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Electron Paramagnetic Resonance in non-stoichiometric cobaltite Na_xCoO_2 and study of the influence of degradation processes on properties of Na_xCoO_2 system

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Electron Paramagnetic Resonance (EPR) measurements of non-stoichiometric cobaltite Na_xCoO_2 in the sodium concentration range $x = 0.53; 0.58; 0.64; 0.75; 0.76; 0.79$ were carried out and the effect of degradation processes on the properties of Na_xCoO_2 system were studied. ESR signal was detected in sample with maximum sodium concentration $\text{Na}_{0.79}\text{CoO}_2$. Analysis of the obtained results on EPR allows us to say that the observed resonance signal is due to the magnetic ions Co^{4+} the appearance of which in the system under study is associated with sodium non-stoichiometry and possible presence of anti-structural defects caused by the localisation of cobalt ions in sodium positions. At low temperatures a sharp decrease in the width of the resonance line, g -factor and integral intensity of resonance signal was observed that indicates that in the $\text{Na}_{0.79}\text{CoO}_2$ sample the magnetic phase transition takes place. It has been established that after long-term storage under ambient conditions EPR signal in the sample $\text{Na}_{0.79}\text{CoO}_2$ disappear. The structural and electron microscopic studies carried out show that as a result of long-term storage of samples, the essential changes of phase composition take place.

Keywords: EPR, cathode materials, non-stoichiometric systems, magnetism, phase transitions.

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1. Introduction

Much attention in recent decades has been paid to compounds of type $A_x\text{MX}_2$ (A = alkali metal, M = transition metal, $X = \text{O}, \text{S}, \text{Se}$). These compounds have a laminar structure and mixed ion-electronic conductance. Ionic conductance is associated with the presence of mobile alkali ions, and electronic conductance is several orders of magnitude higher and, as a rule, presents a metallic character, characteristic of most compounds with a laminar structure [1]. The structural and transport properties of these compounds allow their use as electrode materials for lithium (sodium)-ion batteries. One of the representatives of this type of compound is sodium cobaltite with the chemical formula NaCoO_2 . Sodium cobaltite NaCoO_2 is attractive from the point of view of application as a cathode material for sodium-ion batteries, reviewed as an alternative to lithium-ion batteries [2], as well as thermoelectric materials [3]. Compared to lithium, sodium has a low cost, is widespread in nature and the oxidation-reduction potential of sodium (-2.71 V) is close to lithium (-3.04 V), which allows to review it as an alternative to the traditionally used LiCoO_2 . At the same time, the practical values of the electrical capacity of the considered cobaltites turn out to be noticeably lower than theoretical estimates, which is associated with various kinds of structural imperfections and phase transformations. Indeed, LiCoO_2 and NaCoO_2 compounds can have a certain degree of nonstoichiometry

in terms of both oxygen, lithium, and sodium. As has been found, the level of sodium content in Na_xCoO_2 is a determining factor for the magnetic, electronic and other properties of the compound, i.e. coefficient value x . For example, a high value of the Seebeck coefficient was found at a value of $x = 0.5$, which makes this material promising for thermoelectric devices [4]. Therefore, it is important to obtain data on potential changes in the phase composition of samples in various operating and storage conditions. This paper presents the results of EPR measurements and the results of structural measurements using X-ray diffraction analysis, scanning electron microscopy, and energy-dispersive analysis of the Na_xCoO_2 ($0.5 < x < 0.8$) system.

2. Samples and methods

Samples with different sodium content x (0.53; 0.58; 0.64; 0.75; 0.76; 0.79) were obtained in this paper using the standard solid-phase method, by mixing Co_3O_4 , Na_2CO_3 in appropriate proportions, and subsequent annealing at a temperature of 800°C [5]. EPR measurements were carried out using a Bruker spectrometer at a frequency of 9.23 GHz in the temperature range of 20–300 K. Low temperatures were achieved by using a helium purge, which is a flow system for helium gas passing through the microwave cavity of the spectrometer. An ampoule with a sample and a thermocouple were placed directly into this flow system.

