phases in particularly high temperature studies of oxygen non-stoichiometry, thermal expansion and conductivity. The room temperature crystal structure of $LnMnO_{3-\delta}$ and similar phases are described in literature but there are only few reports on high temperature structural studies along with thermal expansion of unit cell parameters and volume.

Thus, the purpose of this work was the systematic study of crystal structure and properties of complex oxide compounds $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) in order to establish the relationship between the chemical composition, structure and functional physicochemical properties. Therefore, the following tasks were assigned to this work:

- 1. Synthesis of $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) complex oxides and study of crystal structure at room temperature and high temperature.
- 2. Investigation of temperature dependence for oxygen non-stoichiometry and absolute value of oxygen content at room temperature.
- 3. Study of thermal expansion coefficient and comparison of the data obtained from dilatometry and HT-XRPD measurements.
- 4. Measurements of total conductivity and Seebeck coefficient for $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) versus temperature in air.

- 5. Determination of thermal and chemical compatibility of the $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ cathode material with the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte.
- 6. Impedance spectroscopy measurement in order to estimate the cathode performance in SOFCs.

2. EXPERIMENTAL TECHNIQUES

2.1 Characteristics of raw materials and sample synthesis

Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3- δ} were synthesized by a citrate-nitrate combustion technique where A = Ba, Sr and Ca; x = 0, 0.25; B = Mn, Fe, Co, Ni. Nd₂O₃ (Lanhit, 99.99%), Mn(CH₃COO)₂×4H₂O (Merck, \geq 99%), FeC₂O₄×2H₂O (Vekton, \geq 99.9%), Co(NO₃)₂×6H₂O (Merck, \geq 99%), Ni(CH₃COO)₂ (Merck, \geq 99%), BaCO₃ (Lanhit, 99.99%), SrCO₃ (Aldrich, \geq 99.9%) and CaCO₃ (Khimreaktivsnab, >99%), were used as initial reagents. Before synthesis, BaCO₃, SrCO₃ and CaCO₃ were calcined at 500 °C for 5 hours to remove adsorbed gases and moisture. The amount of hydrated water in Nd₂O₃ was determined by thermogravimetric analysis of the sample while heating from room temperature to 1000 °C in a synchronous thermal analyzer Netzsch STA 409 PC. The weight of the starting material was calculated on the required final mass of the synthesized oxide according to the following formula:

$$m_j = \frac{m_{ox} \cdot M_j \cdot i_{ox}}{M_{ox} \cdot i_j} \tag{2.1}$$

where m_j and M_j are the weighed and molar mass of component j respectively; m_{ox} is the final mass of oxide; M_{ox} is the molar mass of oxide; i_j and i_{ox} are the indices of this metal element in the formula of the initial component *j* and in the formula of the oxide being synthesized, respectively.

Scheme 1 shows the systematic synthesis procedure of the powder oxide materials. First of all, the initial reagents were dissolved in dilute nitric acid. Next, the solutions were mixed in a porcelain dish with the addition of citric acid monohydrate. The required weight of citric acid monohydrate can be calculated by equation (2.2),

$$m_{(C_6H_8O_7 \times H_2O)} = n \cdot \frac{m_{ox}}{M_{ox}} \cdot M_{(C_6H_8O_7 \times H_2O)}$$
(2.2)

where the number of moles per citric acid is *n* and $M_{(C_6H_8O_7 \times H_2O)}$ is the molar mass.



Scheme 1 – The synthesis process of powder oxide materials

The obtained solution was slowly evaporated on a hot plate at temperatures 150-200 $^{\circ}$ C until the ignition of the mixture and the formation of a dry grey residue. The resulting dry residue was ground to a powder using an agate mortar. Then the powder in alumina crucible was placed in a furnace and slowly heated (50 degrees / hour) to 1000 $^{\circ}$ C to remove unburned organic precursor residues and carbon.

In order to complete synthesis, the samples were annealed three times at 1100 °C in air for 20 hours and with intermediate grinding using ethanol. In order to study transport properties and thermal expansion, the dense ceramic was prepared. The obtained powders were uniaxially pressed into bars ($2 \times 4 \times 30$ mm) or tablets (15 mm in diameter) under pressure of 20 bar and sintered at 1350 °C in air for 20 hours. The density of the ceramic samples, as a rule, was \geq 90% of the theoretical value obtained from X-ray structural analysis data.

To obtain dense $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ ceramic, stoichiometric amount of prior annealed samarium oxide Sm_2O_3 and $Ce(NO_3)_3 \times 6H_2O$ was dissolved in dilute nitric acid. Next, an equimolar amount of citric acid monohydrate was added while stirring and then the solution was evaporated. The obtained dry residue was annealed at 1000 °C for 12 hours in air. Finally, the powder was uniaxially pressed into tablets under a pressure of 20 bar and sintered at 1600 °C in air for 20 hours.

2.2 X-ray Diffraction phase analysis

X-ray Powder Diffraction (XRPD) phase analysis was used to study the phase composition and crystal structure of the studied compounds. The XRPD is based on the fact that each individual phase has its own set of interplanar distances (d) and relative x-ray scattering intensities (I/I₀). Interplanar distances can be calculated by the Wulff–Bragg's formula:

$$2d\sin\theta = n\,\lambda\tag{2.3}$$

where d is the interplanar distance; θ is the scattering angle of x-ray beam; n is the order of reflection (n = 1); λ is the wavelength of the incident radiation. Bragg diffraction occurs when radiation, with a wavelength comparable to atomic spacings, is scattered in a specular fashion by the atoms of a crystalline system and undergoes constructive interference.

The study was carried out at room temperature on diffractometers Equinox 3000 (FWHM ~ 0.05 °) and Maxima XRD-7000 (FWHM ~ 0.01 °) using Cu-K α radiation ($\lambda = 1.5418$ Å). In the case of Maxima XRD-7000 diffractometers, the structural analysis was carried out in the range of 10 ° $\leq 2\theta \leq 120$ ° with a step of 0.02 ° and an exposure of 10 s at a point. The data for phase analysis were obtained in the range of angles of 10 ° $\leq 2\theta \leq 90$ ° with a step of 0.04 ° and an exposure of 2–4 s. When using an Equinox 3000 diffractometer with a position-sensitive detector, the survey was carried out in

the range of angles of 10 $^\circ \leq 2\theta \leq 90$ $^\circ$ with an exposure time of 30 to 60 minutes.

The phase identification of the samples was performed in the program "Match!" using the PDF-2, ICDD 2010 database. Refinement of unit cell parameters and atomic coordinates of the studied samples were performed using the Le Bail method (profile-matching mode) and the Rietveld method using the Fullprof software [108]. The program compares an experimental profile of diffraction pattern with theoretically calculated for the corresponding crystal structure. This software program can simulate and deliver the details of structural parameters (atomic coordinates, occupancy of positions) and profile parameters (line widths, scale factor, a function parameter describing a profile, constant crystal cell, background coefficients, total heat factor. The criteria for the quality of refinement are reliability factors, such as profile - R_{p} , weighted profile - R_{wp} , Bragg - R_{Br} , structural - R_{f} and expected - R_{exp} .

2.3 Determination of oxygen non-stoichiometry

2.3.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to determine the temperature dependences of oxygen nonstoichiometry (δ) of complex oxides $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca and B = Mn, Fe, Co, Ni; x = 0 and 0.25). Measurements were performed using a NETZSCH STA 409 PC Luxx thermal analysis instrument (**Fig. 2.2**). The mass changes of the samples were recorded in the temperature range of 30-1100 ° C, while the sample was in a continuous flow of air at the rate of 50 ml / min.

A single-phase sample in the form of powder was placed in an alumina crucible, previously annealed at 1100 ° C in air. The initial 2-3 g mass of oxide was taken. The exact mass of the initial oxide sample was determined using Sartorius BP221S analytical balance with an accuracy of $\pm 5 \times 10^{-4}$ g. The

powder into the crucible was heated at $1100 \circ C$ at a rate of $1.5 \circ C / min$, followed by cooling with an exposure of 12-20 hours every 100 ° C. The exposure time required to establish equilibrium in the sample (the mass of the sample remained unchanged for 2–3 hours) varied depending on the composition of oxide. To measure the temperature dependent mass change of studied samples with more accuracy, a correction was made by removing the baseline for an empty alumina crucible.



Figure 2.1 – Schematic image of a NETZSCH STA 409 PC instrument: 1 - weight unit; 2 - vacuum flange; 3 - gas inlet; 4 - vacuum tight alumina protective trumpet; 5 – an oven; 6 - a crucible with a sample; 7 - gas outlet; 8 - furnace lifting mechanism.

In the dynamic mode, the mass change of the sample was continuously recorded at heating and cooling rate of 1-2 K / min from room temperature to 1373 K in air. Reversible changes of the sample mass indicated that the exchange between solid and gas phase occurs only in oxygen by the reaction:

$$Nd_{1-x}A_{x}MnO_{3-\delta_{0}} \leftrightarrow Nd_{1-x}A_{x}MnO_{3-\delta_{i}} + \frac{\Delta\delta}{2}O_{2}(gas)$$
(2.4)

$$Nd_{1-x}A_{x}BO_{3-\delta_{0}} \leftrightarrow Nd_{1-x}A_{x}BO_{3-\delta_{i}} + \frac{\Delta\delta}{2}O_{2}(gas)$$
 (2.5)

$$Nd_{1-x}A_{x}Mn_{0.5}B_{0.5}O_{3-\delta_{0}} \leftrightarrow Nd_{1-x}A_{x}Mn_{0.5}B_{0.5}O_{3-\delta_{i}} + \frac{\Delta\delta}{2}O_{2} (gas)$$
(2.6)

where B = Mn, Fe, Co and Ni; $\Delta \delta = \delta_i - \delta_0$ is the relative oxygen nonstoichiometry; δ_0 – the absolute value of oxygen nonstoichiometry at initial conditions T°, PO₂°; δ_i – the absolute value of oxygen nonstoichiometry at the final state T_i, PO_{2i}.

The value $\Delta \delta = \delta_i - \delta_0$ is associated with the recorded mass changes of the samples for the transition from the initial to the final state by the following relationship:

$$\Delta \delta = \delta_i - \delta_0 = \frac{\Delta m \cdot M}{m_0 \cdot M_0} \tag{2.7}$$

where Δm is the mass change of the samples during the transition from the initial to the final state; m_0 – sample mass at fixed parameters T°, PO₂°, taken as a reference point; M – molecular weight of oxide; M₀ is the atomic mass of oxygen.

2.3.2. Iodometric titration technique

Iodometric titration method was performed to determine the absolute value of oxygen nonstoichiometry in $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; B = Mn, Fe, Co and Ni) at room temperature. The iodometric method (indirect) is based on the titration of iodine released during interaction of the oxidizing

agent with an excess of potassium iodide (KI). In this method, iodometric titration was performed with sodium thiosulfate.

Solution of sodium thiosulfate (Na₂S₂O₃×5H₂O) was prepared and standardized using the exact concentration of potassium dichromate (K₂Cr₂O₇). The concentration of sodium thiosulfate solution was determined six times for more accuracy. The sample of potassium dichromate with exactly known weight (~ 0.005 g) was dissolved in hydrochloric acid solution (1: 2) containing potassium iodide. During this process, oxidative-reduction reaction (2.8) with iodine release occurs. Next, the released iodine was titrated by ~ 0.025 (N) sodium thiosulfate solution (2.9).

$$Cr_2O_7^{2-} + 14H^+ + 9I^- \rightarrow 2Cr^{3+} + 3I_3^- + 7H_2O$$
 (2.8)

$$I_3^- + 2S_2 O_3^{2-} \to 3I^- + S_4 O_6^{2-} \tag{2.9}$$

The concentration of the studied solution of sodium thiosulfate was calculated by the following formula:

$$N_{Na_2S_2O_3} = \frac{6 \cdot m_{K_2Cr_2O_7}}{M_{K_2Cr_2O_7} \cdot V_{Na_2S_2O_3}}$$
(2.10)

where $m_{K_2Cr_2O_7}$ is the weight of K₂Cr₂O₇, g; $M_{K_2Cr_2O_7}$ is the molar mass of K₂Cr₂O₇, (g / mol); $V_{Na_2S_2O_3}$ is volume of sodium thiosulfate, (ml), followed by titration of this sample K₂Cr₂O₇.

Iodometric titration was performed using automatic potentiometric titrator ATP-02 (NPF "Akvilon") with a silver chloride electrode as reference electrode and platinum as indicator electrode. In this case, the titrator automatically added titrant solution $(S_2O_3^{2-})$, measured the potential (φ) of platinum oxidation recovery electrode relative to silver chloride and plotted the titration curve $\varphi = f$ $(V_{S_2O_3})$. The potential of the platinum electrode, which was determined potential for the pairs: I₂/I⁻, after - $S_4O_6^{2-}/S_2O_3^{2-}$ indicated an equivalent point at the end of the titration, a sharp and significant change in the potential of the platinum
electrode was observed. The accuracy of titrant volume determination is ± 0.002 ml, the indicator potential platinum electrode was determined with an accuracy of ± 0.1 V.

Experiments to determine the oxygen content in complex oxides were performed in the following way. Precise weights of $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca and B = Mn, Fe, Co, Ni; x = 0 and 0.25) were dissolved in hydrochloric acid solution in the presence of potassium iodide at a constant stirring.

