

The laboratory technology for nanodispersed raw products and fine-grained ceramics

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Abstract

The laboratory technology based on a modified sol-gel method or its combination with sonochemistry techniques was proposed. It allows obtaining with high reproducibility large amounts of ultrafine powdery raw materials for fine grained functional ceramics for wide application. Ultradispersed powders of the following composition: 20 wt.% $Ce_{0.09}Zr_{0.91}O_2$ / 0.4 wt.% MgO - 79.6 wt.% Al_2O_3 for medical ceramics with a relative density close to 99%. The ultrafine composite powders based on nano-carbon and Mo- and W-oxides were obtained by using a combination of modified sol-gel method and techniques of sonochemistry, these composites are relevant raw materials for new materials for energy. The developed method for producing chemically homogeneous ultradispersed powdery compositions opens the big prospects for the production of highly efficient photocatalysts and fine-grained ceramic materials for energy with a uniform distribution of components in volume. Furthermore, a method of engineering of interface in the composite materials is proposed, which allows production of materials with the specified electrophysical properties.

1. Introduction

The range of fine-grained ceramics applications is very wide and has been described in numerous publications since the end of the last century (Kahan 1974). The multiplicity of the raw products with a specific set of physicochemical properties is a necessary condition for the creation of new materials for various purposes (Azad 2006, Maca 2007, Graves 2010, Yang 2012). Aluminum, bismuth, cerium, cobalt, chromium, copper, magnesium, molybdenum, tungsten, yttrium, zinc and zirconium oxides nanopowders are most promising raw products for the next generation fine-grained ceramics both functional and structural assignments.

In the last decade there has been a growing interest of researchers in graphene-ceramic composites. It is connected with that graphene improves the strength, electrical and thermal properties of ceramics. Composites based on graphene and

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ultrafine metal oxides are attractive raw products for a wide range of application materials: anodes for Li-ion batteries, supercapacitors, transistors, catalysts, solar cells, sensor materials, fuel cells and electrochromic devices (Pati 2011, Yang 2011, Guo 2012). The paper presents the last 5-6 years results of the lab of wet method synthesis of ultradispersed metal (II-XII groups of periodic table) oxide powders (<100 nm) to create a laboratory technology of obtaining the large quantities of ultradispersed metal oxide powders

2. Modified sol-gel technique

The essence of modified sol-gel method is the formation of high dispersed sol particles coated with an organic covering at the first step. These particles have the sizes not exceed a few tens nanometers. At the next step the gelation process was carried out at temperature 90-95°C. The increasing of the dispersed phase concentration leads to coagulation contacts between the sol particles and the 3D-gel formation. Next, at temperature 180-200°C a solvent was removed from gel, and xerogel was formed. Subsequently thermal treatment of xerogel leads to formation of a metal oxide crystal structure. Feature of the developed approach is the use of low molecular weight sol stabilizers: hexamethylenetetramine (HMTA), N,N-dimethyloctylamine (DMOA), tetraethylammonium hydroxide (TEAH) and monoethanolamine (MEA).

3. Sol-gel technique combined with sonication

As it is known the wet methods of synthesis of ultradispersed metal oxides have well proven themselves among a plurality of methods for producing powdery raw products (Trusova 2013) These methods are environmentally friendly, use relatively low operating temperatures, and they are technically readily exercisable. Simultaneously W.S. Hammers (1958) method is the most often used for obtaining of graphene, which is found on the potassium permanganate oxidation of graphite in sulfuric acid, that results to the destruction of delocalized π -electron system by various oxygen-containing groups.

It is known that during the reduction of graphene oxide its structure, as well as its properties is not restored. In this research we developed the method for producing graphene-containing compounds in the soft conditions without the formation of a graphene oxide. The combination of modified sol-gel method with sonication was used for obtaining of the graphene-metal oxide composites.

The as-prepared Mo- or W-containing sols were added to the graphene suspension obtained from a synthetic graphite at pH value equal to 3 with use of ultrasonic treatment of substrate. Ammonium molybdate or paratungstate were used as the metal sources, and N,N-dimethyloctylamine was used as stabilizer of metal-contained sols or graphene suspension. The heat treatment of obtained mixed gels was carried out at 320-340°C in air. The obtained composites were investigated with use of TEM, Raman and FT-IR spectroscopy.

