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Article

Synthesis and Electrophysical Characterization of a Three-Phase Ca–Nd–Mn–Ni–O Oxide System

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Abstract

The three-phase Ca–Nd–Mn–Ni–O oxide system was synthesized by a conventional solid-state ceramic method. The phase composition was investigated by X-ray diffraction (XRD) analysis using the PDF-5+/Rigaku SmartLab Studio II software package and was further confirmed by Rietveld refinement employing the GSAS-II software suite. According to the WPPF/Rietveld refinement results, the synthesized material predominantly consists of the Nd_{0.25}Ca_{0.75}MnO₄ phase (67.2 wt.%), together with the perovskite-like Ca_{0.5}Nd_{0.5}Mn_{0.97}Ni_{0.03}O₃ phase (25.6 wt.%) and a minor (Ni_{0.94}Mn_{0.06})O phase (7.2 wt.%). SEM analysis revealed an agglomerated granular morphology with porous regions, while elemental mapping confirmed the presence of Ca, Nd, Mn, Ni, and O in the synthesized material. FTIR spectroscopy showed characteristic metal–oxygen vibrational bands associated with [MnO₆] and [NiO₆] octahedral units. The electrical properties were investigated in the temperature range of 293–483 K at a frequency of 1 kHz. The material exhibited semiconducting behavior, and the calculated activation energies of electrical conduction were found to be 0.49 and 0.56 eV for the temperature intervals of 293–353 K and 393–483 K, respectively.

Keywords: neodymium, calcium, nickel-manganite, electrophysics

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1. Introduction

Perovskite-like oxides represent a broad class of compounds with the universal ABX₃ structure, where the A-site is occupied by large cations (La³⁺, Nd³⁺, Sr²⁺, Ba²⁺), and the B-site by transition metals (Mn, Ni, Co, Fe) forming BX₆ octahedra. This architecture is highly flexible: substitutions at both A- and B-sites allow fine tuning of the magnetic, electrical, and structural properties of the material. Such structural universality makes perovskites a unique platform for designing materials with tailored characteristics. In recent years, research has focused on how controlled substitutions at the A- and B-sites enable new combinations of properties, including magnetic, ferroelectric, thermoelectric, and catalytic effects [1].

Owing to the combination of structural flexibility and functional diversity, perovskites find applications in a wide range of fields. In energy technologies, they are employed in fuel cells and energy storage systems; in photovoltaics, they serve as the basis for next-generation solar cells demonstrating record efficiencies; in spintronics and magnetic devices, they are utilized due to

colossal magnetoresistance and controllable phase transitions; in catalysis, they act as effective materials for oxidation and reduction reactions; and in thermoelectrics, they function as stable converters of heat into electricity [2–4]. Thus, perovskites represent a universal platform in which chemical modification is directly linked to practical applicability.

Of particular interest in this context are manganites with the general formula $R_{1-x}A_xMnO_3$, where R is a trivalent rare-earth cation and A is a divalent alkaline-earth metal. In these compounds, variation of composition and doping level enables control over phase transitions, magnetic ordering, and conductivity [5, 6].

Particular attention has been devoted to Mn-containing double perovskite oxides with the general formula $A_2BB'O_6$. In these materials, a strong interplay exists between crystal structure, the degree of cation ordering in the B-sublattice, magnetic ordering, and transport properties. Variations in the Ni–O–Mn bond angles and bond lengths, along with the presence of antisite disorder, play a crucial role in determining the magnetic and electrophysical properties, including electrical conductivity, magnetoresistance, and ferromagnetic behavior [7–15].

Manganites exhibit a wide range of functional properties—from giant and colossal magnetoresistance (GMR, CMR) to ferroelectric and magnetocaloric effects—which underpins their application in magnetic field sensors, high-density recording heads, and magnetic refrigeration systems [16, 17]. Substitution of La^{3+} by smaller rare-earth cations, such as Nd^{3+} , leads to significant changes in perovskite properties, as confirmed by studies of the double perovskite Nd_2NiMnO_6 [18]. The influence of monovalent doping (K, Na) on the magnetocaloric properties of $Nd_{0.6}Sr_{0.4-x}M_xMnO_3$ has also demonstrated the promise of such compounds for magnetic refrigeration at room temperature [19].

Modification of manganites by transition metals (Ni, Co, Fe) is one of the most actively developed directions. Such substitutions affect not only the electronic properties of the lattice but may also lead to the formation of secondary phases, including intermetallic compounds. For example, Ni doping in the $La_{0.67}Ba_{0.33}Mn_{1-x}Ni_xO_3$ system reduces the phase transition temperature to $T = 302$ K at $x = 0.075$, making the material promising for magnetic refrigeration [20]. In the case of Mn substitution by Fe, Co, and Ni in $La_{0.7}Ca_{0.3}MnO_3$, a significant influence on ferromagnetic–paramagnetic and metal–semiconductor transitions is observed, although photoemission studies did not reveal noticeable changes in the electronic structure [21]. Similarly, weak Ni doping in $La_{0.2}Sr_{0.8}MnO_3$ was confirmed by EDS spectroscopy, and conductivity in the range of 300–420 K demonstrated frequency dependence [22]. The influence of Ni^{2+} ions on the structural, magnetic, and transport properties of $La_{0.67}Ca_{0.33}MnO_3$ has also been studied in detail [23].

Recent studies demonstrate that perovskite materials possess a unique set of electrophysical properties, including conductivity, dielectric relaxation, and magnetic correlations. In the review by Tayari et al. [24], it is emphasized that, owing to the flexibility of crystal chemistry and the possibility of targeted cation substitution at lattice sites, perovskites exhibit a wide range of electrical and dielectric characteristics. These properties define their potential for applications in energy-efficient devices, sensors, and functional materials. Particular attention is given to the relationship between structural distortions and changes in electrical conductivity, which makes such systems especially attractive for both fundamental and applied research.

In Ni-substituted manganites, current-induced resistivity effects and pronounced nonlinearity in current–voltage characteristics are observed, which are associated both with Joule heating and with specific features of charge transport mechanisms [25]. These phenomena make such systems promising for the investigation of functional properties of oxide materials.

