Приложение А

Introduction

Preparation of dense fine-grained ceramics is a complex problem, retaining its wider application. Getting the dense ceramics by conventional technology is difficult because of the relatively high-temperature synthesis of ceramic powders and the narrow range of sintering. To solve this problem, superfine and ultrafine powders are used.

Nanostructured materials exhibit superior properties such as excellent strength, toughness, and hardness, as obvious from the presence of refined grains. The nanostructured coatings/structures experience superior and novel properties; thus, the importance of achieving such tremendous improvement in performance cannot be neglected by researchers.

Global market for Nanocomposites is projected to reach 1.5 billion pounds (lbs) by the year 2017. Nanopowders market in Russia was involved in commercialization stage. Despite the fact that the number of scientific developments on ceramic nanopowders is considerable, the problem of reliable suppliers of raw materials for industry is very urgent. With the development and introduction of new technologies Russian enterprises are often forced to purchase nano-sized ceramic powders from other countries. In this regard, the development of new methods of synthesis nano particles should be guided by raw materials produced in the territory of the Russian Federation, on the technologies that actually implement in the workplace.

1. Literature review

1.1. METHODS OF SYNTHESIS ALUMINUM AND ZIRCONIUM OXIDES

1.1.1. Synthesis Al_2O_3 and ZrO_2 nanoparticles by hot-air spray pyrolysis

Spray pyrolysis is a powerful technique to synthesize a wide variety of ceramic nanoparticles like Al_2O_3 and ZrO_2. Large quantity of metal oxide particles with homogeneous particle and crystallite size less than 100 nano meters has been produced by this method. This is a simple method to allow continuous production of nano ceramic particles which offer the opportunity to tailor materials on a nano scale because of its small crystallites.

Рисунок 1 - горячего воздуха пиролиза распыления (*hot-air spray pyrolysis*)

Hot-air spray pyrolysis is more effective and it provides a substantially wider spectrum of possibilities such as mass production with automated process, simple and inexpensive process, yielding high surface area particles with quite reduced particle size and free flowing structure. The present method helps in controlling the particle size and texture of Al_2O_3 and ZrO_2 nanoparticles. The present spray pyrolyser is an automated system which provides significant benefits such as scale up the productivity in a manufacturing environment. Further, these methods are used to achieve high purity products with less aggregated particles. It may be identified as the desirable method for large scale production of mono dispersed Al_2O_3 and ZrO_2 nanoparticles with high surface area and quite uniform diameter.

The synthetic Bayer liquor (sodium aluminium hydroxide) was extracted from raw bauxite using Bayer process. The detailed extraction process was given in our previous paper [10]. Bayer liquor is used as a precursor for the synthesis of Al_2O_3 nanoparticles. The extracted Bayer liquor (250 ml) was hydrolysed through drop by drop addition of 6 M HNO_3 (Merck GR, 69%) solution under constant stirring. An amorphous hydrated aluminium oxide was precipitated at pH 7. A characteristic white precipitate of $Al(OH)_3{\cdot}H_2O$ appeared at this stage of the reaction. The obtained precipitate was filtered using Whatman (Grade No.: 40) filter paper and washed several times in double distilled and deionised water until it was free from sodium nitrate and unreacted components. Further, the precipitate ($Al(OH)_3{\cdot}H_2O$) was dissolved in 500 ml of 1 M HNO_3 solution to obtain the aluminium nitrate solution. The schematic representation of the preparation of aluminium nitrate precursor was shown in Eqs. (1) and (2).

$$NaAl(OH)_4 + HNO_3 \rightarrow Al(OH)_3 \cdot H_2O + NaNO_3 \tag{1}$$

$$Al(OH)_3 \cdot H_2O + 3HNO_3 \rightarrow Al(NO_3)_3 \cdot 4H_2O \tag{2}$$

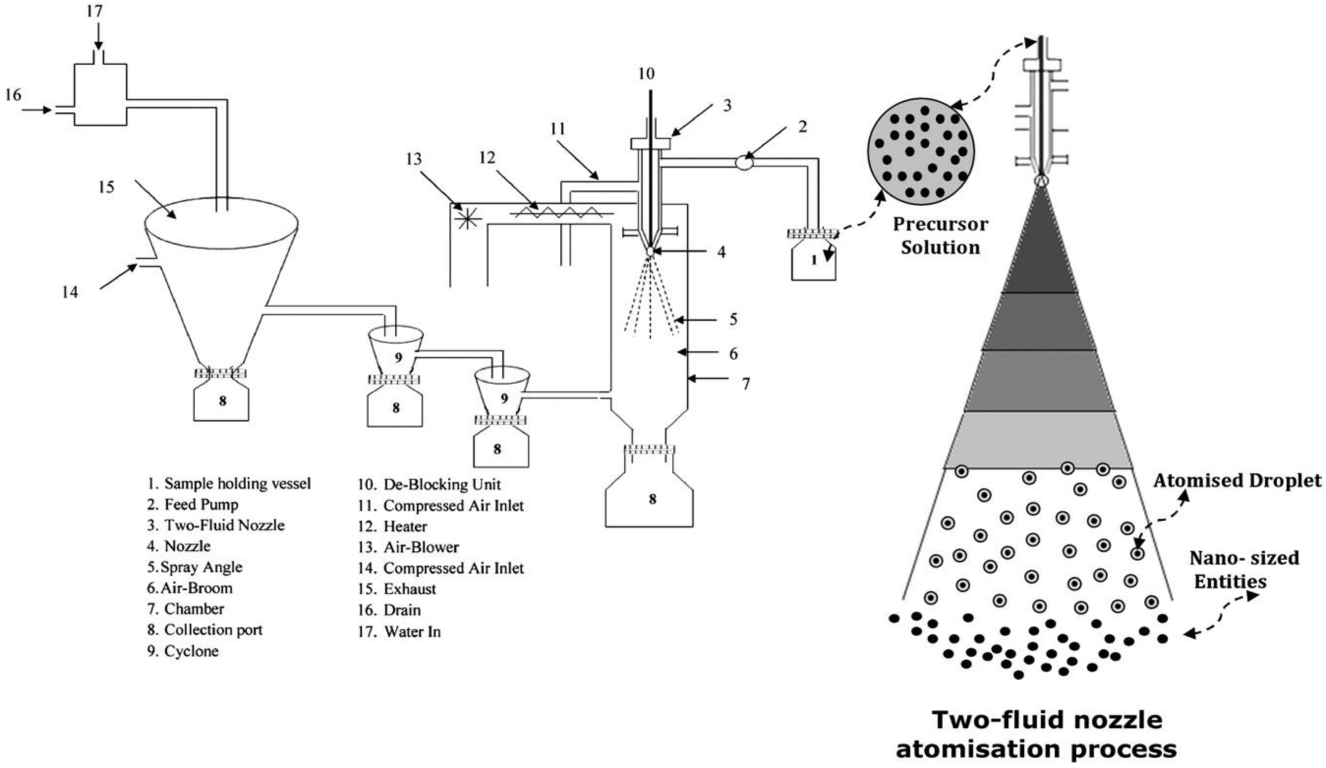


Fig. 2 - Schematic diagram of automated spray pyrolysis experimental set-up.

The perfect uniform solution of aluminium nitrate was used as the starting precursor in spray pyrolysis to get nano sized Al_2O_3 particles. The schematic diagram of automated spray pyrolysis experimental set-up used for mass production of nano Al_2O_3 particles is shown in Fig. 2. The present independent spray pyrolyser experimental set-up primarily consists of a) an atomizer which converts the starting solution into droplets, b) automated anti-blocking unit, c) tubular electric furnace with hot air blower, d) two fluid nozzle with compressed air inlet and sample feeding port, e) feed pump which facilitates the flow rate of precursor, f) reaction chamber, g) cyclonic sample collectors and h) purification system. The total process is automated using a single power control panel which controls the process automatically. The formation of atomizer was controlled by controlling the pressure of compressed air. Then, the atomized nanosized entities of aluminium nitrate droplets were injected into hot air zone, generated through hot air blower in tubular reaction chamber. The temperature of reaction chamber was maintained in the temperature range from 673 to 773 K by adjusting the furnace temperature of hot air blower. In hot air zone, the atomised droplets were dried and the constituent aluminium nitrates were decomposed at 673 K to form nano sized Al_2O_3 particles. The typical decomposition reaction of aluminium nitrate precursor in spray pyrolysis is given in Eq. (3).

$$Zr(NO_3)_3 \rightarrow ZrO_2 + 3NO_2 \uparrow + O_3 \uparrow \tag{3}$$

After the completion of one full cycle, the nano Al2O3 particles obtained were collected in the cyclones. There are two main parts of cyclones which are used for the powder collection such as second and third cyclones. These two cyclones consist of fine powders which are in nano range. The collected samples were characterized as it is without post synthesis treatment such as customization and sintering of the particles. The present spray pyrolyser operating conditions yields 26–28 g of nano powder for the operation of the system for 8 h. The overall output of present mini-modal spray pyrolyser was 74±5%.

The XRD pattern of Al_2O_3 nanoparticles produced through spray pyrolysis is shown in Fig. 3(a). The diffraction patterns of Al_2O_3 nanoparticles are assigned to the cubic phase, indicating that the Al_2O_3 nanoparticles have crystalline γ-Al_2O_3 phase with cubic symmetry. The obtained XRD pattern of Al_2O_3 nanoparticles is in well agreement with the standard powder diffraction data (JCPDS File No.: 79–1558). From the XRD data, it is found that Al_2O_3 particles have cubic crystalline phase with an average crystallite size of 5 nm.

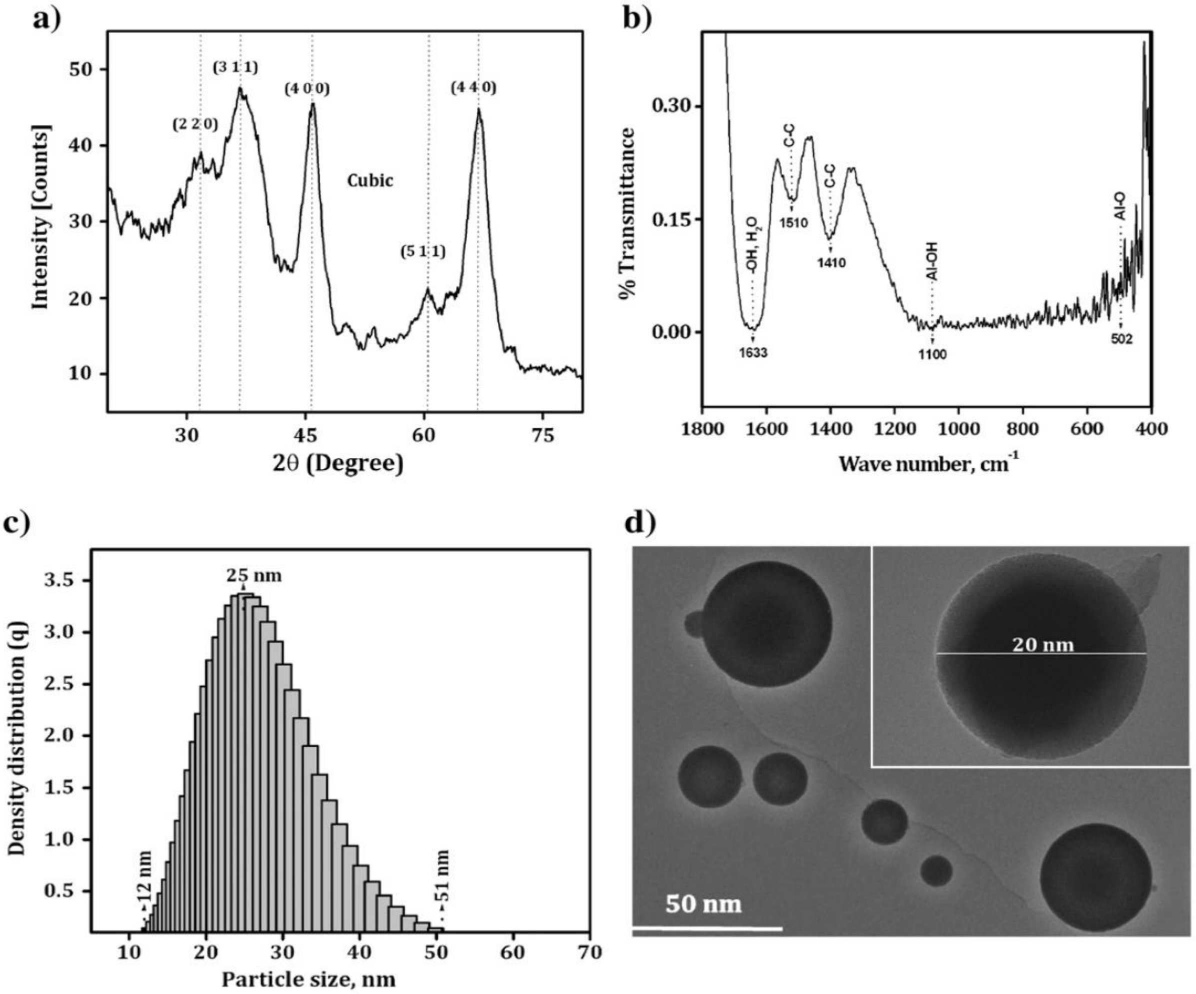


Figure 3 - Characterization of Al_2O_3 nanoparticles produced through spray pyrolysis, a) XRD pattern, b) FTIR spectra, c) PSD and d) TEM picture.