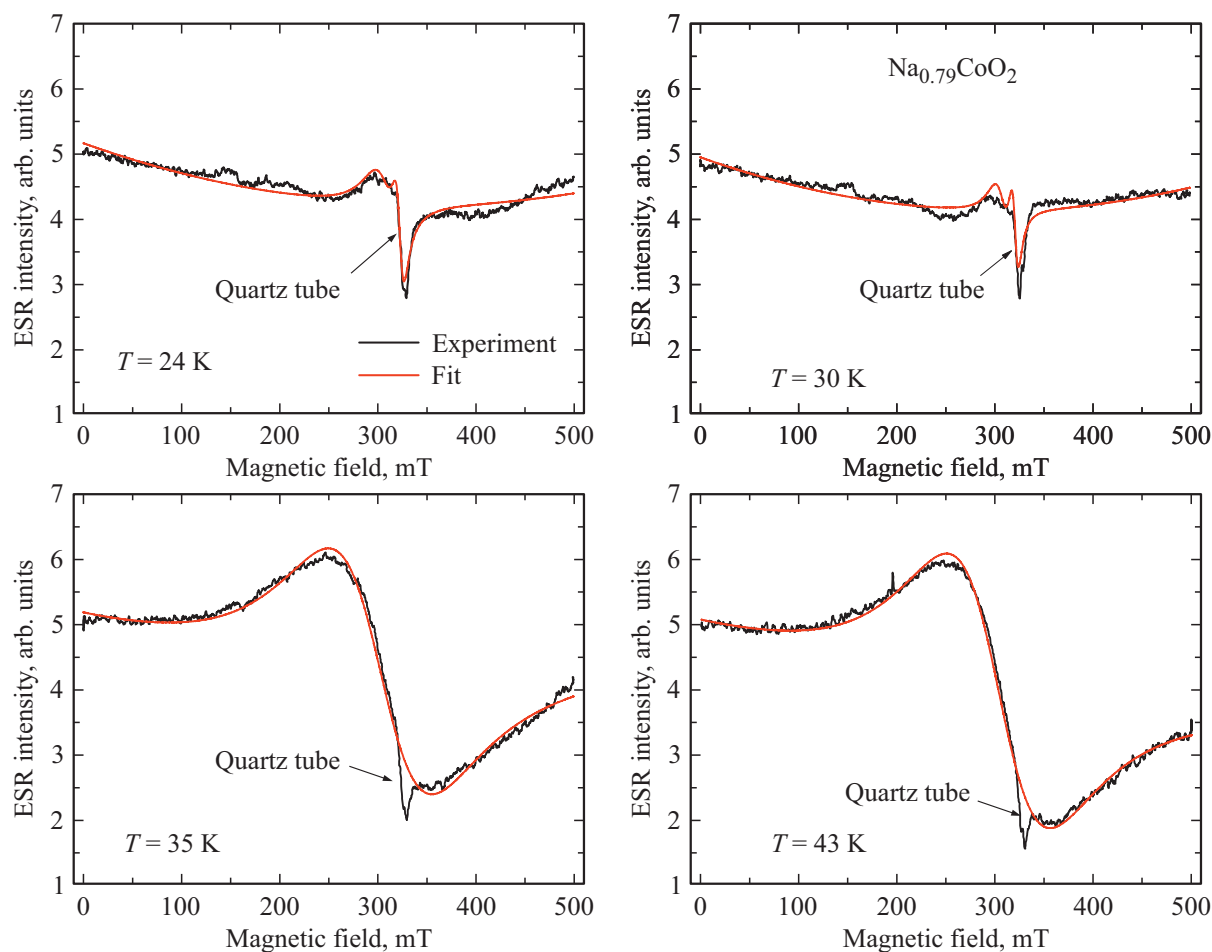


Figure 1. EPR spectra of $\text{Na}_{0.79}\text{CoO}_2$ at different temperatures: 24, 30, 35 and 43 K. The results of approximation of the spectra using the Lorentz shape of the absorption line are shown by red lines.

High-resolution scanning electron microscopy (SEM) Carl Zeiss EVO 50XVP with an energy-dispersive X-ray elemental microanalyzer was used to study the surface morphology of Na_xCoO_2 samples. The samples were studied at room temperature.

Identification of samples and determination of the parameters of their crystal structure were carried out using X-ray diffraction analysis. The studies were performed using DRON-7 diffractometer (CuK_α radiation). The spectra were processed using the Maud program.

3. Findings and discussion

X-ray diffraction patterns of Na_xCoO_2 samples with different sodium contents $x = 0.53; 0.58; 0.64; 0.75; 0.76; 0.79$ show that the resulting samples are single-phase and have a hexagonal $\gamma\text{-Na}_x\text{CoO}_2$ structure [6].

3.1. EPR studies

The EPR was measured on all obtained Na_xCoO_2 samples in a broad temperature range of 20–300 K. It

was found that of all the samples studied, the EPR signal was observed only in the sample with the highest sodium concentration $x = 0.79$.

The measurements performed show that the EPR signal, its width and amplitude differ significantly for different temperatures. Experimental EPR spectra of the $\text{Na}_{0.79}\text{CoO}_2$ sample recorded at various temperatures are shown in Figure 1.

There is an additional narrow resonance signal (radical center) from the quartz tube in which the sample is placed in the spectra as can be seen in the figure. Let us note also that the spectra are recorded with a base line, which has a parabolic shape, which may be related to the conductance of the sample. A theoretical fitting of the experimentally observed resonance lines was carried out using the Lorentz line shape for a detailed analysis of the temperature dependence of the EPR spectra. A good agreement between the experimental and theoretical absorption lines was obtained using the Lorentz shape of the resonance line as can be seen from Figure 1, which indicates the presence of exchange interaction between them in the system of magnetic ions. Indeed, the studies of the electron density distribution based

on X-ray synchrotron radiation measurements demonstrated a direct observation of the formation of hybridized states between the $3d$ and $2p$ electron levels Co-Na, respectively, in the Na_xCoO_2 system with the increase of a sodium concentration [5]. Figure 2 shows the temperature dependences of the g -factor, the absorption linewidth and the integral intensity of the observed EPR signal.