In recent years, multiphase manganite oxide systems have attracted considerable attention due to the coexistence of phases with different crystal structures, electronic states, and charge-transport mechanisms. Such heterogeneous materials may exhibit complex electrical and dielectric behavior associated with interfacial polarization, phase separation, oxygen nonstoichiometry, and charge transport across grain boundaries. The presence of multiple manganese-containing oxide phases

can significantly affect the electrical conductivity, dielectric response, magnetic ordering, and the nature of phase transitions [26].

Multiphase manganese-based oxide systems are considered promising functional materials due to their structural flexibility, mixed-valence states of manganese, and the strong correlation between crystal structure and physical properties. Interfacial interactions and the coexistence of different oxide phases can give rise to unusual transport and magnetic effects, including interfacial polarization, phase separation, and tunable electrical properties [27].

In Ca–Nd–Mn–Ni-containing systems, high-temperature ceramic synthesis may be accompanied by the formation of several oxide phases with different crystal structures and electrophysical properties. Such multiphase manganite systems are of particular interest due to the relationship between phase composition, structural heterogeneity, and the functional properties of the material. Previous studies have shown that composite manganites containing multiple phases can exhibit modified magnetic, transport, and electrical characteristics compared with single-phase systems [28].

Recent studies indicate that multiphase oxide systems based on manganites are of particular interest due to the coexistence of phases with different crystal structures and transport mechanisms. Such heterogeneous ceramics may exhibit complex electrophysical behavior associated with interfacial polarization, mixed-valence manganese states, oxygen nonstoichiometry, and grain-boundary charge transport. In systems containing Ca, Nd, Mn, and Ni, the formation of secondary oxide phases during high-temperature ceramic synthesis can significantly influence electrical conductivity and dielectric response.

In the present work, a three-phase Ca–Nd–Mn–Ni–O oxide system synthesized by the conventional ceramic method is investigated. According to WPPF/Rietveld analysis, the obtained material consists predominantly of $\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$ together with $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ and minor (Ni, Mn)O phases. The coexistence of these phases provides a convenient model system for studying the relationship between phase heterogeneity, crystal structure, and electrophysical properties.

Thus, the aim of the present study is the synthesis and investigation of the structural and electrophysical properties of the multiphase Ca–Nd–Mn–Ni–O oxide system.

2. Results and Discussion

To verify the correctness of the chosen methodology for dielectric and electrophysical measurements, BaTiO_3 samples, widely used as a model material, were first investigated. The obtained values of dielectric permittivity showed good agreement with literature data, confirming the reliability of the experimental procedure and data processing. The dielectric permittivity of a standard BaTiO_3 sample measured at 1 kHz and 293 K was 1296, which is consistent with the recommended value of (1400 ± 250) [29–31].

After validating the measurement methodology using BaTiO_3 , the electrophysical properties of the three-phase Ca–Nd–Mn–Ni–O oxide system were investigated. According to the WPPF/Rietveld analysis, this system consists of $\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$, $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$, and minor $(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$ phases. The numerical values of dielectric permittivity and electrical resistance for this system are presented in Table 1, while their temperature dependences are shown in Figure 1.

Table 1. Results of Electrophysical Measurements.

T, K	R, Ohm	ϵ	$\lg \epsilon$	$\lg R$, Ohm
293	867,100	4012	3.60	5.94
303	342,100	11,042	4.04	5.53
313	239,900	17,097	4.23	5.38
323	204,900	21,891	4.34	5.31

333	178,100	27,976	4.45	5.25
343	152,700	35,618	4.55	5.18
353	133,900	40,720	4.61	5.13
363	163,200	31,573	4.50	5.21
373	615,500	7766	3.89	5.79
383	1,020,000	4453	3.65	6.01
393	1,120,000	4674	3.67	6.05
403	1,091,000	5425	3.73	6.04
413	1,014,000	6497	3.81	6.01
423	899,500	8603	3.93	5.95
433	694,600	14,593	4.16	5.84
443	546,400	23,764	4.38	5.74
453	476,600	32,443	4.51	5.68
463	377,500	49,915	4.70	5.58
473	341,500	58,297	4.77	5.53
483	257,900	99,305	5.00	5.41

