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RESEARCH ARTICLE

Technology of synthesis and electronic structure of triple barium–strontium–calcium carbonates for cathodes of microwave devices

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Abstract
Objectives. Triple barium–strontium–calcium carbonates of various grades are widely used for depositing oxide coatings on cathodes of electrovacuum devices. Of all types of cathodes used in electrovacuum devices, oxide cathodes are among the most common, due to combining efficiency, durability, operation at relatively low temperatures, and a relatively low cost. The aims of this work were to: create a technology for the synthesis of triple barium–strontium–calcium carbonates with nonequilibrium phase compositions that comprise the triple carbonate proper and a pure barium carbonate phase; develop a quality control procedure for such a carbonate for using it as a component of the cathode material for microwave devices; study how the electronic structure of barium oxide crystallites is affected by doping microimpurities from other phases of the cathode material.
Methods. The study used precision X-ray diffraction analysis and electron spectroscopy.
Results. A technology was developed for the co-precipitation of triple barium–strontium–calcium carbonates from their nitrate salts. Under optimal precipitation conditions, this produces triple carbonate powders with nonequilibrium phase compositions. Electron spectroscopy showed that the parameters of the electronic structure of the crystallites are significantly affected by doping impurities of calcium, strontium, and nickel in barium oxide crystallites formed by heat treatment of triple carbonates.
Conclusions. Calcium and strontium have a synergistic effect on the doping of barium oxide with the two other chemical elements. As well as efficiently controlling the quality of the nonequilibrium phase composition of triple carbonates, which is formed during the synthesis of triple carbonates by the titration method, precision X-ray diffraction analysis can be used to efficiently control the processes of agglomeration of nanoparticles or recrystallization of nanostructured phases formed during the synthesis of triple carbonates.

Keywords: porous-metal cathodes, cathode material, thermionic emission, electronic structure, X-ray diffraction analysis

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НАУЧНАЯ СТАТЬЯ

Технология синтеза и электронная структура тройных карбонатов бария-стронция-кальция для катодов СВЧ-приборов

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Резюме

Цели. Тройные карбонаты бария-стронция-кальция различных марок широко используются для нанесения оксидных покрытий на катоды электровакуумных приборов. Из всех типов катодов в электровакуумных приборах оксидные катоды являются одними из самых распространенных, т.к. сочетают в себе эффективность, долговечность, работу при относительно небольших температурах и сравнительно невысокую стоимость. Цели работы – разработка технологии синтеза тройных карбонатов бария-стронция-кальция с неравновесным фазовым составом, состоящим из собственно тройного карбоната и фазы чистого карбоната бария, разработка методики контроля качества такого карбоната для применения его в качестве компонента катодного материала для СВЧ-приборов, а также исследование влияния на электронную структуру кристаллитов оксида бария легирующих микропримесей из состава других фаз катодного материала.

Методы. Использована методика прецизионного рентгеноструктурного анализа и методы электронной спектроскопии.

Результаты. Разработана технология совместного осаждения тройных карбонатов бария-стронция-кальция из их азотнокислых солей, которая при выборе оптимального режима осаждения позволяет получать порошки тройного карбоната с неравновесным фазовым составом. Методами электронной спектроскопии показано, что легирующие примеси кальция, стронция, никеля в кристаллитах оксида бария, формирующихся при термообработке тройных карбонатов, существенно влияют на параметры электронной структуры кристаллитов.

Выводы. Совместное влияние кальция и стронция свидетельствует о наличии так называемого синергетического эффекта при легировании оксида бария двумя другими химическими элементами. Методика прецизионного рентгеноструктурного анализа позволяет эффективно контролировать качество неравновесного фазового состава тройных карбонатов, формирующегося при синтезе тройных карбонатов методом титрования и контролировать процессы агломерации наночастиц либо рекристаллизации наноструктурированных фаз, формирующихся при синтезе тройных карбонатов.

Ключевые слова: металлопористые катоды, катодный материал, термоэлектронная эмиссия, электронная структура, рентгеноструктурный анализ

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INTRODUCTION

Triple barium–strontium–calcium carbonates have been widely used as components of various types of cathodes for microwave electrovacuum devices – in particular, as the main component of a nickel oxide cathode. The chief characteristics of triple carbonates are determined by their chemical composition and particle size distribution [1, 2]. While there are various technologies for the synthesis of triple carbonates [3–11], the functional efficiency of cathodes using these materials strongly depends on the technology used for their synthesis. Figure 1a shows the equilibrium ternary phase diagram of ternary carbonates [12], and Fig. 2b presents that of ternary oxides [13], which are formed by the decomposition of ternary carbonates during activation of cathodes by heating at a temperature of about 1000°C. The shaded areas in the diagrams indicate compositions of materials used in cathode electronics.