In the Raman spectrum of sample C-WO₃ (Fig. 1) it is observed the broad bands of graphene D (1350 cm⁻¹) and G (1580 cm⁻¹) of approximately equal intensity. Strong

fluorescent background and absence of signal in the second order region of bands D and G ($2600-2900\text{ cm}^{-1}$) indicates the presence of amorphous graphite. At the same time the bands corresponding to WO_3 absent in the spectrum. With increasing of the laser power from 0.5 up to 5.0 mW there were a decrease of fluorescent intensity of the background and the appearance of strong bands: 178 and 254 cm^{-1} (the deformation vibrations of the group O-W-O), as well as 687 and 799 cm^{-1} (valence vibrations of groups O-W-O). The appearance of WO_3 bands with the intensity many times higher than D and G bands one, possibly, is connected with strengthening of laser radiation, which leads to the destruction of chemical bonds WO_3 -graphene and remove the carbon from WO_3 surface.

Fig. 2 shows TEM image of C- MoO_3 composite. It is clearly seen that MoO_3 rods with size 50-200 nm are coated with a thin layer of amorphous carbon. Elemental analysis showed the presence of molybdenum, carbon and oxygen. So, the efficiency of sonication of synthetic graphite in the colloid stabilized by N,N-dimetiloktilamine has been proven.

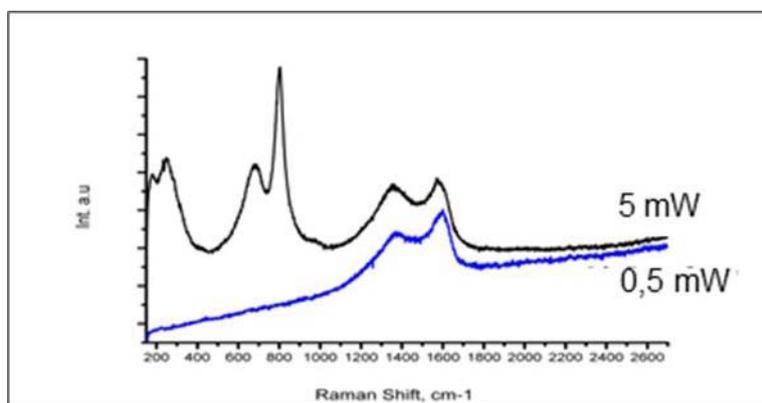


Fig. 1. Raman spectrum of C- WO_3 composite at excitation of laser with 514 nm wavelength (TRIAX 552, Jobin Yvon).

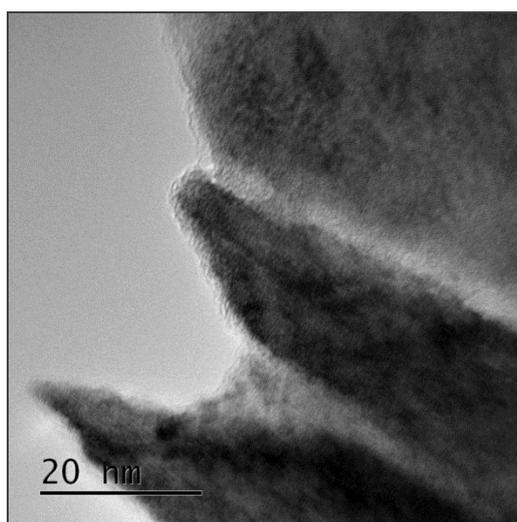


Fig. 2. TEM image of C- MoO_3 composite (LEO 912 ab Omega Carl Zeiss instruments)

4. Ultradispersed powder mixture for dense fine-grained ceramics

The laboratory technology of ultradispersed Al_2O_3 powders, an important raw material for fine grained ceramics of wide applications, was developed based on the modified sol-gel method (Trusova 2013). Aluminum nitrate was used as the metal source, and MEA was used as sol stabilizer. This method allows producing powders of gamma- Al_2O_3 with a crystallite size of 10-25 nm, with high reproducibility.