When dissolving samples in a solution of hydrochloric acid containing an excess of KI, the following processes occur:

$$2Mn^{n+} + 3(n-2)I^{-} \rightarrow 2Mn^{2+} + (n-2)I_{3}^{-}$$
(2.11)

$$2B^{n+} + 3(n-2)I^{-} \rightarrow 2B^{2+} + (n-2)I_{3}^{-}$$
(2.12)

where n^+ is the average oxidation state of 3*d* metals in Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3- δ} (A = Ba, Sr, Ca and B = Mn, Fe, Co, Ni; x = 0 and 0.25).

The condition of electroneutrality for all studied samples can be written in the following way:

$$3(1-x) + 2x + n = 2(3-\delta)$$
(2.13)

Using the electroneutrality condition and the law of chemical equivalence, the final expression for calculating absolute non-stoichiometry for $Nd_{1-x}A_{x}Mn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Co), $Nd_{0.75}A_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Sr and Ca), $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ and $NdMn_{0.5}Ni_{0.5}O_{3-\delta}$ are:

$$\delta = \frac{-5000.m + 1240426.N.V - 283100.N.V.x + 15431.N.V.y - 5000.x.m)}{(79997.N.V - 10000.m)}$$
(2.14)

where $N_{Na_2S_2O_3}$ - normality of the Na₂S₂O₃ solution, mol eq / 1; $V_{Na_2S_2O_3}$ - is the volume of sodium thiosulfate, ml, followed by titration of this sample; m is the weight of the investigated oxide; *x* – alkaline earth metal; *y* is transition metal.

2.4 Method for determining thermal expansion

2.4.1 Dilatometric analysis

Measurement of linear thermal expansion coefficient (LTEC) of ceramic materials is necessary to determine the possibility of obtaining a strong contact of material with other parts of the electrochemical device (electrodes, current paths, sealants, etc.).

Dilatometric measurements were carried out in air using a Netzsch DIL402 dilatometer (**Fig. 2.2**) in the temperature range 30-1300 °C with heating / cooling rate of 2 K / min. The measurements were carried out on sintered ceramic samples of a length of 10–15 mm, which were previously mechanically polished so that the bar had strictly parallel faces.



Figure 2.2 – Schematic image of a dilatometer DIL 402 C: 1 - displacement sensor; 2-thermostatically controlled housing; 3 - vacuum flange; 4 – holder sample; 5 - pusher; 6 - sample; 7 - thermocouple; 8 - oven; 9 - gas output for analysis; 10 – entrance gas; 11 - the fixing nut; 12 - dilatometer base; 13 - vacuum tight alumina trumpet.

The measurement error of the change in the length of the sample is 0.01 microns. The initial sample length (L_0) was measured with a micrometre with an accuracy of 0.01 mm. The isobaric linear coefficient of thermal expansion was determined according to the equation:

$$LTEC = \sqrt[3]{\alpha_P} = \sqrt[3]{\frac{1}{V}(\frac{\partial V}{\partial T})_P} = \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_P \qquad (2.15)$$

from the slope of the experimental dependences $\Delta L / L = f(T)$, where α_P is the thermal extension coefficient, L_0 - sample length at room temperature, ΔL - current length change of the sample, T is the temperature.

2.4.2 High temperature x-ray diffraction phase analysis

For high-temperature X-ray phase analysis the following hightemperature camera: HTK 1200N (Anton Paar) installed on a Maxima XRD-7000 diffractometer was used. Measurements at various temperatures were carried out in the range of 30-1300 ° C in air with a step of 100 ° C. The instrumental parameters were the same as for measurements at room temperature.

The thermal expansion coefficients were calculated in the approximation that the samples under study are polycrystalline materials in which crystallites are randomly oriented [109]. In this case, the volumetric expansion (α_V) for the orthogonal samples can be determined by the following formula:

$$\alpha_V = \frac{1}{V_0} \left(\frac{dV}{dT} \right)_{\rm p} = \frac{1}{a_0} \left(\frac{da}{dT} \right)_{\rm p} + \frac{1}{b_0} \left(\frac{db}{dT} \right)_{\rm p} + \frac{1}{c_0} \left(\frac{dc}{dT} \right)_{\rm p}$$
(2.16)

where V_0 and a_0 , b_0 , c_0 denote the unit cell volume and the unit cell parameters at room temperature respectively. In this case, LTEC can be calculated by the

following equation:
$$\alpha_L = \frac{1}{3} \left(\frac{1}{a_0} \left(\frac{da}{dT} \right)_p + \frac{1}{b_0} \left(\frac{db}{dT} \right)_p + \frac{1}{c_0} \left(\frac{dc}{dT} \right)_p \right) \quad (2.17)$$

2.5 Methods of measuring electrical conductivity and Seebeck coefficient

The total conductivity of the studied compounds was measured using a four-probe DC method. The samples of the investigated oxides were polycrystalline bars with the sizes of $1 \times 3 \times 10 \text{ mm}^3$. For measuring the voltage drop on the sample during the experiment, potential contacts of platinum wire were attached to sample strictly parallel to the ends of the bar, after which the sample was placed vertically in the experimental setup between the two current leads. For a better electrical contact of the current leads with the sample, a pressing mechanism consisting of springs, alumina tube.

Potential contacts were connected respectively with the lower and upper S-type thermocouples. Thermocouples were connected to three voltmeters in such a way that two of them recorded the voltage on the thermocouples themselves, and the third one took the voltage off potential contacts. The current source and voltmeters used for measuring are part of the R-318 module included in a Zirconia-MR automatic partial pressure regulator. Measurements were carried out in air at the temperature range of 30–1000 ° C in the cooling mode with a step of 50 °C. From the obtained experimental data, the values of the total electrical conductivity (σ) and the Seebeck coefficient (S) can be calculated by the following formulas:

$$\sigma = \frac{I}{U} \cdot \frac{l}{s_c} \tag{2.18}$$

where *I* is the current supplied to the sample; *U* is the voltage drop on the sample; *l* is the distance between potential contacts; S_c is the cross-sectional area of the bar.

$$S = -\frac{U_0 - E_0}{\Delta T \cdot 0.001} + S^{Pt}(T_{av})$$
(2.19)

where U_0 is the measured value of thermo-emf; E_0 is the voltage across the cell at zero temperature gradient; ΔT is the temperature difference between the upper and lower potential contact; $S^{Pt}(T_{av})$ is the Seebeck coefficient of platinum receiving contacts with an average temperature T_{av} [110].

The obtained values of electrical conductivity and the Seebeck coefficient refer to the average temperature:

$$T_{av} = \frac{T_{up} + T_{down}}{2} \tag{2.20}$$

where T_{up} is the temperature of the upper thermocouple; T_{down} - temperature of the lower thermocouple.

2.6 Method of chemical compatibility test

To study the chemical compatibility of $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ oxides with solid electrolyte $Ce_{0.8}Sm_{0.2}O_{2-\delta}$, a mixture of aforementioned oxides with the 1: 1 weight ratio were prepared. After thorough grinding in an agate mortar, the mixture was placed into an alumina crucible and annealed at 1100 ° C for 70 hours in air. Before and after annealing, the powder mixtures were analyzed by XRD.The identification of the phase composition of the resulting powder mixtures was performed in the "Match!" Program using the PDF-2 database, ICDD 2010.

2.7 Method of impedance spectroscopy

То the measure impedance of the symmetrical cell with Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-δ} (NBMF55) electrodes, ultrasound was applied on the suspension of samples in alcohol. This ultrasound helps to reduce the particle size of the sample. The alcohol content sample was painted on both sides of the Ce_{0.8}Sm_{0.2}O_{2-δ} (SDC) pellet and then annealed at 1100 °C for 1 h in air. The measurements were performed using an Elins Z-2000 instrument in the 500-850 °C temperature interval and frequency range of 0.1 Hz to 2 MHz with an excitation voltage of 300 mV.

3. SYNTHESIS AND CRYSTAL STRUCTURE OF Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3- δ} (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25)

3.1 Room temperature crystal structure of $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25)

 $3.1.1 Nd_xA_{1-x}MnO_{3-\delta}$ (A = Ba, Sr and Ca; x =0 and 0.25)

XRPD patterns of $Nd_xA_{1-x}MnO_{3-\delta}$ (A = Ba, Sr and Ca; x =0 and 0.25) revealed that these oxides adopted the perovskite-like structure. According to the results of the Rietveld refinement performed with the help of the Fullprof program [108] all obtained oxides possesses the orthorhombic structure (*Pnma* space group) (**Fig. 3.1**). These are in good agreement with previously described results for $Nd_{1-x}A_xMnO_3$ [15, 25, 26]. The refined unit cell parameters and *R*-factors are listed in **Table 3.1**.

Table 3.1 – The unit cell parameters and R-factors for the $Nd_{1-x}A_{x}MnO_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) solid solutions.

Sample	Sp.gr.	a, Å	b, Å	c, Å	V, Å ³	$R_{b,}$ %	$R_f \%$
NMO	Pnma	5.723(4)	7.567(3)	5.406(1)	234.19(1)	16.8	10.9
NBMO	Pnma	5.495(1)	7.756(2)	5.478(1)	233.50(1)	12.2	10.1
NSMO	Pnma	5.466(3)	7.694(1)	5.452(3)	229.35(4)	13.1	9.43
NCMO	Pnma	5.481(2)	7.653(2)	5.409(1)	226.91(1)	11.3	8.76

Although the ionic radii of Nd³⁺ (1.27 Å) is smaller than those for alkali earth elements the unit cell volume of NdMnO_{3- δ} (NMO) is the largest compared to the A-substituted solid solutions (Table 3.1). This phenomenon can be explained by the raise of oxidation state of manganese from Mn³⁺ to Mn⁴⁺ due to the hetero-valent substitution [85]. The order of the unit cell volumes for the substituted oxides: Nd_{0.75}Ba_{0.25}MnO_{3- δ} (NBMO) > Nd_{0.75}Sr_{0.25}MnO_{3- δ} (NSMO) > Nd_{0.75}Ca_{0.25}MnO_{3- δ} (NCMO) is correlated with the relative sizes of dopant cations. The changes of unit cell parameters versus composition are more complicated and couldn't be explained simply by the size factor.



Figure 3.1 – Refined XPRD profiles of $Nd_{1-x}A_xMnO_{3-\delta}$ (A = Ba, Sr and Ca; x =0 and 0.25). The open red circles, black lines, the bottom blue lines and green vertical bars represent the experimental data, calculated pattern, difference curves and Bragg positions, respectively.

The refined relative atomic coordinates for $Nd_xA_{1-x}MnO_{3-\delta}$ (A = Ba, Sr and Ca; x =0 and 0.25) are listed in **Table 3.2.** Although the Rietveld refinement for all XRPD patterns of $Nd_xA_{1-x}MnO_{3-\delta}$ have better fit using the orthorhombic unit cell (sp.gr. *Pnma*) but the experiment of $Nd_{1-x}Ca_xMnO_3$ (0.3 $\leq x \leq 0.5$) and $Pr_{0.7}A_{0.3}MnO_3$ (A = Sr, Ca) using high resolution electron microscopy demonstrated monoclinic distortion at room temperature [33, 111]. So, it could be concluded that synthetic or heat treatment condition is very much important for the crystal structure of perovskite oxide. In order to establish a particular condition for the possible structural transformation between these structures additional structural studies are needed.

Table 3.2 – Relative atomic coordinates of the $Nd_{1-x}A_xMnO_{3-\delta}$ (A = Ba, Sr and Ca; x =0 and 0.25) crystal structure obtained by the Rietveld method.

Samples	NMO	NBMO	NSMO	NCMO
Nd	Nd	Nd/Ba	Nd/Sr	Nd/Ca
X	0.4376(8)	0.508(1)	0.5279(6)	0.5414(5)
У	0.25	0.25	0.25	0.25
Z	0.0138(2)	-0.000(1)	-0.0098(8)	-0.0082(9)
Mn	Mn	Mn	Mn	Mn
X	0	0	0	0
У	0	0	0	0
Z	0	0	0	0
O (1)	O (1)	O (1)	O (1)	O (1)
X	0.4769(4)	0.47(1)	0.492(4)	0.492(3)
У	0.25	0.25	0.25	0.25
Z	0.5800(3)	0.54(2)	0.47(1)	0.436(5)
O (2)	O (2)	O (2)	O (2)	O (2)
X	0.1798(9)	0.26(1)	0.714(4)	0.767(5)
У	0.0498(4)	0.01(1)	-0.02(1)	0.016(3)
Z	0.2187(3)	0.26(1)	0.23(1)	0.319(4)

$3.1.2 Nd_{1-x}A_{x}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x =0 and 0.25)

The obtained XRPD patterned of single phase $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x =0 and 0.25) exposed the orthorhombic perovskite-like structure which is in good agreement with the literature [112-117], although the synthesized nanostructured $La_{1-x}A_xFe_{0.5}Mn_{0.5}O_{3-\delta}$ series was indexed as cubic [118]. The Rietveld refined XPRD profiles of the studied samples are shown in

Fig. 3.2. 50% iron doped NdMn_{0.5}Fe_{0.5}O_{3- δ} (NMFO) was claimed as orthorhombic phase with *Pnma* or *Pbnm* space group [38, 39, 114, 119,120]. So. the preliminary refinements for the prepared **NMFO** and $Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (NBMFO) were performed using the reported orthorhombic based structural model (Fig. 3.2) and we obtained better fittings with calculated pattern reported in [114]. The results of Rietveld refinement are model in Table 3.3. The similar presented was applied for $Nd_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (NSMFO) and $Nd_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (NCMFO) but a closer inspection of the refined XRPD pattern for NCMFO exposed that the experimental peak near $2\theta \approx 44^{\circ}$ was not properly fitted with calculated one (see the inset in **Fig. 3.2**). Similarly, the disagreement between the experimental results and calculated profile for the refined XRPD pattern of NSMFO was detected near the peak at $2\theta \approx 54^{\circ}$. Further refinement of NSMFO and NCMFO using monoclinic unit cell with sp. gr. P21/n revealed better agreement of experimental XRPD pattern with the calculated profile. The unit cell parameters, volume, R-factors and crystal structure parameters refined by the Rietveld method for Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3- δ} (A = Ba, Sr and Ca; x =0 and 0.25) are summarized in Tables 3.3 and 3.4.