In the first instance, of course, there is a question about the nature of the observed EPR signal. It is known that the cobalt ions have the valency Co^{3+} in stoichiometric NaCoO_2 and are in the low-spin configuration of t_{2g}^6 . This state corresponds to a completely filled $3d$ orbital. This configuration has zero spin and is characterized by the absence of an EPR signal. Indeed, most published papers indicate the absence of an EPR signal in sodium stoichiometric NaCoO_2 samples. The presence of sodium nonstoichiometry in Na_xCoO_2 samples is characterized by a change in the valence state of cobalt ions in the proportion $\text{Co}_x^{3+}/\text{Co}_{1-x}^{4+}$ depending on the content of sodium ions. This means the occurrence of magnetic Co^{4+} ions in the studied system and the possibility of observing an EPR signal on them. Thus, indeed, an EPR signal in Na_xCoO_2 on samples with $x = 0.65$; 0.7 and 0.75 was observed in paper [6]. The occurrence of Co^{4+} ions can also be caused by antisite defects, when during the synthesis some cobalt ions fill the positions of another cation — sodium, and vice versa, some sodium ions fill the cobalt positions. In this case, the cobalt ion goes into the charge state $4+$, donating an electron to the structure of local bonds, when localized in sodium positions. The occurrence of such antisite centers of transition elements was found in various systems [7,8]. The results of numerous experimental and theoretical studies [9–12] indicate very complex structural changes that occur in this above-mentioned region of sodium concentrations, which also cause corresponding changes in the electronic and magnetic properties of the system. Indeed, a change of the sodium concentration in the Na_xCoO_2 system results in significant changes of the crystal lattice parameters. For instance, it was found in Ref. [9] that the magnetic moments of cobalt ions depend significantly on the distance between the cobalt ions and sodium ions. The electronic structure of the Co^{3+} ions and its valence state do not change as the distance Co-Na decreases, while the probability of the occurrence of Co^{4+} ions increases as this distance increases. Thus, if the distances between the cobalt and sodium ions determine the valence state and magnetic moments of the cobalt ions, then the effects of magnetic interaction in such a system become significantly more complicated, since the sodium ions are randomly distributed over their positions in the corresponding layers in the nonstoichiometric Na_xCoO_2 . As can be seen from Figure 2, the EPR linewidth, the g factor and the integral intensity of the EPR signal behave monotonically in the region of high temperatures, without demonstrating a significant variation of values. In particular, the behavior of the integral intensity of the resonance line is characteristic of the magnetic susceptibility of a paramagnet

