Conference materials
UDC 544.032
DOI: https://doi.org/10.18721/JPM.173.239

Composition of Al/Zn nanoparticles produced in a gas discharge

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Abstract. In this work, we investigated the size and elemental composition of a binary of aluminum/zinc nanoparticles synthesized in a gas discharge generator. Al_xZn_{1-x} nanoparticles were produced in inert atmosphere by simultaneous erosion of aluminum hole cathode and a zinc anode. Mass fractions of aluminum x were varied from 0.05 to 0.29 by changing the surface area of the aluminum electrode. It was found that the mass fraction of aluminum in binary composition increased 2.6 times when erosion surface of the Al cathode dropped from 188.5 to 37.7 mm^2. The average sizes of primary nanoparticles were in the range from 12.8 to 18.6 nm, which formed submicron agglomerates. Also, when the erosion process occurred in an air atmosphere, we produced zinc aluminate $AlZn_2O_4$ with luminescence in ultraviolet (UV) range.

Keywords: nanoparticles, zinc aluminate, size measurement, gas discharge, TEM, erosion

Funding: This work was financially supported by the Russian Science Foundation (project no. 22-19-00311, https://rscf.ru/en/project/22-19-00311/).

Citation: Novosyolov A.K., Sanatulina A.F., Vershinina O.V., Lizunova A.A., Gudkova S.A., Urazov M.N., Composition of Al/Zn nanoparticles produced in a gas discharge, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 17 (3.2) (2024) 196–200. DOI: https://doi.org/10.18721/JPM.173.239

Материалы конференции
УДК 544.032
DOI: https://doi.org/10.18721/JPM.173.239

Состав наночастиц Al/Zn, полученных в газовом разряде

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Аннотация. В этой работе мы исследовали размер и элементный состав бинарных наночастиц алюминия/цинка, синтезированных в газоразрядном генераторе. Наночастицы Al_xZn_{1-x} были получены в инертной атмосфере путем одновременной эрозии алюминиевого катода с отверстием и цинкового анода. Массовую долю алюминия x варьировали от 0.05 до 0.29 изменяя площадь поверхности алюминиевого электрода. Было обнаружено, что массовая доля алюминия в бинарной композиции увеличилась в 2,6 раза, когда эрозионная поверхность алюминиевого катода снизилась со 188.5 до 37.7 мм^2. Средние размеры первичных наночастиц находились в диапазоне от 12.8 до 18.6 нм, которые образовывали субмикронные агломераты. Кроме того, когда процесс эрозии происходил в воздушной атмосфере, мы получали алюминат цинка $AlZn_2O_4$ с люминесценцией в ультрафиолетовом (УФ) диапазоне.

Ключевые слова: наночастицы, алюминат цинка, измерение размеров, газовый разряд, ПЭМ, эрозия

Финансирование: Работа выполнена при финансовой поддержке Российского научного фонда (проект № 00311-19-22, https://rscf.ru/en/project/22-19-00311/).

Ссылка при цитировании: Новосёлов А.К., Санатулина А.Ф., Вершинина О.В., Лизунова А.А., Гудкова С.А., Уразов М.Н. Состав наночастиц Al/Zn, полученных в газовом разряде // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2024. Т. 3.2 № .17. С. 196–200. DOI: https://doi.org/10.18721/JPM.173.239

Introduction

Gas discharge [1] is an excellent method for producing chemically pure metal nanoparticles (NP), semiconductors, and several component compounds [2]. Complex two-component NPs can be made using electrodes of the required complex chemical composition for erosion. However, not all materials can be used to make required electrodes, therefore, a manufacturing method with simultaneous erosion [3] of the cathode and anode from different materials is relevant, allowing to produce NP of substances that cannot be mixed on a macroscopic scale [4].

To vary the composition of two-component particles using different anode and cathode materials, it is necessary to regulate the energy and type of electric pulse supplied to the electrodes [5], as well as the flow rate of the carrier gas in the setup [3]. In this work we proposed alternative method to control the composition of binary nanomaterials, based on varying the surface area of electrodes. This approach leads to a change in the energy density of the surface for erosion of the electrodes, allowing for a different ratio of mass fractions of the particle components. Using aluminum and zinc as electrodes, it is possible to obtain a promising material – zinc aluminate.