The ultradispersed powdery mixture having the following composition 20 wt.% $\text{Ce}_{0.09}\text{Zr}_{0.91}\text{O}_2$ / 0.4 wt.% MgO - 79.6 wt.% Al_2O_3 (calculated as oxides) was developed for the preparation of bio-inert, wear-resistant and durable material (De Aza 2002, Trusova 2012, Trusova and Khrushcheva 2013). According to XRD data (DRON-3M, CuK_α , Russia), the mixture has phase composition: 20.6 wt.% $\text{Ce}_{0.09}\text{Zr}_{0.91}\text{O}_2$ (tP6) / 37.4 wt.% $\text{MgAl}_6\text{O}_{10}$ (cF16) – 42.0 wt.% gamma- Al_2O_3 (cF56). The crystallite size was calculated by the Rietveld method, and this value was 3-10 nm. The average particle size of the aerosol diffusion spektrometroscopy data (DAS-2702, Russia) was 45 nm; BET surface was equal 50 m^2/g .

Magnetic pulse compression followed by sintering (1) and hot pressing (2) were used for nanopowder mixture consolidation. In the first case obtained powders were shaped by the magnetic pulsed technique (amplitude of pulsed pressure was up to 1.6 GPa; pulse duration was 300-500 s) into disks of 15 mm in diameter and 2-4 mm thick. Obtained green bodies were sintered at 1550°C during 1 h. The hydrostatic density of the ceramics was 3.83 g/cm^3 , and relative density of the ceramics was 93.5%. By SEM data the ceramic samples sintered from obtained powders were fine-grained material with granules size about 3 μm (Fig. 3). The microphoto clearly shows the rods with a diameter less than 0.5 μm , which play an important role in the formation of high mechanical properties of ceramics for constructional purposes. Investigation of the obtained ceramics by SEM/EDS method showed a high chemical homogeneity of the material: a uniform distribution of O, Al, Ce and Zr in volume is clearly seen on the microphotos in Figs. 4.