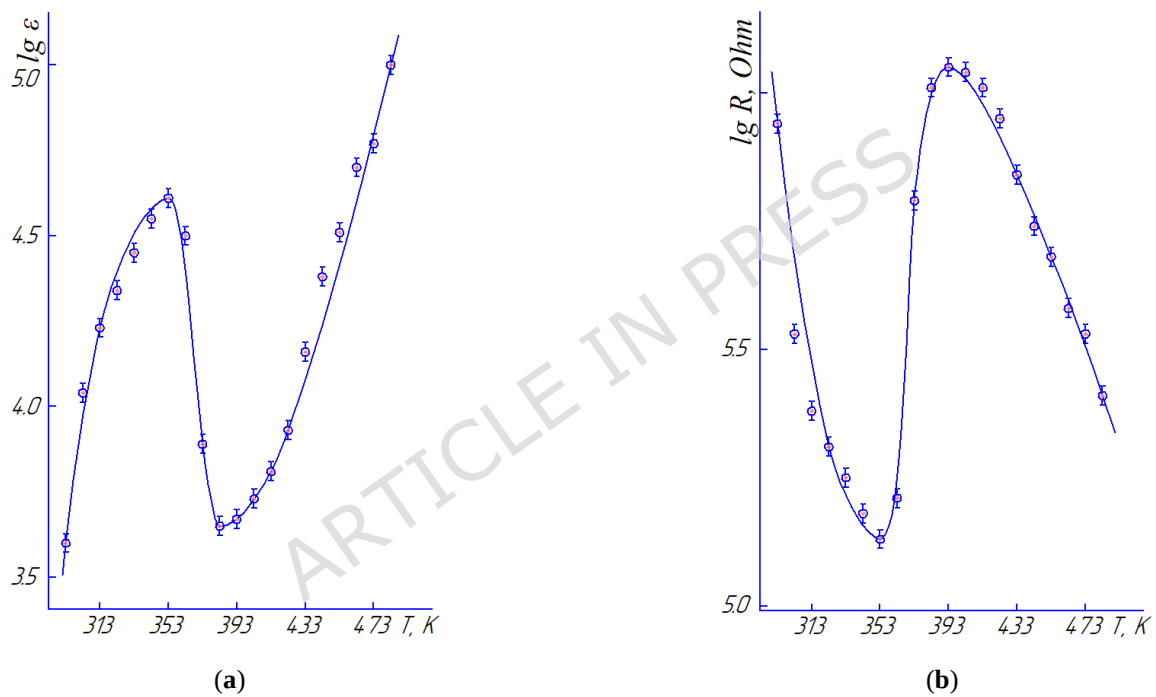


Figure 1. Temperature dependence of (a) dielectric permittivity and (b) electrical resistance of the three-phase Ca-Nd-Mn-Ni-O oxide system measured in the temperature range of 293–483 K at a frequency of 1 kHz; - experimental data.

Since the investigated material is a three-phase oxide system, the measured electrical response reflects the combined contribution of all crystalline phases and interphase boundaries. Therefore, the calculated activation energies should be interpreted as effective transport parameters of the entire multiphase oxide system rather than intrinsic values of an individual phase.

To analyze the temperature dependence of electrical conductivity, the resistance values were converted into conductivity according to the following relation:

$$\sigma = \frac{1}{R}, \quad (1)$$

Based on the $\ln(\sigma) \sim 1/T$ dependence, the slope (m) was extracted and subsequently employed to calculate the effective activation energy of electrical conduction (E_a) according to the following relation:

$$E_a = 2 \times k \times |m|, \quad (2)$$

where $k = 8.617 \times 10^{-5}$ eV/K — the Boltzmann constant.

Figure 2 presents the temperature dependence of electrical conductivity, highlighting the experimental data obtained in the ranges of 293–353 K and 393–483 K.

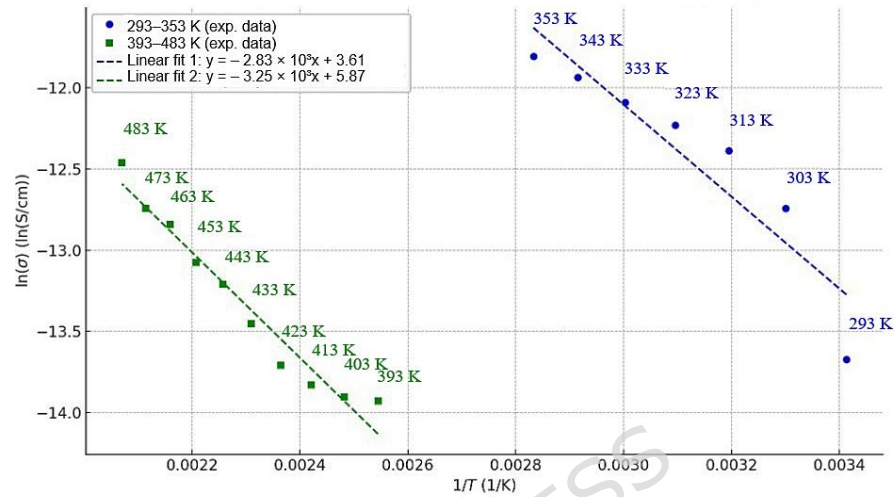


Figure 2. Temperature dependence of electrical conductivity of the three-phase Ca–Nd–Mn–Ni–O oxide system in the temperature ranges of 293–353 K and 393–483 K. Symbols denote experimental data, and solid lines represent the linear fits used for activation energy evaluation.

Figure 2 illustrates the temperature dependence of electrical conductivity. The blue markers and fitted line correspond to the experimental data in the range of 293–353 K, whereas the green markers and fitted line represent the experimental results and linear approximation obtained for 393–483 K.

For the temperature range of 293–353 K:

$$y = -2.83 \times 10^3 x + 3.61, \quad (3)$$

the slope $m_1 = -2830$.

For the temperature range of 393–483 K:

$$y = -3.25 \times 10^3 x + 5.87, \quad (4)$$

the slope $m_2 = -3250$.

By inserting the slope values into equation (2), the effective activation energies of electrical conductivity were determined as $E_{a1} = 0.49 \pm 0.09$ eV for 293–353 K and $E_{a2} = 0.56 \pm 0.04$ eV for 393–483 K. The uncertainties were estimated from the standard error of the slope obtained by linear regression of the $\ln(\sigma)$ versus $(1/T)$ dependence.

The obtained results confirm the semiconducting nature of the electrical conductivity of the material over a wide temperature range. The observed increase in the effective activation energy with increasing temperature may be associated with a change in the dominant charge-transport mechanism, as well as with variations in the relative contribution of the three coexisting phases.

In the three-phase system, phases with different crystal structures and, apparently, different manganese oxidation states coexist. In such multiphase materials, the electrical response is generally determined by the combined contribution of all phases and interfacial boundaries. Therefore, the calculated activation energies should be regarded as effective transport parameters of the entire multiphase oxide system rather than as intrinsic characteristics of any individual phase [29, 32].

As a result of the synthesis, a nickel-substituted calcium–neodymium manganite three-phase composite was successfully obtained. According to the WPPF/Rietveld refinement results, the material consists of the $\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$ and $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ phases, together with a minor amount of the $(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$ phase. The multiphase nature of the sample was unambiguously confirmed by the presence of well-defined diffraction peaks corresponding to all three phases.