XRD powder patterns of ZrO_2 nanoparticles produced through spray pyrolysis are shown in Fig. 4(a). From the XRD data, it was found that the synthesized nano ZrO_2 particles have 96% monoclinic and 4% tetragonal crystal structure which well agreed with the standard powder diffraction data (JCPDS File No.:81–1314 and 80–2155).

An average crystallite size of monoclinic crystal phase is obtained as 18 nm from the observed eleven different reflections. On the other hand, the grain size of tetragonal phase is found to be 26 nm from a reflection obtained at 2θ=30.272. All the reflection peaks are well recognized and are wide widths with uniform crystalline size distribution in the range from 11 to 31 nm. From the above XRD analysis, it is evident that spray pyrolysis yields crystalline ZrO_2 particles with low grain size.

Hot-air spray pyrolysis has some advantages such as easy scaling for mass production, uniform morphology with free flowing structure and controlled particle size over other classical process, particularly precipitation and sol–gel route. Further, the spray pyrolyser is one of the direct processes for conversion of

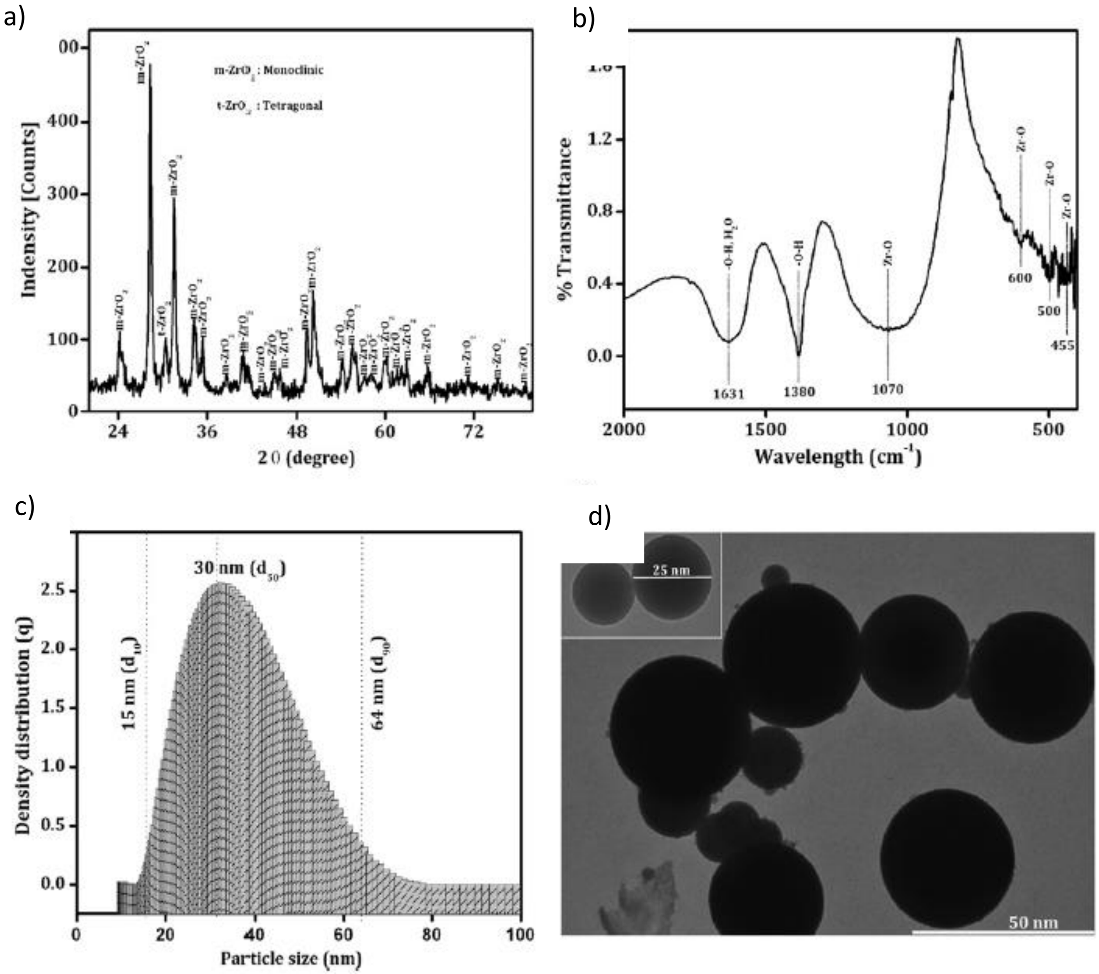


Figure 4 - Characterization of ZrO_2 nanoparticles produced through spray pyrolysis, a) XRD pattern, b) FTIR spectra, c) PSD and d) TEM image

aluminium nitrate and zirconyl nitrate solution into Al_2O_3 and ZrO_2 nanoparticles.

1.1.2. Synthesis Al_2O_3 and ZrO_2 by CO_2 laser vaporization (LAVA)

In order to prepare ceramic nanoparticles by CO_2 laser vaporization (LAVA) coarse ceramic powders (e.g. ZrO_2, Al_2O_3, and TiO_2) were used as raw materials. Work scheme of CO_2 laser vaporization (LAVA) was showed in figure 5.

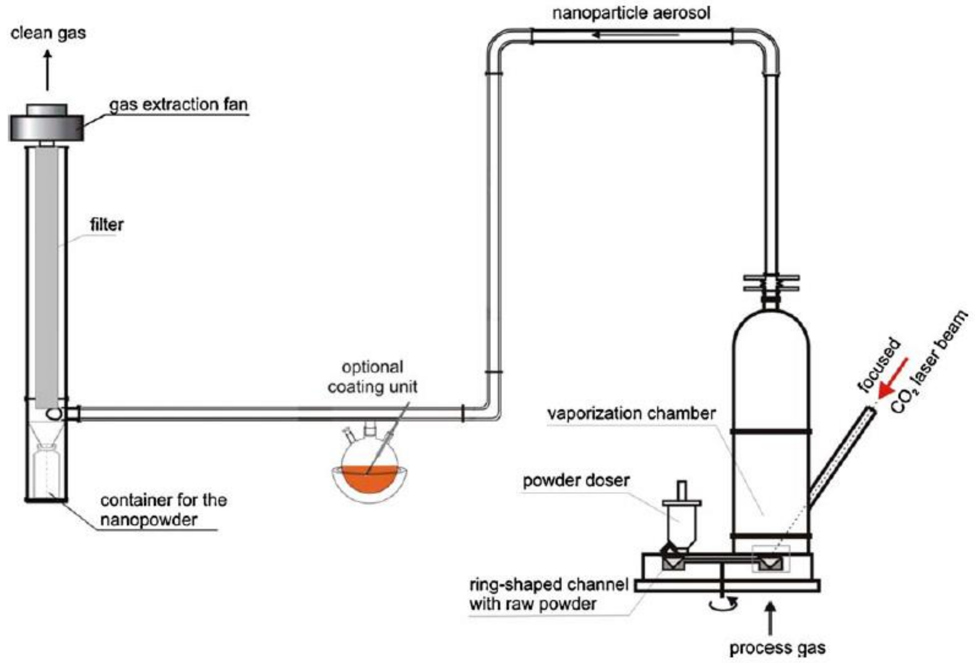


Fig. 5. Schematic representation of the LAVA laboratory system.

The LAVA process and thereby the quality of the ceramic nanopowders is controlled by the relevant process parameters such as laser power, continuous or pulsed laser operation, and also volume flow and thermal conductivity of the process gas within the zone of particle condensation. To allow for a further customization or conditioning of the laser-generated nanoparticles, the basic process can be varied or supplemented by the co-laser vaporization (Co-LAVA) method or the in-process coating of the aerosol particles, respectively. The Co-LAVA method is used to achieve multi-phase or single-phase mixed-oxide nanoparticles. For this purpose homogeneous mixtures of at least two ceramic raw powders are co-laser evaporated in one single process (Fig. 5). Starting from a mixture of several oxides the composition of the resulting nanoparticles depends on the thermal behavior of the raw components, their reactivity within the mixture as well as on their mixing ratios. In general the components of the raw mixture have different rates of vaporization. Therefore it is not possible to map the mixing ratio of the raw components onto the phase composition of the resulting nanoparticles. To obtain defined phase ratio in the nanopowder, the mixing ratio of the raw powders has to be determined experimentally. In order to prevent the depletion of Fig. 6. Principle of the co-laser vaporization process. the component with the higher vaporization rate in the raw mixtures, fresh mixtures have to be supplied continuously during the co-vaporization process.

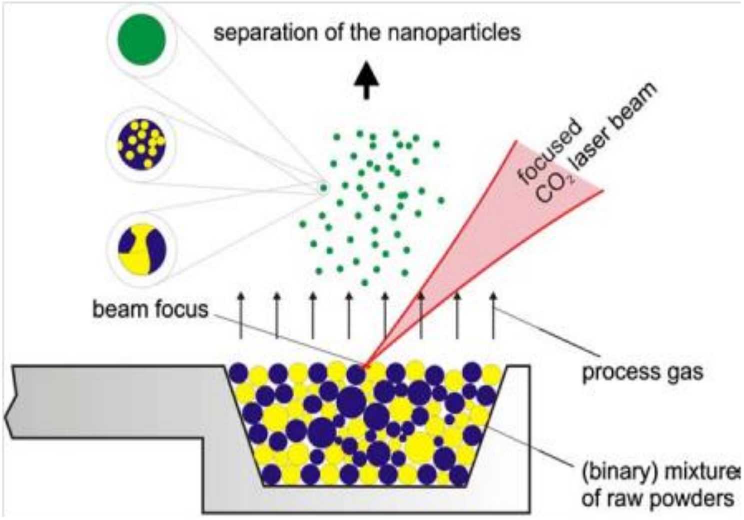


Figure 6- Principle of the co-laser vaporization process

The LAVA method allows for the production of a wide range of ceramic nanopowders. Zirconium dioxide (zirconia, ZrO_2), aluminum oxide (alumina, Al_2O_3) and titanium dioxide (titania, TiO_2) were selected to discuss the particle formation and the characteristic features of single phase, unmodified LAVA nano powders. As raw powders for the laser vaporization corundum (α-Al_2O_3, Alcoa, A16SG), yttrium stabilized tetragonal zirconia (ZrO_2, Tosoh Corp., TZP-3Y) and anatase (TiO2,VWR BDH Prolabo, GPR Rectapur 20732.298) were used. These raw materials were vaporized under air applying a continuous laser radiation with the maximum power of $P = 2$ kW and an additional air jet through the nucleation zone. Production rates of 27 g, 24 g, and 17 g nanopowder per hour were achieved, respectively. Transmission electron microscopic (TEM) micrographs reveal the typical morphology of LAVA generated ceramic nanoparticles (Fig. 7).