Table 3.3 – The unit cell parameters and R-factors refined by the Rietveld method of $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) solid solutions.

Samples	Sp. gr	a, Å	b, Å	c, Å	V, Å	$R_{B_{i}}\%$	$R_f \%$
NMFO	Pnma	5.673(2)	7.679(4)	5.431(3)	236.56(1)	4.82	4.80
NBMFO	Pnma	5.503(1)	7.776(3)	5.511(7)	235.89(2)	7.67	7.67
NSMFO	P21/n	5.462(3)	5.480(1)	7.723(4)	231.24(2)	5.16	7.32
	Pnma	5.464(3)	7.723(1)	5.479(4)	231.19(2)	8.80	12.7
NCMFO	P21/n	5.418(1)	5.488(3)	7.684(1)	228.53(1)	5.74	8.43
	Pnma	5.489(1)	7.685(3)	5.419(1)	228.59(1)	6.12	8.92
	Pnma	5.489(1)	7.685(3)	5.419(1)	228.59(1)	6.12	8.92



Figure 3.2 – Refined XPRD profiles for $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25). The open red circles, black lines, the bottom blue lines and green vertical bars represent the experimental data, calculated pattern, difference curves and Bragg positions, respectively.

The monoclinic distortion of NSMFO and NCMFO at room temperature could be compared with the reported for $Nd_{1-x}Ca_xMnO_3$ ($0.3 \le x \le 0.5$) and $Pr_{0.7}A_{0.3}MnO_3$ (A = Sr, Ca) materials studied using high resolution electron microscopy (HREM) [33, 111]. The authors claimed that the observed monoclinic distortions in $Nd_{1-x}Ca_xMnO_3$ ($0.3 \le x \le 0.5$) at room temperature could be the evidence of charge ordering [33, 121,122]. So, there is a possibility of charge ordering in NSMFO and NCMFO at low temperature. The unit cell volume decreases in the row NBMFO > NSMFO > NCMFO (**Table 3.3**) due to the decreasing radius of substituent cation [85]. **Table 3.5** shows the

comparative Me-O bond lengths analysis in $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ where the doping of Ba in NMFO led to a decrease in the Mn/Fe-O1 and Mn/Fe-O2 bond lengths. The latter may indicate a partial oxidation of the 3d-metals to higher oxidation states as it decreases their radius [85].

Table 3.4 – Structural parameters of the $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) solid solutions obtained by the Rietveld refinement.

Samples	NMFO	NBMFO	NSMFO	NCMFO
Space group	Pnma	Pnma	P21/n	P21/n
Nd	Nd	Nd/Ba	Nd/Sr	Nd/Ca
X	0.0567(3)	0.0142(4)	-0.002(2)	-0.0077(9)
У	0.25	0.25	0.030(3)	0.0404(3)
Z	0.0105(6)	0.001(2)	0.247(2)	0.248(1)
Fe/Mn	Fe/Mn	Fe/Mn	Fe/Mn	Fe/Mn
X	0	0	0.5/0	0.5/0
У	0	0	0/0.5	0/0.5
Z	0.5	0.5	0/0	0/0
O (1)	O (1)	O (1)	O (1)	O (1)
X	0.480(3)	0.504(5)	0.08(1)	0.079(4)
У	0.25	0.25	0.493(4)	0.484(3)
Z	-0.096(3)	-0.054(9)	0.25(1)	0.24 (2)
O (2)	O (2)	O (2)	O (2)	O (2)
X	-0.309(3)	0.238(9)	0.71(2)	0.70(1)
У	-0.044(2)	-0.033(5)	0.31(1)	0.30(1)
Z	-0.290(3)	-0.227(6)	0.038(9)	0.029(6)
O (3)	O (3)	O (3)	O (3)	O (3)
X	_	_	0.72(2)	0.72(1)
У	_	_	0.26(1)	0.28(1)
Z	—	_	0.46(1)	0.447(6)
β	90°	90°	89.989°	89.979°

Earlier, it was stated that the oxidation of GdBaMnFeO₅ to GdBaMnFeO₆ is correlated with the promotion of oxidation state of Mn ions from +2 to +4

while the oxidation state of Fe remained unchanged (+3) [123]. Partial substitution of Nd^{3+} by Ba^{2+} in NBMFO promotes changes from Mn^{3+} to Mn^{4+} (along with the formation of oxygen vacancies) to compensate the negative charge of acceptor-type dopant at the A-site. This contribution is the reason of decreasing unit cell volume with the Ba doping in NMFO. The value of β -angle is almost 90° (Table 3.4.) for both NSMFO and NCMFO which indicates that monoclinic distortions are very subtle at room temperature. So, it is unlikely to ordering (compared with $Nd_{0.7}Ca_{0.3}MnO_3$ expect **B**-site [121] and Nd_{0.5}Sr_{0.5}MnO₃ [122]) due to difference between Mn-O and/or Fe-O bond lengths, especially since this difference lies within the experimental error of XRPD (**Table 3.5**).

Table 3.5 – The selected Me-O bond lengths in the $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) solid solutions obtained by the Rietveld refinement

Selected bonds		Bone	d length d, Å	
	Nd	Nd/Ba	Nd/Sr	Nd/Ca
Nd-O1	2.29(2)	2.46(5)	2.34(6)	2.34(2)
Nd-O2	2.38(2)	n/a	2.34(8)	2.39(5)
Nd-O3	n/a	n/a	2.46(8)	2.35(5)
Mn-O1	n/a	n/a	2.09(1)	2.0(1)
Mn-O2	n/a	n/a	2.09(8)	1.99(5)
Mn-O3	n/a	n/a	2.03(8)	2.00(5)
Fe-O1	n/a	n/a	2.0(1)	1.9(1)
Fe-O2	n/a	n/a	1.91(9)	1.97(5)
Fe-O3	n/a	n/a	1.91(7)	1.98(5)
Mn/Fe-O1	1.993(4)	1.97(8)	n/a	n/a
Mn/Fe-O2	1.94(2)	1.93(4)	n/a	n/a

$3.1.3 Nd_{1-x}A_{x}Mn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25)

The initial Rietveld refinement of the X-ray powder diffraction data for $NdMn_{0.5}Co_{0.5}O_{3-\delta}$ was performed based on the orthorhombic settings with *Pnma* space group similar to earlier studied NdMnO₃ [124] and NdCoO₃ [125, 126] samples. It is well known that the orthorhombic *Pnma* space group does not allow B-site ordering due to the presence of only one crystallographic position 4b (1/2, 0, 0) for B-element [127]. In contrast the Rietveld refinement was performed based on the monoclinic settings with $P2_1/n$ space group to find the possibility of B-site ordering like that described for La₂CoMnO₆ [128]. This monoclinic space group has two non-equivalent crystallographic B-positions, B(1): 2c $(0, \frac{1}{2}, 0)$ and B(2): 2d $(\frac{1}{2}, 0, 0)$. The Rietveld refinement with monoclinic space group shows lower reliability factors compared to orthorhombic one (Table 3.6). Fig. 3.3 shows the Rietveld refinement of XPRD profiles of our studied samples. The refined unit cell parameters, and unit cell volumes with corresponding space groups for the studied $NdMn_{0.5}Co_{0.5}O_{3-\delta}$ (NMCO), $Nd_{0.75}Ba_{0.25}Mn_{0.5}Co_{0.5}O_{3-\delta}$ (NBMCO), $Nd_{0.75}Sr_{0.25}Mn_{0.5}Co_{0.5}O_{3-\delta}$ (NSMCO) and $Nd_{0.75}Ca_{0.25}Mn_{0.5}Co_{0.5}O_{3-\delta}$ (NCMCO) samples are listed in **Table. 3.6**.

Table 3.6 – The unit cell parameters refined by the Rietveld method, space group and R-factors for the $Nd_{1-x}A_xMn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) solid solutions.

Samples	Sp.gr.	a, Å	<i>b</i> , Å	<i>c</i> , Å	V , Å ³	$R_{b,}$ %	$R_f \%$
NMCO	P21/n	5.416(1)	5.534(1)	7.681(1)	230.32(8)	6.64	6.95
	Pnma	5.533(1)	7.681(1)	5.416(5)	230.23(7)	11.6	9.71
NBMCO	Pnma	5.445(8)	7.711(2)	5.469(8)	229.69(6)	11.9	13
NSMCO	P21/n	5.438(4)	5.430(4)	7.672(8)	226.60(1)	10.6	9.48
	Pnma	5.430(7)	7.671(3)	5.436(1)	226.47(3)	8.67	6.78
NCMCO	P21/n	5.391(6)	5.423(7)	7.625(2)	222.98	5.71	7.06
INCIVICO	Pnma	5.385(4)	7.626(3)	5.414(3)	222.36(9)	13.3	15.1

NBMCO was refined based on a structural model using orthorhombic phase with *Pnma* space group; it exhibited similarity with iron doped NBMFO. Sr and Ca doped oxides NSMCO and NCMCO were refined using orthorhombic and monoclinic settings with *Pnma* and $P2_1/n$ space groups respectively. Better *R*-factors assumes the orthorhombic structure for NSMCO unlike NSMFO, which was better described in terms of monoclinic structure (**Table 3.6**).



Figure 3.3 – Refined XPRD profiles of $Nd_{1-x}A_xMn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25). The open red circles, black lines, the bottom blue lines and green vertical bars represent the experimental data, calculated pattern, difference curves and Bragg positions, respectively.

Samples	NMCO	NBMCO	NSMCO	NCMCO
Sp.gr.	P21/n	Pnma	Pnma	P21/n
Nd	Nd	Nd/Ba	Nd/Sr	Nd/Ca
X	0.9891(2)	0.0098(4)	0.4686	-0.0060(6)
Y	0.0476	0.25	0.25	0.03622
Z	0.2533(2)	-0.0029(2)	-0.0020(9)	0.2489
Co/Mn	Co/Mn	Co/Mn	Co/Mn	Co/Mn
X	0/0.5	0	0	0.5/0
У	0.5/0	0	0	0/0.5
Z	0/0	0.5	0	0/0
0(1)	O (1)	O (1)	0(1)	O (1)
X	0.0695(7)	-0.0289(2)	0.1609(5)	0.0585(7)
y	0.4883(5)	0.25	0.0129(1)	0.5025(7)
Z	0.2800(9)	0.5399(1)	0.3090(5)	0.2255
O (2)	O (2)	O (2)	O (2)	O (2)
X	0.7978(9)	-0.2457(5)	0.4953(1)	0.7547(3)
y	0.1991(8)	0.4682(5)	0.25	0.3460
Z	-0.0326(7)	-0.7073(3)	0.4525(5)	0.0204(9)
O (3)	O (3)	O (3)	O (3)	O (3)
X	0.7792(4)	NA	NA	0.7133(6)
y	0.2125(9)	NA	NA	0.2820
Z	0.5543(4)	NA	NA	0.4438(1)
β	90.01°	90°	90°	90.07

Table 3.7 – Structural parameters of the $Nd_{1-x}A_{x}Mn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca) solid solutions obtained by the Rietveld refinement.

The unit cell volume of the $Nd_{1-x}A_xMn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) series is found to be decreased with the doping by relatively smaller atom in the row Ba, Sr and Ca. The sequence of unit cell volume of the samples is NMCO > NBMCO > NSMCO > NCMCO similarly to the pure

manganites and iron doped manganites. The value of β -angle is almost 90° (**Table 3.7**) for NMCO, NSMCO and NBMCO which indicates that monoclinic distortions are very subtle or absent at room temperature but rising of β value in Ca-doped NCMCO indicates the increase of monoclinic distortion. The structural parameters and space group of the studied Nd_{1-x}A_xMn_{0.5}Co_{0.5}O_{3- δ} (A = Ba, Sr and Ca; x = 0 and 0.25) solid solutions are summarized in **Table 3.7**.

$$3.1.4 NdNi_{0.5-x}T_xMn_{0.5}O_{3-\delta}$$
 (T = Co, Cu; x=0-0.5)

Fig. 3.4 shows the XRPD pattern of $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$ powder oxide refined by the Rietveld method. The initial refinement was performed using the orthorhombic model similar to the NdMn_{0.5}Fe_{0.5}O_{3- δ} sample, however better results were obtained when the XRPD pattern refined as the double phase containing the perovskite solid solution with monoclinic structure (sp.gr. *P2*₁/*n*) and impurity phase of NiO (sp.gr. *Fm3m*). **Fig. 3.4** reveals that the calculated profile satisfactorily describes the experimental data with *R*_B and *R*_f factors <5% with \approx 1% of NiO impurity. The tabulated structural parameters and selected bond lengths (**Table 3.8**) are in good agreement with reported neutron powder diffraction (NPD) results performed at 210 K in air [50]. The authors described the studied oxide with monoclinic structure containing two different octahedral positions occupied by Ni and Mn ions [50].