3. Experimental Part

The synthesis was initially aimed at obtaining the nickel-substituted manganite $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ by conventional ceramic processing using high-purity precursors. According to the WPPF/Rietveld refinement of the X-ray diffraction data, the final product represents a three-phase Ca–Nd–Mn–Ni–O oxide system consisting predominantly of $\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$ together with $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ and minor $(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$ phases. The starting materials included neodymium(III) oxide (“puriss. spec.” grade, TU 48-4-523-90, 99.5%, $m = 2.7134$ g; Chem Craft, Kaliningrad, Russia), nickel(II) oxide (“p.a.” grade, TU 6-09-4125-80, 99.0%, $m = 1.2046$ g; LLC Granchem, Chelyabinsk, Russia), manganese(III) oxide (“p.a.” grade, TU 6-09-2165-77, 99.0%, $m = 1.2731$ g; Yugraaktiv, Rostov-on-Don, Russia), and calcium carbonate (“p.a.” grade, GOST 4530-76, 99.0%, $m = 3.2285$ g; Chem Craft, Kaliningrad, Russia)

Prior to synthesis, all precursor materials were dehydrated at 400 °C to remove residual moisture. Stoichiometric quantities of the components were then homogenized by thorough mixing and grinding in an agate mortar. The homogenized precursor mixture was subsequently subjected to a multi-stage thermal treatment procedure, resulting in the formation of the final multiphase oxide system.

The synthesis was conducted in an alumina crucible using a SNOL furnace under controlled thermal conditions. The procedure involved an initial calcination at 600 °C for 10 h, followed by sequential heating steps at 800 °C, 1000 °C, and a final treatment at 1200 °C for 15 h. After each stage, the sample was cooled to room temperature, re-ground, and homogenized to enhance phase uniformity.

Following high-temperature sintering, the material was subjected to an additional low-temperature annealing at 400 °C for 10 h. This final treatment was performed to stabilize the crystal structure and to ensure chemical, thermal, and mechanical integrity for subsequent applications.

Thus, the formation of the secondary $(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$ phase should be considered a consequence of secondary redox processes occurring during high-temperature solid-state synthesis due to changes in the valence states of manganese and nickel, rather than as evidence of an incomplete primary reaction.

During the synthesis process, additional oxygen release occurs due to the thermal decomposition of calcium carbonate and precursor oxides. These processes may contribute to changes in oxygen nonstoichiometry and the redistribution of the valence states of Mn and Ni, leading to the formation of a secondary nickel–manganese oxide phase [33–36].

Figure 3 presents the X-ray diffraction (XRD) pattern of the three-phase Ca–Nd–Mn–Ni–O oxide system, illustrating the results of phase composition analysis and WPPF/Rietveld refinement.

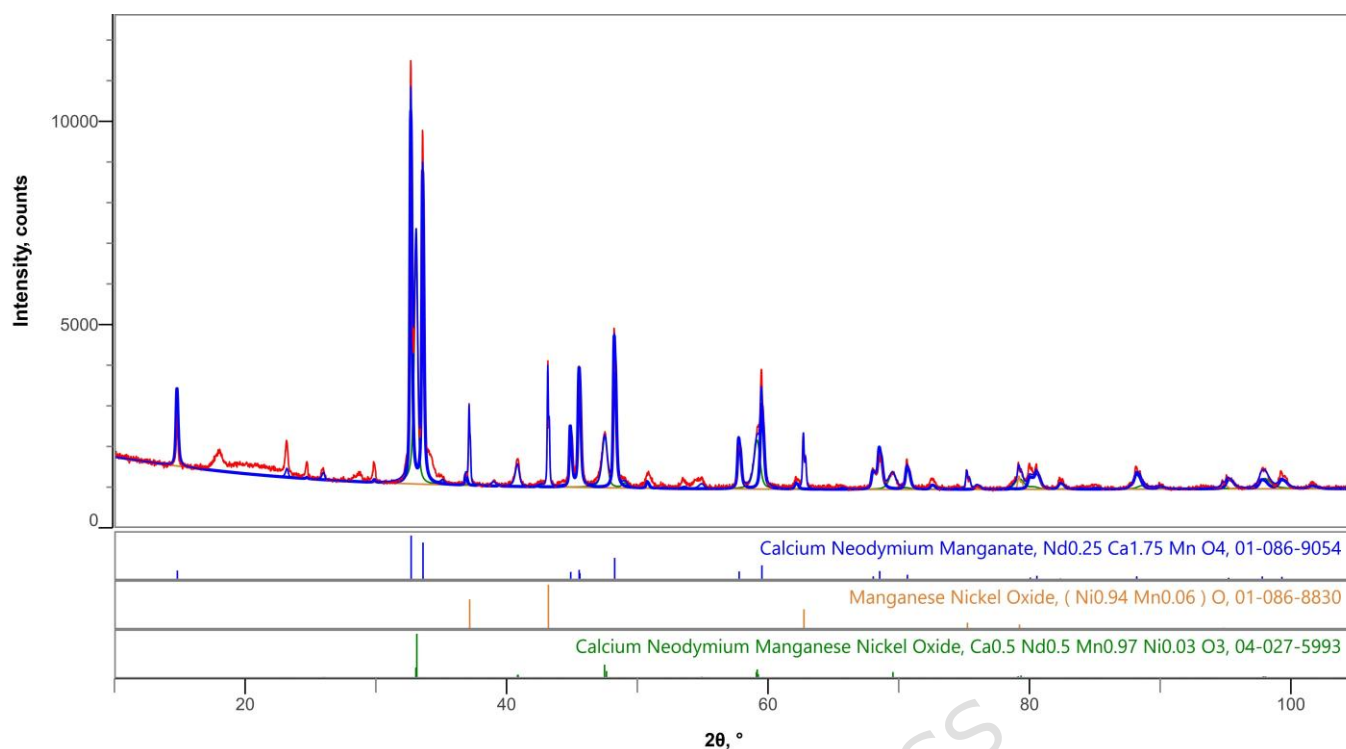


Figure 3. X-ray diffraction pattern and WPPF/Rietveld refinement of the three-phase Ca–Nd–Mn–Ni–O oxide system showing the coexistence of Nd_{0.25}Ca_{1.75}MnO₄, Ca_{0.5}Nd_{0.5}Mn_{0.97}Ni_{0.03}O₃, and minor (Ni_{0.94}Mn_{0.06})O phases.