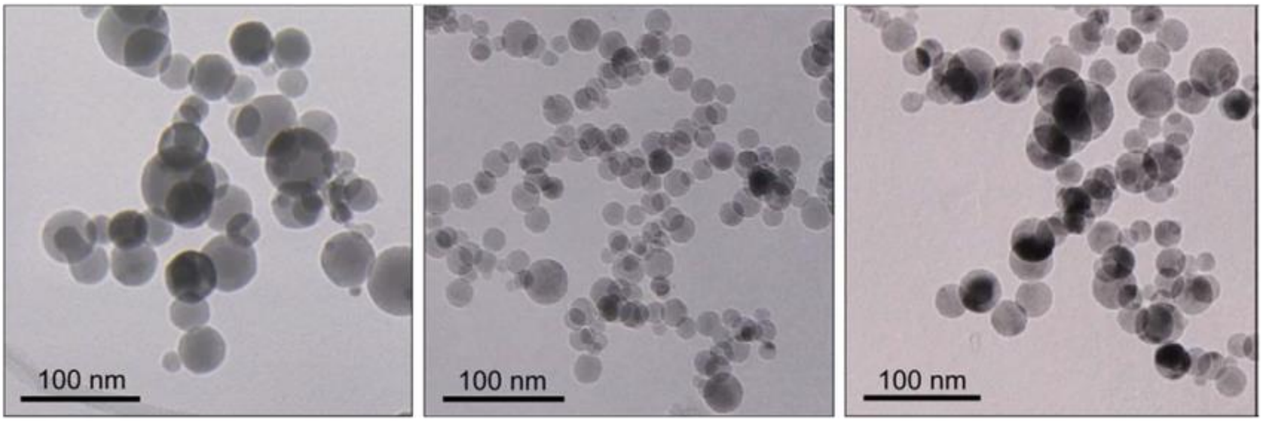


Figure 7 – TEM micrographs of LAVA prepared ZrO_2, Al_2O_3, and TiO_2 nanoparticles (from left to right) applying continuous laser radiation.

The density and cumulative particle diameter distributions of these three powder samples were derived from statistical TEM analysis (Fig. 8, upper row). The particle diameters show unimodal log-normal distributions.

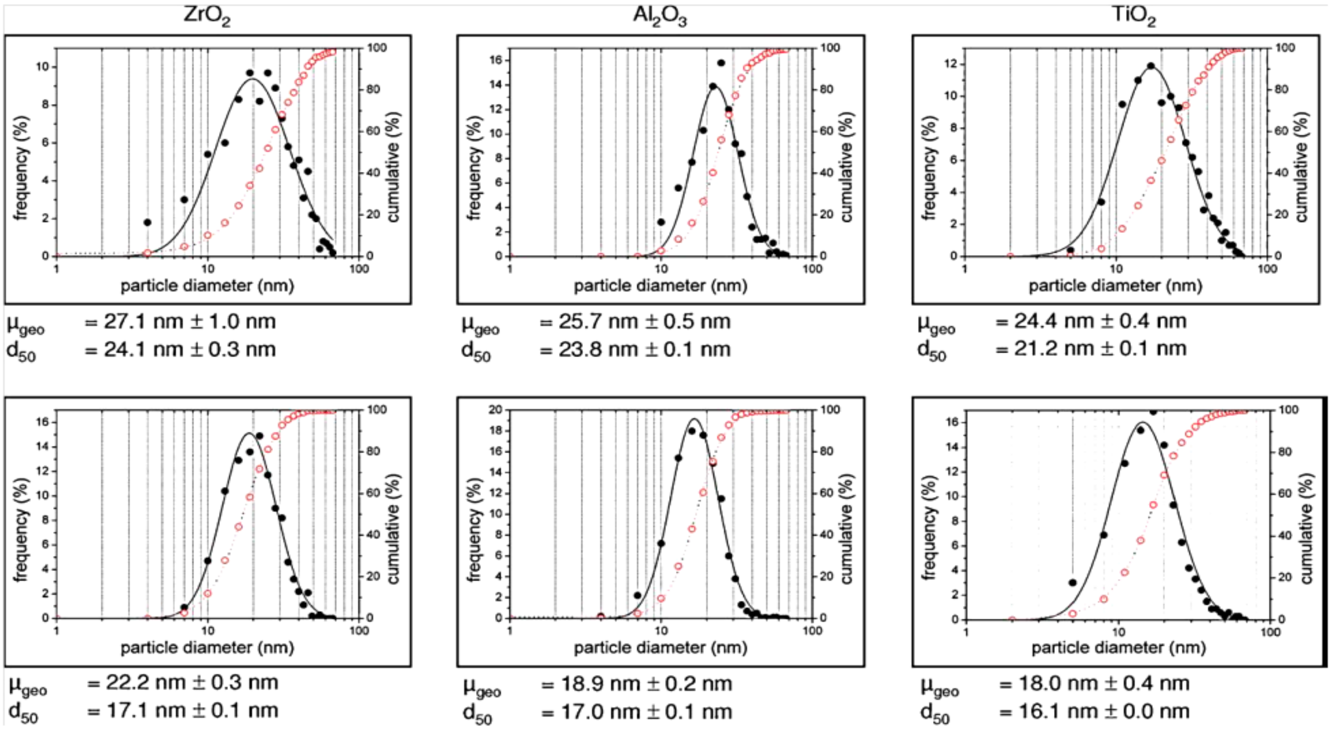


Figure 8 - Particle diameter distributions of the LAVAprepared ZrO_2, Al_2O_3, and TiO_2 nanopowders (from left to right) applying continuous (upper row) and pulsed laser radiation (lower row): density (—,●)_) and cumulative distributions (...,○) on number basis, geometric mean values μ_{geo} and $d50$ values (50% of the particles have smaller diameters than this value) of the particle diameters.

The nanoscaled particles are of spherical shape and merely softly agglomerated by weak van der Waals forces. Only a marginal fraction of particles is firmly bonded by solid state bridges (sinter necks). These findings reflect the

LAVA principle (Fig. 7): starting with the evaporation of the ceramic raw powder into a plasma particle formation proceeds through various time-temperature dependent stages.

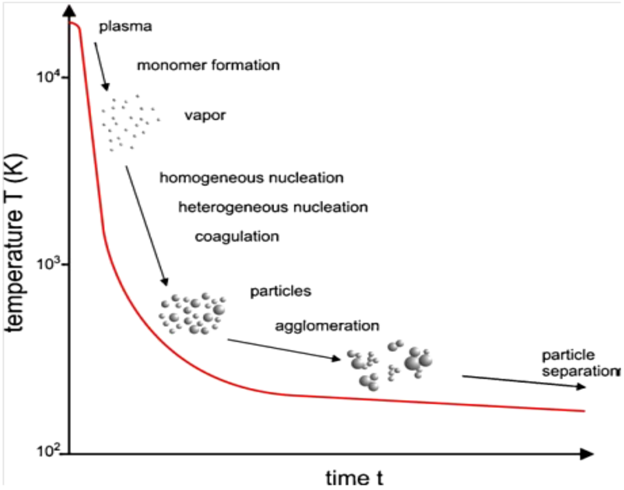


Figure 9 - Time-temperature dependent stages of particle formation within the LAVA process.

1.1.3. Synthesis of ZrO2 by CO_2 laser vaporization glycothermal processing

This technique can produce fine, high purity and stoichiometric particles of single and multi-component metal oxides. Furthermore, if the process conditions such as solution pH, solute concentration, reaction temperature, reaction time, seed materials, and the type of solvent are carefully controlled, the ceramic particles with desired shape and size can be produced. Chuah et al, reported that the reaction time and temperature and the pH of reaction medium are important factors that determine the surface area of zirconium. The influence of reaction is explained in terms of the enhanced agglomeration of primary particles during reaction and the strengthening of the network structure. The preparation flow of zirconia powder is schematically illustrated in Fig.1. Zirconia precursors were precipitated from 0.1 mol/L $ZrCl_2O \cdot 8H_2O$ solution by slowly adding NH_4OH water with rapid stirring, in which the pH of starting solutions varied between 7 and 11. The precipitated zirconia precursors were washed by respected cycles of centrifugation and redispersion in water. Washing was performed for a minimum of five times in ethanol.

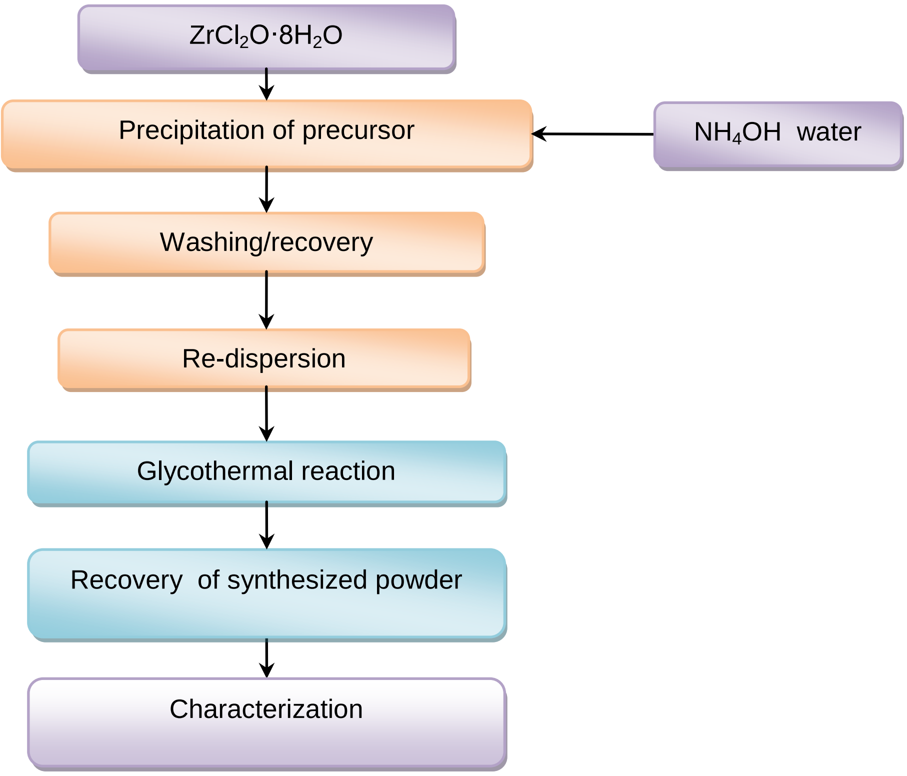


Figure 10 - Experimental flow chart of synthesized zirconia powders by glycothermal processing

Excess solution was decanted after the final washing and the wet precursor was re-dispersed in 200 mL ethylene glycol under vigorous stirring. The resulting suspension was placed in a 1 L stainless steel pressure vessel. The vessel was then heated to 270 °C at a rate of 10 °C/min for 6 h.