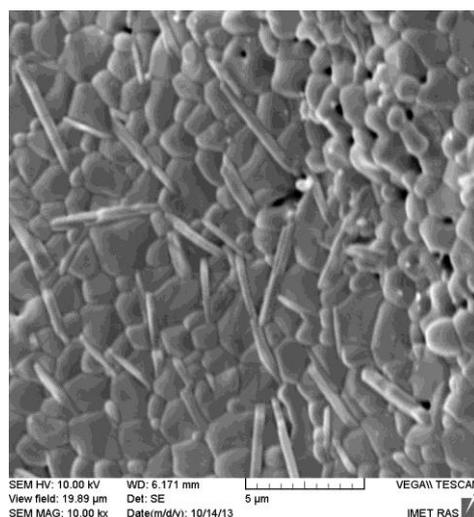
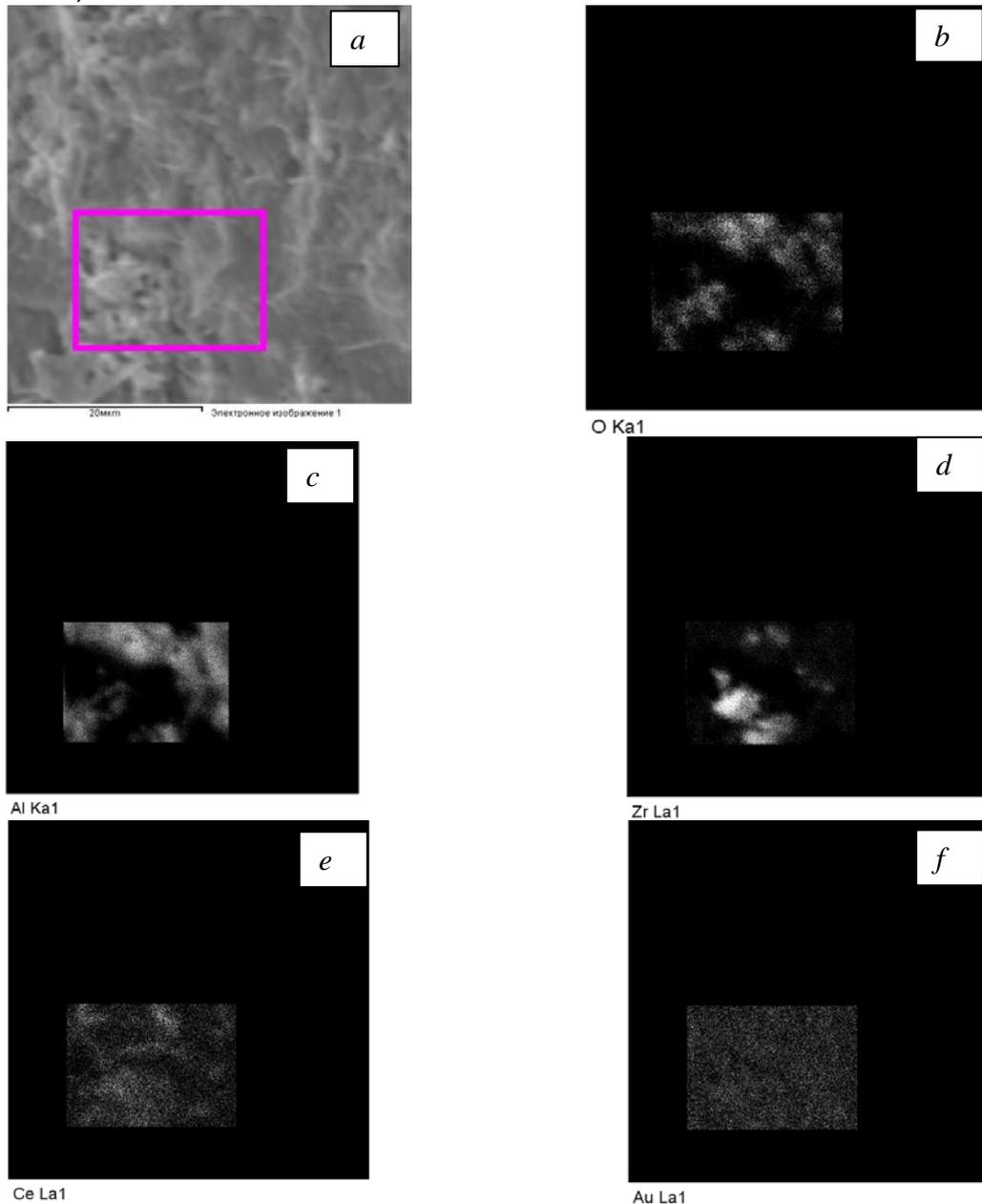
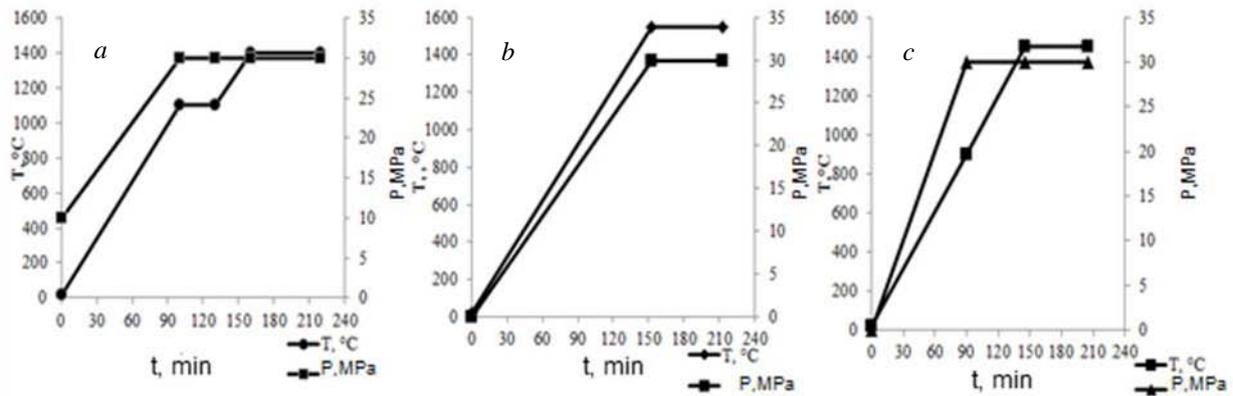


Fig. 3. SEM image of the ceramic obtained by magnetic pulse compression (VEGA TESCAN Czech Republic).