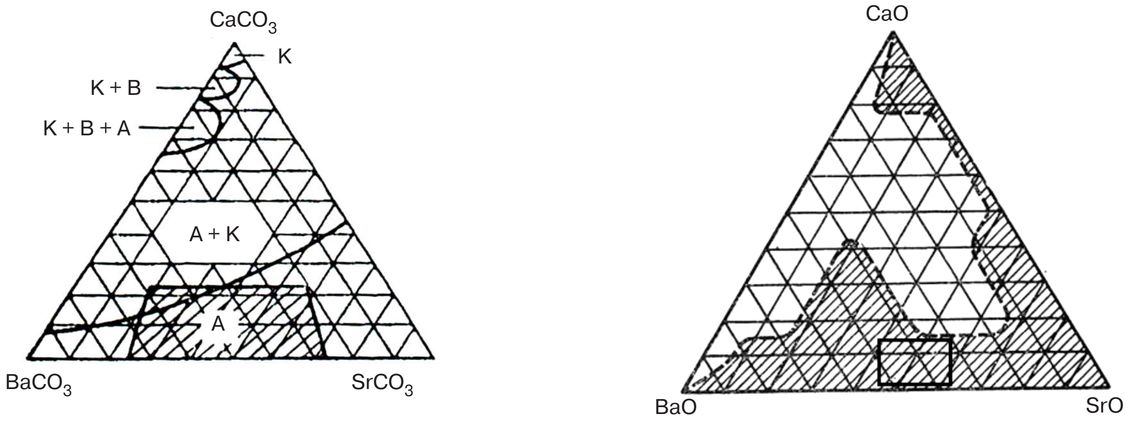
Examples of practically used materials consisting of triple carbonates include aragonite having a rhombohedral crystal structure, comprising a ternary solid carbonate solution. In the case of the thermal decomposition of such a triple carbonate during activation of cathodes and the formation of a ternary solid solution of barium–strontium–calcium oxides, the work function of such a material is known to be higher than that of pure barium oxide [14]. It is noted in the literature that the phase composition of triple carbonates and, hence, their efficiency in the manufacture of cathodes strongly depends on their synthesis conditions [12, 15].

The aims of this work were to create a technology for the synthesis of triple barium–strontium–calcium carbonates with nonequilibrium phase compositions that comprise the triple carbonate proper and a pure barium carbonate phase, as well as developing a quality control procedure for such a carbonate for using it as a component of the cathode material for microwave devices and studying how the electronic structure of barium oxide crystallites is affected by doping microimpurities from other phases of the cathode material.

TRIPLE CARBONATE SYNTHESIS TECHNOLOGY

Triple barium–strontium–calcium carbonates of KTA-1-6 grade were prepared by rapidly adding a 3.5 molal aqueous ammonium carbonate solution stabilized with ammonia to a 1 molal aqueous solution of the corresponding nitrate salts at room temperature. Triple barium–strontium–calcium carbonate of KTA-1-6 grade was obtained by adding a 0.9 molal aqueous solution of the corresponding nitrate salts heated to 45°C to a 3.5 molal aqueous ammonium carbonate solution stabilized with ammonia.

When developing a technology for the synthesis of triple carbonates with nonequilibrium phase compositions, various synthesis conditions were tested. These differed in the rate of addition of the precipitating

