Microstructure and elemental composition of multicomponent systems based on silicon, titanium and zirconium oxides

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Abstract. The paper presents the results of studying the microstructure and elemental composition of multicomponent systems based on silicon, titanium and zirconium dioxides. These systems are of great practical interest for the medical, food, and microbiological industries due to their unique optical, photocatalytic, and bactericidal properties. Studies have shown that multicomponent systems based on silicon, titanium, and zirconium dioxides obtained by the sol-gel method have an amorphous structure, while the samples exhibit a deviation from stoichiometry towards an increase in the oxygen content, which is explained by the presence of oxo-, hydroxo-, and aqua complexes. The structure and shape of multicomponent oxide particles are determined by the component that prevails in the system. The presence of additional components and possible chemical interactions between them determines the process of nucleation, which, in turn, affects the polydispersity of the obtained samples.

1. Introduction
In the modern world, there is a constant development and improvement of technologies and materials. Dispersed materials based on silicon, titanium, and zirconium dioxides are of practical interest from a medical point of view due to their high biocompatibility [1-5]. The photocatalytic activity [6, 7] of titanium dioxide opens up the possibility of using materials based on it in the food and microbiological industries, and also allows to find applications in wastewater treatment plants [8-10]. The combination of titanium dioxide treatment with UV treatment allows disinfection without the formation of carcinogenic, mutagenic, and strong-smelling compounds. In addition, oxides of silicon, titanium, and zirconium and materials based on them are widely used in the production of paints, plastics, cosmetics, hydrophobic coatings, aerogels, etc [11-17].

The purpose of this work is to establish the relationship between the features of synthesis of the multicomponent systems based on silicon, titanium, and zirconium oxides and their phase composition, structure, and shape.

2. Methods
Multicomponent systems based on silicon, titanium, and zirconium dioxides were obtained by the sol-gel method, by co-precipitation of components from aqueous-alcoholic solutions. The following precursors were used: tetraethoxysilane (grade A), titanium tetraisopropylate (pure grade), 2-aqueous zirconyl nitrate (analytical grade). Aqueous-alcoholic solutions were prepared on the basis of ethyl alcohol of the "Extra" brand (GOST 51652-2000) and deionized water (GOST R 52501-2005). The precipitation of silicon, titanium, and zirconium hydroxides was carried out by an aqueous solution of...
ammonia (analytical grade). The developed method for the preparation of multicomponent systems based on silicon, titanium, and zirconium dioxides consists of several stages.

At the first stage, aqueous-alcoholic solutions of precursors were mixed. Then, to activate the hydrolysis process with constant stirring, a 12.5% ammonia solution was slowly dripped until the neutral value of the active acidity of the medium (pH = 6 - 7). At the second stage, to form an aggregative stable gel of the multicomponent oxide system, the samples were placed for 24 hours in a dark cool place. At the third stage, the resulting gels were washed by centrifugation and then dried at a temperature of 100 °C.

This technique [18] was used to obtain 4 series of samples of multicomponent oxide systems. In the first series of SiO\(_2\)-TiO\(_2\) samples, the titanium dioxide content was varied in the range from 10 to 90 wt.%. In the second and third series of samples, the content of zirconium dioxide varied from 0.1 to 3% (wt.). In the fourth series of samples, the content of titanium dioxide varied from 3 to 10% (wt.), And zirconium dioxide from 0.1 to 3% (wt.) The characteristics of the multicomponent oxide systems are presented in Table 1. The mass content of silicon, titanium, and zirconium dioxides, for ease of comparison with the results of energy dispersive analysis, have been converted into atomic percentages of the corresponding elements.