Figure 3 presents the experimental X-ray diffraction pattern and the results of the WPPF/Rietveld refinement of the three-phase Ca–Nd–Mn–Ni–O oxide system. It was established that the investigated sample predominantly consists of the Nd_{0.25}Ca_{1.75}MnO₄ phase, together with the perovskite-like Ca_{0.5}Nd_{0.5}Mn_{0.97}Ni_{0.03}O₃ phase and a minor (Ni_{0.94}Mn_{0.06})O phase. A satisfactory agreement between the experimental and calculated diffraction profiles was observed, confirming the validity of the selected structural model and the phase composition of the system.

The main intense reflections in the $2\theta \approx 32\text{--}35^\circ$ and $45\text{--}50^\circ$ regions arise from the overlap of contributions from several phases, which is characteristic of complex multiphase manganite systems. The presence of weak additional reflections confirms the existence of a secondary nickel–manganese oxide phase. The vertical tick marks at the bottom of the figure correspond to the positions of the Bragg reflections of the identified Nd_{0.25}Ca_{1.75}MnO₄, Ca_{0.5}Nd_{0.5}Mn_{0.97}Ni_{0.03}O₃, and (Ni_{0.94}Mn_{0.06})O phases.

According to the WPPF/Rietveld refinement results, the phase fractions were determined to be 67.2 wt.% for Nd_{0.25}Ca_{1.75}MnO₄, 25.6 wt.% for Ca_{0.5}Nd_{0.5}Mn_{0.97}Ni_{0.03}O₃, and 7.2 wt.% for (Ni_{0.94}Mn_{0.06})O. The obtained results indicate the formation of a heterogeneous multiphase oxide system in which the coexistence of phases with different crystal structures may significantly influence the electrophysical properties of the material.

Approaches to the structural analysis of multiphase oxide composites and the interpretation of phase coexistence are widely discussed in the literature for complex perovskite systems. It has been shown that interfacial interactions can manifest as variations in relative peak intensities, peak broadening, and slight shifts of diffraction maxima, and can significantly affect the overall electrophysical properties of the material due to the contribution of interfacial boundaries [32, 37–39].

Figure 3 presents the experimental X-ray diffraction pattern and the results of the WPPF/Rietveld refinement of the three-phase Ca–Nd–Mn–Ni–O oxide system. The sample predominantly consists of the Nd_{0.25}Ca_{1.75}MnO₄ phase and also contains the perovskite-like Ca_{0.5}Nd_{0.5}Mn_{0.97}Ni_{0.03}O₃ phase together with a minor (Ni_{0.94}Mn_{0.06})O phase. The satisfactory

agreement between the experimental and calculated diffraction profiles confirms the validity of the selected structural model and the phase composition of the system [40].

The main intense reflections in the $2\theta \approx 32\text{--}35^\circ$ and $45\text{--}50^\circ$ regions arise from the overlap of contributions from several phases, which is characteristic of complex multiphase manganite systems [41]. The presence of weak additional reflections confirms the existence of a secondary nickel–manganese oxide phase. The vertical tick marks at the bottom of the figure correspond to the positions of the Bragg reflections of the identified $\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$, $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$, and $(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$ phases.

According to the WPPF/Rietveld refinement results, the phase fractions were determined to be 67.2 wt.% for $\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$, 25.6 wt.% for $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$, and 7.2 wt.% for $(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$. These results indicate the formation of a heterogeneous multiphase oxide system in which the coexistence of phases with different crystal structures may significantly influence the electrophysical properties of the material [2, 28].

According to the literature data, calcium-containing manganites subjected to high-temperature treatment can exhibit pronounced oxygen-exchange and redox behavior associated with changes in oxygen nonstoichiometry and the valence state of manganese. Additional oxygen release during synthesis may occur due to the thermal decomposition of calcium carbonate and precursor oxides, thereby affecting phase formation and promoting the formation of secondary oxide phases [42].

Structural analysis of the synthesized three-phase oxide system was performed by X-ray diffraction (XRD), including phase identification and refinement of crystallographic parameters, using widely accepted approaches for the investigation of oxide systems and nanocrystalline materials reported in the literature [43].

Table 2. Crystal structure of the oxide complex.

Parameters	$\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$	$\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$	$(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$
PDF Card Number:	01-086-9054 QM: S	04-027-5993 QM: I	01-086-8830 QM: I
I/Ic (RIR):	3.150	5.592	4.749
Crystal System:	Tetragonal	Orthorhombic	Cubic
Space Group:	I41/acd:2	Pbnm	Fm-3m
a:	5.29930 Å	5.37620 Å	4.19200 Å
b:	5.29930 Å	5.39300 Å	4.19200 Å
c:	23.74950 Å	7.59260 Å	4.19200 Å
α :	90.000°	90.000°	90.000°
β :	90.000°	90.000°	90.000°
γ :	90.000°	90.000°	90.000°
Volume:	666.947 Å ³	220.139 Å ³	73.665 Å ³
Z:	8	4	4
Radiation Source:	CuK α 1	CuK α 1	CuK α 1
Wavelength:	1.54060 Å	1.54060 Å	1.54060 Å
2 θ Range:	0.00000 – 150.00000	10.00000 – 150.00000	20.00000 – 150.00000

Table 2 presents the crystallographic parameters of the phases identified in the investigated three-phase Ca–Nd–Mn–Ni–O oxide system according to the WPPF/Rietveld refinement results. The table includes the unit-cell parameters, unit-cell volume, number of formula units per unit cell (Z), calculated and crystallographic densities, as well as refinement quality indicators. The obtained structural parameters confirm the coexistence of the $\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$ and $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ phases together with a minor $(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$ phase in the synthesized material.

According to the WPPF/Rietveld refinement results, the synthesized sample represents a three-phase oxide system. The refinement demonstrated a satisfactory agreement between the experimental and calculated diffraction profiles, with reliability factors of $R_{wp} = 7.30\%$, $R_p = 5.07\%$, $S = 2.6424$, and $\chi^2 = 6.9822$. The main phase was identified as the calcium–neodymium manganate

$\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$ with a phase fraction of 67.2(3) wt.%. The refined unit-cell parameters of this phase were determined to be $a = 5.3306(3) \text{ \AA}$, $b = 5.3306(3) \text{ \AA}$, and $c = 23.8866(15) \text{ \AA}$.