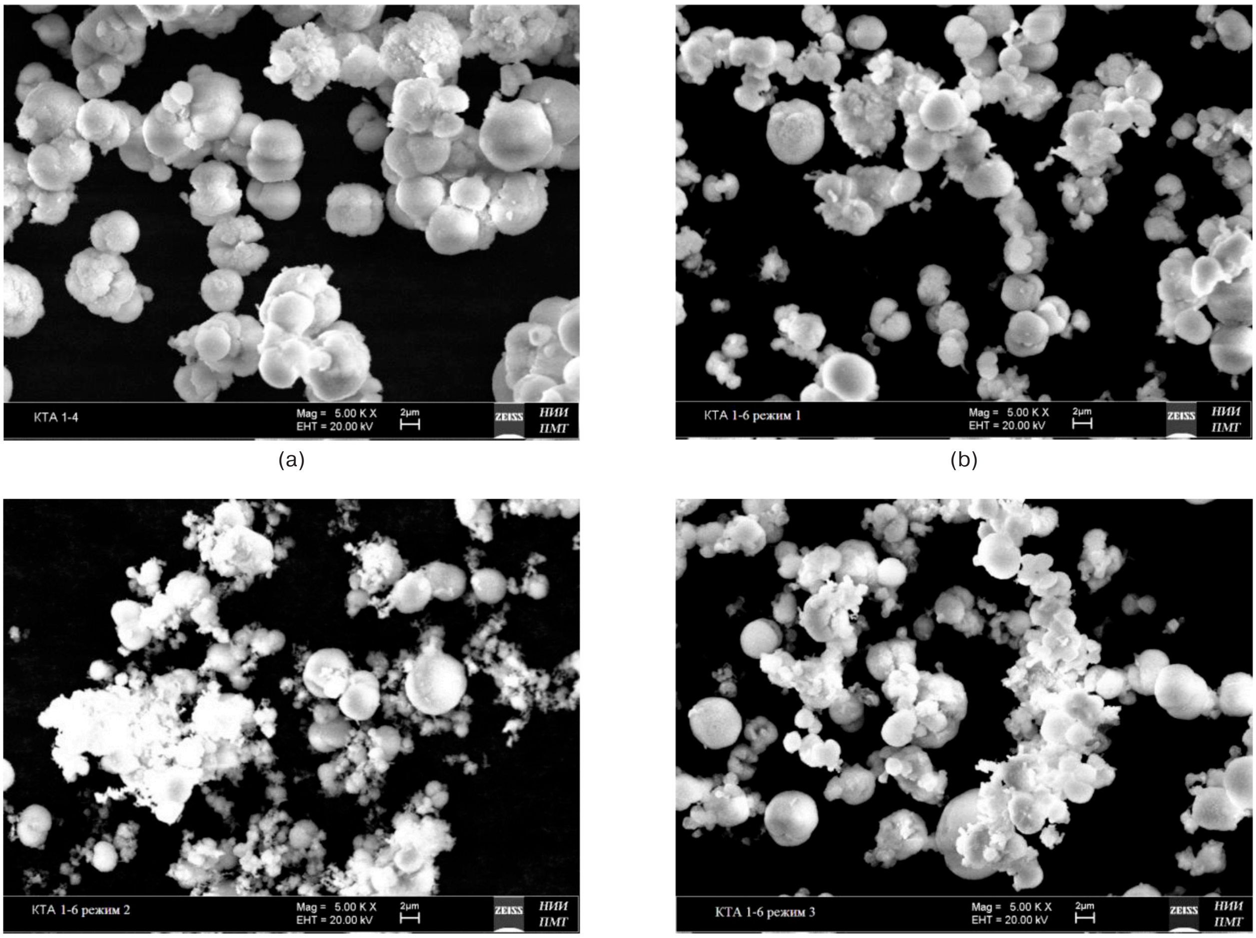


(a) (b)

Fig. 1. Phase diagrams of the (a) $BaCO_3$–$SrCO_3$–$CaCO_3$(a) [1] and (b) BaO–CaO–SrO [2] systems

Table 1. Conditions of synthesis of triple barium–strontium–calcium carbonates

Parameter	Variants of synthesis products			
	KTA-1-4	KTA-1-6, conditions 1	KTA-1-6, conditions 2	KTA-1-6, conditions 3
Morphology of product	Fig. 2a	Fig. 2b	Fig. 2c	Fig. 2d
Average grain size, μm (measured with PSKh-10a, LabNauchPribor, Russia)	3.9	1.9	0.9	2.0
Composition $BaCO_3$:$SrCO_3$:$CaCO_3$, %	50:43:6	50:43:6	50:43:6	54:40:5
Temperature of nitrate solution, °C	46	26	30	30
Molar concentration of nitrate solution	0.9	1	1	1



(a) (b) (c) (d)

Fig. 2. Micrographs of particles of triple barium–strontium–calcium carbonate

component to the solution of nitrate salts, as well as the rate of mixing of the reacting solutions.

The structure of the powders of the synthesis products was studied by electron spectroscopy, while the phase composition was studied by X-ray powder diffraction analysis. Table 1 presents the conditions of the synthesis of triple carbonates, while Fig. 2 shows the morphology of particles of the synthesis products.

INVESTIGATION OF THE PHASE COMPOSITION OF SYNTHESIS PRODUCTS

The synthesis products were studied by X-ray powder diffraction analysis. Since the parameters of the crystal structure of germanium are known up to the fifth decimal place, a germanium powder was added to the material to be analyzed at a concentration of 20% to function as an internal standard. Preliminarily, pure barium carbonate