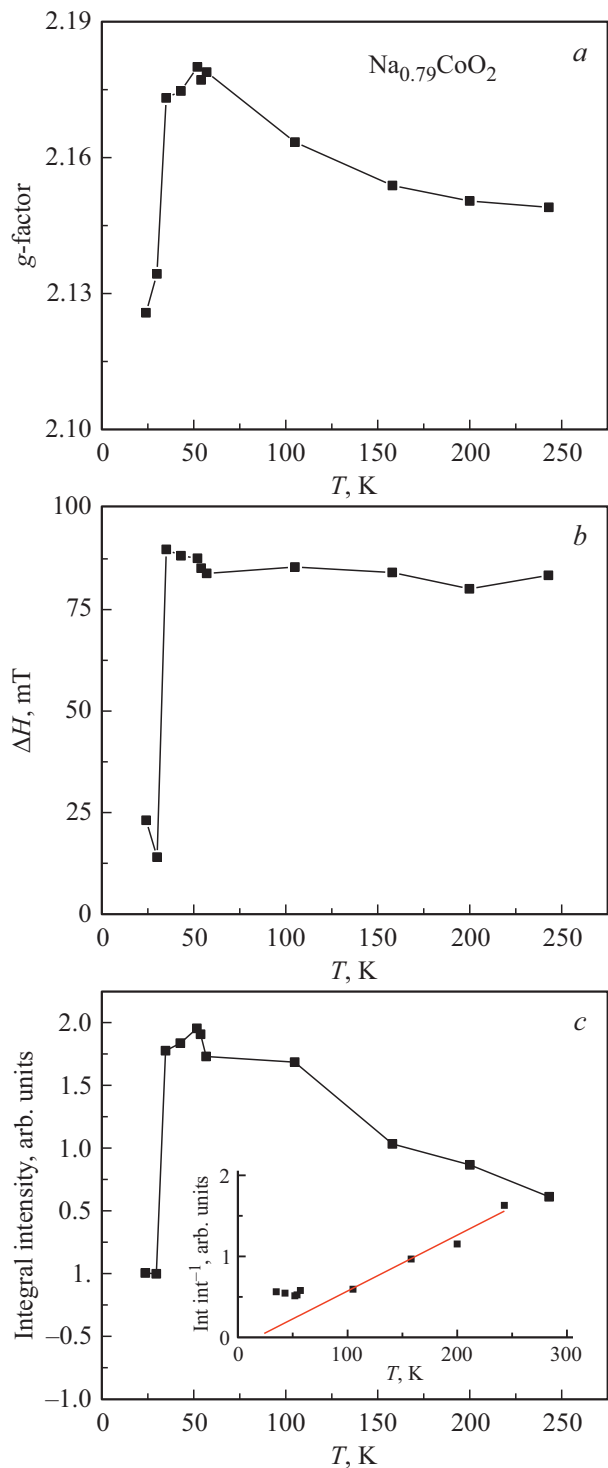


Figure 2. The temperature dependence of EPR spectrum parameters for $\text{Na}_{0.79}\text{CoO}_2$: (a) g -factor; (b) absorption line width; (c) integral intensity.

described by the Curie-Weiss law in accordance with the expression

$$\chi = C/(T - \theta), \quad (1)$$

where θ — temperature of Curie-Weiss.

A sharp decrease of the EPR linewidth, g factor and integral intensity is observed with the decrease of the temperature $T < 50$ K. Figure 2 shows that the line width decreases by almost a factor of 4 and the integral intensity drops to almost zero. This means a significant change of the magnetization towards its decrease in the specified temperature range. There is no doubt that this is primarily determined by those exchange processes that are realized in the system of magnetic moments associated with Co^{4+} ions. As already noted, the magnitudes of the magnetic moments of Co ions depending on their localization positions in the crystal lattice and the distance between Co and sodium ions were theoretically calculated in paper [9]. It was shown that the magnetic ions Co^{4+} will also be randomly distributed in the crystal lattice since sodium ions are distributed randomly over their localization positions in the nonstoichiometric system Na_xCoO_2 . In this case, the dominant interaction between magnetic cobalt ions will be short-range magnetic correlations between nearby magnetic ions, which leads, as a rule, to a magnetic state of the spin glass type, when the magnetic moments freeze in random orientations. The existence of magnetically correlated regions caused by structural defects and the presence of ions of different valences was also observed in Ref. [13,14].

3.2. Structural studies

It was found that sodium ions in nonstoichiometric Na_xCoO_2 have high mobility, which is natural, since unoccupied positions are required for diffusion processes. There is no doubt that the phase composition of Na_xCoO_2 samples with different sodium concentrations will significantly depend on operating conditions. Indeed, the high ionic mobility of sodium and its reactivity (for instance, Na ions readily react with molecules present in the surrounding atmosphere to form NaOH or sodium carbonates) significantly complicated the monitoring of Na levels. For this reason it was of interest to conduct morphological and structural studies of these samples of Na_xCoO_2 , stored in the ambient conditions for 6 months.

The surface morphology of the Na_xCoO_2 samples was studied by high-resolution scanning electron microscopy (SEM) using a Carl Zeiss EVO 50XVP electron microscope with an energy-dispersive X-ray elemental microanalyzer. SEM images of the surface of the studied Na_xCoO_2 samples are shown in Figures 3–8.

The obtained micrographs show that the morphology of the surface of the samples behaves extremely inconsistently (ambiguously) if we approach the analysis from the point of view of finding certain patterns associated with an increase of sodium concentration. It can be said that there are surface types depending on the surface morphology of the samples. *Ia* — „needle-like particles“ were found on the surface of samples of this type. *Ib* — non-ideal prism-like shape were found on the surface of samples of this type.

Table 1. Average values of the obtained Na/Co ratio values

Sample	Xnom.	Average value Na/Co ratio (atomic, %)	Types surface
1	0.53	0.27	II
2	0.58	0.76	<i>Ia</i>
3	0.64	0.56	<i>Ib</i>
4	0.75	1.81	<i>Ia</i>
5	0.76	3.01	<i>Ib</i>
6	0.79	2.37	<i>Ia</i>

II — the surface of these samples is a laminar structure. This is clearly visible from the SEM micrographs of samples with different sodium concentrations below.

The obtained electron microscopic images show the presence of white particles of various sizes on all samples. Let us note that there were similar white particles on the surface of $\text{Na}_{0.88}\text{CoO}_2$ single crystals after exposure to the surrounding atmosphere [15]. It was assumed that as a result of interaction with the environment, particles of sodium hydroxide (NaOH) and sodium carbonates appear on the surface of single crystals.

Table 1 shows the results of energy-dispersive analysis (EDA) of Na_xCoO_2 samples and, in particular, the average values of the obtained Na/Co ratios are presented. The measurements were performed at several points on areas of 400×300 microns.

Based on the results of EDA of the Na_xCoO_2 samples, it is possible to say that a deviation of the Na/Co ratio from the initial value x is observed in each of such sample, which indicates the heterogeneity of the samples.