Zinc aluminate is an important functional material with unique properties such as high thermal stability, optical transparency and luminescence [6]. These properties also make it possible to use zinc aluminate as a cathodoluminophore in modern sources of visible and ultraviolet radiation. Therefore, it is an important task to develop various methods for the synthesis of zinc aluminate, which make it possible to obtain particles with various characteristics. Methods for the synthesis of zinc aluminate are known: sol-gel method [7], method of co-deposition [8], solid-phase mechanochemical synthesis [9], hydrothermal and microwave methods [8].

Thus, the purpose of this work was to study the elemental composition of binary Al_xZn_{1-x} nanoparticles produced in gas discharge in inert atmosphere when changing the geometric parameters of the aluminum cathode with constant geometry of the zinc anode. And estimate the possibility of synthesis nanosized zinc aluminate in air atmosphere, characterized the size, morphology, phase and optical properties of obtained nanoparticles.

Materials and Methods

The synthesis was carried out on a setup consisting of a gas discharge chamber and a gas path [2]. A capacitor 107 nF was used for discharge, a voltage of 1.5 kV and a current value of 60 mA were set on the generator, which made it possible to achieve a discharge frequency of 500 Hz. Pure Ar 4.8 with a flow rate of 600 ml/min was used as the carrier gas, in which self-passivation of the obtained particles was carried out for 20 hours after synthesis. To study the particle elemental composition and size, depending on the geometry of the aluminum cathode, we manufactured two types of hole cylindrical Al electrodes with different surface area: the first type of the electrodes had fixed external diameter 8 mm and variable internal one: 2, 4.5, 5.3, 6 mm; the second type of the electrodes characterized fixed internal diameter 2 mm and external diameter 4, 5.3, 6.3 and 8 mm. Thus, the surface area of the end of the Al electrodes was from 37.7 mm^2 to 188.5 mm^2. Energy density stored in the capacitor and released between the electrodes was calculated as the ratio of the energy on the capacitor, equal to 120.4 MJ, to the surface area of the erosion of the aluminum electrode. Studies of the crystal structure, particle sizes and elemental composition of nanoparticles, were carried out using transmission electron microscopy (TEM) JEM-2100 (JEOL, Ltd., Tokyo, Japan) with energy dispersive X-ray analysis (EDX) Oxford X-MaxN, data on the particle size distribution of agglomerates were obtained using the aerosol spectrometer TSI SMPS 3936. The crystal structure of the samples was studied by X-ray diffraction on a Drawell DW-XRD-2700A diffractometer, China. The studies were carried out in the Bregg-Brentano geometry using a copper X-ray tube with a wavelength of 1.54 E. The scanning speed was 0.5 deg./min.

Results and Discussion

Based on the images obtained on the TEM (Fig. 1, *a*), a primary particle size distribution was obtained for each surface area of the electrodes. It was found that the particle sizes range from 12.8 ± 3.9 nm to 18.6 ± 6.3 nm regardless of the size of the aluminum electrode. To determine the elemental composition of the obtained nanoparticles, elemental spectra of agglomerates were performed using energy dispersion analysis on TEM (Fig. 1, *b*), from which the mass fraction of each element of the mixture of NPs was calculated. The minimum value of the ratio of the mass fraction of zinc to aluminum is 2.5 witHh an Al electrode area of 37.7 mm^2 and increases to 20 when the area is 188.5 mm^2 (Fig. 1, *c*). That means we can regulate the composition of Al/Zn nanoparticles and get binary material from $Al_{0.05}Zn_{0.95}$ to $Al_{0.29}Zn_{0.71}$ by ranging the energy density of an electric pulse between the electrodes. The size distribution of agglomerates of the particles obtained during synthesis using an aerosol spectrometer was also determined. A range of sizes of nanoparticle agglomerates was obtained: from 88 ± 2 nm to 139 ± 1 nm and is described by an increasing linear function (Fig. 1, *d*).

Particles were also synthesized in air with an electrode with an erosion area of 188.5 mm^2,