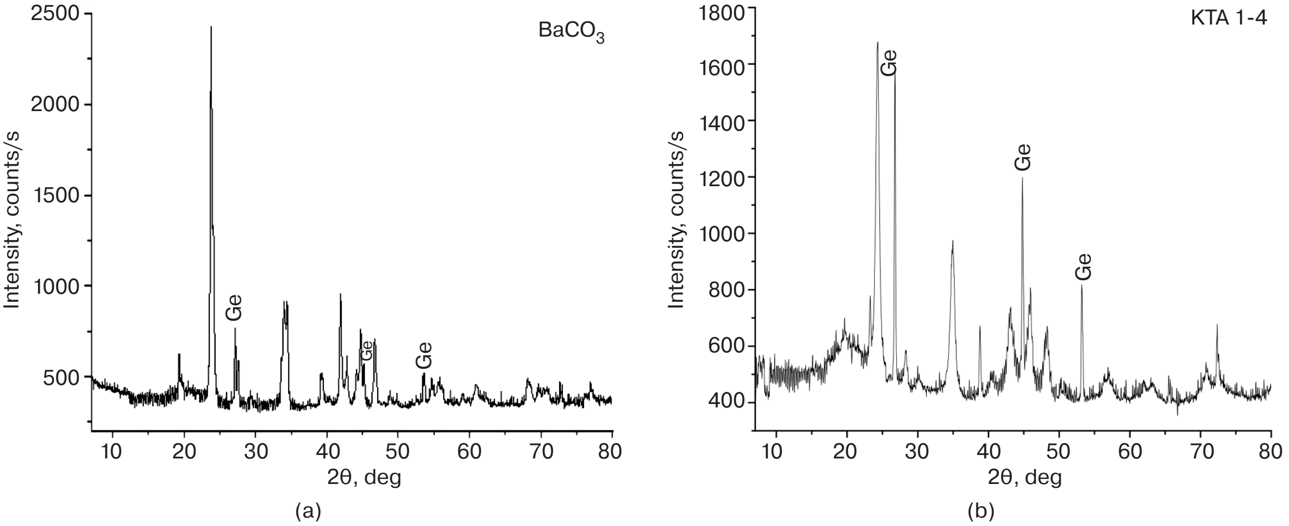


Fig. 3. X-ray powder diffraction patterns of (a) carbonate $BaCO_3$ and (b) triple carbonate of grade KTA-1-4

was studied, the X-ray powder diffraction pattern of which is shown in Fig. 3a. As an example, Fig. 3b presents the X-ray powder diffraction pattern of the synthesized KTA-1-4 grade triple carbonate.

Along with solid solutions of triple carbonates, the analysis of the phase composition of triple carbonate synthesis products demonstrated the presence of pure barium carbonate, which content strongly depends on the synthesis conditions. Table 2 presents the most significant characteristics of the X-ray powder diffraction analysis of the synthesis products of triple carbonates along with the characteristics of pure barium carbonate.

By analyzing the recorded X-ray powder diffraction patterns along with the parameters given in Table 2, it was possible to formulate quality control criteria for triple barium–strontium–calcium carbonates to permit the efficient use of this material as a component of microwave device cathodes. Figure 4 illustrates the selection of quality criteria for triple carbonate using a portion of the X-ray powder diffraction pattern in the 2θ range 22°–28°.

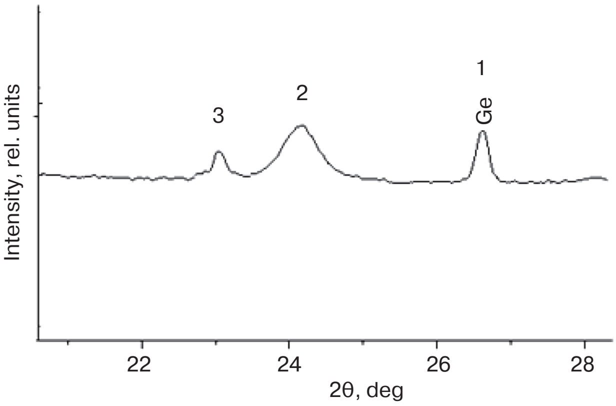


Fig. 4. Selection of quality control parameters for triple carbonates

In Fig. 4, peak 1 is the germanium peak used as an internal standard for determining the positions of other peaks in the X-ray powder diffraction pattern up to the fifth decimal place. Peak 2 characterizes a solid triple carbonate solution phase, while peak 3 corresponds to a phase of pure barium carbonate. To summarize the results of this

Table 2. Quality control parameters for triple carbonates

Parameter	Material				
	$BaCO_3$	KTA-1-4	KTA-1-6, conditions 1	KTA, conditions 2	KTA, conditions 3
a, position of peak of triple carbonate, deg	–	23.318	23.654	24.673	23.644
d, interplanar distance at peak of triple carbonate, Å	–	3.660	3.611	3.608	3.613
δθ, broadening of peak of triple carbonate, deg	–	0.40	0.43	0.46	0.42
a_0, position of peak of barium carbonate, deg	23.778	23.262	23.660	24.22	23.618
Δ*a*, shift of peak of barium carbonate, deg	Standard	−0.516	−0.118	0.442	–0.160
$\delta\theta_0$, broadening of peak of barium carbonate, deg	0.31	0.20	0.06	0.07	0.10
I, barium carbonate to triple carbonate peak area ratio in sample, %	100	7.5	1.1	3.8	2.3

study, physical criteria can be formulated for the quality of triple barium–strontium–calcium carbonate for its use as a component of the cathode materials for microwave devices:

- the position of peak 2 (triple carbonate) represents the composition of the solid solution of triple carbonate;
- the width of peak 2 (triple carbonate) represents the scatter in the composition of triple carbonate;
- the position of peak 3 (pure barium carbonate) represents the level of doping with microimpurities, including calcium and strontium;
- the width of peak 3 (pure barium carbonate) represents the size of crystallites of pure barium carbonate;
- the ratio of the areas of peaks 3 and 2 represents the content of pure barium carbonate in the synthesis product.