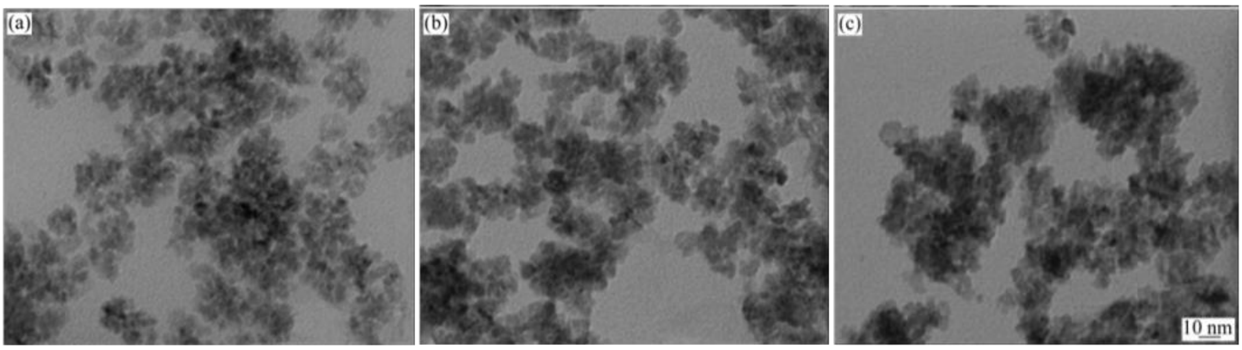


Figure 11 - TEM images of synthesized zirconia powders at different pH values: (a) pH=7; (b) pH=9; (c) pH=11

1.1.4. Synthesis of α-Al_2O_3 nanopowders by the polyacrylamide gel method

The polyacrylamide sol–gel method is a simple, fast and cheap method used for the synthesis of a wide variety of nanopowders. The precursors prepared from $Al(NO_3)_3.9H_2O$ and $AlCl_3.6H_2O$ are denoted as AN and AC, respectively. Synthesis of nanoparticles was carried out by dissolving the appropriate amount of these precursors, followed by the addition of acrylamide (AM) and N,N′-methylene bisacrylamide (MBAM) monomers in a molar ratio of 22:1 (AM:MBAM), producing a transparent solution after stirring. Freshly made 10% (w/v) ammonium persulfate (APS) and 1% (v/v) N,N,N′,N′-tetramethyl ethylene diamide (TEMED) were added to the premixed solution to act as an initiator and an accelerator, respectively. A rapid polymerization was observed, forming a transparent polymeric gel without any precipitation, followed by homogenization in a ceramic mortar. Different samples were obtained after subsequent thermal treatment using an Ex.1200-2LA laboratory furnace.

It has been reported that, in the polyacrylamide gel method, the presence of the polymeric network can effectively inhibit the aggregation of powders at high temperatures. Therefore, due to the high calcination temperatures of Al_2O_3 (1100–1200 °C), protecting the polymeric network from thermal degradation is critical to maintaining good control over particle size and morphology. SEM images from the synthesized powders using different heating rates, shown in Fig. 12, demonstrate that a lower heating rate produces finer particles. In order to support this observation, further investigation was carried out using XRD analysis.

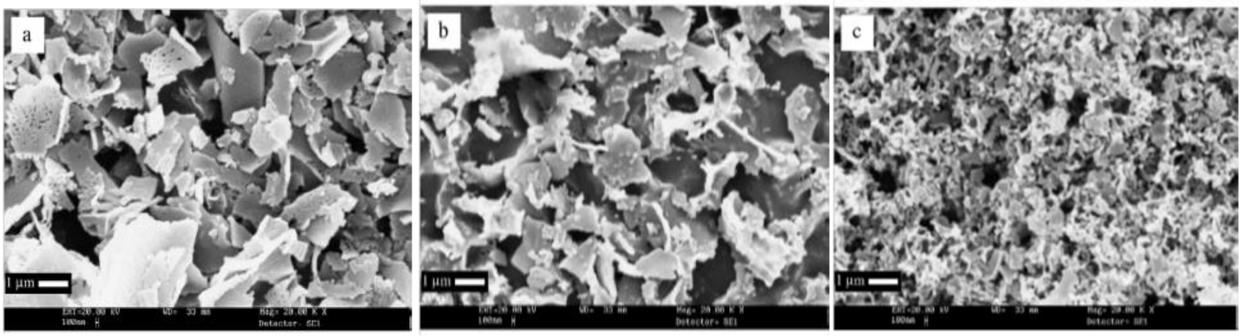


Figure 12 - SEM images of α-Al2O3 powders prepared at different heating rates (a) 20 (b) 10 and (c) 5 °C/min under two-stage atmospheres and (c) 5 °C/min under two-stage atmospheres.

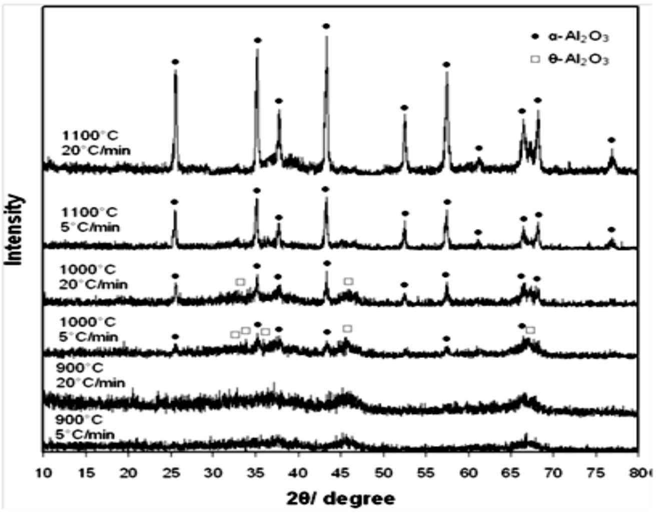


Figure 13 – XRD patterns of Al_2O_3 powders calcined at 900, 1000 and 1100 °C using two heating rates of 5 and 20 °C/min.

Fig. 13 displays the XRD patterns of alumina powders calcinated at 900, 1000 and 1100 °C using two heating rates of 5 and 20 °C/min. γ-Al_2O_3 synthesis was poor for both heating rates at 900 °C. Further heating up to 1000 °C revealed the presence of θ-Al_2O_3 and α-Al_2O_3. The latter is dominant using the 20 °C/min heating rate, indicating acceleration in the phase transformation from θ-Al_2O_3 to α-Al_2O_3. α-Al_2O_3 was the main product observed when the synthesized particles were heated to 1100 °C during calcination, and the intensity of the pattern was greater for the higher

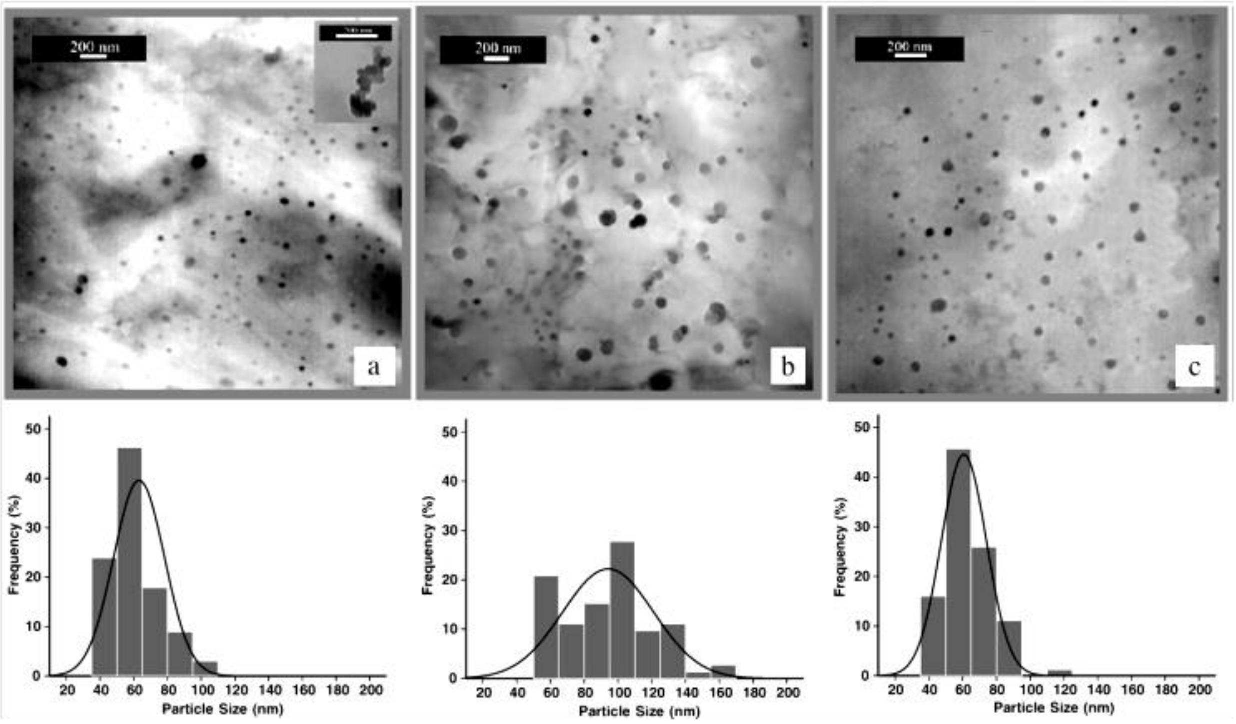


Figure 14 – TEM images and SD curves of α-Al_2O_3 powders obtained with different conditions: (a) M/S=2, Concentration=80 wt.% (b) M/S=1, Concentration=80 wt.% and (c) M/S=2, Concentration=50

heating rate.

The results show an increase in thermal stability with an increase in M/S ratio. At 0.5 M/S ratio, 92% loss of the original mass was observed when heated to 200 °C, but, as this ratio was increased, the rate of polymeric decomposition was reduced, resulting in less aggregation and producing finer nanoparticles. TEM images and SD curves (Fig.14a and 14b) support the above claims, indicating an increase from 65 nm to 100 nm particle size using M/S ratios of 2 and 1, respectively.