The identification of samples and determination of the parameters of their crystal structure were carried out using the X-ray diffraction analysis. The studies were performed using DRON-7 diffractometer (CuK_α radiation). The spectra were processed using the Maud program. (The software for the analysis of X-ray diffraction data based on an iterative procedure for minimizing the deviation between the experimental and calculated X-ray patterns using the combined Rietveld method [16]).

Figures 9–10 shows the X-ray diffraction patterns of Na_xCoO_2 (0.53; 0.79) samples stored in the normal conditions for 6 months. The results of processing of X-ray images using the Maud program are listed in Table 2.

Thus, X-ray diffraction analysis shows that the phase composition of samples significantly changes as a result of their long-term storage. A significant presence of the $\text{Na}_{0.57}\text{CoO}_2$ phase (81.1%, 56.0% and 81.3%, respectively) and the $\text{Na}_{0.78}\text{CoO}_2$ phase (18.9, 44.0 and 18.7% respectively) is found in Na_xCoO_2 samples with sodium contents of $x = 0.58, 0.75$ and 0.76 . The presence of the $\text{Na}_{0.84}\text{CoO}_2$ phase was found in an amount of 29.4% and 52.1%,

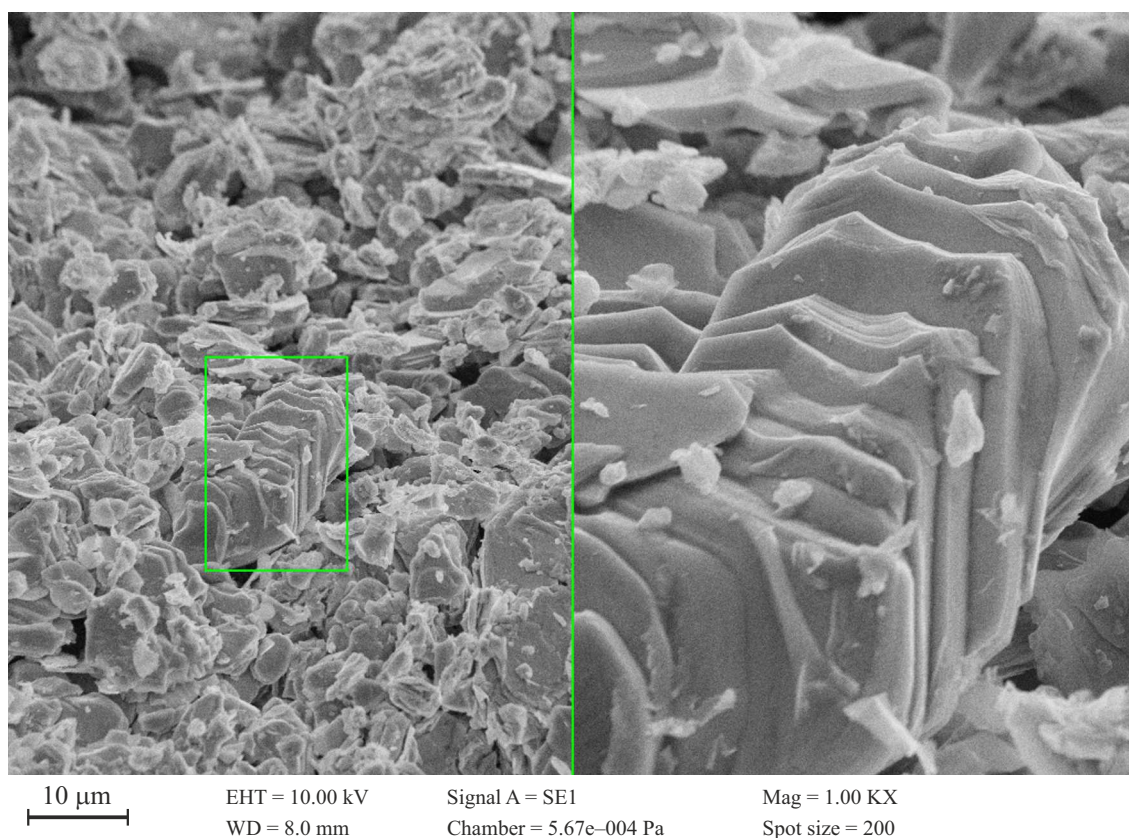


Figure 3. SEM micrograph of sample $\text{Na}_{0.53}\text{CoO}_2$ with surface type II.