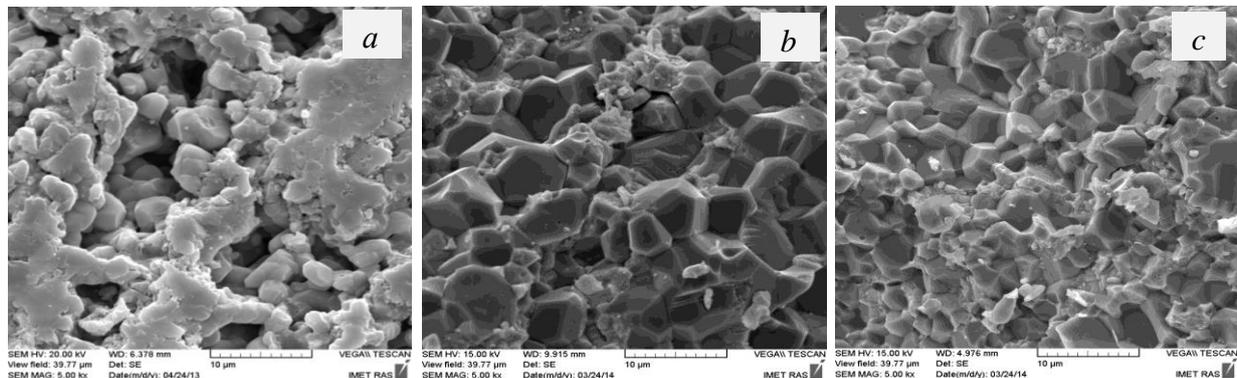
Also it was carried out a series of experiments on compaction and sintering of nanopowder mixture of the same composition by hot pressing in a furnace (Thermal technology inc. high temperature experts model HP20-3560-20). Optimization of temperature and pressure change graphs was also carried out. (Figs. 5a-c). According to hydrostatic weighing, density of ceramic samples increased from 3.5 to 4.14 g/cm³ at optimization of graphs of temperature and pressure (Fig. 5a-c), in the latter case, relative density of the ceramics was 98.7%. It was found that the optimization of the temperature and pressure increase modes leads to disappearance of the open pores (Figs. 6a-c).



Figs. 4. SEM image of the obtained ceramics (a), map of O-, Al-, Zr- and Ce-elements over the scanned area (b-e) and Au coated plate for sample (f). (Scanning electron microscope VEGA TESCAN with an attachment for local XRD analysis)



Figs. 5a-c. Graphs of temperature and pressure changes during hot pressing of nanopowder mixture composition: $\text{Ce}_{0.09}\text{Zr}_{0.91}\text{O}_2/\text{MgO}-\text{Al}_2\text{O}_3$ (20/80, wt.%)



Figs. 6a-c. SEM micrographs of ceramic samples obtained under three different schedules of pressure and temperature changes, shown at the Figs. 5a-c, respectively. (VEGA TESCAN, Czech Republic).

5. Decorated ZnO nanoparticles

Ultradispersed ZnO powders are important and promising raw materials for production of fine grained ceramics for nanoelectronics, semiconductors, (photo)catalysts, etc. However, on obtaining of such materials the problem of preparation of chemically homogeneous powders occurs because nanopowdery mixtures tend to delamination, which leads to problems in quality of green body and discredits the nanopowdery raw materials for the production of fine grained ceramics. Therefore, the development of new materials for next-generation electronics requires the new approaches to the directed formation of structure of ultradispersed powdery raw products. As it is well known, for creating durable ceramic materials and materials for electronic devices, it is important to uniform distribute of the components of the mixture in the volume of the green body. We believe that chemical decoration of ZnO nanoparticles with other components of mixture is a reliable way to obtain of chemically

homogeneous mixtures, since this method allows fixing the minor components of ultradispersed mixture on the surface of ZnO nanoparticles. Previously, we reported our way of decoration, which is based on a modified sol-gel method (Trusova and Vokmintcev 2014).

The oxides of second and third metals (Bi, Ce, Cr, Cu, Ni, Y, Zr) were coated on the surface of ZnO nanoparticles, calcined at 500°C. The obtained ultradispersed ZnO based powdery composites were studied by FT-IR spectroscopy (Trusova and Vokmintcev 2014) in order to investigate a nature of interaction between the decorating metal oxides and ZnO nanoparticle surface and to prove the fact of chemical decoration. Fig. 7 shows FT-IR the spectra of ZnO, decorated with NiO, Bi₂O₃ and both these oxides simultaneously. In FT-IR spectrum of powder ZnO, decorated with Bi₂O₃, in the region 800-1100 cm⁻¹ corresponding to the Zn-O bond overtones, two bands are observed: 850 и 1014 cm⁻¹. In the spectrum of powder ZnO, decorated with NiO, in this region there are three bands of Zn-O bonds are: 875, 813 and 1030 cm⁻¹. In the case of a ternary system in the 800-1100 cm⁻¹ region of Zn-O bond overtones, it was found impact of both oxides simultaneously: NiO and Bi₂O₃. The spectrum of the ternary system is not a simple superposition of the spectra of two binary systems. Practically all of the bands are shifted, which indicates the existence of the structural elements interaction of all three oxides in composition. This is proof of chemical nature of interaction between ZnO particles surface and decorating metal oxides and the formation of 2D-interface between them, which is not shown in XRD pattern.