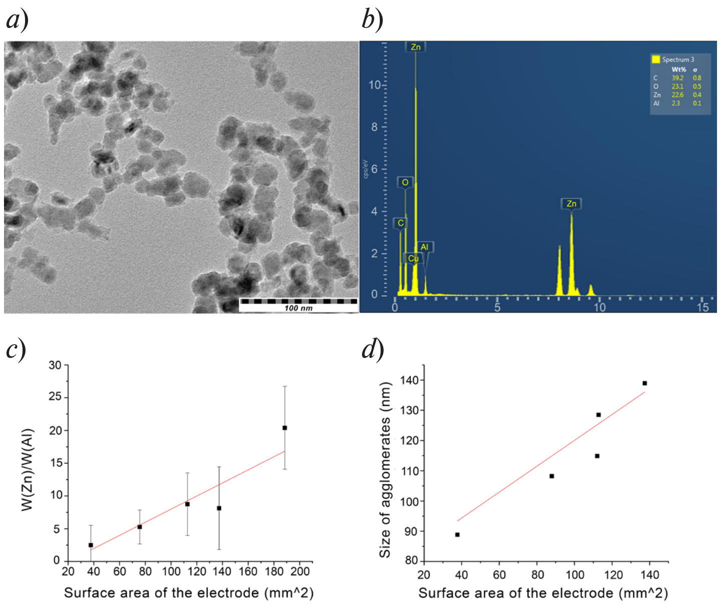

Fig. 1. Characterization of nanoparticles: typical TEM image of primary nanoparticles in agglomerate (area of erosion of aluminum electrode is 112 mm^2) (*a*); EDX spectra of agglomerate (area of erosion of aluminum electrode is 112 mm^2) (*b*); dependence of ratio of mass fractions of zinc and aluminum on the surface area of the aluminum electrode (*c*); dependence of size of agglomerates on surface area of aluminum electrode (*d*)

since this option gives a minimum aluminum content, which, according to literature data, can provide a luminescent material. Photoluminescent spectrum of obtained mixed powder reveal the ultraviolet luminescence in the wide range with a maximum at 375 nm (Fig. 2, *a*). The XRD spectrum shows that we have a mixture of several phases in the air – zinc oxide, aluminum oxide and zinc aluminate (Fig. 2, *b*). We have considered two synthesis options with the same energy density of 638.6 J/m^2 (surface area of 188.5 mm^2): in an inert environment and in the air. Using

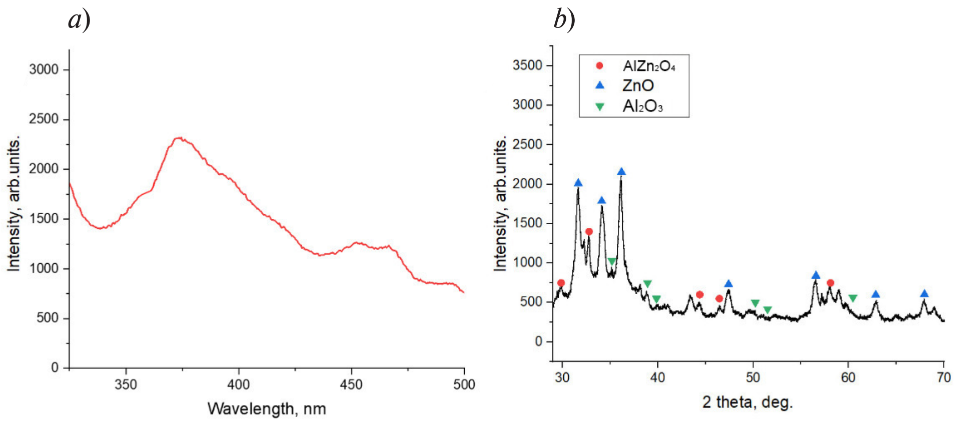

Fig. 2. Characterization of powder obtained in air with simultaneous erosion of aluminum cathode with area of 188.5 mm^2 and zinc anode: PL-spectra (*a*); XRD-spectra (*b*)

EDX analysis of the surface of the electrodes, it was obtained that the mass fraction of oxygen on both electrodes, which was constant and approximately equal to 2% in an inert medium, became equal to 34% in the air, which indicates the formation of metal oxides.

Conclusion

It was found that by changing the geometry of aluminum cathode in gas discharge generator, the elemental composition of binary Al_xZn_{1-x} nanoparticles produced in inert atmosphere can be adjusted in the range of x from 0.05 to 0.29. At the same time, the average diameter of obtained nanoparticles varied from 12.8 nm to 18.6 nm regardless of the erosion surface of the aluminum electrode. The sizes of agglomerates linearly increase from 88 nm to 139 nm and the ratio of the mass fraction of zinc to the mass fraction of aluminum increases from 2.5 to 20 when the erosion surface increases from 37.7 mm^2 to 188.5 mm^2. XRD analysis of NPs synthesized in air showed the presence of a multicomponent mixture: zinc aluminate, zinc oxide and aluminum oxide, which have maximum photoluminescence in UV range.

Acknowledgments

This work was financially supported by the Russian Science Foundation (project № 22-19- 00311, https://rscf.ru/en/project/22-19-00311/).

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Received 31.07.2024. Approved after reviewing 16.08.2024. Accepted 17.08.2024.