Приложение Б

РЭМ ИЗОБРАЖЕНИЯ ОКСИДОВ АЛЮМИНИЯ И ЦИРКОНИЯ

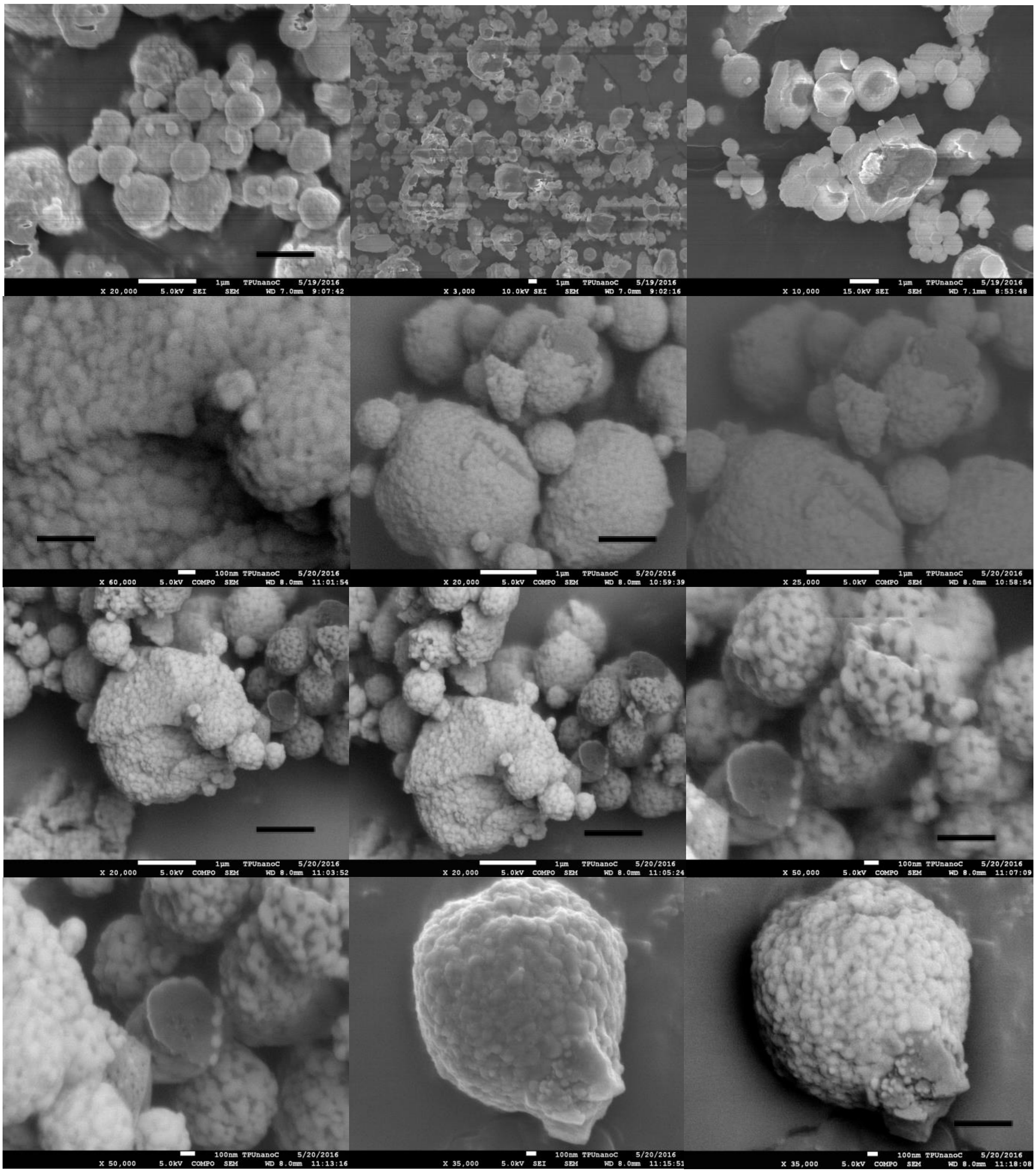


Рисунок Б 1 – РЭМ порошков Al_2O_3-ZrO_2 полученных методами распылительной сушки из 1 М $Al_2(NO_3)_3$ и 1 М $ZrOCl_2$ с добавлением 1 NH_4OH . Отжиг 1200 °С 1 часа;

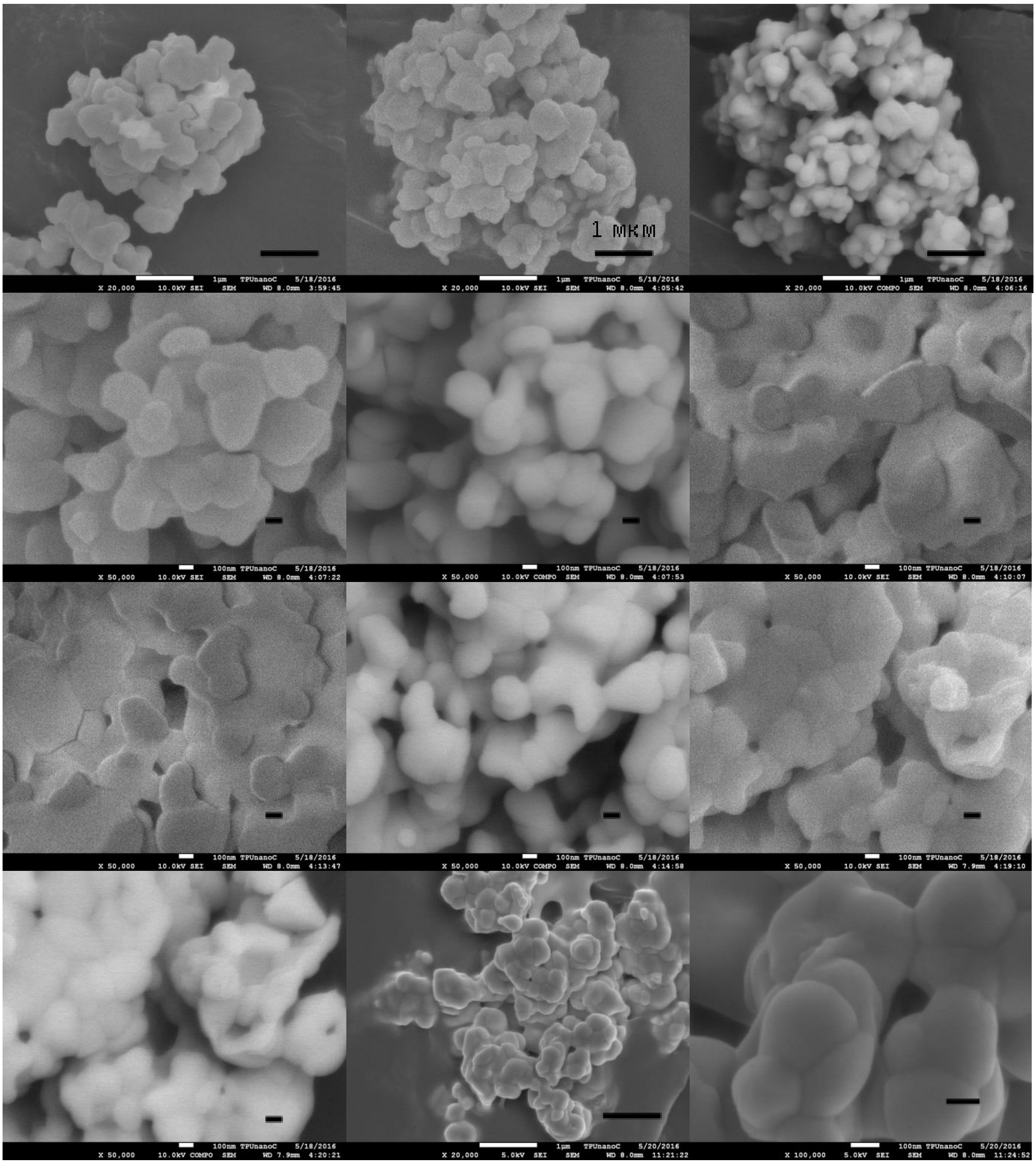


Рисунок Б2 – РЭМ порошков Al_2O_3-ZrO_2 полученных обратное осаждение из 1 М $Al_2(NO_3)_3$ и 1 М $ZrOCl_2$ с добавлением 0,25 H_3Cit . Отжиг 1200 °С 1

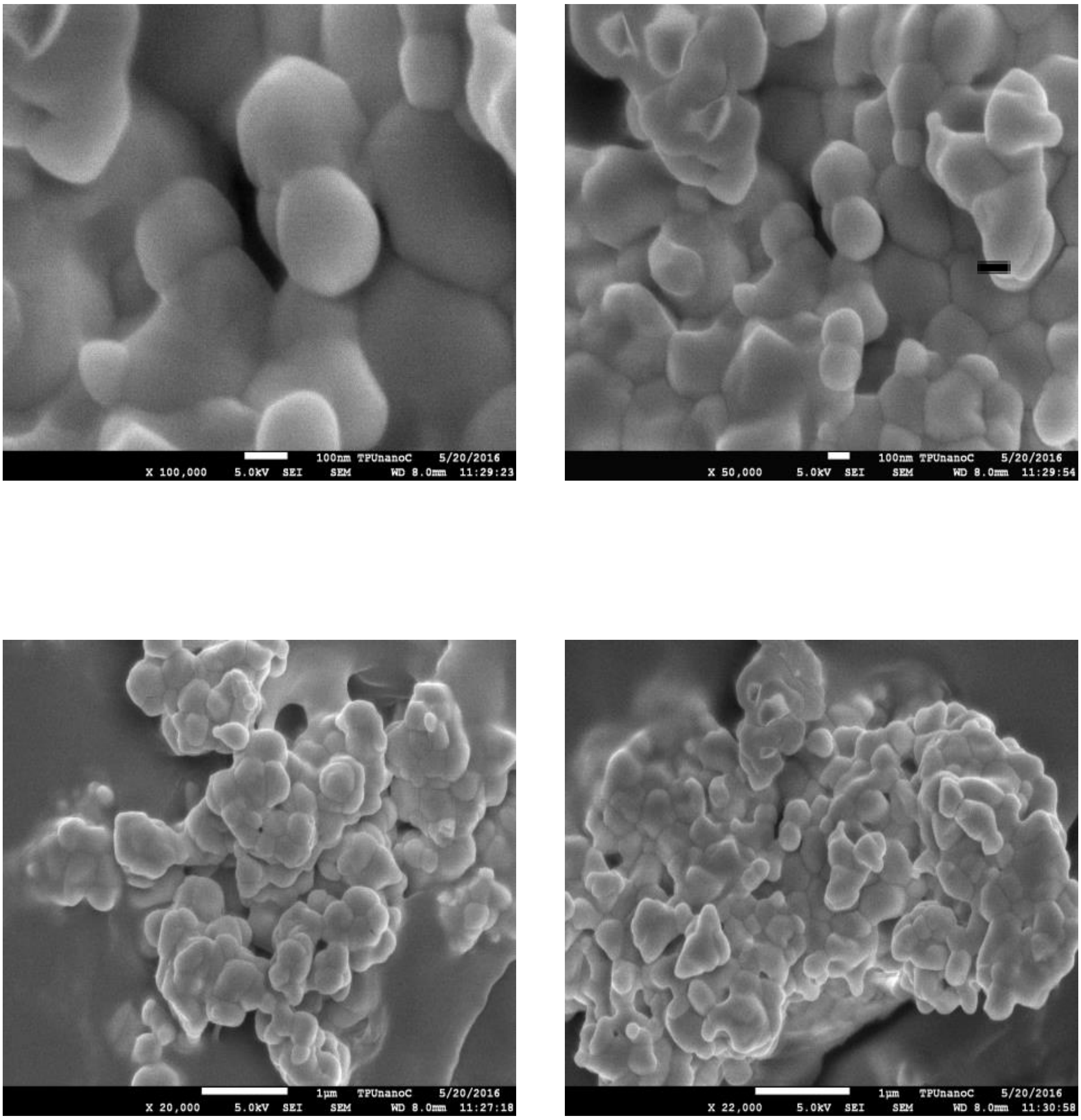


Рисунок Б 3 – РЭМ порошков Al_2O_3-ZrO_2 полученных обратное осаждение из 1 М $Al_2(NO_3)_3$ и 1 М $ZrOCl_2$ с добавлением 0,25 H_3Cit . Отжиг 1200 °С 1 часа;