To further verify the selected phase model, Rietveld refinement was performed using the GSAS-II software package.

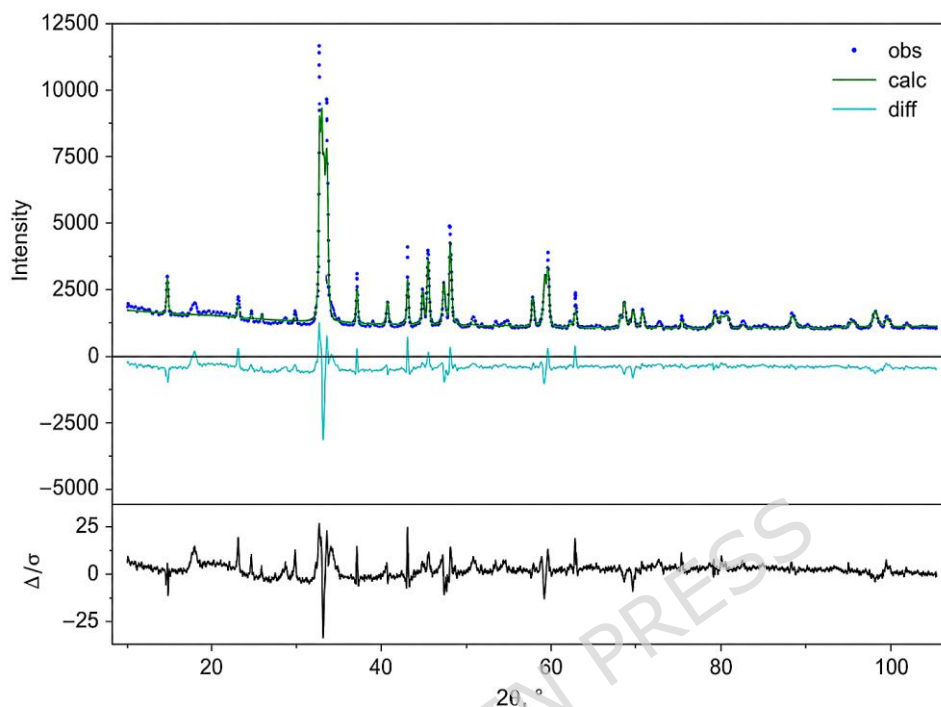


Figure 4. Rietveld refinement profile of the synthesized three-phase Ca–Nd–Mn–Ni–O oxide system obtained using GSAS-II. The blue points correspond to the experimental diffraction intensities, the green line represents the calculated diffraction profile, the cyan line shows the difference curve ($Y_{\text{obs}} - Y_{\text{calc}}$), and the lower black curve represents the normalized residual Δ/σ .

The refinement model also included three crystalline phases: Calcium Neodymium Manganate, Calcium Neodymium Manganese Nickel Oxide, and Manganese Nickel Oxide. The refinement converged successfully and demonstrated an acceptable agreement between the experimental and calculated diffraction profiles, with $R_{\text{wp}} = 9.27\%$ and $\chi^2 = 11.26$. The slight differences in the numerical values of the reliability factors obtained using the Rigaku and GSAS-II software packages are attributed to differences in the profile refinement algorithms, background description, peak-shape functions, number of refined parameters, and methods used for calculating the statistical criteria. Nevertheless, both approaches consistently confirm the same principal result, namely the formation of a three-phase oxide system.

The refinement results indicate that the synthesized material is a complex multiphase managanite system. The presence of overlapping reflections and minor residual discrepancies near several intense peaks may be associated with similar interplanar spacings of the coexisting phases, preferred crystallite orientation, microstrain effects, and local structural heterogeneity characteristic of multiphase transition-metal oxides. Nevertheless, the satisfactory agreement between the experimental and calculated diffraction profiles, together with the consistency of the results obtained using two different software approaches, confirms the validity of the proposed three-phase model.

Microstructural characterization of the compound was performed using scanning electron microscopy (SEM) at the Interdisciplinary Research Center of the Kazakh National Women's Teacher Training University (Almaty) (Figures 5–7). The SEM analysis was carried out on powder samples obtained after synthesis.

Figure 5 shows the microstructure of the three-phase Ca–Nd–Mn–Ni–O oxide system at a magnification corresponding to a 5 μm scale. The SEM image reveals agglomerated granular particles with a porous morphology characteristic of oxide ceramics synthesized by the conventional solid-state method [44, 45]. Such morphology is typical of multiphase manganite systems prepared via high-temperature ceramic processing.

The observed microstructure indicates the presence of irregularly shaped grains forming porous agglomerates with intergranular voids. Such morphology may contribute to the occurrence of intergranular effects and interfacial polarization, which can influence the electrophysical properties of the material. The selected magnification allows detailed visualization of the surface morphology and possible structural heterogeneity of the synthesized oxide system.

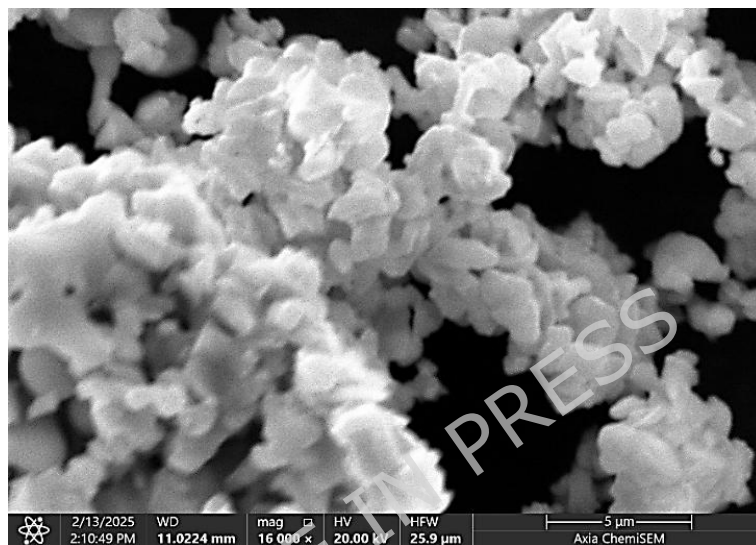


Figure 5. SEM microstructure of the three-phase Ca–Nd–Mn–Ni–O oxide system at a scale of 5 μm .