INVESTIGATION OF THE ELECTRONIC STRUCTURE OF MATERIALS

Along with triple barium–strontium–calcium carbonate, another component of nickel oxide cathodes is nickel powder having a particle size of 15–25 µm. In addition to functioning as a metal phase to increase the thermal and electrical conductivity of the material, nickel acts as a catalyst for the decomposition of triple carbonate to the corresponding barium–strontium–calcium oxides. In addition, nickel atoms entering the crystal lattice of barium oxide affect the parameters of the electronic structure of the oxide. Obviously, the functions of a catalyst and an alloying element can be performed more efficiently by nickel nanoparticles introduced into the cathode material as an additional component. In this context, we studied the electronic structure of the material of the composition 0.9Ni + 0.1 (KTA-1-6-grade triple carbonate + 0.1Ni (nano)). The nanopowder comprised a nickel powder with a particle size of 80 nm, which was produced by electrical nickel wire explosion by our order at NPK Peredovye poroshkovye tekhnologii (Tomsk, Russia).

The electronic structure of the materials was investigated using a Theta Probe high-resolution electron spectrometer (Thermo Fisher Scientific, USA) equipped with a high-resolution spherical mirror analyzer, an X-ray source, and several types of electron gun. This permits the study of materials by chemical analysis and characteristic electron energy loss spectroscopy.

The initial components of test samples were a KTA-1-6 grade triple carbonate powder (OST 11-OD0.028.002-76[1], Pluton, Russia); a PNK-1L7 grade nickel powder with particle sizes of 15–25 µm (Kolskaya GMK, Russia), and a nano nickel powder (TU 1791-003-36280340-2008, Peredovye poroshkovye tekhnologii,[2] Russia). After mixing the components in a turbula-type mixer (PASM1.000.001, NPK ISTEL, Russia), the samples of the materials were placed into molybdenum vessels (made by hand according to GOST 25442-82[3] from a sheet of MCh grade molybdenum, sheet thickness of 0.22 mm, PO Volfram, Russia) with an alundum-coated molybdenum insert (made by alunding molybdenum sheets according to the internal technology of the enterprise) on nickel plates and sintered in bulk in a vacuum furnace (SShVE-1-2,5/25-I2, NPO TsNIITMASh, Russia) with a gradual temperature rise to 1200°C for 2 h. The materials to be studied were compacted into pellets 1 mm thick and 7.6 mm in diameter on a laboratory press Vaneox 25t (FLUXANA GmbH & Co.KG., Germany) in steel molds at a specific pressing force of $P_{sp} \sim 4.5–5$ t/cm^2.

Figure 5 shows the electronic spectrum of barium states in the studied sample of the material of the composition 0.9Ni + 0.1 (KTA-1-6-grade triple carbonate + 0.1Ni(nano)), while Table 3 presents the results of the interpretation of this spectrum.

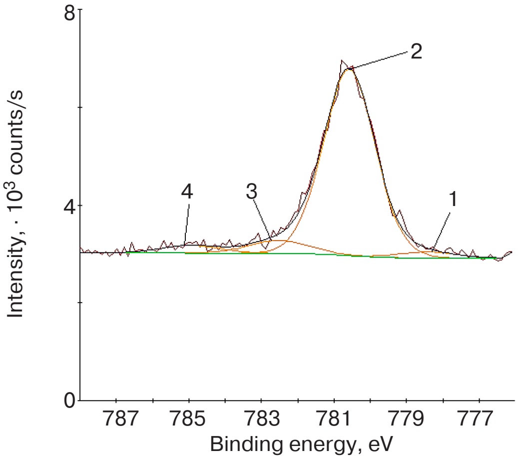


Fig. 5. Electronic spectrum of barium in a sample of the material 0.9Ni + 0.1(KTA + 0.1Ni (nano))

Characteristic electron energy loss spectroscopy was used to study the electron plasma energy losses upon excitation of bulk and surface plasmons in the oxide phases listed in Table 3. Figure 6 shows the characteristic electron energy loss spectrum after its differentiation in order to more clearly distinguish the peaks of characteristic losses.

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[1] OST 11-OD0.028.002-76. Electro-vacuum devices. Carbonate of alkaline-earth metals of barium, strontium, calcium. Specifications. http://www.docum.ru/ost.asp?id=262135. Accessed October 28, 2022 (in Russ.).

[2] http://www.nanosized-powders.com. Accessed October 28, 2022 (in Russ.).

[3] GOST 25442-82. Interstate standard. Molibdenum annealed strips for deep drawing. Specifications. Moscow: Izd. Standartov; 2004 (in Russ.).