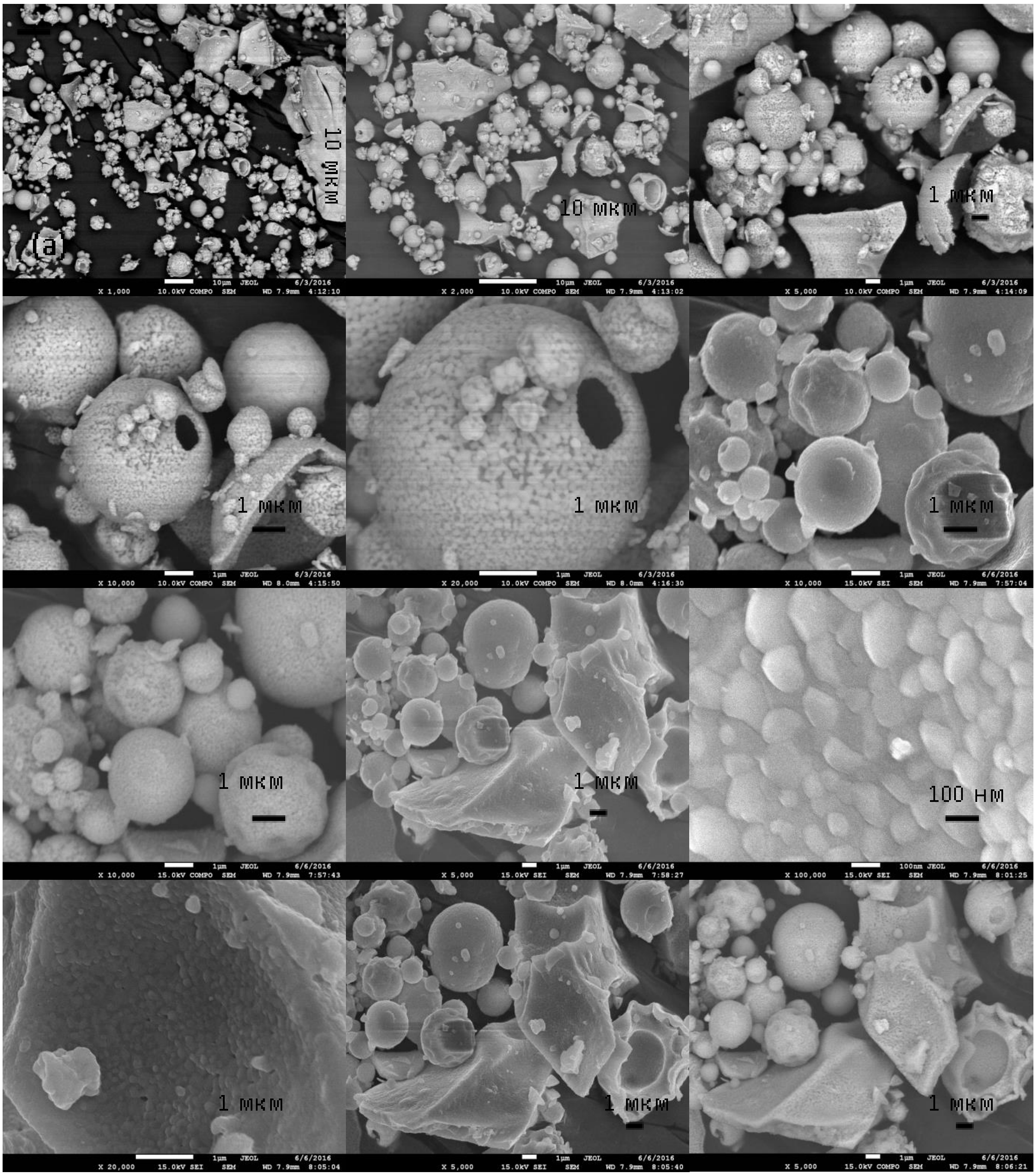
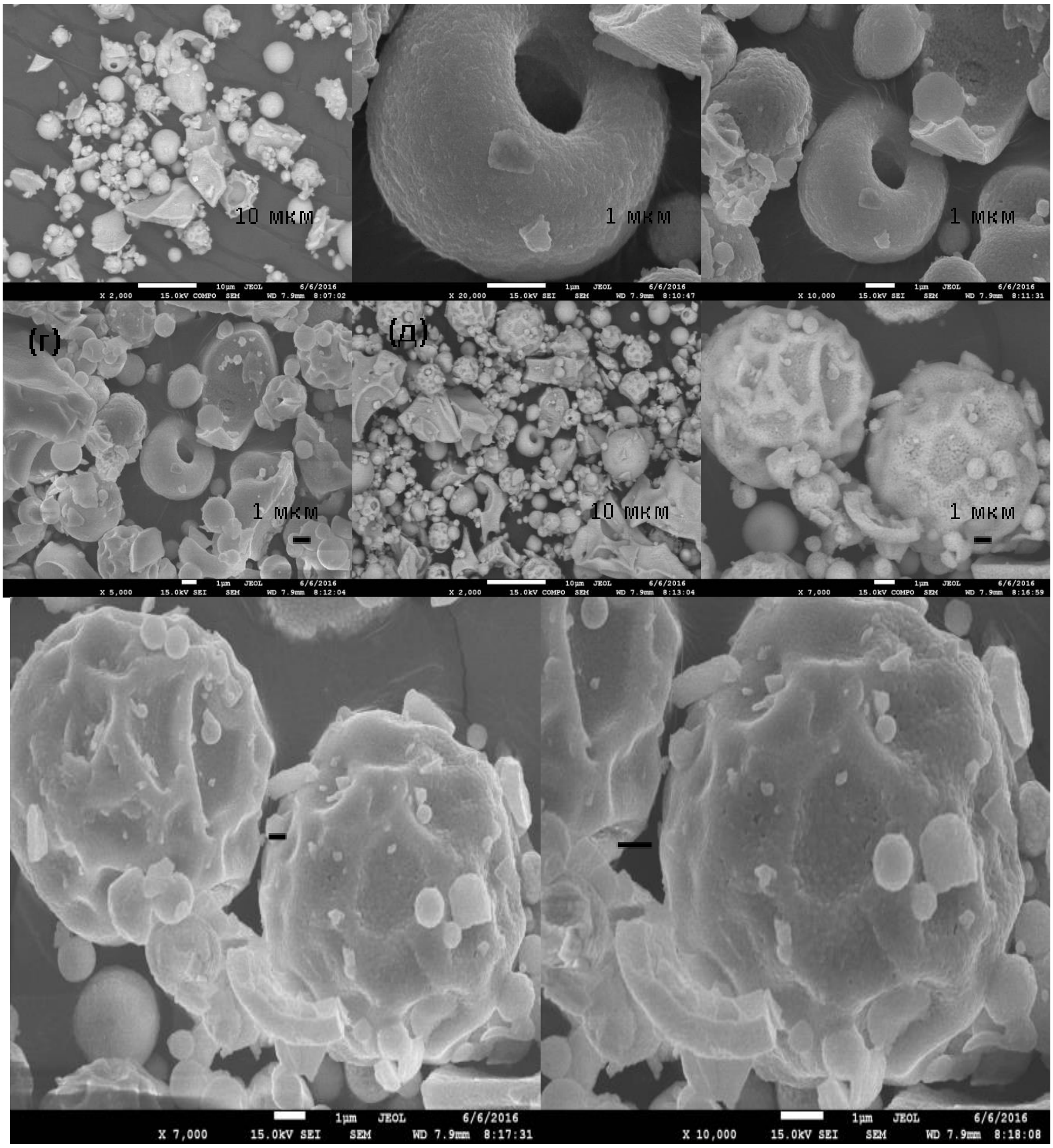
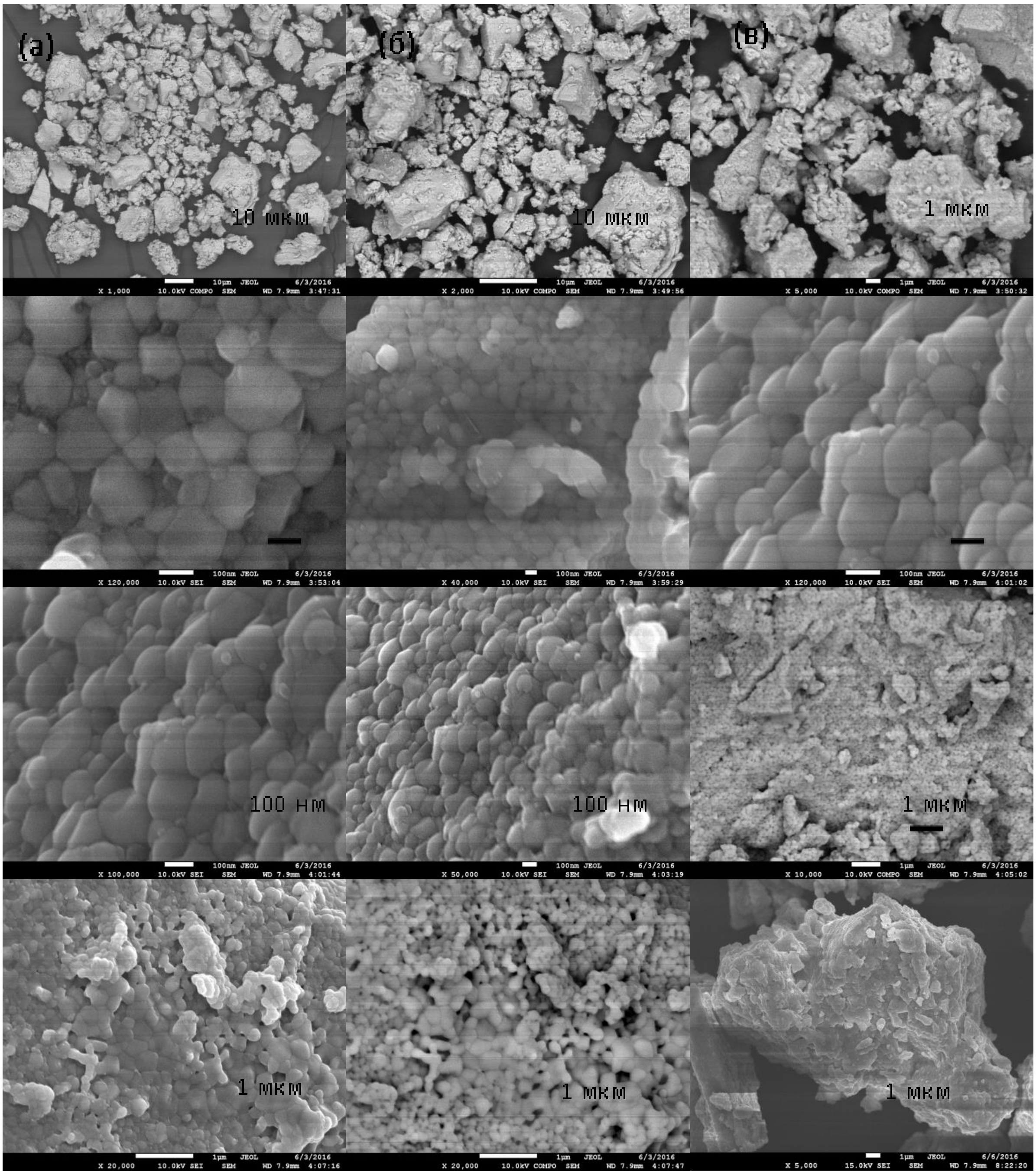