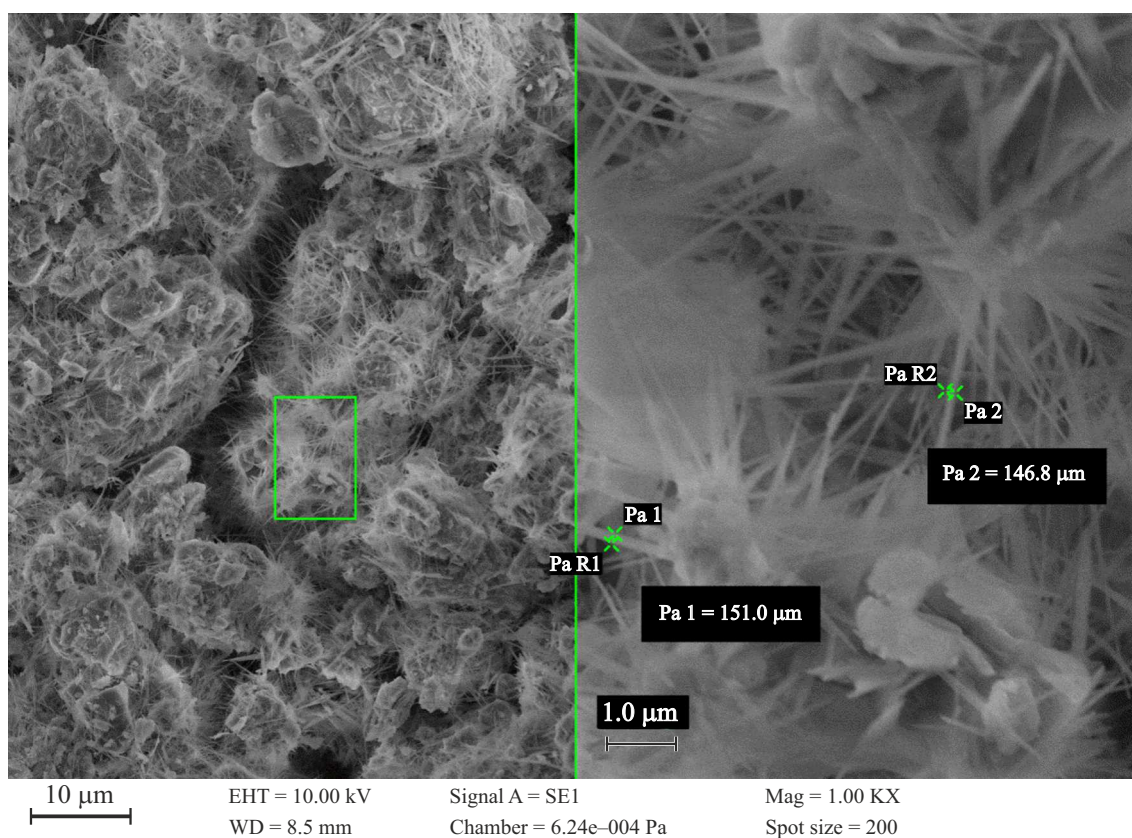


Figure 4. SEM micrograph of a sample $\text{Na}_{0.58}\text{CoO}_2$ with surface type Ia.