Table 3. Interpretation of the electronic spectrum of barium in a sample of the material 0.9Ni + 0.1(KTA + 0.1Ni (nano))

No. of peak	Peak energy, eV	Peak intensity, counts/s	Peak width, eV	Barium in compound
1	778.43	124.17	1.96	$Ba(OH)_2 \cdot 2H_2O$
2	780.58	3806.47	1.74	$Ba_{(1-y)}O_{(1-x)}Ni_y$
3	782.51	262.61	1.98	$BaO_{(1-x)}$
4	784.94	159.08	1.95	$Ba_{(1-y)}O_{(1-x)}Ca_y$

Table 4. Parameters of characteristic losses in the oxide phases of the material 0.9Ni + 0.1(KTA + 0.1Ni (nano))

No. of phase	Phase composition	Parameter				
		E_s, eV	E_b, eV	N_s, m^{-3}	N_b, m^{-3}	N_s/N_b
1	$BaO_{(1-x)}$	1.96	2.56	$4.84 \cdot 10^{24}$	$4.15 \cdot 10^{24}$	1.17
2	$Ba_{(1-y-z)}O_{(1-x)}Ca_ySr_z$	3.40	5.42	$1.05 \cdot 10^{25}$	$1.33 \cdot 10^{25}$	0.79
3	$Ba_{(1-y)}O_{(1-x)}Ni_y$	7.81	10.84	$4.76 \cdot 10^{25}$	$4.60 \cdot 10^{25}$	1.03

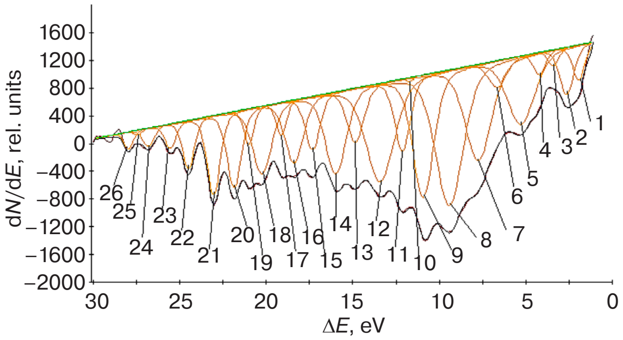

Fig. 6. Characteristic electron energy loss spectrum of the material 0.9Ni + 0.1(KTA + 0.1Ni (nano))

Barium oxide, which is formed by the heat treatment of the material and contains oxygen vacancies, is a donor-type semiconductor, whereas the other carbonate or oxide phases in the cathode material are dielectrics. Therefore, when the surface of the material is bombarded by medium-energy electrons, they undergo characteristic energy losses due to the excitation of bulk and surface plasmons—collective oscillations of oxygen vacancy electrons. Their energies, E_b and E_s, respectively, are found from the well-known expressions

$$\Delta E_b = \sqrt{\frac{e^{*2}\hbar^2 N_b}{\varepsilon\varepsilon_0 m^*}}, \qquad (1)$$

$$\Delta E_s = \sqrt{\frac{e^{*2}\hbar^2 N_s}{\varepsilon\varepsilon_0 m^*}}, \qquad (2)$$

where e^* is the effective charge of an oxygen vacancy, m^* is the effective mass of oxygen vacancy electrons, $\hbar$ is the Planck constant, ε_0 is the vacuum permittivity, $\varepsilon = 3.6$ is the high-frequency permittivity of barium oxide, N_b is the bulk concentration of oxygen vacancies, and N_s is the surface concentration of oxygen vacancies.

The total losses ΔE due to the excitation of plasmon oscillations are written as

$$\Delta E = n_1 E_b + n_2 E_s, \qquad (3)$$

where n_1 and n_2 are integers.

Characteristic loss peaks 1–26 in Fig. 6 are well grouped into 9 groups, which (three rows each) correspond to the phases $BaO_{(1-x)}$, $Ba_{(1-y)}O_{(1-x)}Ni_y$, $Ba_{(1-y)}O_{(1-x)}Ca_y$. Table 4 presents summary data on the parameters of the characteristic electron energy losses, along with the calculated values of the volume and surface concentrations of oxygen vacancies in various phases of barium oxide.

CONCLUSIONS

It is shown that the technology of coprecipitation of triple barium–strontium–calcium carbonates from their nitrate salts can be used under optimal precipitation conditions to produce powders of triple carbonates having nonequilibrium phase compositions.

The results of the study of the electronic structure of carbonates containing a nickel nanopowder suggested the following conclusions:

(1) The higher bulk and surface concentrations of oxygen vacancies in the $Ba_{(1-y)}O_{(1-x)}Ni_y$ phase than in the simple $BaO_{(1-x)}$ phase should be accompanied by a lower work function of this phase and, hence, a higher thermal emission current density.

(2) Although the bulk concentration of vacancies is lower in the $Ba_{(1-y-z)}O_{(1-x)}Ca_ySr_z$ phase than in the $Ba_{(1-y)}O_{(1-x)}Ni_y$ phase, the ratio of the bulk and volume concentrations of vacancies is significantly less than unity; i.e., the surface is depleted in oxygen

vacancies, which should be accompanied by a decrease in the upward curvature of the energy bands, i.e., a decrease in the work function of the material.