The summarized bond lengths in **Table 3.8** suggest that most of the B-site cations species existed in a form of Ni²⁺ and Mn⁴⁺, although small amounts of Ni³⁺ and Mn³⁺ could be present. This statement is in agreement with Sánchez-Benítez et al. [50] who clarified it by the charge disproportionation process Ni³⁺ + Mn³⁺ \rightarrow Ni²⁺ + Mn⁴⁺ and claimed that from the structural point of view this compound can be considered as a double perovskite of composition Nd₂NiMnO₆ [50]. Though, the degree of long-range ordering between Ni and Mn sites was equal to 88.4%. Taking into account these facts, it could be assumed that observed monoclinic distortions in NdNi_{0.5}Mn_{0.5}O_{3-δ} arise because

of the different size of MO_6 octahedra, formed by Ni^{2+} and Mn^{4+} , which are statistically located one after another (because of their equal concentrations) in three directions of the perovskite network [129].

Table 3.8 – The unit cell parameters, structural parameters and selected Me–O bond lengths for the monoclinic $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$ phase at room temperature obtained by the Rietveld method.

Atom	Site	Ref	ined coordinat	Selected	Bond length,	
Atom	Sile	x	у	Z.	bonds	Å
					Nd-O1	2.38(2)
Nd	4e	-0.0091(6)	0.0441(2)	0.250(1)	Nd–O2	2.40(5)
					Nd–O3	2.39(4)
					Ni–O1	2.09(5)
Ni	2c	0.5	0	0.5	Ni–O2	2.14(4)
					Ni–O3	2.11(4)
					Mn–O1	1.83(5)
Mn	2d	0.5	0	0	Mn–O2	1.81(4)
					Mn–O3	1.83(4)
01	4e	0.074(4)	0.482(3)	0.268(5)		
O2	4e	0.690(8)	0.265(8)	0.044(6)		
03	4e	0.727(8)	0.309(6)	0.461(6)		
						e (1) 9

sp. gr. P21/n, a = 5.4078(1) Å, b = 5.4792(1) Å, c = 7.6662(1) Å, V = 227.152(7) Å3, $\beta = 90.069^{\circ}$



Figure 3.4 – XPRD pattern of $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$ at RT refined by the Rietveld method

Fig. 3.5 shows the XRPD pattern of $Nd_2Ni_{1-x}Co_xMnO_{6-\delta}$ (0.2 $\leq x \leq$ 0.5) solid solutions refined by the Rietveld method. The formula of the studied samples is shown as the formula for double perovskite to make easier understanding of doping component. The initial refinement was performed using monoclinic structure (sp.gr. *P*2₁/n). The unit cell parameters, volume and structural parameters are summarized in **Table 3.9** and **Table 3.10** respectively based on the Rietveld refinement.



Figure 3.5 – XPRD pattern for $Nd_2Ni_{1-x}Co_xMnO_{6-\delta}$ (0.2 $\leq x \leq 0.5$) solid solutions at RT refined by the Rietveld method.

Samples	a, Å	b, Å	c, Å	V , Å ³	β	Rb, %	Rf %	χ^2
x = 0.2	5.410(2)	5.497(6)	7.676(6)	228.33(1)	90.064	5.22	6.01	2.00
x = 0.3	5.411(6)	5.500(1)	7.677(6)	228.52(4)	90.054	4.85	6.40	2.25
x = 0.4	5.412(9)	5.501(2)	7.678(3)	228.62(1)	90.047	4.86	5.73	1.96
x = 0.5	5.413(5)	5.509(4)	7.678(6)	229.00(0)	89.94	3.85	4.85	1.88

Table 3.9 – The unit cell parameters refined by the Rietveld method and R-factors for the $Nd_2Ni_{1-x}Co_xMnO_{6-\delta}$ (0.2 $\leq x \leq 0.5$) solid solutions.

Fig. 3.6 represents the variations of the refined unit cell parameters, volume and β -angle with the concentration of Co-substitution at room temperature. The unit cell parameters and unit cell volume increase with the increasing concentration of cobalt. In this complex system the substitution of Ni²⁺ by Co²⁺ enforces to produce the mixed oxidation state of transition metal ions which might be the reason of increasing unit cell parameters [85]. The β -angle value found to gradually decreases with the concentration of cobalt. This phenomenon implies that the higher concentration of cobalt leads to a transformation from monoclinic phase to orthorhombic phase at room temperature.

The metal-oxygen bond length of each cation is summarized in **Table 3.11**. The increase of Mn–O bond length and the decrease of Ni–O bond length observed after small amount of cobalt was incorporated instead of Ni in NdNi_{0.5}Mn_{0.5}O_{3. δ} confirms the fact that most of the Mn cations existed in mixed oxidation states Mn³⁺ and Mn⁴⁺ and Ni presumably existed in Ni²⁺ state. Introduction of Co seems to shift the distribution of oxidation states: Co slightly increases the mean oxidation state of 3-d ions in Ni-sites, and consequently decreases the mean oxidation state in Mn-Sites. The Mn–O bond length also found to increase with the increasing doping concentration of Co. This might be corelated with the increasing concentration of Mn³⁺ due to decreasing bond length of Ni/Co–O [85]. This bond length data has good agreement with the

increasing unit cell volume with cobalt concentration [85]. It worth noting that since the accuracy of XRD for determination of light atom coordinates like oxygen is low, further structural study is needed in order confirm the aforementioned conclusions.

Table 3.10 – Structural parameters of the $Nd_2Ni_{1-x}Co_xMnO_{6-\delta}$ (0.2 $\leq x \leq 0.5$) solid solutions obtained by the Rietveld refinement.

Samples	x = 0.2	x = 0.3	x = 0.4	x = 0.5
Sp. Gr.	P21/n	P21/n	P21/n	P21/n
Nd	Nd	Nd	Nd	Nd
Χ	-0.0064(2)	-0.0057(7)	-0.0092(1)	-0.0092(2)
Y	0.0459(5)	0.0458(2)	0.0454(1)	0.0468(4)
Z	0.2441(1)	0.2535(1)	0.2525(3)	0.2523(9)
Ni/Co	Ni/Co	Ni/Co	Ni/Co	Ni/Co
Χ	0	0	0	0
Y	0.5	0.5	0.5	0.5
Z	0	0	0	0
Mn	Mn	Mn	Mn	Mn
Χ	0.5	0.5	0.5	0.5
Y	0	0	0	0
Z	0	0	0	0
0(1)	0(1)	0(1)	0(1)	0(1)
Χ	0.0823(3)	0.0788(1)	0.0778(9)	0.0882(2)
Y	0.4850(3)	0.4794(4)	0.4789(4)	0.4868(1)
Z	0.2360(4)	0.2474(2)	0.2337(7)	0.2277(3)
O (2)	O (2)	O (2)	O (2)	O (2)
Χ	0.7740(5)	0.7035(2)	0.6851(2)	0.7261(9)
Y	0.1885(1)	0.3257(2)	0.2670(7)	0.2987(4)
Z	-0.0461	0.0446(3)	0.0388(1)	0.0392(1)
O (3)	O (3)	O (3)	O (3)	O (3)
Χ	0.8138(3)	0.6971(1)	0.7142(5)	0.6925(9)
Y	0.2507(9)	0.2354(6)	0.3146(2)	0.2918(1)
Ζ	0.5385(7)	0.4603(3)	0.4626(5)	0.4579(1)



Figure 3.6 – The variation of (a, b) unit cell parameters, (c) unit cell volume, (d) β angle with the concentration of Co-substitution in Nd₂Ni_{1-x}Co_xMnO_{6- δ} (0.2 \leq x \leq 0.5) at room temperature.

Table	3.11	—	Selected	М-О	bond	lengths	for	the	monoclinic	Nd_2Ni_{1-}
_x Co _x M	nO _{6-δ}	(0.2	$2 \le x \le 0.5$	5) phase	e at roc	om tempe	ratur	e obt	ained by the	Rietveld
metho	d.									

Atoms		x = 0.2	x = 0.3	x = 0.4	x = 0.5
Atom	Atom	d 1, 2 (Å)			
1	2				
Nd	01	2.324(3)	2.338(3)	2.365(3)	2.308(3)
Nd	O2	2.354(5)	2.38(6)	2.412(7)	2.425(8)
Nd	O3	2.462(5)	2.428(6)	2.36(6)	2.349(8)
Ni Co	01	1.867(5)	1.85(5)	1.847(6)	1.814(5)
Ni Co	O2	2.031(5)	1.95(6)	2.901(6)	1.871(8)
Ni Co	O3	2.207(5)	2.024(6)	1.988(6)	1.941(7)
Mn	01	2.076(5)	2.083(5)	2.097(6)	2.115(5)
Mn	02	1.846(5)	1.862(5)	1.874(6)	1.933(7)
Mn	03	1.726(6)	2.212(6)	1.874(6)	2.005(8)

Fig. 3.7 shows the XRPD pattern for $Nd_2Ni_{1-x}Cu_xMnO_{6-\delta}$ ($0.2 \le x \le 0.5$) solid solutions refined by the Rietveld method. The refinement of the series was performed using monoclinic structure with $P2_1/n$ space group. The refined unit cell parameters, unit cell volume and structural parameters are summarized in **Table 3.12** and **Table 3.13**.



Figure 3.7 - XPRD pattern of $Nd_2Ni_{1-x}Cu_xMnO_{6-\delta}$ ($0.2 \le x \le 0.5$) solid solutions at RT refined by the Rietveld method.

Fig. 3.8 represents the dependencies of the refined unit cell parameters, unit cell volume and β -angle with the concentration of copper at room temperature. The unit cell parameters (*a*,*b*) increased compared to undoped sample and exhibited tiny raise with the increasing of copper content while c parameter first increases compared to the undoped Nd₂NiMnO_{6- δ}, but then monotonically decreases unlike cobalt series. The unit cell volume is slightly increases with the

increasing of Cu content, which is in agreement with the size factor since the ionic radius of copper (rCu²⁺/Cu³⁺ 0.87/0.68 Å; CN = 6) is slightly larger than that for nickel (rNi²⁺/Ni³⁺ = 0.79/0.72 Å; CN = 6) [85]. It is interesting to note that unlike Co-doped samples, β angle value found to gradually increase with the concentration of copper. This illustrates that Cu-substitution increases monoclinic distortions of the perovskite structure while Co incorporation leads to the increase of symmetry.



Figure 3.8 – The variation of (a, b) unit cell parameters, (c) unit cell volume, (d) β angle with the concentration of Cu-substitution in Nd₂Ni_{1-x}Cu_xMnO_{6- δ} (0.2 \leq x \leq 0.5) at room temperature.

Samples	a, Å	b, Å	c, Å	V, Å ³	β	R <i>b</i> %	R f %
x = 0.2	5.413(8)	5.494(1)	7.669(1)	228.11(2)	90.063	4.50	5.68
x = 0.3	5.414(5)	5.496(1)	7.668(6)	228.20(1)	90.071	5.27	6.74
x = 0.4	5.416(6)	5.500(1)	7.667(6)	228.43(6)	90.076	4.72	5.63
x = 0.5	5.418(2)	5.507(1)	7.663(5)	228.67(1)	90.085	4.66	5.47

Table 3.12 – The unit cell parameters refined by the Rietveld method and R-factors for the $Nd_2Ni_{1-x}Cu_xMnO_{6-\delta}$ (0.2 $\leq x \leq 0.5$) solid solutions.

Table 3.13 – Structural parameters of the $Nd_2Ni_{1-x}Cu_xMnO_{6-\delta}$ ($0.2 \le x \le 0.5$) solid solutions obtained by the Rietveld refinement.

Samples	x = 0.2	x = 0.3	x = 0.4	x = 0.5
Sp. Gr.	P21/n	P21/n	P21/n	P21/n
Nd	Nd	Nd	Nd	Nd
X	-0.0072	-0.0088	-0.0062	-0.0085
У	0.0452	0.0447	0.0456	0.0461
Z	0.2539	0.2525	0.2446	0.2451
Ni/Co	Ni/Cu	Ni/Cu	Ni/Cu	Ni/Cu
X	0	0	0	0
У	0.5	0.5	0.5	0.5
Z	0	0	0	0
Mn	Mn	Mn	Mn	Mn
X	0.5	0.5	0.5	0.5
У	0	0	0	0
Z	0	0	0	0
0(1)	0(1)	0(1)	0(1)	0(1)
X	0.0795	0.0845	0.0726	0.0775
У	0.4844	0.4813	0.4840	0.4822
Z	0.2391	0.2285	0.2750	0.2793
O (2)	O (2)	O (2)	O (2)	O (2)
X	0.6942	0.7063	0.6951	0.6953
У	0.2731	0.2730	0.2933	0.3048
Z	0.0375	0.0442	0.0383	0.0474
O (3)	O (3)	O (3)	O (3)	O (3)
X	0.7132	0.7216	0.7161	0.7294
y	0.3048	0.3079	0.2927	0.2774
Ζ	0.4524	0.4658	0.4468	0.4604

The values of metal-oxygen bond length are summarized in **Table 3.14**. The slight increase of Mn-O bond length found after small amount doping of copper ion in B site suggests that small amount of Mn cations coexisted in mixed form Mn³⁺ and Mn⁴⁺. The Mn–O bond length monotonically decreases and the Ni/Cu–O bond length increases with the increasing doping concentration of Cu which may due to the increasing concentration of Mn⁴⁺ and Ni²⁺ respectively [85]. To confirm this data obtained from XRPD refinement, we need further structural investigation using neutron or electron diffraction methods.