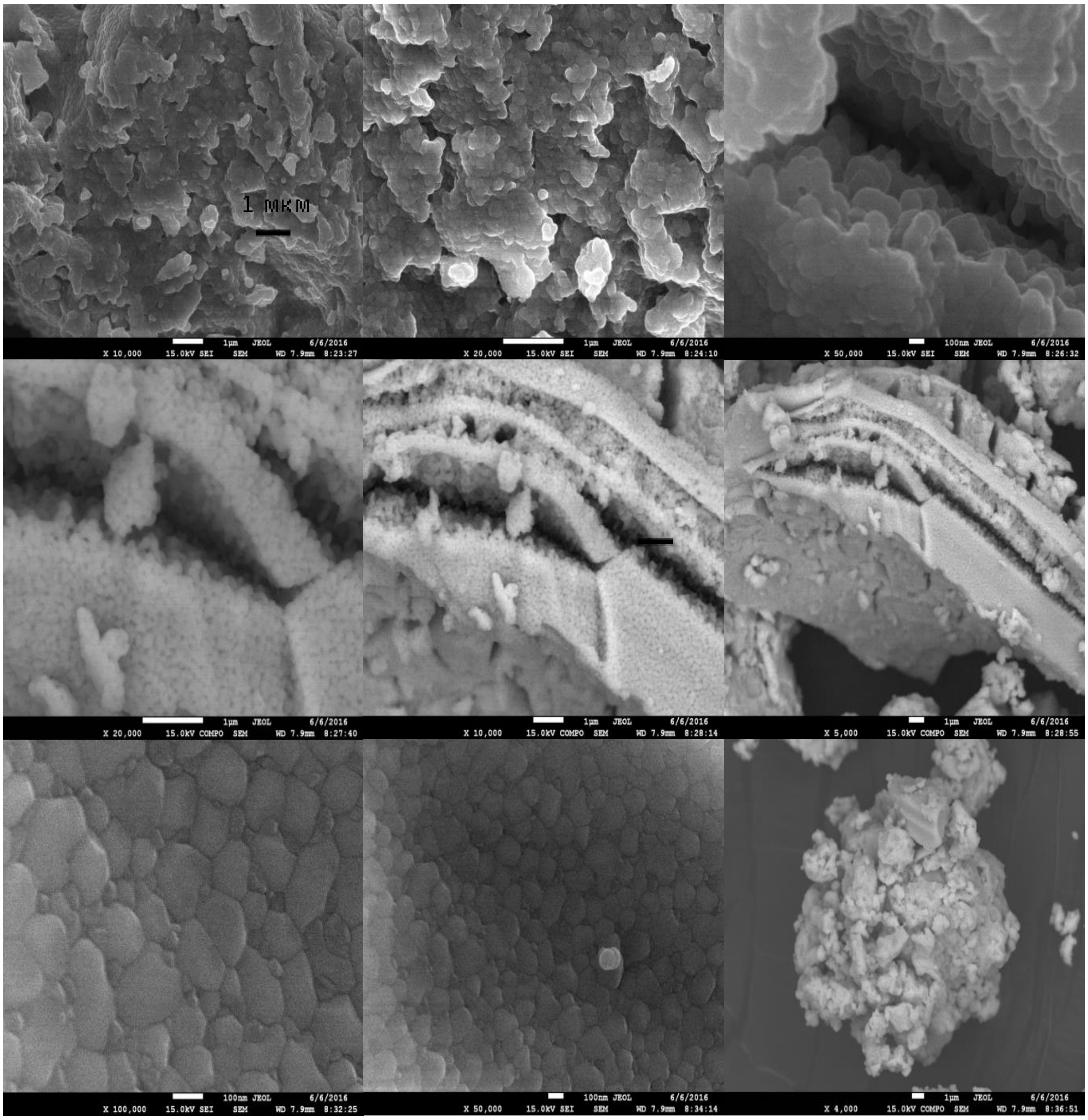
Рисунок Б 4– РЭМ порошков Al_2O_3-ZrO_2 полученных методами распылительной сушки из 1 M $Al_2(NO_3)_3$ и 1 M $ZrOCl_2$ с добавлением 0,12 H_3Cit . Отжиг 1200 °C 1 часа;



Б 5 – РЭМ порошков Al_2O_3-ZrO_2 полученных методами распылительной сушки из 1 М $Al_2(NO_3)_3$ и 1 М $ZrOCl_2$ с добавлением 0,12 H_3Cit . Отжиг 1200 °С 1 часа

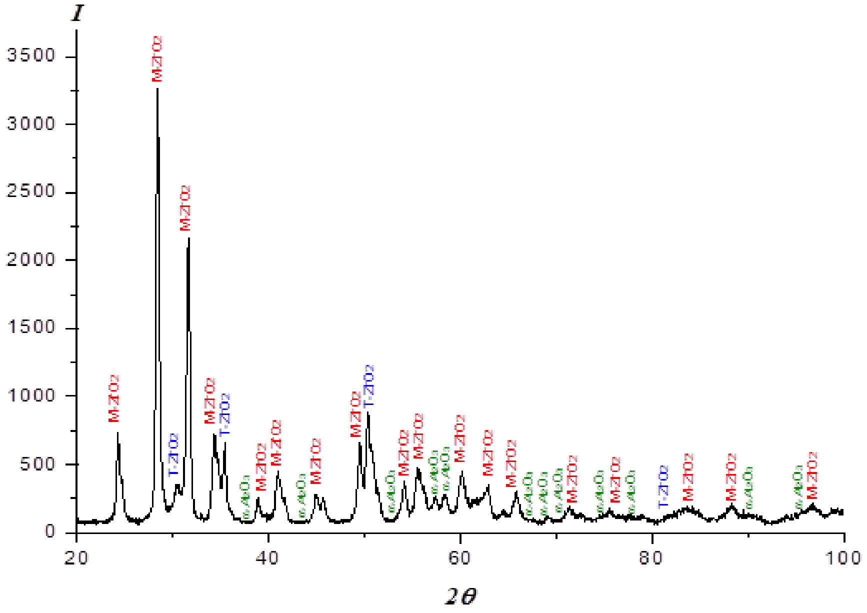


Б 6– РЭМ порошков Al_2O_3-ZrO_2 полученных химическим осаждением из 0,25 М $Al_2(NO_3)_3$ и 0,25 М $ZrOCl_2$ с добавлением аммиака . Отжиг 1200 °C 1 часа;



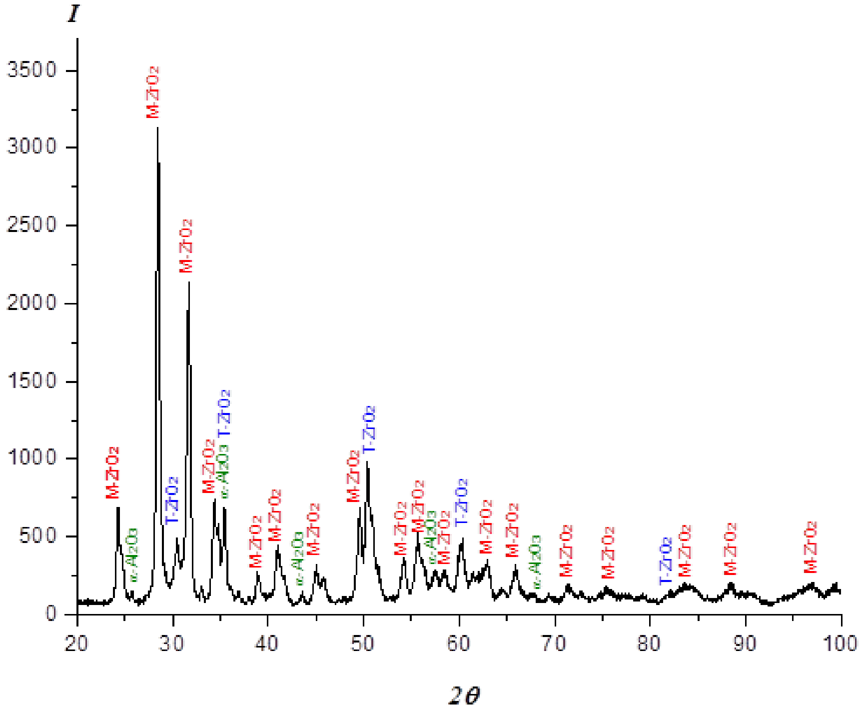
Б 7– РЭМ порошков Al_2O_3-ZrO_2 полученных химическим осаждением из 1 М $Al_2(NO_3)_3$ и 1 М $ZrOCl_2$ с добавлением аммиака . Отжиг 1200 °С 1 часа:

Приложение В
ДИФРАКТОГРАММЫ ПОРОШКОВ ОКСИДОВ АЛЮМИНИЯ И ЦИРКОНИЯ



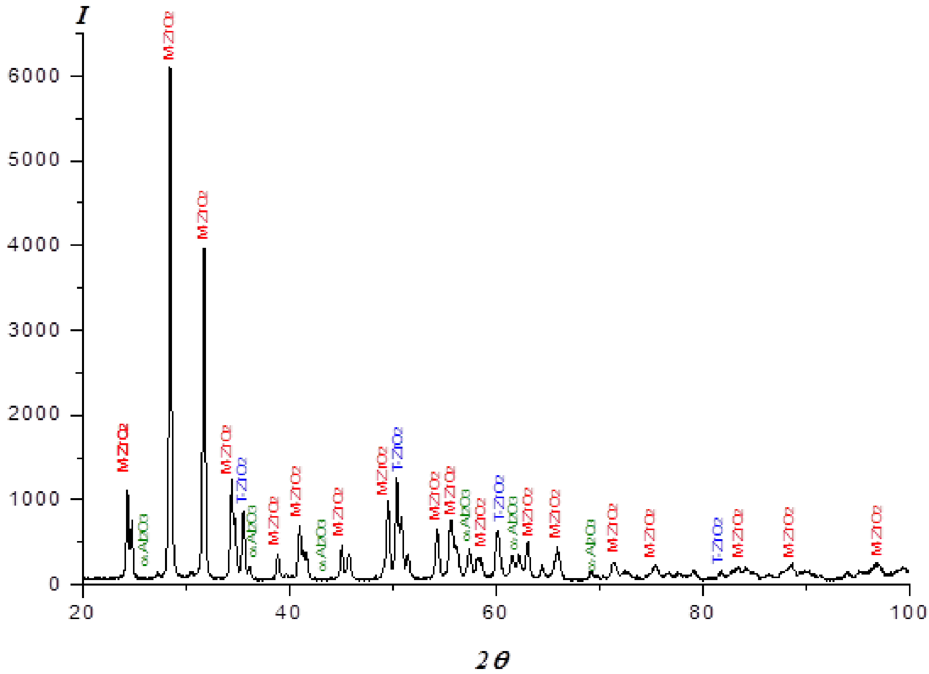
AlNO$_3$+ZrOCl$_2$+NH$_4$OH

NS [0,5:0,5]



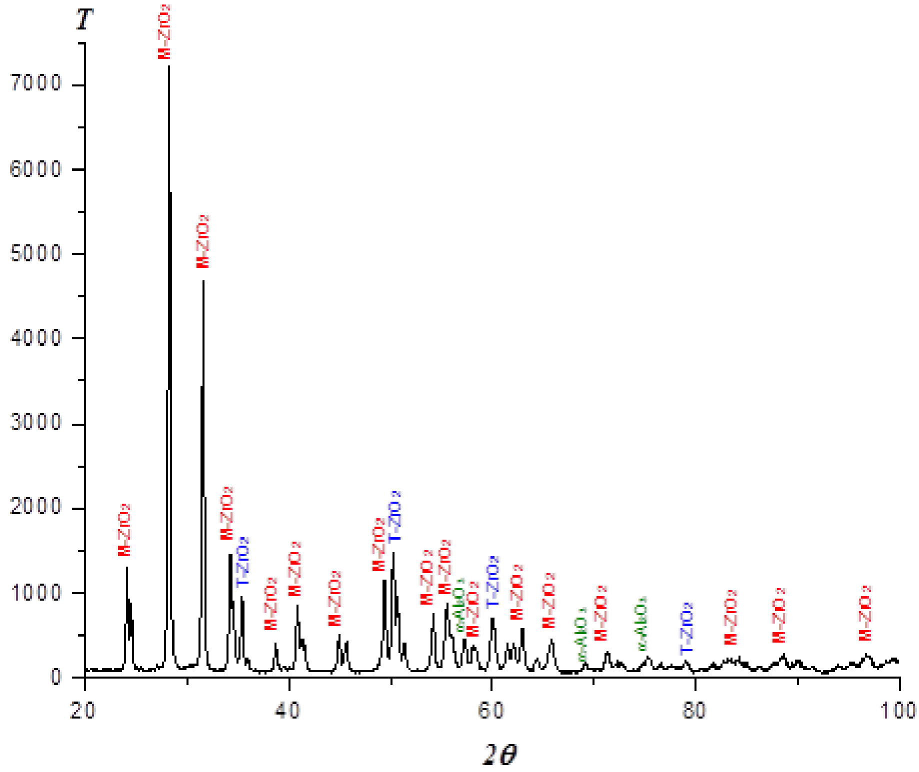
AlNO$_3$+ZrOCl$_2$+NH$_4$OH

NS [1:1]