(3) Calcium and strontium have a synergistic effect on the doping of barium oxide with the two other chemical elements.

The results of the study of the crystal structure of triple carbonates synthesized by the titration method suggest the following conclusions:

- Precision X-ray diffraction analysis efficiently controls the quality of the nonequilibrium phase composition of triple carbonates, which is formed during the synthesis of triple carbonates by the titration method.
- (5) Precision X-ray diffraction analysis can be used to efficiently control the processes of agglomeration of nanoparticles or recrystallization of nanostructured phases formed during the synthesis of triple carbonates.

Authors' contributions

V.I. Kapustin—definition of the research concept; study of the electronic structure of materials; analysis and interpretation of data; writing the initial text of the article.

I.P. Li—investigation of the powder structure of synthesized products via electron spectroscopy; analysis and interpretation of data; participation in writing the initial text of the article.

N.E. Kozhevnikova—development of technology for the synthesis of non-equilibrium phase compositions of triple carbonates; conducting the synthesis of triple carbonates of KTA-1-6, KTA-1-4 grades; preparation of samples of materials to study their electronic structure; participation in writing the initial text of the article.

E.F. Khudaigulova—investigation of the phase composition of powders of synthesized products via X-ray phase analysis; participation in writing the initial text of the article.

All authors have approved the final manuscript for publication.

REFERENCES

1. Nikonov B.P. *Oksidnyi katod* (*Oxide Cathode*). Moscow: Energiya; 1979. 240 p. (in Russ.).
2. Kapustin V.I., Li I.P., Kozhevnikova N.E., Khudaigulova E.F. New criteria for quality control of raw barium-strontium-carbonates calcium. *Elektronnaya tekhnika. Seriya 2: Poluprovodnikovye pribory*. 2021;3(262):94–98 (in Russ.). https://www.elibrary.ru/item.asp?id=46663947
3. Karsakova M.B., Petrova O.B. Processes of crystal formation of triple carbonates for the technology of cathodes of electrovacuum devices. In: *Youth and 21st century 2022*. Proceedings of the 12th International Youth Scientific Conference. In 4 v. Kursk; 2022. V.1. P. 32–36 (in Russ.).
4. Mosin A.D., Pastushkova A.A. Study of the structure of triple carbonates. In: *Scientific and technological progress: information, technology, mechanism the collection*. Collection of articles on results of the International Scientific and Practical Conference. Sterlitamak; 2020. P. 83–87 (in Russ.).
5. Kapustin V.I., Li I.P., Kozhevnikova N.E., Karsakova M.B., Khudaigulova E.F. Synthesis and analysis of nanoscale crystallites of triple barium–strontium–calcium carbonates for cathodes of microwave devices. In: *XI Vserossiskaya nauchno-tekhnicheskaya konferentsiya* “*Elektronika i mikroelektronika SVCh*” (*The 11th All-Russian Scientific and Technical Conference “Microwave Electronics and Microelectronics*.” Collection of reports. St. Petersburg. May 30 – June 3, 2022). St. Petersburg: SPbGETU LETI. P. 427–431 (in Russ.). Available from URL: https://mwelectronics.etu.ru/assets/files/2022/427-431.pdf

СПИСОК ЛИТЕРАТУРЫ

1. Никонов Б.П. *Оксидный катод*. М.: Энергия; 1979. 240 с.
2. Капустин В.И., Ли И.П., Кожевникова Н.Е., Худайгулова Э.Ф. Новые критерии контроля качества тройных карбонатов бария-стронция-кальция. *Электронная техника. Серия 2: Полупроводниковые приборы*. 2021;3(262):94–98. https://www.elibrary.ru/item.asp?id=46663947
3. Карсакова М.Б., Петрова О.Б. Процессы кристаллообразования тройных карбонатов для технологии катодов электровакуумных приборов. В сб.: *Молодежь и XXI век – 2022*. Материалы 12-й Международной молодежной научной конференции: в 4-х т. Курск; 2022. Т. 4. С. 32–36.
4. Мосин А.Д., Пастушкова А.А. Исследование структуры тройных карбонатов. В сб.: *Научно-технический прогресс: информация, технологии, механизм*. Сборник статей по итогам Международной научно-практической конференции. Стерлитамак; 2020. С. 83–87.
5. Капустин В.И., Ли И.П., Кожевникова Н.Е., Карсакова М.Б., Худайгулова Э.Ф. Синтез и анализ наноразмерных кристаллитов тройных карбонатов бария-стронция-кальция для катодов СВЧ приборов. В сб.: *XI Всероссийская научно-техническая конференция «Электроника и микроэлектроника СВЧ»*. Сборник докладов. Санкт-Петербург. 30 мая – 3 июня 2022 г. СПб.: СПбГЭТУ «ЛЭТИ». С. 427–431. URL: https://mwelectronics.etu.ru/assets/files/2022/427-431.pdf
6. Александров Е.М., Шофман Г.С., Лубянецкая К.Ф., Фельдман Ф.С. *Способ изготовления эмиссионного материала для оксидных катодов*: пат. 2019878 РФ. Заявл. 26.02.1992; опубл. 15.09.1994.