Table 3.14 – Selected M–O bond lengths for the monoclinic $Nd_2Ni_{1-x}Cu_xMnO_{6-\delta}$ ($0.2 \le x \le 0.5$) phase at room temperature obtained by the Rietveld method.

Atoms		x = 0.2	x = 0.3	x = 0.4	x = 0.5
Atom 1	Atom 2	d 1,2 (Å)	d 1,2 (Å)	d 1,2 (Å)	d 1,2 (Å)
Nd	01	2.331(6)	2.353(3)	2.364(1)	2.369(4)
Nd	O2	2.396(5)	2.408(6)	2.388(1)	2.318(7)
Nd	03	2.3640(5)	2.413(6)	2.432(1)	2.458(8)
Ni Cu	01	2.335(6)	2.234(5)	2.149(1)	2.181(4)
Ni Cu	O2	2.091(5)	2.049(6)	2.022(1)	2.007(7)
Ni Cu	03	2.064(4)	2.01(5)	1.983(1)	1.95(8)
Mn	01	1.983(6)	1.824(5)	1.774(1)	1.748(4)
Mn	O2	1.862(4)	1.901(6)	1.958(1)	2.005(7)
Mn	03	1.913(5)	1.858(6)	1.836(1)	1.815(9)

$3.1.5 Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$

In order to study the structure of mixed ferrite manganite of Nd and Ba with 1:1 ratio complex oxide with the Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3- δ} (NBMF55) overall composition was prepared at 1350°C in air. The XRPD pattern of NBMF55 refined by the Rietveld method is shown in **Fig. 3.9**. This sample crystallized in the ideal cubic perovskite structure (sp. gr. *Pm3m*) with *a* = 3.89824(7) unlike to the Ba-poorer samples NMFO and NBMFO, which

possessed the orthorhombic distortions. The comparable studies have been done by several research groups with similar materials [130-137]. The absolute δ value and the average oxidation state of 3d-metals (Z) of disordered sample were equal to 2.86(2) and +3.22 at room temperature, respectively.



Figure 3.9 – Rietveld refined XPRD profile of $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$. The open red circles, black lines, the bottom blue lines and green vertical bars represent the experimental data, calculated pattern, difference curve and Bragg reflections, respectively.

3.2 HT structural analysis of $Nd_{1-x}Ba_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (x=0.25 and 0.5), $Nd_{0.75}Ba_{0.25}Mn_{0.5}Co_{0.5}O_{3-\delta}$ and $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$

<u> $3.2.1 Nd_{1-x}Ba_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (x 0.25 and 0.5)</u>

Fig. 3.10 shows the results of high temperature XRPD (HT-XRPD) measurements for NBMFO sintered at 1350 °C in air. It has the orthorhombic structure with sp. gr. *Pnma*, which is remained unchanged within the whole temperature range studied 25–1000 °C. The small impurity phase appeared at T = 200 °C, which peaks appear in the range $31^{\circ} \le 2\theta \le 32^{\circ}$ whose intensity remains almost constant until T = 1000 °C. These additional peaks can be attributed to BaFeO_{2.5} or BaMnO₃ [114].



Figure 3.10 – HT-XRPD patterns of NBMFO. Inset shows the enlargement view of peak.

The NBMFO sample cannot be obtained as a single phase at 1100 °C in air but it lies very close to the homogeneity range limit according to the phase diagram for the NdMnO₃–BaMnO₃–BaFeO_{2.5}–NdFeO₃ system [114]. An increase in the synthesis temperature up to 1350 °C permitted to obtain singlephase NBMFO which was supported by room temperature XRPD of the sample cooled down at the rate of 100 °C/h. This result confirmed that 100 °C/h cooling rate allowed to "freeze" high-temperature single-phase state, i.e. the sample did not have enough time to equilibrate with atmospheric oxygen. In contrast, the HT-XRPD experiment with slow heating with 1 h dwell every 100 °C allowed NBMFO to gain an equilibrium oxygen content and Mn oxidation state. As a result, the increase in Mn⁴⁺ concentration led to the formation of aforementioned impurities.



Figure 3.11 – HT-XRPD patterns of NBMF55. Inset shows the enlargement view of peak.

High-temperature XRPD measurements were performed for NBMF55 up to 1000 °C. The XRPD data were collected at each 200° C step. **Fig. 3.11** shows the HT-XRPD profiles for $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ indicated that the cubic phase with sp. gr. *Pm3m* which was stable up to 1000°C in air with no decomposition and structural transitions observed in the temperature range studied.

<u>3.2.2 NdNi_{0.5}Mn_{0.5}O_{3-δ}</u>

The HT-XRPD measurements for $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$ indicated that the monoclinic phase remains stable up to 1000°C in air (**Fig. 3.12**). There was no decomposition and structural transitions observed in the whole temperature range studied. The inset of **Fig. 3.12** shows the overlapping of peaks with temperature near 32.8° which can be explained by an increase in unit cell parameters resulting in the shifting of peaks towards the smaller 20 values.



Figure 3.12 – HT-XPRD patterns of $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$. Inset shows the enlargement view of peak.

$3.2.3 Nd_{0.75}Ba_{0.25}Mn_{0.5}Co_{0.5}O3_{-\delta}$

Fig. 3.13 shows the XRPD pattern of NBMCO at room temperature and 900 °C refined by the Rietveld method. A precise inspection of XRPD results reveals the presence of small amount of impurity. The refinement was performed using double phase model with impurity phase for XRD pattern collected at RT while triple phase model was performed for the XRD pattern collected at 900 °C.



Figure 3.13 – HT-XPRD patterns of NBMCO. The open black circles, red lines, the bottom blue lines and green vertical bars represent the experimental data, calculated pattern, difference curve and Bragg reflections, respectively.

The refined data suggests that the presence of cubic $(Co,Mn)_3O_4$ impurity phase ($\approx 1\%$) at room temperature. Triple phases refinement at 900 °C demonstrated that some amount of $(Co,Mn)_3O_4$ impurity have disappeared due to reduction process and the formation of (Co,Mn)O phase, but still tiny amount of $(Co,Mn)_3O_4$ has been found $\approx 0.25\%$ (**Fig. 3.13**). The unit cell parameters and volume of NBMCO at 900 °C are a = 5.528 Å, b = 7.824 Å, c = 5.519 Å, V = 238.77 Å³, respectively.

4. TEMPERATURE DEPENDENCE OF PHYSICAL AND CHEMICAL PROPERTIES

4.1 Oxygen non-stoichiometry of $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25).

4.1.1 $Nd_xA_{1-x}MnO_{3-\delta}(A = Ba, Sr and Ca; x = 0 and 0.25)$

Fig. 4.1 shows the temperature dependence of mass losses (Δ m/m) for Nd_xA_{1-x}MnO_{3-δ} (A = Ba, Sr and Ca; x = 0 and 0.25) associated with oxygen release. The observed curves show relatively weak temperature dependence of oxygen content. The maximum mass loss (~0.5%) was found for the undoped NMO sample at 1000°C. It is known that neodymium manganite NMO possesses oxygen excess at relatively low temperature and sharp drop of mass at T>600 °C is associated with the release of oxygen excess. Introduction of alkaline earth metals significantly decreases the oxygen content, and they become oxygen deficient even at room temperature [61-64].

If we assume NMO as ideal crystal, then partial substitution of Nd by alkali earth metal causes at least two accompanied processes in order to maintain electroneutrality condition, which can be written using the Kröger-Vink notation as follows:

1. Partial substitution of Nd by alkali earth metals leads to increase in Mn oxidation state:

$$2AO + 2Nd_{Nd}^{\times} + 2Mn_{Mn}^{\times} + \frac{1}{2}O_2 \to 2A'_{Nd} + 2Mn_{Mn}^{\bullet} + Nd_2O_3 \quad (4.1)$$

2. Partial substitution of Nd by alkali earth metals leads to formation of oxygen vacancies:

$$2AO + 2Nd_{Nd}^{\times} + O_0^{\times} \to 2A_{Nd}' + V_0^{\bullet \bullet} + Nd_2O_3$$
(4.2)

3. The release of oxygen upon heating can be written as follows:

$$2Mn_{Mn}^{\bullet} + 0_0^{\times} \to \frac{1}{2}O_2 + 2Mn_{Mn}^{\times} + V_0^{\bullet\bullet}$$
(4.3)

The release of oxygen for all A-site doped samples starts at 600-700°C and can be described by eq. (4.3).



Figure 4.1 – Temperature dependencies of relative mass loss for $Nd_xA_{1-x}MnO_{3\pm\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) in air.

4.1.2 $\underline{Nd_{x}A_{1-x}Mn_{0.5}Fe_{0.5}O_{3-\delta}(A = Ba, Sr and Ca; x = 0 and 0.25)}$

Table 4.1 shows the absolute values of oxygen non-stoichiometry for $Nd_xA_{1-x}Mn_{0.5}Fe_{0.5}O_{3\pm\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) in air at room temperature, calculated from the results of chemical analysis: dichromatometric titration with Mohr salt (δ_1) or iodometric titration (δ_2). The oxygen deficiency increases with the substitution of Nd by alkali earth metals (Ba, Sr or Ca), since the latter serve as acceptor-type dopants. If we assume Nd³⁺Mn³⁺_{0.5}Fe³⁺_{0.5}O²⁻ as an ideal state, then the formation of oxygen vacancies V^{••} with introduction of

alkali earth metals can be written by using Kröger-Vink notation similarly as described in equations (4.2) and (4.3).

Table 4.1 – Oxygen non-stoichiometry δ and average oxidation state Z⁺ of 3dmetals in Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3- δ} (A = Ba, Sr and Ca; x =0 and 0.25) at RT; δ_1 denotes results of dichromate titration with Mohr salt, δ_2 – results of iodometric titration.

Sample name	Z^+	δ_1	δ_2
NdMn _{0.5} Fe _{0.5} O _{3-δ}	3.01	-0.003 ± 0.02	n/a
$Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	3.16	0.067 ± 0.02	n/a
$Nd_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	2.94	0.15 ± 0.02	0.17 ± 0.02
$Md_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	2.87	0.19 ± 0.02	0.21 ± 0.02

Table 4.1 shows the δ_1 and δ_2 values, which are in good agreement with each other within the experimental error; although, the slightly higher values were obtained from the iodometric titration results. These two techniques are based on slightly different fundamental concept: only Mn cations participate in redox reaction with Mohr salt while in iodometric titration both cations are reduced to +2 oxidation state. Thus, it can be assumed that while most Fe cations are in +3 oxidation state in NSMFO and NCMFO, but some small amount of Fe²⁺ is present in the samples.

The experimental curve of $\delta = f(T)$ and $Z^+ = f(T)$ in air for Nd_xA₁. _xMn_{0.5}Fe_{0.5}O_{3- δ} (A = Ba, Sr and Ca; x = 0 and 0.25) compounds is shown in **Fig. 4.2**, where Z⁺ is an average oxidation state of 3*d*-metals. The experimental curves illustrate relatively weak dependency of oxygen non-stoichiometry versus temperature, which is in good agreement with the data reported for La_{1-x}Sr_xMn_{0.5}Fe_{0.5}O_{3- δ} [138].

The release of oxygen for NMFO and NBMFO starts only at 750–800 °C, while for NSMFO and NCMFO oxygen deficiency visibly increases already at comparatively lower temperature (350–400 °C).



Figure 4.2 – Temperature dependencies of oxygen non-stoichiometry δ and average oxidation state of 3d-metals Z⁺ in Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3- δ} (A = Ba, Sr and Ca; x = 0 and 0.25) in air.

The doping with alkaline earth metals affects the oxidation state of 3*d*metals which is obviously seen from the calculated values of average oxidation state Z⁺ (**Fig. 4.2**). Here at the first approximation we assumed that all iron atoms are existed as Fe³⁺, i.e. we neglected Fe²⁺ ions and assumed that only Mn cations changed their oxidation state in Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3- δ}. Such approach had been used earlier for this type of oxides [123]. The Z⁺ values higher than 3 for NBMFO and Z⁺ values < 3 for NSMFO and NCMFO respectively (**Fig. 4.2**,) demonstrate the presence of Mn⁴⁺ in the Ba-containing phase, while Mn²⁺ appears in the Sr- and Ca-doped compounds. Such result appears from the experimental fact of noticeably lower oxygen deficiency for NBMFO compared to NCMFO. The coexistence of point defects in Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3- δ} can be shown by the electroneutrality condition:

$$[Mn_{Mn}^{\bullet}] + 2[V_0^{\bullet\bullet}] = [A'_{Nd}] + [Mn'_{Mn}] + [Fe'_{Fe}]$$
(4.4)

where $[Mn'_{Mn}]$ and $[Mn^{\bullet}_{Mn}]$ represent the electron and electron hole localized on Mn^{3+} cations, respectively; $[Fe'_{Fe}]$ signifies the electron localized on Fe³⁺ cation.