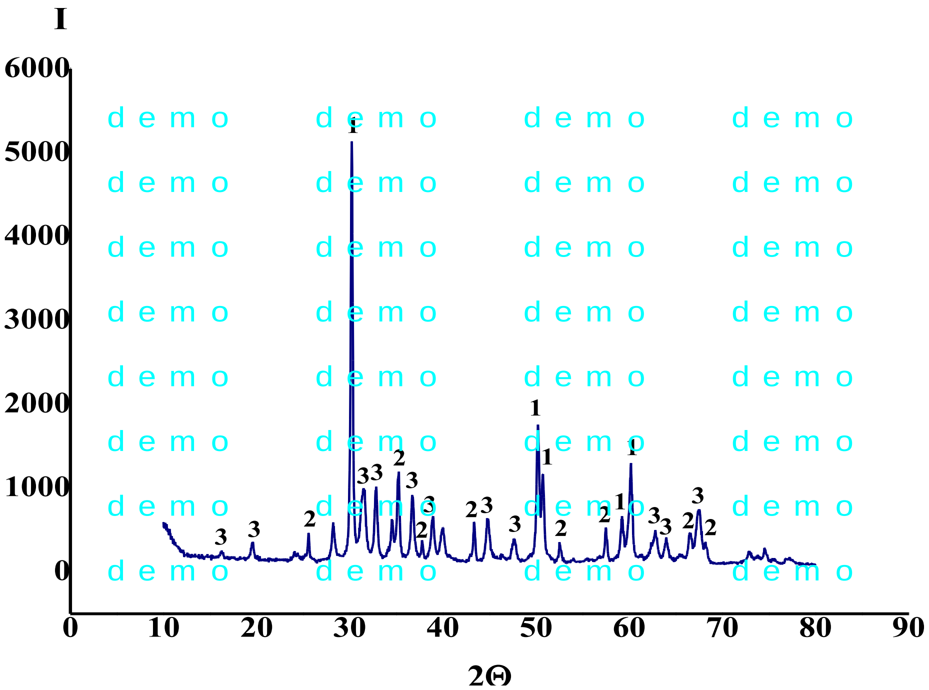
$AlNO_3$+$ZrOCl_2$+ H_3Cit

ФИЛЬТРАЦИЯ [1:1:0,5]



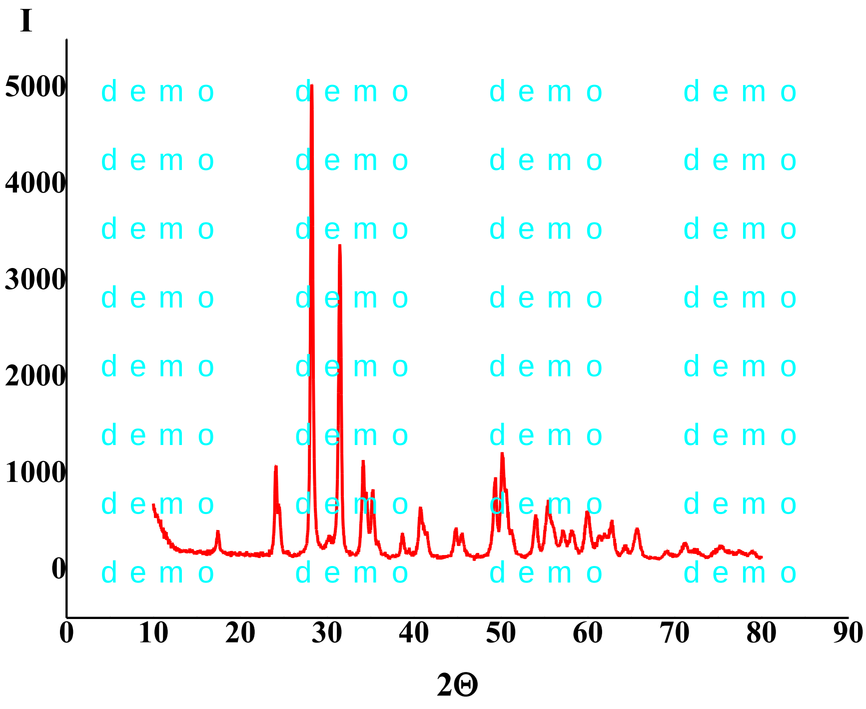
$AlNO_3$+$ZrOCl_2$+H_3Cit

NS [1:1:0,5]



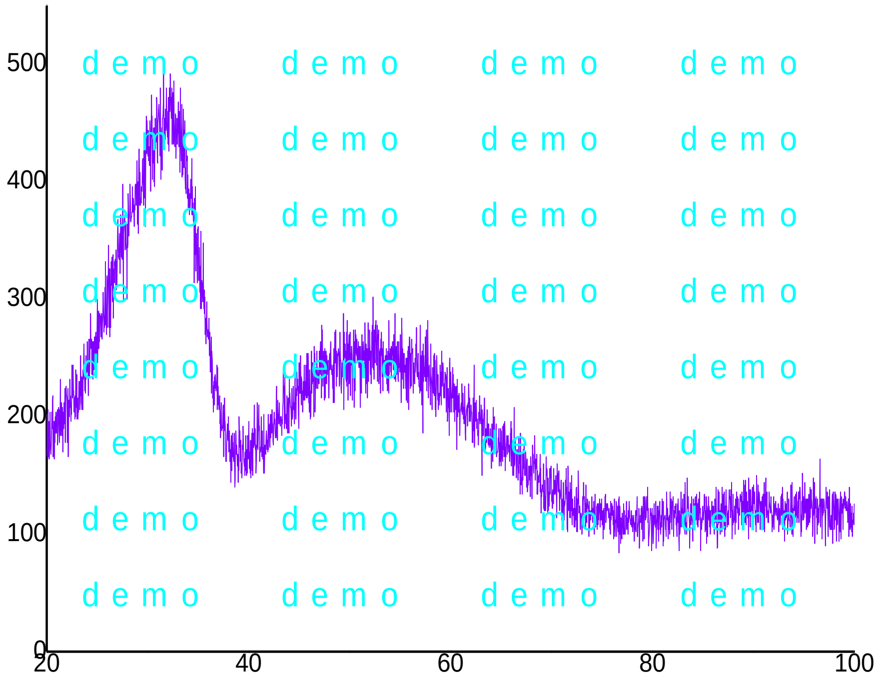
AlNO$_3$+ZrOCl$_2$+NH$_4$OH

ФИЛЬТРАЦИЯ [1:1]

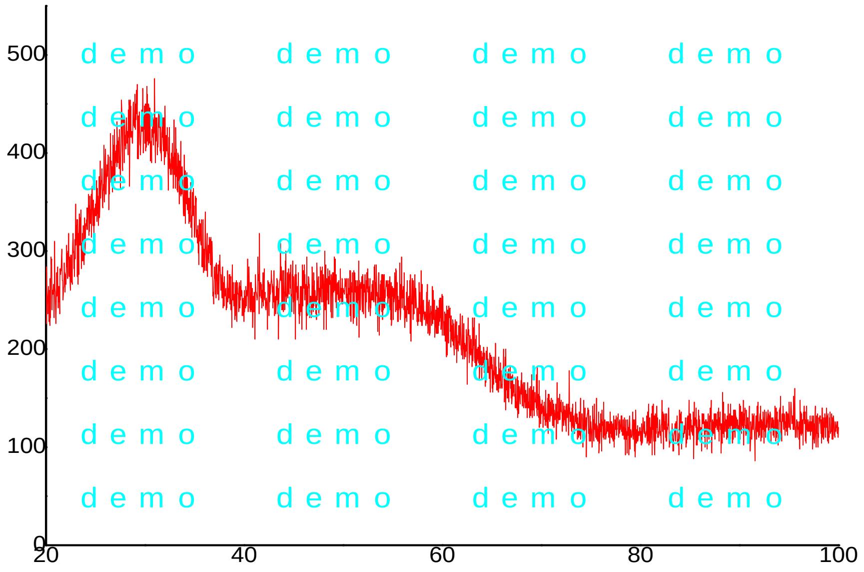


AlNO$_3$+ZrOCl$_2$+NH$_4$OH

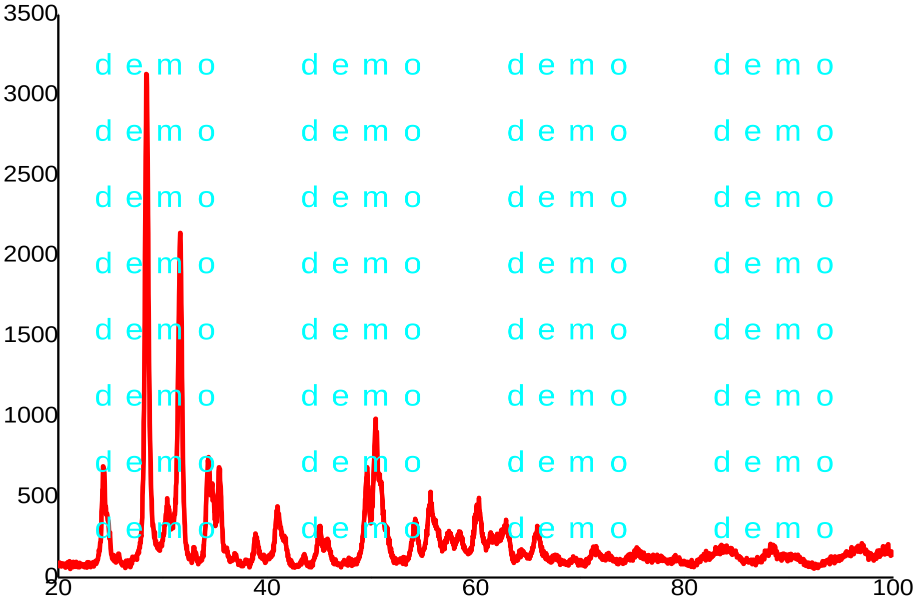
ФИЛЬТРАЦИЯ [0,75:0,25]



$AlNO_3+ZrOCl_2+NH_4OH$ 450°C
ФИЛЬТРАЦИЯ [1:1]

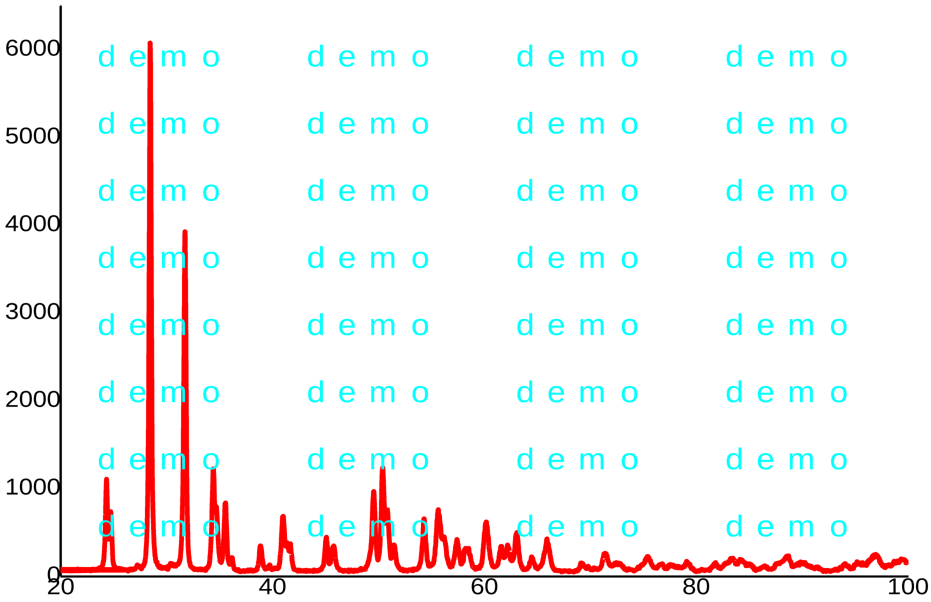


$AlNO_3+ZrOCl_2+NH_4OH$ 100°C
ФИЛЬТРАЦИЯ [1:1]



AlNO$_3$+ZrOCl$_2$+ H$_3$Cit

NS [0,25:0,25:0,12]



AlNO$_3$+ZrOCl$_2$+ H$_3$Cit

ФИЛЬТРАЦИЯ [1:1:0,5]