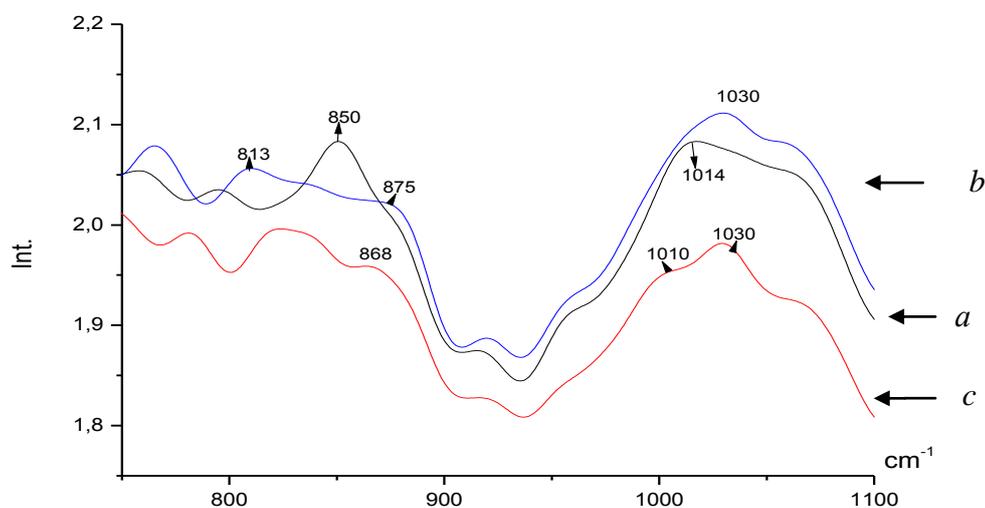


Fig. 7. FT-IR spectra of ultradispersed powders: ZnO-Bi₂O₃ (a), ZnO-NiO (b) and ZnO-Bi₂O₃-NiO (c).

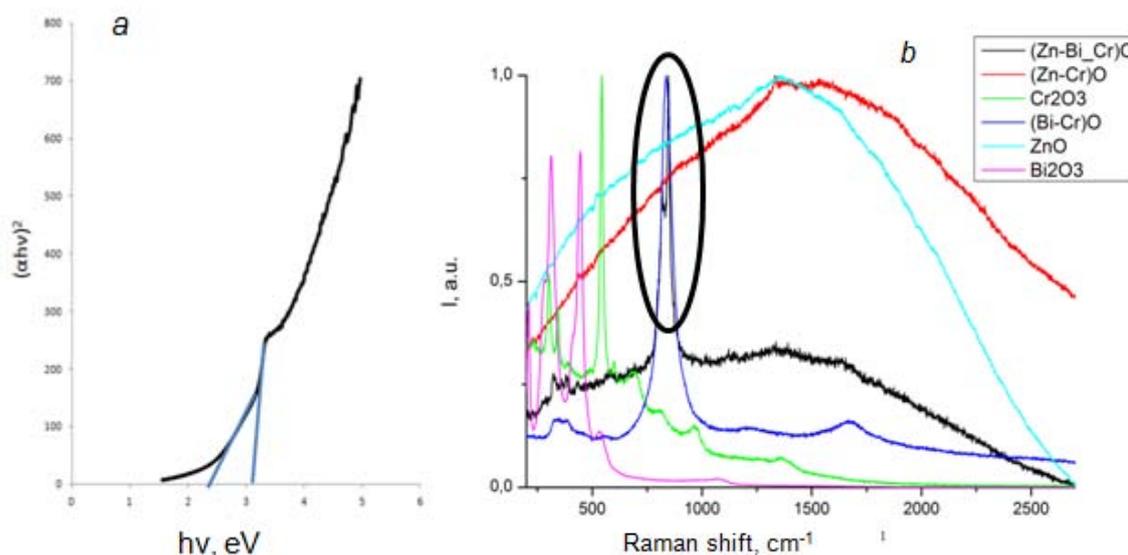
To determine the effect of decoration on the physico-chemical properties of ultradispersed powders the comparative study of decorated composites was carried out by use of UV and Raman spectroscopy. The band gap of obtained powders was calculated by J. Tauc method (1968) based on the results of UV spectroscopy (Table 1).