The gradual decrease in the oxidation state of Mn cations from Mn^{+4} to Mn^{+2} for NBMFO, NSMFO, NCMFO respectively, probably the effect of radius decreases at the A-site, which allows the radius increase at the B-site and, thus, promotes the reduction from Mn^{4+} to Mn^{2+} [85].

4.1.3 $\underline{Nd_{1-x}A_{x}Mn_{0.5}Co_{0.5}O_{3-\delta}}$ (A = Ba, Sr and Ca; x = 0 and 0.25)

Temperature dependencies of oxygen non-stoichiometry (δ) and average oxidation state of 3d metals in air for $Nd_{1-x}A_{x}Mn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) have shown in **Fig. 4.3**. All the samples show very small oxygen release rate below the 700 °C. The release of oxygen for $Nd_{1-x}A_{x}Mn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25) solid solutions starts at 750-800°C which is very similar to the iron doped series. For all studied samples a sharp TGA drop was observed between 800 and 900 °C. This data clearly indicate that all the studied samples might contain some impurities, for example, Mn-doped cobalt oxide or Co-doped Mn oxide. This assumption has been confirmed by the aforementioned results of HT-XRD measurements for NBMCO (Fig. 3.13). It is known that during heating in air Co_3O_4 reduces to CoO at 900-910 °C [158]. This equilibrium is reversible and usually a reverse oxidation takes place at the same temperature on cooling. Partial substitution of Co by Mn should enhance the stability of (Co,Mn)₃O₄ and therefore increased the transformation temperature in air. However, earlier it was shown that the oxidation temperature of (Co,Mn)O annealed for some time at 1300°C shifted to the significantly lower values compared to the reduction temperature down to 800°C. Here, the presented TGA data was collected during cooling of the samples which were equilibrated for prolonged period at 1100 °C down to room
temperature. So, the oxygen uptake starts during cooling and we also observed a visible mass increase due to the oxidation process in vicinity of 800°C, which is in good agreement with the results reported by Bordeneuve et al. [158].



Figure 4.3 – Temperature dependencies of oxygen non-stoichiometry (δ) and average oxidation state of 3*d*-metals (Z+) in Nd_{1-x}A_xMn_{0.5}Co_{0.5}O_{3- δ} (A = Ba, Sr and Ca; x = 0 and 0.25) solid solutions in air.

The absolute values of δ measured by iodometric titration at room temperature are summarized in Table 4.2. The room temperature δ value of undoped NMCO is 0.08±0.02 which is in a good agreement with reported one for LaMn_{0.5}Co_{0.5}O_{3- δ} [139]. Yanez-Vilar et al [139] synthesized LaMn_{0.5}Co_{0.5}O_{3- δ} at different temperature and claimed that the sample which was annealed at the

lowest temperature (900°C) only showed oxygen stoichiometric and other materials showed a very similar δ (0.04-0.05) value.

Based on the XPS results Meng et al [140] found the presence of mixedvalent $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ coupling in $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (x = 0, 0.5 and 0.75) system at room temperature. It was reported that 25% doping by alkali earth metals increases the oxidation state of 3*d*-metals while the variation of oxygen content in doped samples maintained the electroneutrality condition. TGA results revealed that temperature raise increases the oxygen deficiency and decrease the oxidation state of 3*d*-metals (Fig. 4.3).

Table 4.2 – Room temperature oxygen non-stoichiometry δ and average oxidation state Z+ of 3*d*-metals in Nd_{1-x}A_xMn_{0.5}Co_{0.5}O_{3- δ} (A = Ba, Sr and Ca; x = 0 and 0.25).

Compositions	Z+	δ	Ref
NdMn _{0.5} Co _{0.5} O _{3-δ}	2.84	0.08	Current work
LaMn _{0.5} Co _{0.5} O _{3-δ}	2.9	0.05	[139]
$Nd_{0.75}Ba_{0.25}Mn_{0.5}Co_{0.5}O_{3-\delta}$	3.34	0.005	Current work
$Nd_{0.75}Sr_{0.25}Mn_{0.5}Co_{0.5}O_{3\text{-}\delta}$	3.22	0.011	Current work
$La_{0.5}Sr_{0.5}Mn_{0.5}Co_{0.5}O_{3-\delta}$	2.99	0.25	[140]
$Nd_{0.75}Ca_{0.25}Mn_{0.5}Co_{0.5}O_{3\text{-}\delta}$	3.2	0.02	Current work

4.1.4 NdNi_{0.5}Mn_{0.5}O_{3-δ}

Fig. 4.4 shows oxygen non-stoichiometry in NdNi_{0.5}Mn_{0.5}O_{3- δ} obtained in the dynamic mode during heating (heating rate 1–2 K/min). The average value of oxygen non-stoichiometry at room temperature equal to 0.15 ± 0.02 is practically temperature-independent in whole studied temperature range within the experimental error.



Figure 4.4 – Temperature dependencies of oxygen non-stoichiometry (δ).

The calculated average Z+ value for 3*d*-metals in NdNi_{0.5}Mn_{0.5}O_{2.85} is +2.7 at room temperature, which mean that 3*d*-metals adopted M³⁺ and M²⁺ states. However if we assume that all Ni atoms are existed in Ni²⁺ state, then average oxidation state of Mn cations will be equal to +3.4, and formula of oxide can be represented as $NdNi_{0.5}^{2+}Mn_{0.3}^{3+}Mn_{0.2}^{4+}O_{2.85}$. Indeed, it could be expected that equilibrium for the reaction Ni³⁺ + Mn³⁺ = Ni²⁺ + Mn⁴⁺ is more likely shifted to the right hand side [50,141].

$$4.1.5 Nd_{1-x}Ba_{x}Mn_{0.5}Fe_{0.5}O_{3-\delta}$$

The temperature dependencies of oxygen non-stoichiometry (δ) and the average oxidation state of transition metals (Z⁺) in Nd_{1-x}Ba_xMn_{0.5}Fe_{0.5}O_{3- δ} is shown in **Fig. 4.5**. The oxygen deficiency and average oxidation state of 3*d*-metals increases with the increase of acceptor-type dopant concentration. The inset in **Fig. 4.5** shows that oxygen non-stoichiometry increases almost linearly with x at room temperature. The release of oxygen from NBMF55 starts at T \approx 330 °C, which is significantly lower in comparison with NMFO and NBMFO.



Figure 4.5 – Temperature dependencies of oxygen non-stoichiometry and average oxidation state of 3d-metals in $Nd_{1-x}Ba_xMn_{0.5}Fe_{0.5}O_{3-\delta}$. Inset shows the oxygen non-stoichiometry (δ) vs concentration of Ba in $Nd_{1-x}Ba_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ at room temperature.

The value of average oxidation state of 3*d*-metals in Nd₁₋ _xBa_xMn_{0.5}Fe_{0.5}O_{3- δ} (x = 0–0.5) indicated an increase in electron hole concentration with x, which localized on Mn³⁺ forming Mn⁴⁺ cations [123]. Moreover, **Fig. 4.5** demonstrates that the concentration of Mn⁴⁺ in NBMF55 expressively decreases with oxygen release, according to the following quasichemical reaction [142]:

$$O_0^{\times} + 2Mn_{Mn}^{\cdot} = V_0^{\cdot} + 2Mn_{Mn}^{\times} + 1/2O_2$$
(4.5)

The absolute value of oxygen content and the average oxidation state of 3*d*-metals (Z) in NBMF55 were 2.86(2) and +3.22 respectively at room temperature. If we assume all the Fe ions remain as Fe³⁺ then average oxidation state of Mn ions is equal to +3.44, i.e. the ratio of the Mn⁴⁺/Mn³⁺ is 11:14 and the formula can be rewritten as $Nd_{0.5}Ba_{0.5}Mn_{0.22}^{4+}Mn_{0.28}^{3+}Fe_{0.5}^{3+}O_{2.86}$.

4.2 TEC measurements

4.2.1 TEC of $Nd_{1-x}Ba_{x}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (x = 0.25 and 0.5) and $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$ using HT-XRPD

The thermal expansion of NBMFO was calculated from the results of HT-XRPD measurements (**Fig. 3.13**). The refined unit cell parameters and unit cell volume are plotted against temperature in **Fig. 4.6**. It can be seen that practically linear dependencies was observed with a small increase in slope at 800 °C (except for the *c* parameter). This change in slope correlated with the beginning of oxygen release (**Fig. 4.6**) and can be interpreted as chemical expansion due to formation of oxygen vacancies and decrease in the average oxidation state of 3*d*-metals [70].

The values of thermal expansion coefficients (TECs) along a (α_a), b (α_b), c (α_c) directions and for the unit cell volume (α_V) of the NBMFO orthorhombic unit cell were calculated from the slope of corresponding temperature dependencies and presented in **Table 4.3**. For instance, α_V can be calculated using eq. (2.16).

The LTEC of NBMFO ceramics can be estimated in approximation of non-textured polycrystalline material with randomly oriented crystallites [109, 143]. In this case LTEC can be calculated by eq. (2.17).

The calculated value of α_L is presented in **Table 4.3** in comparison with LTECs for Nd_{0.8}Ba_{0.2}Mn_{0.5}Fe_{0.5}O_{3- δ} [119] and La_{0.78}Ba_{0.22}Mn_{0.6}Fe_{0.4}O_{3- δ} [144] determined by the dilatometric measurements. The TEC value obtained from HT-XRPD are in good agreement with the reported data only in the temperature range of 100–800 °C where LTECs for Nd_{0.8}Ba_{0.2}Mn_{0.5}Fe_{0.5}O_{3- δ} and La_{0.78}Ba_{0.22}Mn_{0.6}Fe_{0.4}O_{3- δ} were obtained using dilatometry in dynamic mode with relatively slow heating/cooling rate (2 K/min). The data collected using dilatometry in the dynamic mode cannot reflect the complete contribution of

chemical expansion while the sample was equilibrated at each experimental temperature at least for 1 h during the HT-XRPD study.



Figure 4.6 – Temperature dependencies of the unit cell parameters (a, b, c) and unit cell volume (V) for NBMFO.

Table 4.3 – TEC values for NBMFO and related materials at different temperature range.

$Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	200–800°C	800–1000°C
$\alpha_V imes 10^6$, K ⁻¹	41.5	50.5
$\alpha_a \times 10^6$, K ⁻¹	13.6	16.4
$\alpha_L \times 10^6$, K ⁻¹	13.8	16.8
Nd _{0.8} Ba _{0.2} Mn _{0.5} Fe _{0.5} O _{3-δ} [119]		
$\alpha_L imes 10^6, \mathrm{K}^{-1}$	11.10±0.2 (30–1300°C)	
$La_{0.78}Ba_{0.22}Mn_{0.6}Fe_{0.4}O_{3-\delta}$ [144]		
$\alpha_L \times 10^6$, K ⁻¹	12.7±0.2 (20-1100°C)	

The LTEC value for NBMFO is smaller than that for $Nd_{0.8}Ba_{0.2}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ [119] and $La_{0.78}Ba_{0.22}Mn_{0.6}Fe_{0.4}O_{3-\delta}$, [144] which may

be due to the La ($r_{XII} = 1.36$ Å) substitution by Nd ($r_{XII} = 1.27$ Å) and partial oxidation of Mn³⁺ cations to Mn⁺⁴ oxidation state following the Ba doping [85]. Since the nature of elements and their occupancies sites of the identical type of crystal structure change very subtle in the row NBMFO, Nd_{0.8}Ba_{0.2}Mn_{0.5}Fe_{0.5}O_{3-δ} and La_{0.78}Ba_{0.22}Mn_{0.6}Fe_{0.4}O_{3-δ} and it is usual that the larger unit cell should be expanded greater than the smaller one with temperature.

The study of thermal expansion of NBMF55 using HT-XRPD is shown in **Fig. 4.7**. The refined unit cell parameter and volume demonstrates that the *a*-parameter and unit cell volume showed linear temperature dependencies with an increase in slope at T > 800 C. Similar behaviour was observed for NBMFO which was ascribed to the chemical expansion contribution due to oxygen release and formation of oxygen vacancies.



Figure 4.7 – Temperature dependencies of the *a*-parameter and unit cell volume (V) for NBMF55.

The linear (α_a) and volumetric (α_V) thermal expansion coefficients (TECs) for NBMF55 were calculated from the slope of corresponding temperature dependencies using eq. (2.16) and (2.17). The calculate α_a and α_V values were equal to $14.4 \times 10^{-6} \text{ K}^{-1}$ and $43.75 \times 10^{-6} \text{ K}^{-1}$ in the temperature range of 25–800 °C, and $16.44 \times 10^{-6} \text{ K}^{-1}$ and $50.59 \times 10^{-6} \text{ K}^{-1}$ in the 800–1000 °C interval, respectively. The increase of barium content in Nd_{1-x}Ba_xMn_{0.5}Fe_{0.5}O_{3-\delta} (x = 0.25 and 0.5) series leads to the rise in TEC values, which can be explained by the size factor [85].

The refined lattice parameters and unit cell volume as a function of temperature for $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$ are shown in **Fig. 4.8**. It was found that unit cell expands predominantly in a and c directions. The Me–O bond lengths analysis revealed that strong distortion of the MnO6 octahedra may be responsible for the observed anisotropy.