6. Aleksandrov E.M., Shofman G.S., Lubyanetskaya K.F., Fel'dman F.S. *Method for manufacturing emission material for oxide cathodes*: RF Pat. 2019878. Publ. 15.09.1994 (in Russ.).
7. Artyushenko A.I., Batura Z.E., Krivobok V.I., Nakhodnova A.P. *Method for obtaining fine powders of triple and double carbonates of alkaline earth elements*: RF Pat. 180572. Publ. 19.03.1966 (in Russ.).
8. Dorzhin G.S., Neznaev G.N., Kitaeva T.I. Rusakova Zh.P. *Method for obtaining mixed carbonates of alkaline earth metals*: RF Pat. 520330. Publ. 05.07.1976 (in Russ.).
9. Evstigneeva N.K., Kalinina I.D. *Method for obtaining powders of double or triple carbonates of alkaline earth metals*: RF Pat. 880983. Publ. 15.11.1981 (in Russ.).
10. Smorodinova L.A., Aryanina T.G. *Emission material*: RF Pat. 873301. Publ. 15.10.1981 (in Russ.).
11. Kiselev A.B., Lobova E.V., Nikonov B.P. *Method for manufacturing an active coating of oxide cathodes*: RF Pat. 383109. Publ. 23.05.1973 (in Russ.).
12. Bol'shakov A.F., Abalduev B.V., Popov A.I. Phase inhomogeneity of mixed crystals of alkaline earth metal carbonates and its influence on the properties of an oxide cathode. *Izvestiya AN SSSR. Ser. Neorganicheskiye materialy*. 1977;13(7):1270–1274 (in Russ.).
13. Moizhes B.Ya. *Fizicheskie protsessy v oksidnom katode* (*Physical processes in the oxide cathode*). Moscow: Nauka; 1968. 480 p. (in Russ.).
14. Kapustin V.I., Li I.P. *Teoriya, elektronnaya struktura i fizikokhimiya materialov katodov SVCh priborov: monografiya* (*Theory, electronic structure and physical chemistry of microwave device cathode materials*). Moscow: INFRA-M; 2020. 370 p. (in Russ.). ISBN 978-5-16-015560-9
15. Chistyakova M.A., Podkopaeva N.N., Konikova R.A. Investigation of structural-phase transformations of the oxide coating of cathodes during the formation and service life. *Elektronnaya tekhnika. Seriya 4. Elektrovakuumnye i gazorazryadnye pribory*.1977;4:106–113 (in Russ.).

7. Артюшенко А.И., Батура З.Е., Кривобок В.И., Находнова А.П. *Способ получения мелкодисперсных порошков тройных и двойных карбонатов щелочноземельных элементов*: пат. 180572 РФ. Заявка № 809296/23-4; заявл. 19.12.1962; опубл. 19.03.1966. Бюл. № 8.
8. Доржин Г.С., Незнаев Г.Н., Китаева Т.И., Русакова Ж.П. *Способ получения смешанных карбонатов щелочноземельных металлов*: пат. 520330 РФ. Заявка № 2013007; заявл. 05.04.1974; опубл. 05.07.1976.
9. Евстигнеева Н.К., Калинина И.Д. *Способ получения порошков двойных или тройных карбонатов щелочноземельных металлов*: пат. 880983 РФ. Заявка № 2895040; заявл. 04.01.1980; опубл. 15.11.1981.
10. Смородинова Л.А., Арянина Т.Г. *Эмиссионный материал*: пат. 873301 РФ. Заявка № 2860081; заявл. 27.12.1979; опубл. 15.10.1981.
11. Киселев А.Б., Лобова Э.В., Никонов Б.П. *Способ изготовления активного покрытия оксидных катодов*: пат. 383109 РФ. Заявка № 1608332/26-25; заявл. 04.01.1971; опубл. 23.05.1973.
12. Большаков А.Ф., Абалдуев Б.В., Попов А.И. Фазовая неоднородность смешанных кристаллов карбонатов щелочноземельных металлов и ее влияние на свойства оксидного катода. *Известия АН СССР. Сер. Неорганические материалы*. 1977;13(7):1270–1274.
13. Мойжес Б.Я. *Физические процессы в оксидном катоде*. М.: Наука; 1968. 480 с.
14. Капустин В.И., Ли И.П. *Теория, электронная структура и физикохимия материалов катодов СВЧ приборов: монография*. М.: ИНФРА-М; 2020. 370 с. ISBN 978-5-16-015560-9
15. Чистякова М.А., Подкопаева Н.Н., Коникова Р.А. Исследование структурно-фазовых превращений оксидного покрытия катодов в процессе формирования и срока службы. *Электронная техника. Серия 4. Электровакуумные и газоразрядные приборы*. 1977;4:106–113.

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