Figure 6 illustrates the microstructure of the three-phase Ca–Nd–Mn–Ni–O oxide system at a scale of 30 μm .

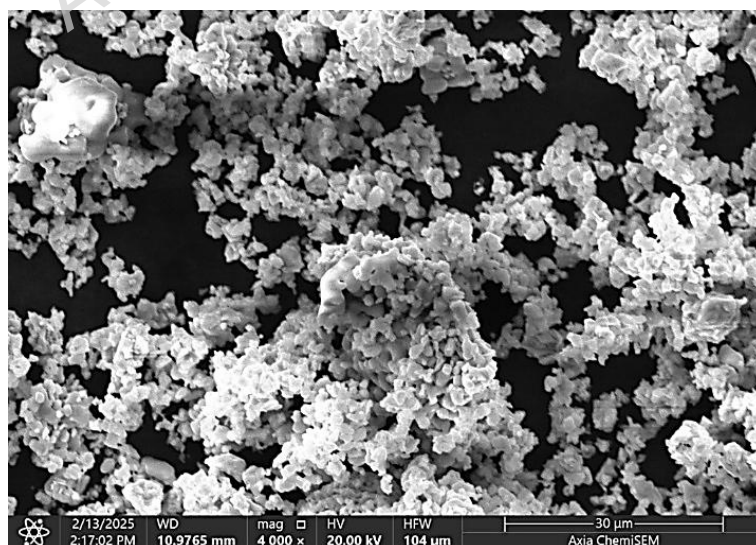


Figure 6. SEM microstructure of the three-phase Ca–Nd–Mn–Ni–O oxide system at a scale of 30 μm .

Figure 6 shows the microstructure of the three-phase Ca–Nd–Mn–Ni–O oxide system at a magnification corresponding to a 30 μm scale. The SEM image reveals a heterogeneous granular morphology consisting of agglomerated particles of different sizes and irregular shapes. Such

morphology is characteristic of multiphase oxide ceramics synthesized by the conventional solid-state method.

The particles form porous agglomerates with a nonuniform spatial distribution and well-developed intergranular regions, indicating the structural heterogeneity of the synthesized material. The observed morphology may influence the electrophysical properties of the oxide system due to intergranular effects and interfacial polarization processes.

The elemental distribution of Ca, Nd, Mn, Ni, and O within the structures was assessed (Figure 7).

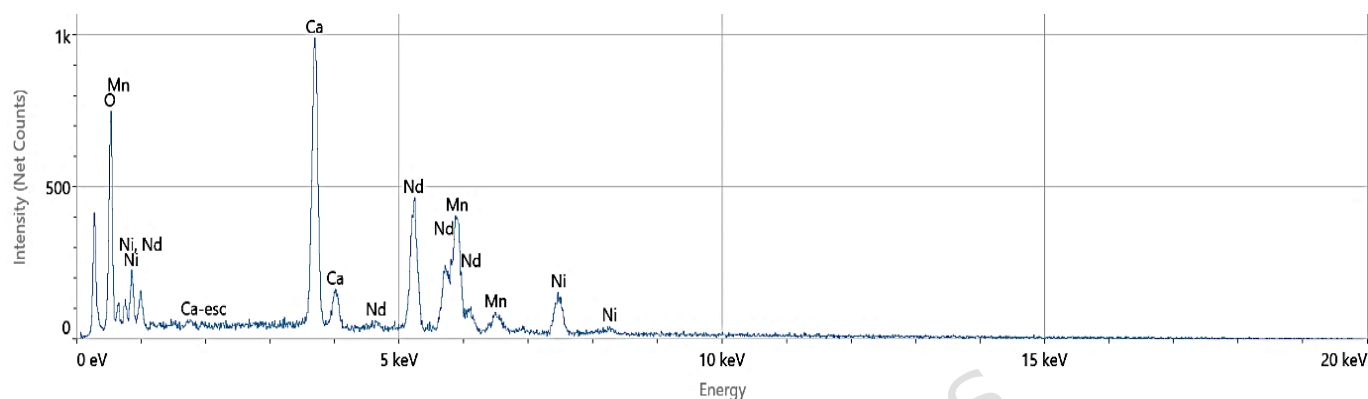


Figure 7. Elemental distribution across the surface.

The elemental mapping results show that Ca, Nd, Mn, Ni, and O are distributed relatively uniformly throughout the investigated material, which is consistent with the formation of a multiphase oxide system. According to the WPPF/Rietveld refinement results, the major phase of the sample is $\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$ (67.2 wt.%), whereas the perovskite-like $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ phase is present in a smaller amount (25.6 wt.%). The minor $(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$ phase accounts for approximately 7.2 wt.% and is likely localized in separate intergranular regions.

Manganese is present in all identified phases, whereas nickel is predominantly associated with the secondary nickel–manganese oxide phase and partially incorporated into the perovskite-like $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ structure. Oxygen participates in the formation of the octahedral framework characteristic of manganite oxide structures. The overall elemental composition of the sample (at.%) was determined to be: O — 56.0%, Ca — 17.6%, Mn — 11.7%, Ni — 6.5%, and Nd — 8.2%.

The FTIR spectrum presented in Figure 8 was obtained using the attenuated total reflection (ATR) method in the range of 1000–600 cm^{-1} . The spectrum corresponds to the investigated three-phase Ca–Nd–Mn–Ni–O oxide system. Two characteristic absorption bands are observed in the spectrum: an intense band at 710.10 cm^{-1} assigned to the stretching vibrations of metal–oxygen bonds, predominantly Mn–O bonds in $[\text{MnO}_6]$ octahedra characteristic of manganite oxide structures, and a less intense band at 684.09 cm^{-1} , also associated with vibrations in $[\text{MnO}_6]$ and/or $[\text{NiO}_6]$ octahedra, which may reflect the mixed nature of Mn–O and Ni–O bonds.