$NdNi_{0.5}Mn_{0.5}O_{3-\delta}$	<i>Т</i> =25–200°С	<i>Т</i> =200-1000°С
$\alpha_V \times 106$, K-1	25.2	29.98 ± 0.5
$\alpha_a \times 106, \text{K-1}$	11.87	13.73 ± 0.05
$\alpha_b \times 106, \text{K-1}$	2.05	4.58 ± 0.17
$\alpha_c \times 106, \text{K-1}$	12.04 ± 0.07	12.04 ± 0.07
a _L × 106, K-1	8.65	10.12 ± 0.19
$Pr_2NiMnO_{6-\delta}$ [2]	T=50-800°C	
$a_L \times 106$, K-1	10.6	
La _{0.95} Ni _{0.5} Ti _{0.5} O ₃₋₈ [141]	<i>T</i> =250–650°C	<i>T</i> =750–950°C
<i>α_L</i> × 106, K -1	9.99 ± 0.01	11.96 ± 0.01

Table 4.4 – TEC values for NdNi_{0.5}Mn_{0.5}O_{3- δ} and related materials in air.

The thermal expansion coefficients for unit cell parameters of $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$ were determined from the slopes of the corresponding temperature dependencies as described in eq. (2.16) and (2.17). The LTEC was

estimated in approximation of non-textured polycrystalline material with randomly oriented crystallites [109]. The calculated TEC values are summarized in **Table 4.4** with similar ordered material [129, 141]. The LTEC value of NdNi_{0.5}Mn_{0.5}O_{3- δ} shows moderate thermal expansion and it is compatible with well-known electrolyte materials [145].



Figure 4.8 – Temperature dependencies of the unit cell parameters (a, b, c) and the unit cell volume (V) in NdNi_{0.5}Mn_{0.5}O_{3- δ}.

4.2.2 TEC of $Nd_{0.75}Ba_{0.25}Mn_{0.5}(Fe, Co)_{0.5}O_{3-\delta}$ using dilatometry

Fig. 4.9 shows the comparative temperature dependent relative elongation $(\Delta L/L_o)$ of NBMFO and NBMCO solid solutions and inset shows the

enlargement view for NBMCO at high temperature. The slop of $\Delta L/L_o$ plot (attributed to the beginning of oxygen release) was found to shift towards higher value for NBMCO sample compared to NBMFO. A significant hysteresis between the heating and cooling regimes appears for cobalt doped sample while iron doped sample has practically no hysteresis. TGA results (**Fig. 4.2** and **Fig. 4.3**) clearly indicated that NBMFO had relatively weak dependency of oxygen non-stoichiometry versus temperature while NBMCO exhibited significantly higher oxygen release. Therefore, the kinetics of oxygen release/uptake with heating/cooling can be a reason for the hysteresis observed on the dilatometric curve for NBMCO.

The inset of **Fig. 4.9** shows the deviation of temperature dependent relative elongation near about 930 °C during heating. The reported thermogravimetric analysis of $(Co,Mn)_3O_4$ spinel showed that partial substitution of Co by Mn enhance the stability and increases the reduction temperature that reflected in weight loss during heating [158]. In the case of dilatometry measurement of NBMCO sample the observed deviation from linearity near 930 °C during heating, might be the reason of the $(Co,Mn)_3O_4$ spinel impurity presence. It is also confirms previously reported difference in the reduction-oxidation transformations during heating and cooling processes [158]. The thermal expansion coefficient values were calculated from the dilatometry data using eq. (2.15).

The TEC values calculated from the slope of linear fitting of $\Delta L / L_0$ vs T for NBMFO and NBMCO solid solution are summarized in **Table 4.5**. The TEC value obtained for iron doped NBMFO sample from dilatometry measurements was smaller compared to that calculated from HT-XRPD measurements. In case of dilatometry, the measurements were performed in the dynamic mode (heating/cooling rate of 2 K/min) while HT-XRPD study has been done in equilibrium state at each experimental temperature (the sample

was equilibrated at least for 1 h). Thus, the data collected using dilatometry in the dynamic mode cannot reflect the complete contribution of chemical expansion. The calculated TEC value for studied NBMCO is smaller than for pure cobaltite perovskite [146]. The TEC value $(10.98 \times 10^6 \text{ K}^{-1})$ obtained at 100-500 is comparable with well-known electrolytes such as YSZ, LSGM, $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ which suggest that NBMFO could be a potential cathode material for low temperature SOFCs.



Figure 4.9 – Temperature dependencies of $\Delta L / L_0$. The enlargement view of NBMCO at high temperature (inset)

Table 4.5 – Thermal expansion coefficient values for NBMFO and NBMCO using dilatometry data at different temperature range.

Temperature range, °C	$Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	$Nd_{0.75}Ba_{0.25}Mn_{0.5}Co_{0.5}O_{3-\delta}$
100-500	$10.98 \times 10^{6} \text{ K}^{-1}$	$14.65 \times 10^{6} \text{ K}^{-1}$
400-800	$11.92 \times 10^{6} \text{ K}^{-1}$	$14.79 \times 10^{6} \text{ K}^{-1}$
500-1000	$12.66 \times 10^{6} \text{ K}^{-1}$	$14.95 \times 10^{6} \text{ K}^{-1}$
800-1000	$13.27 \times 10^{6} \text{ K}^{-1}$	$14.47 \times 10^{6} \text{ K}^{-1}$

4.3 Total conductivity (σ) and the Seebeck coefficient (S) of Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3- δ} (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25)

4.3.1 $Nd_xA_{1-x}MnO_{3-\delta}(A = Ba, Sr and Ca; x = 0 and 0.25)$

The total conductivity (σ) and the Seebeck coefficient (S) versus temperature for Nd_{1-x}A_xMnO_{3- δ} (A = Ba, Sr and Ca; x = 0 and 0.25) are shown in **Fig. 4.10.** The figure demonstrates that total conductivity of the samples possessed semiconductor-type behaviour within all studied temperature range. The lowest conductivity found for NMO compared to doped samples and reaching the maximal value of 56 S/cm at 1000 °C. The total conductivity increased in the row NCMO < NSMO < NBMO at *T* > 600°C. NBMO possessed the highest conductivity of 205 S/cm at 1000 °C. These data confirmed that the studied samples could be used as cathode materials in SOFCs [2, 147].



Figure 4.10 – Temperature dependence of total conductivity (σ) and Seebeck coefficient (S) for Nd_{1-x}A_xMnO_{3- δ} (A = Ba, Sr and Ca; x = 0 and 0.25) in air.

The linear shape of the $\ln(\sigma T) = f(1/T)$ plotted in Fig. **4.11** indicates that conduction is thermally activated. Inset shows the activation energy of the corresponding materials. The values of activation energy for the doped oxides are very close to each other since they originate by hopping mechanism for charge carriers between Mn³⁺ and Mn⁴⁺. Significant amount of Mn⁴⁺ ions exists according to the reaction (4.2) even at relatively low temperature. The activation energy for undoped NMO included also energy of charge carrier formation which noticeably increased its value.



Figure 4.11 – The linear plot of temperature dependencies of total conductivity.

Fig. 4.10 (right) shows temperature dependencies of the Seebeck coefficient for $Nd_{1-x}A_xMnO_{3-\delta}$ (A = Ba, Sr and Ca; x = 0 and 0.25). The Seebeck coefficient slowly decreases with temperature for all studied samples. The highest Seebeck coefficient was found for NMO at room temperature and remained positive up to 1000°C, demonstrating that the electron holes (*p*-type conductivity) are the main charge carriers in NMO. On the contrary, the S values for NSMO and NCMO transformed the sign from positive to negative at

high temperature, while NBMO showed only negative S values in the whole studied temperature range. Thus, the doping of alkaline earth metals for neodymium resulted in an alteration of the major charge carriers from electron holes to electrons (*n*-type conductivity) in Nd_{1-x}A_xMnO_{3- δ} (A = Ba, Sr and Ca; x = 0 and 0.25). However, both types of electrical conduction should be considered as comparable in the studied samples.

4.3.2 $Nd_xA_{1-x}Mn_{0.5}Fe_{0.5}O_{3-\delta}(A = Ba, Sr and Ca; x = 0 and 0.25)$

Fig. 4.12a and **Fig. 4.12c** show the temperature dependencies of total conductivity (σ) and the Seebeck coefficient (S) respectively for Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3- δ} (A = Ba, Sr and Ca; x=0, 0.25) in air. The increase of conductivity with temperature indicates semiconducting-like behaviour (**Fig. 4.12a**). In this series, NBMFO shows the highest value of total conductivity (25 S/cm) at 1000 °C which is much smaller than that for the Fe-free manganite system. The observed values of total conductivity mainly reflect the electronhole transport in the studied oxides as the oxygen-ion conductivity in manganites and ferrites is lower by few orders of magnitude compared to the electronhole one [148, 149].



Figure 4.12 – Temperature dependencies of total conductivity (a, b) and Seebeck coefficient (c) for $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x=0, 0.25) in air.

The Seebeck coefficient of $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x=0, 0.25) is positive at low temperatures indicating p-type conduction (**Fig. 4.12c**). The Seebeck coefficient values go down to negative region with increase in temperature suggesting n-type conduction at high temperatures. Similar results obtained for neodymium manganite system. The temperature dependencies of the Seebeck coefficient of $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x=0, 0.25) suggest that both electrons and electron holes participate in the electronic transport. It could be considered that electron type defects are localized at the manganese cations Mn^{3+} forming Mn^{4+} (electron holes) and Mn^{2+} (electrons).

The linear shape of $\ln(\sigma T) = f(1/T)$ dependence plotted in **Fig. 4.12(b)** indicates that conduction is thermally activated. The values of activation energy are typical for the small polaron hopping mechanism of conduction in $Nd_{1-x}A_{x}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x=0, 0.25). Hence, the total conductivity and Seebeck coefficient can be interpreted as follows [150]:

$$\sigma = \frac{A}{T} \exp(-\frac{E_{\sigma}}{RT})$$
(4.4)

$$S = \pm \frac{R}{F} \left(B + \frac{Q}{RT} \right) \tag{4.5}$$

where A and B signify the temperature independent constants; E_{σ} and Q are the activation energy of total conductivity and the heat of transfer, respectively; R and F are the universal gas constant and the Faraday constant, respectively. Eq (4.8) is considerable at relatively low temperature while the concentration of electrons and/or electron holes keeps constant as well as the oxygen content. The activation energy E_{σ} and the heat of transfer Q can be linked by the following equation [151, 152, 153]:

$$W_{\rm H} = E_{\sigma} - Q \tag{4.6}$$

where W_H is the energy required to produce the equivalency of the two neighbouring positions in the hopping i.e. polaron hopping energy.

Table 4.6 shows the calculated values of E_{σ} and Q from the experimental data plotted in the form of corresponding dependencies $\ln(\sigma T) = f(1/T)$ and S = f(1/T) for each studied composition. The positive values of $W_H > 0$ for all studied oxides confirm that electron hole transport can be described by the small polaron hopping mechanism [150, 151, 152, 153]. The decrease in activation energy E_{σ} in the row NBMFO, NSMFO, NCMFO, associates with the decrease in total conductivity (**Fig. 4.12a**). However, the heat of transfer Q (the energy required for a formation of polaron [151]) in the row from NBMFO to NCMFO increases demonstrating that localized electron holes Mn_{Mn}^{\bullet} are more mobile species compared to localized electrons Mn_{Mn}' in Nd_{0.75}A_{0.25}Mn_{0.5}Fe_{0.5}O_{3- $\delta}$} (A = Ca, Sr, Ba). Since NBMFO contains the highest concentration of electron holes (see Fig. 4.2 (b)) compared to other homologous phases, it reveals the highest conductivity value. The higher value of activation energy for NMFO oxide compared to the alkali earth oxides has probably same origin as for the Fe-free manganites.

Table 4.6 – The energy parameters of electron-hole transport in Nd₁₋ $_{x}A_{x}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x=0, 0.25).

Composition	E _σ , kJ/mol	T, °C	Q, kJ/mol	W _H ,
				kJ/mol
NdMn _{0.5} Fe _{0.5} O _{3-δ}	33.87±0.3	100-750	13.8±0.4	20.1±0.5
$Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	26.89±0.2	150-800	2.82 ± 0.2	24.1±0.28
$Nd_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	24.72±0.18	25-450	3.95 ± 0.05	20.8±0.19
$Nd_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$	23.01±0.26	25-400	6.98 ± 0.2	16.0±0.33

The comparative study of temperature dependencies of total conductivity (σ) and the Seebeck coefficient (S) for Nd_{1-x}Ba_xMn_{0.5}Fe_{0.5}O_{3- δ} are shown in **Fig. 4.13**. NBMF55 composition showed the highest conductivity value of 25 S/cm at 1000 °C. The Arrhenius plot (inset **Fig. 4.13**) for NBMF55 showed that conduction was thermally activated with the activation energy (E_a) of 31.84

kJ/mol in the 25–1000 C range. It can be seen that significant increase in Ba content from 25% to 50% has not affected the conductivity value. This allow to draw a conclusion that raise of Ba content from 25 to 50% has mainly increased the oxygen vacancy concentration according to eq. (4.2) rather than manganese oxidation state due to eq. (4.1). The Seebeck coefficient of NBMF55 decreased with temperature similar like NMFO and NBMFO and remained positive at all studied temperatures (**Fig. 4.13**) indicating that electron holes localized on manganese were the main charge carriers.