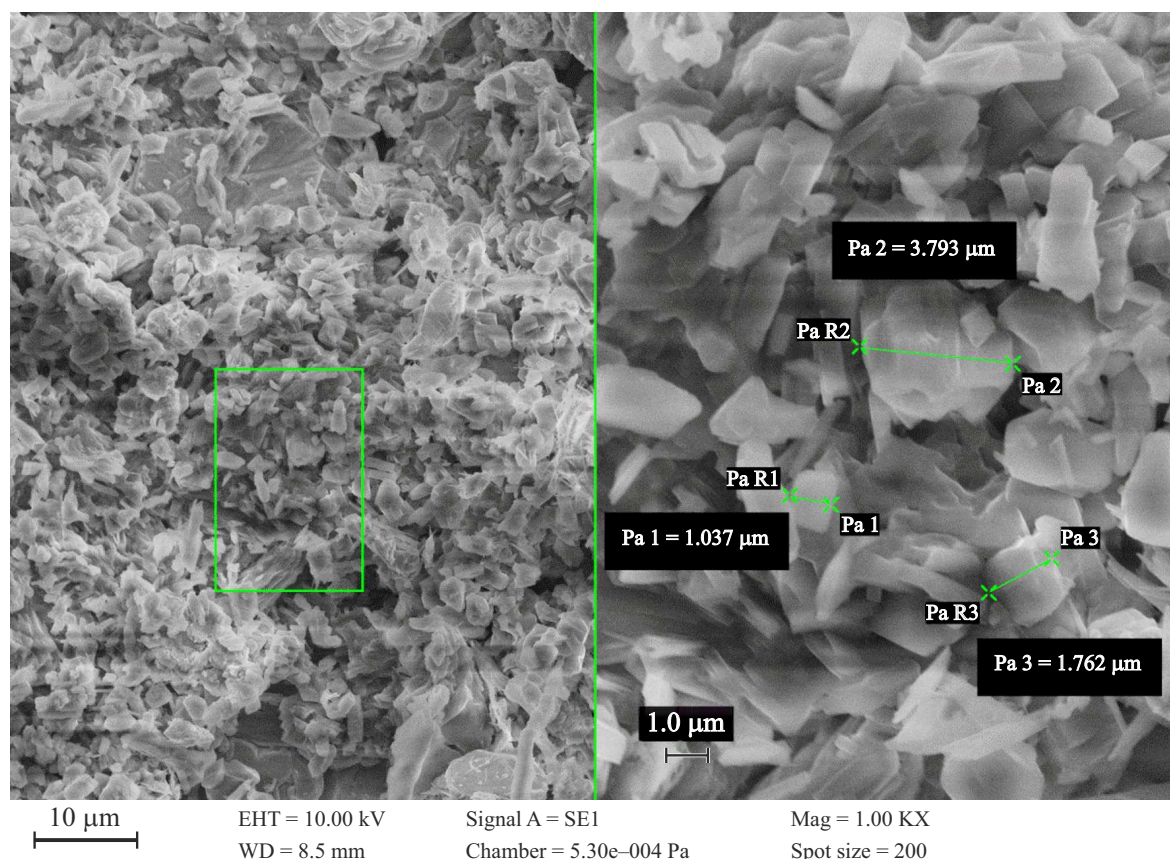


Figure 5. SEM micrograph of a sample $\text{Na}_{0.64}\text{CoO}_2$ with surface type Ib .

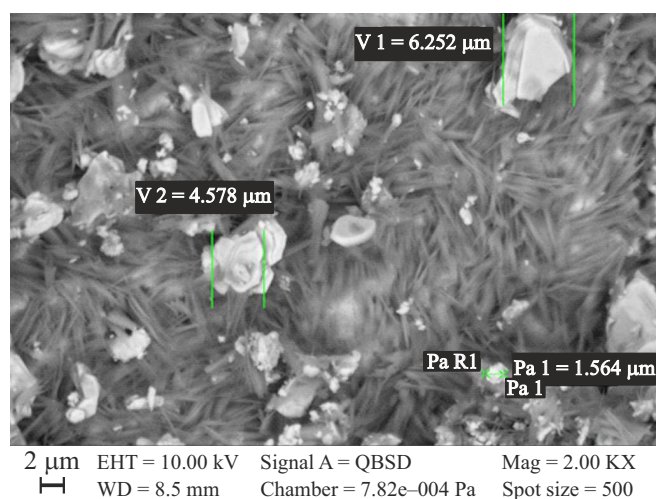


Figure 6. SEM micrograph of a sample of $\text{Na}_{0.75}\text{CoO}_2$ with surface type Ia .

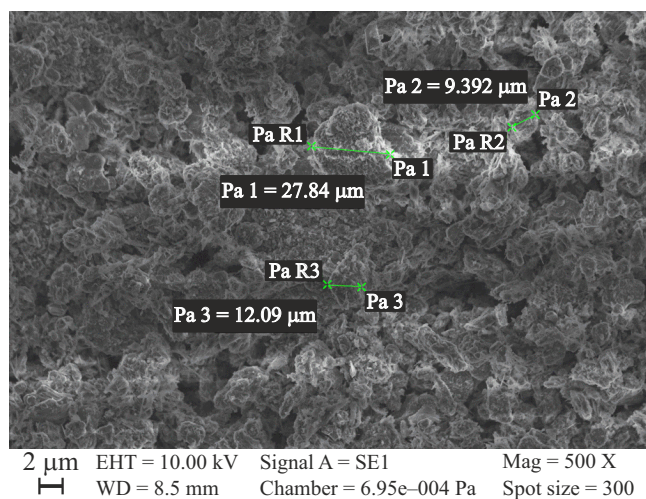


Figure 7. SEM micrograph of a sample of $\text{Na}_{0.76}\text{CoO}_2$ with surface type Ib .

respectively, in the samples with the lowest sodium concentration $x = 0.53$ and the highest sodium concentration $x = 0.79$. Meanwhile, H_3NaO_2 phase was observed in the last two samples. This phase comprises a sodium hydroxide monohydrate, white crystals. Comparing the

results of energy-dispersive analysis with X-ray diffraction data, it is clear that the surface properties of Na_xCoO_2 differ from the bulk properties, which is undoubtedly associated with the active properties of the surface of this compound.

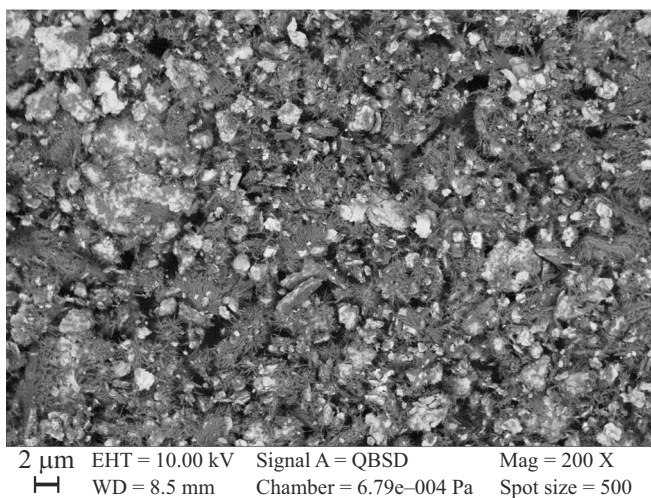


Figure 8. SEM micrograph of a sample of $\text{Na}_{0.79}\text{CoO}_2$ with surface type Ia.