It was shown that the decoration of ZnO nanoparticles has a significant influence on their band gap, and its value varies in the range from 2.81 to 3.15 eV.

Table 1. Band gap (E_g) of ultradispersed ZnO powder, the particles of which was decorated with metal oxides

Composition	E_g , eV	Composition	E_g , eV	Composition	E_g , eV
ZnO-Cr ₂ O ₃	3.00	ZnO-CuO	3.04	ZnO-Bi ₂ O ₃ -CuO	3.15
ZnO-Bi ₂ O ₃	2.81	ZnO-CeO ₂	3.08	ZnO-Bi ₂ O ₃ -CeO ₂	3.10
ZnO-Y ₂ O ₃	2.81	ZnO-NiO	3.06	ZnO-Bi ₂ O ₃ -Y ₂ O ₃	2.97
ZnO-ZrO ₂	3.12	ZnO-Bi ₂ O ₃ -NiO	2.87	ZnO-Bi ₂ O ₃ -Cr ₂ O ₃	3.02, 2.33
		ZnO-Bi ₂ O ₃ -ZrO ₂	3.03		

Particularly noteworthy is the composite ZnO-Bi₂O₃-Cr₂O₃, in which structuring of ZnO band gap was observed. It was manifested in the formation of an impurity level (2.33 eV) inside the band gap due to doping of surface ZnO monolayers with Bi³⁺ and Cr³⁺ ions, resulting in E_g value decreasing to 3.02 eV. Tauc plot in coordinates $(\alpha h\nu)^2 - h\nu$ by UV absorption shows the presence of two linear sections, which indicates the two-stage absorption in the composite ZnO-Bi₂O₃-Cr₂O₃ (Fig. 8a).



Figs. 8: a – Tauc plot for ZnO-Bi₂O₃-Cr₂O₃ composite, b - Raman spectra of the powders and composites based on ZnO, Bi₂O₃ and Cr₂O₃.

For an interpretation of the observed effect the powder composites based on ZnO, Bi₂O₃, Cr₂O₃ were studied by Raman spectroscopy (Fig. 8b). It can be seen that the spectrum of ZnO-Bi₂O₃-Cr₂O₃ composite has the same band as the spectrum of Bi-Cr-oxides binary system. The detailed examination of region 810-850 cm⁻¹ (marked by the oval in Fig. 8b) shows that in the case of ternary system separated peak is split, which

indicates a change in the symmetry of Cr-O-Bi chain and the formation of additional vibrational level. The established fact can be considered as evidence of the formation of 2D-interface between the ZnO nanoparticle surface and decorating Bi₂O₃ and Cr₂O₃ additives that causes the changes in short-range order of ZnO structure and leads to band gap change.

6. Conclusion

So, the laboratory technology based on a modified sol-gel method or its combination with sonochemistry technique is proposed. It allows obtaining with high reproducibility large amounts of ultrafine powdery raw products for fine grained functional ceramics for wide application. First of all, it's ultra-fine powders for ceramic materials for medical purposes of the following composition: 20 wt.% Ce_{0.09}Zr_{0.91}O₂ / 0.4 wt.% MgO - 79.6 wt.% Al₂O₃. The conditions of their consolidation were studied, and as a result the optimal conditions were developed for the preparation of ceramic material with a relative density close to 99%. The ultrafine composite powders based on nano-carbon and Mo- and W-oxides were obtained by using a combination of modified sol-gel method and techniques of sonochemistry, these raw products are relevant intermediates for new materials for energy. The developed method for producing the chemically homogeneous ultradispersed powdery compositions opens the big prospects for the production of highly efficient photocatalysts and fine-grained ceramic materials for energy with a uniform distribution of components in volume. Furthermore, a method of engineering of interface in the composite materials is proposed, which allows production of materials with the specified electrophysical properties.

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