Figure 4.13 – Total conductivity and Seebeck coefficient of $Nd_{1-x}Ba_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ versus temperature in air. Inset shows reciprocal temperature dependencies of ln (σ T).

4.3.3
$$Nd_xA_{1-x}Mn_{0.5}Co_{0.5}O_{3-\delta}$$
 (A = Ba, Sr and Ca; x = 0 and 0.25)

The total conductivity of $Nd_{1-x}A_{x}Mn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x=0, 0.25) has shown in **Fig. 4.14 (left).** The conductivity of all oxides has increased

with temperature showing semiconducting behaviour. In this series, undoped NMCO and Ba-doped NBMCO showed lowest and highest conductivity respectively in the whole temperature range studied. NSMCO showed higher conductivity compared with that for NCMCO which is similar to the one for pure manganite and iron doped manganite series. NBMCO sample showed highest total conductivity equal to 285 S/cm at 1000°C. This high conductive material can be considered as promising cathode materials for SOFCs [154].



Figure 4.14 – Temperature dependencies of total conductivity and Seebeck coefficient for $Nd_{1-x}A_{x}Mn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; x=0, 0.25) in air.

 $Nd_{1-x}A_xMn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca; x=0, 0.25) have highest conductivity compared with pure manganite and iron doped manganites. The linear shape of the $ln(\sigma T) = f(1/T)$ dependence plotted in Fig. **4.15** indicates that conduction is thermally activated. Inset shows the activation energy of the corresponding materials. Similar behaviour obtained for pure manganite and iron doped series.



Figure 4.15 – The linear plot of temperature dependencies of total conductivity.

The Seebeck coefficient of undoped NMCO and 25% alkali metal doped oxides shows different behaviour compared to that for pure manganite and iron doped manganite series. The temperature dependencies of Seebeck coefficient for $Nd_{1-x}A_xMn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr and Ca x=0, 0.25) are shown in **Fig. 4.14** (**right**). The variations of Seebeck coefficient of the studied oxides with temperature are very small and slightly deviate from zero value. At lower temperature all samples showed negative S (except NMCO), which become positive at high temperature. It is worth noting that all doped samples showed practically indistinguishable S values near 500°C. It could be assumed that such behavior is a result of charge compensation mechanism suggested earlier [157] which can be described by the following equation:

$$Co^{3+} + Mn^{3+} = Co^{2+} + Mn^{4+}$$
(4.7)

This equilibrium is shifted to the right hand side at low temperature, i.e. electron holes localized on Mn ions, while electrons are mainly located on Co

ions. An increase of temperature facilitates hopping of charge carriers, changes their mobility but have not significantly changes the ratio of electrons and electron holes. Therefore, the value of Seebeck coefficient small and slightly varied.

Similar to the undoped manganite series, iron-doped and cobalt-doped oxides NdNi_{0.5}Mn_{0.5}O_{3- δ} revealed semiconductor type behaviour (σ) in the whole temperature range studied (**Fig. 4.16**). The obtained σ value of 7.3 S/cm at 800 °C was slightly higher than that (5.7 S/cm) reported for similar material Pr₂NiMnO_{6- δ} at this temperature [2]. The maximal σ value for NdNi_{0.5}Mn_{0.5}O_{3- δ} (15 S/cm) was reached at 1000 °C. The ln(σT) = f(1/T) plot (inset **Fig. 4.16**) exposed that charge transfer was thermally activated signifying a small polaron hopping mechanism. The activation energy increased with temperature from 32.80 kJ/mol (T < 350°C) to 43.41 kJ/mol (T > 350°C).

Comparable behaviour was also detected for $Pr_2NiMnO_{6-\delta}$ at 550 °C [2]. It could be explained by the small elongation of Ni–O–Mn bond lengths with temperature (for instance, the Ni–O1–Mn bond length increased from 3.83 Å at room temperature to 3.85 Å and 3.88 Å at 400 °C and 1000 °C, respectively). The Seebeck coefficient (*S*) for NdNi_{0.5}Mn_{0.5}O_{3- $\delta}$} (inset **Fig. 4.16**) possessed complex temperature dependence and adopted negative values at all studied temperatures presenting that predominant charge carriers in the oxide were electrons localized on Ni³⁺ cations forming Ni²⁺.



Figure 4.16 – Temperature dependencies of total conductivity (σ) and Seebeck coefficient (*S*) for NdNi_{0.5}Mn_{0.5}O_{3- δ} in air.

5. APPLICATION OF Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-δ} AS CATHODS IN SOLID OXIDE FUEL CELLS

5.1 Study of the chemical compatibility of $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ with solid electrolyte $Ce_{0.8}Sm_{0.2}O_{2-\delta}$

The chemical compatibility of NBMF55 in respect to the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) electrolyte has been studied due to the comparable and moderated TEC value and relatively high conductivity of mixed conducting oxide in the intermediate temperature range. NBMF55 and SDC powders, prepared according to the methods described in section 2.6, were mixed in weight ratio 1:1 and annealed at 1100° C for 70 hours in air. The results of X-ray diffraction analysis of the mixture of NBMF55 and SDC after annealing together with XRD patterns for individual components are presented in **Fig. 5.1**.



Figure 5.1 – XRPD patterns of SDC, NBMF55 and the SDC/ NBMF55 mixture annealed at 1100 °C for 70 h in air.

Phase identification results did not reveal the presence of impurity peaks which demonstrated the absence of visible chemical interaction between NBMF55 and SDC.

5.2 Impedance spectroscopic study

The inset of **Fig. 5.2** shows the complex impedance diagrams of symmetrical cells based on NBMF55 electrode materials with SDC electrolyte. The area specific resistance (ASR) value associated to the overall electrode polarization processes versus temperature is shown in **Fig. 5.2** for the NBMF55/SDC symmetrical cell obtained by the fitting of impedance spectra using the equivalent circuit indicated (Fig. 5.2 inset) in which the electrode process displays two major contributions, at intermediate and low frequencies [155-157]. The Zview software was used to fit the impedance spectra to equivalent circuits. The studied impedance spectra have been fitted to a series circuit, using inductance (L₁) caused by the electrochemical setup, ohmic resistance, (R) which associated to the total ion transport in the electrolyte and two parallel RCPE circuits related to processes at the electrode-electrolyte interface and at the electrode surface, taking place at intermediate and low frequencies respectively [59].

The inset of **Fig. 5.2** shows the fitted impedance spectrum measured at 779 °C. The ASR value of NBMF55/SDC symmetrical cell showed 2.2 Ω cm² at 700°C in air which is slightly higher than that for the Gd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3- δ} + GDC/GDC cell and comparable with the values obtained for the state-of-the-art La_{1-x}Sr_xMnO_{3- δ} (LSM) cathode [129]. This is a preliminary result and for a proper comparison the sintering conditions and microstructure should be considered. Therefore, due to the comparable electrode performance for symmetric cells of NBMF55 perovskites, it could be a potential electrode in SOFCs.



Figure 5.2 – The Arrhenius plot of ASR values obtained for the NBMF55/SDC symmetrical cell in comparison with reported data. The inset shows the fitted Nyquist plot at 779 °C and corresponding equivalent circuit.

FINDINGS

According to the results of experimental and theoretical work, the following conclusions can be drawn:

- 1. The X-ray powder diffraction refined by the Rietveld analysis identified the crystal structure of the studied oxides and the variations of unit cell parameters with dopant concentration and temperature: $Nd_xA_{1-x}MnO_{3-\delta}$ (A = Ba, Sr and Ca; x =0 and 0.25) are orthorhombic with *Pnma* space group; $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$ (A = Ba; x =0 and 0.25) possessed orthorhombic crystal structure, but Sr- and Ca-doped $Nd_{1-x}A_xMn_{0.5}Fe_{0.5}O_{3-\delta}$, as well as $NdNi_{1-x}(Co,Cu)_xMn0_5O_{3-\delta}$ samples have monoclinic (*P21/n*) structure; $Nd_{1-x}A_xMn_{0.5}Co_{0.5}O_{3-\delta}$ (A = Ba, Sr x = 0 and 0.25) have orthorhombic crystal structure (*Pnma*) while undoped and Ca-doped samples possessed monoclinic structure. The unit cell volume (V) of all samples increased with an increase in the radius of alkaline earth metals.
- 2. The HT-XRPD analysis of orthorhombic $Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$, cubic $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ and monoclinic $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$ phases demonstrated that no phase transition has been seen for the samples up to $1000^{\circ}C$.
- 3. Thermogravimetric analysis of $Nd_{1-x}A_{x}Mn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0.25) demonstrated that the complex oxides are oxygen deficient and the value of the oxygen nonstoichiometry (δ) increases with increasing temperature and doping by Ba, Sr and Ca respectively.
- 4. The values of thermal expansion coefficient for $Nd_{1-x}Ba_xMn_{0.5}B_{0.5}O_{3-\delta}$ (B = Fe and Co; x = 0.25 and 0.5), and $NdNi_{0.5}Mn_{0.5}O_{3-\delta}$, obtained by dilatometry and HT-XRPD measurements were almost similar for both measurement techniques and comparable with known electrolytes at intermediated temperature range.

- 5. The studied $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) oxides exhibited semiconductor-type conductivity in the whole temperature range studied and can be described within the hopping small polaron mechanism. It was shown that Co-doped series revealed highest conductivity while Fe-doped series possessed lowest conductivity. The values and sign of Seebeck coefficients for depended on the ratio of positive and negative charge carriers associated with the dopant content and oxygen nonstoichiometry.
- 6. It was shown that $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ oxide and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte were chemically inert to each other at 1100° C; no interaction products were detected after annealing for 70 hours.
- 7. The impedance spectroscopy measurements concluded that ASR value of the $Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3-\delta}$ /SDC symmetrical cell is comparable (2.2 Ω cm²) with modern cathode materials.

Further work on this topic will be aimed to study $Nd_{1-x}A_xMn_{0.5}B_{0.5}O_{3-\delta}$ (A = Ba, Sr, Ca; B = Mn, Fe, Co, Ni; x = 0, 0.25) compositions as cathode materials for SOFC based on $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolytes. Using the methods of impedance spectroscopy and scanning electron microscopy, the microstructure of these cathodes will be investigated and its effect on the efficiency of the fuel cell operation will be determined.

List of symbols of letters and adopted abbreviations

- A alkaline earth metals;
- B 3d transition metal;
- a, b, c unit cell parameters;
- V the volume of the unit cell;
- Å Angstrom, unit of measure for length, 10^{-10} m;
- δ oxygen nonstoichiometry value;
- e the elementary charge, $1,60219 \times 10^{-19}$ C;
- E_A the activation energy;
- E_{σ} the activation energy of conductivity;
- E_{s} the activation energy of the Seebeck coefficient;
- F the Faraday constant, 96484,56 C / mol;
- I current strength;
- I/I₀ the relative intensity of X-ray scattering;
- λ the radiation wavelength;
- T temperature;
- X, Y, Z relative coordinates of atoms in the unit cell of oxides;
- x the content of the doping additive in the oxide;
- z the number of formula units in the unit cell;
- TEC thermal expansion coefficient;
- min time unit, 60 s;
- NPD neutron powder diffraction;

sp. gr. - space group; XRPD - X-ray powder diffraction;

S/cm – Siemens/centimeter;

S – Seebeck coefficient;

R_{Br} - Bragg factor;

R_f - structural factor;

R_p - profile factor;

 δ_1 – room temperature oxygen nonstoichiometry measure using dichromate titration with Mohr salt;

 δ_2 - room temperature oxygen nonstoichiometry measure using iodometric titration;

 Z^{+} - oxidation state of transition metals;

Kröger-Vink notation;

 $V_0^{\bullet\bullet}$ - oxygen vacancies;

 $[Mn'_{Mn}]$ - electron localized on Mn³⁺ cations

 $[Mn_{Mn}^{\bullet}]$ - electron hole localized on Mn³⁺ cations;

 $[Fe'_{Fe}]$ - the electron localized on Fe³⁺ cation.

NMO - NdMnO_{$3+\delta$}

NBMO - $Nd_{0.75}Ba_{0.25}MnO_{3-\delta}$

NSMO - $Nd_{0.75}Sr_{0.25}MnO_{3-\delta}$

NCMO - $Nd_{0.75}Ca_{0.25}MnO_{3-\delta}$

NMFO - NdMn_{0.5}Fe_{0.5}O_{3- δ}

NBMFO - $Nd_{0.75}Ba_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$

NSMFO - $Nd_{0.75}Sr_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$

NCMFO - $Nd_{0.75}Ca_{0.25}Mn_{0.5}Fe_{0.5}O_{3-\delta}$

 $NBMF55 \text{ - } Nd_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}O_{3\text{-}\delta}$

NMCO - NdMn_{0.5}Co_{0.5}O_{3-δ}

NBMCO - $Nd_{0.75}Ba_{0.25}Mn_{0.5}Co_{0.5}O_{3-\delta}$

NSMCO - $Nd_{0.75}Sr_{0.25}Mn_{0.5}Co_{0.5}O_{3-\delta}$

NCMCO - $Nd_{0.75}Ca_{0.25}Mn_{0.5}Co_{0.5}O_{3-\delta}$

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