The observed bands confirm the formation of an octahedral oxygen framework characteristic of the perovskite-like and layered manganite phases present in the investigated multiphase system. The obtained FTIR spectroscopic data are in good agreement with the results of the X-ray diffraction analysis and the WPPF/Rietveld refinement.

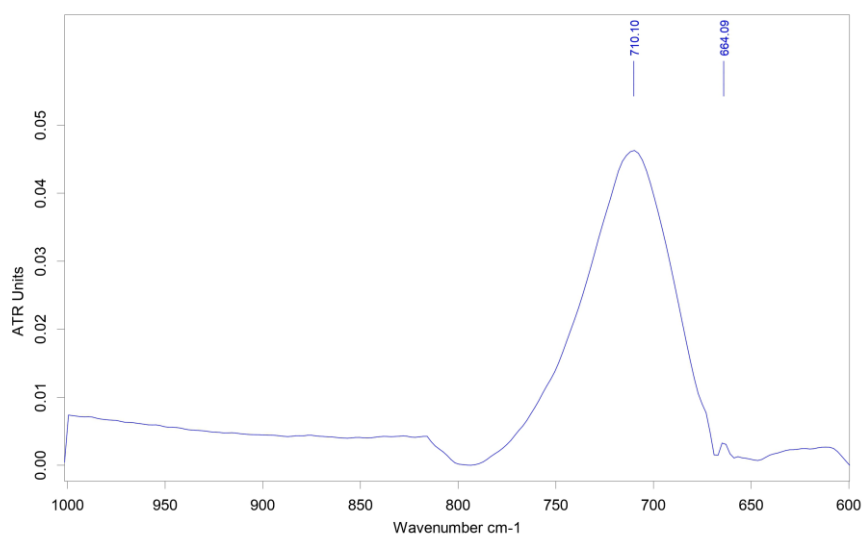


Figure 8. IR spectrum of the $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ –MnNi phase mixture in the range of 1000–600 cm^{-1} .

For LaMnO_3 and CaMnO_3 , the Mn–O stretching vibrations are typically observed in the range of ~ 610 – 630 cm^{-1} , while for NdMnO_3 similar bands are detected in the range of ~ 620 – 640 cm^{-1} [46, 47]. The bands identified in our study are shifted toward higher frequencies. This shift indicates the substitution of Nd^{3+} and Ni^{2+} ions, which influences the bond strength and the local symmetry of the crystal lattice through distortion and tilting of the MnO_6 octahedra [48]. The MnNi phase (an intermetallic compound) usually does not exhibit pronounced bands in the IR region due to the absence of significant dipole moments during vibrational transitions; therefore, its contribution to the spectrum is minimal or negligible [49].

3.1. Characterization

The phase composition of the synthesized sample was investigated by X-ray diffraction (XRD), including phase identification and WPPF/Rietveld refinement of the crystallographic parameters. The measurements were performed using a MiniFlex 300/600 diffractometer (Rigaku Corporation, Tokyo, Japan) with $\text{CuK}\alpha$ radiation operated at 40 kV and 15 mA. The diffraction data were collected in the 2θ range of 10 – 105° with a scanning step of 0.02° and a scanning rate of $5^\circ/\text{min}$, providing detailed analysis of the characteristic diffraction peaks.

The error in determining the interplanar spacings did not exceed $\pm 0.002 \text{ \AA}$, corresponding to the instrumental resolution of the diffractometer. The obtained X-ray diffraction data were processed using the PDF-5+ database and the Rigaku SmartLab Studio II software package. Phase identification and structural analysis were performed taking into account the possible coexistence of phases and the structural heterogeneity of the synthesized oxide system. The applied experimental methodology provided high-quality diffraction data suitable for phase analysis and WPPF/Rietveld refinement.

The electrophysical properties of the system were examined in the temperature range of 293–483 K with 10 K increments, following the procedure described in [50]. Measurements were conducted using a commercial LCR-781 instrument (Taiwan) at a working frequency of 1 kHz. According to the technical specifications, the measurement accuracy for capacitance, relative dielectric permittivity, and electrical resistance (R) is 0.05% [50]. A detailed description of the methodology is provided in this study and in previously reported analogous investigations [51, 52].

4. Conclusions

The three-phase Ca–Nd–Mn–Ni–O oxide system was synthesized by a conventional solid-state ceramic method. According to the WPPF/Rietveld refinement of the X-ray diffraction data,

the synthesized material predominantly consists of the $\text{Nd}_{0.25}\text{Ca}_{1.75}\text{MnO}_4$ phase (67.2 wt.%), together with the $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ phase (25.6 wt.%) and a minor $(\text{Ni}_{0.94}\text{Mn}_{0.06})\text{O}$ phase (7.2 wt.%). The refinement of the crystallographic parameters confirms the formation of a heterogeneous multiphase oxide system. The perovskite-like $\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Mn}_{0.97}\text{Ni}_{0.03}\text{O}_3$ phase is characterized by distorted $[\text{Mn}/\text{NiO}_6]$ octahedra typical of orthorhombic manganite structures.

The microstructure of the synthesized material was investigated by scanning electron microscopy (SEM), which revealed a heterogeneous granular morphology with porous agglomerates and well-developed intergranular regions characteristic of multiphase manganite ceramics prepared by high-temperature solid-state synthesis. Infrared spectroscopy confirmed the formation of metal–oxygen bonds associated with $[\text{MnO}_6]$ and $[\text{NiO}_6]$ octahedral units characteristic of manganite oxide structures.

The electrophysical properties of the investigated three-phase oxide system were studied in the temperature range of 293–483 K. The calculated effective activation energies of electrical conductivity were found to be 0.49 and 0.56 eV in the temperature intervals of 293–353 K and 393–483 K, respectively. The increase in the activation energy with increasing temperature may be associated with a change in the dominant charge-transport mechanism, as well as with the contribution of intergranular and interfacial regions in the heterogeneous multiphase structure. The obtained electrical response should therefore be regarded as an effective transport characteristic of the entire three-phase oxide system rather than of any individual phase.

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