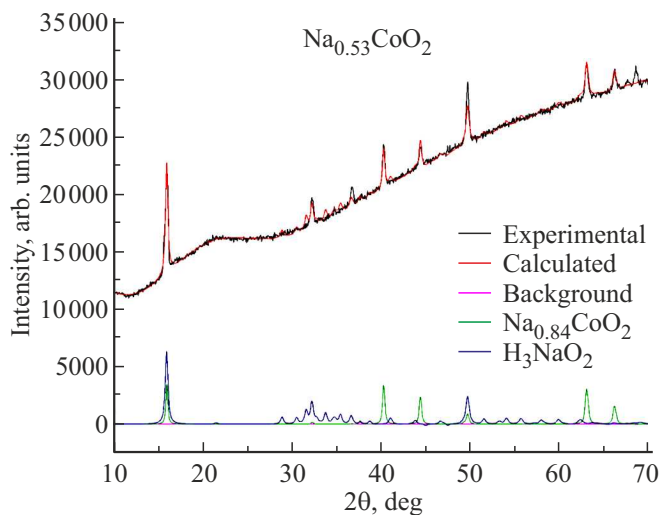


Figure 9. X-ray diffraction pattern of a sample of $\text{Na}_{0.53}\text{CoO}_2$.

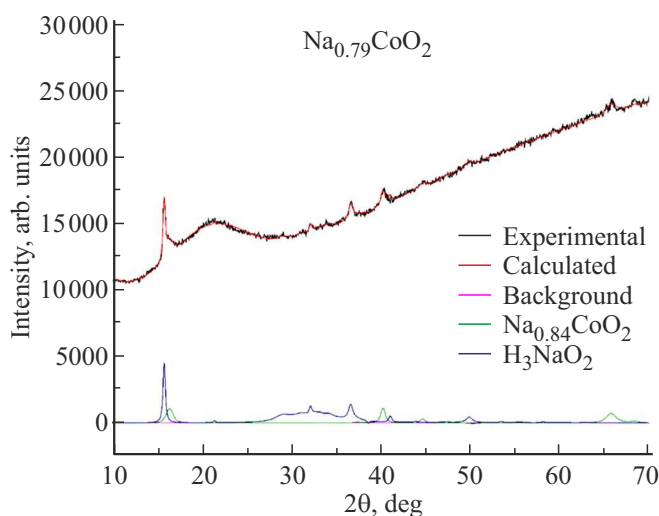


Figure 10. X-ray diffraction pattern of a sample of $\text{Na}_{0.79}\text{CoO}_2$.

Table 2. Results of X-ray image processing using the Maud program

Content Na	Phase content, weight, (%)			
	$\text{Na}_{0.57}\text{CoO}_2$	$\text{Na}_{0.78}\text{CoO}_2$	$\text{Na}_{0.84}\text{CoO}_2$	H_3NaO_2
0.53			29.4	70.5
0.58	81.1	18.9		
0.75	56	44		
0.76	81.3	18.7		
0.79			52.1	47.9

4. Conclusion

EPR was measured in nonstoichiometric cobaltite of Na_xCoO_2 in the sodium concentration range of $x = 0.53$; 0.58; 0.64; 0.75; 0.76; 0.79 and the impact of degradation processes on the properties of the Na_xCoO_2 system was studied in this paper. An EPR signal was detected in the sample with the maximum sodium concentration $\text{Na}_{0.79}\text{CoO}_2$. The analysis of the obtained EPR results allows saying that the observed resonance signal is attributable to magnetic ions Co^{4+} , the appearance of which in the studied system is associated with sodium nonstoichiometry and the presence of antisite defects caused by the localization of cobalt ions in sodium positions. A sharp decrease of the EPR linewidth, g factor and integral intensity of the EPR signal is observed in the region of low temperatures of $T < 50\text{ K}$. This means that the magnetization of the sample significantly decreases in the specified temperature range. Sodium nonstoichiometry in Na_xCoO_2 samples results in the appearance of cobalt ions in the proportion of $\text{Co}_x^{3+}/\text{Co}_{1-x}^{4+}$ depending on the content of sodium ions, at which magnetic Co^{4+} ions and non-magnetic Co^{3+} ions are randomly distributed in the crystal lattice. In this case, the dominant interaction between magnetic cobalt ions will be short-range magnetic correlations between nearby magnetic ions, which leads, as a rule, to a magnetic state of the spin glass type, when the magnetic moments „freeze“ in random orientations. It was found that the EPR signal in the $\text{Na}_{0.79}\text{CoO}_2$ sample disappears after long-term storage under ambient conditions. The conducted structural and electron microscopic studies demonstrate that a significant change of their phase composition is observed as a result of long-term storage of samples. It was found that the changes of the surface properties of Na_xCoO_2 differ from the changes occurring in the volume of the sample, which is undoubtedly associated with the active properties of the surface of this compound.

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Conflict of interest

The authors declare that they have no conflict of interest.

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