**Table 1.** Theoretically calculated elemental composition of multicomponent oxide systems

| Series number | Type of the multicomponent system | Number of sample | Content of elements, at. % |
|---------------|----------------------------------|-----------------|---------------------------|
|               |                                  |                 | Silicon | Titanium | Zirconium | Oxygen |
| Series 1      | SiO\(_2\)-TiO\(_2\)              | 1               | 30.76   | 2.57     | –         | 66.67 |
|               |                                  | 2               | 28.06   | 5.27     | –         | 66.67 |
|               |                                  | 3               | 25.21   | 8.12     | –         | 66.67 |
|               |                                  | 4               | 22.20   | 11.13    | –         | 66.67 |
|               |                                  | 5               | 19.1    | 14.23    | –         | 66.67 |
|               |                                  | 6               | 15.8    | 17.53    | –         | 66.67 |
|               |                                  | 7               | 12.13   | 21.20    | –         | 66.67 |
|               |                                  | 8               | 8.39    | 24.94    | –         | 66.67 |
|               |                                  | 9               | 4.28    | 29.05    | –         | 66.67 |
|               |                                  | 10              | –       | 33.33    | –         | 66.67 |
| Series 2      | TiO\(_2\)-ZrO\(_2\)              | 1               | –       | 33.31    | 0.02      | 66.67 |
|               |                                  | 2               | –       | 33.22    | 0.11      | 66.67 |
|               |                                  | 3               | –       | 33.11    | 0.22      | 66.67 |
|               |                                  | 4               | –       | 32.89    | 0.44      | 66.67 |
|               |                                  | 5               | –       | 32.67    | 0.66      | 66.67 |
| Series 3      | SiO\(_2\)-ZrO\(_2\)              | 1               | 33.32   | –        | 0.01      | 66.67 |
|               |                                  | 2               | 33.25   | –        | 0.08      | 66.67 |
|               |                                  | 3               | 33.17   | –        | 0.16      | 66.67 |
|               |                                  | 4               | 33.00   | –        | 0.33      | 66.67 |
|               |                                  | 5               | 32.83   | –        | 0.50      | 66.67 |
| Series 4      | SiO\(_2\)-TiO\(_2\)-ZrO\(_2\)   | 1               | 30.77   | 2.54     | 0.02      | 66.67 |
|               |                                  | 2               | 30.80   | 2.45     | 0.08      | 66.67 |
|               |                                  | 3               | 30.85   | 2.31     | 0.17      | 66.67 |
|               |                                  | 4               | 30.93   | 2.07     | 0.33      | 66.67 |
|               |                                  | 5               | 31.0    | 1.82     | 0.51      | 66.67 |
The phase composition of the samples was studied by powder diffractometry on a PANalitical Empyrean X-ray diffractometer (PANalitical B.V., Netherlands). The structure and elemental composition of samples of multicomponent oxide systems were investigated on a MIRA3-LMH scanning electron microscope with a module for energy dispersive analysis AZtecEnergy Standart / X-max 20 (standart) (Tescan, Czech Republic).

3. Results and discussion
To determine the phase composition of samples of two and three-component oxide systems after washing and drying, we used the powder diffractometry method. Since the diffraction patterns of the samples had a similar character within each series, one diffractogram was selected from each series (Figure 1).

![Figure 1. Diffraction patterns of multicomponent oxide samples: 1 – SiO₂-TiO₂ (w(Ti) = 29.05 % (at.)); 2 – SiO₂-ZrO₂ (w(Zr) = 0.5 % (at.)); 3 – TiO₂- ZrO₂ (w(Zr) = 0.66 % (at.)); 4 – SiO₂-TiO₂-ZrO₂ (w(Ti) = 1.82 % (at.); w(Z) = 0.51 % (at.))](image)

As can be seen from Fig. 1, the diffraction patterns contain low-intensity broadened peaks. This suggests that all samples of multicomponent oxide have an amorphous structure after drying. The analysis of the diffraction pattern of the samples of multicomponent oxide systems does not allow us to qualitatively and quantitatively identify the crystalline phases included in their composition.

To study the microstructure of the samples and the local elemental composition, we used the method of scanning electron microscopy in combination with energy-dispersive X-ray spectroscopy. Figures 2 and 3 show the EDS spectra of samples from each series. Table 2 shows the elemental composition of all studied samples.
Comparison of the theoretically calculated elemental composition of samples of multicomponent oxide systems (Table 1) and the one, obtained on the basis of energy-dispersive spectroscopy (Table 2) shows us that in the samples after drying there is a deviation from stoichiometry towards an increase in oxygen content. This suggests that in addition to silicon, titanium, and zirconium dioxides, the composition of multicomponent systems after drying includes oxo-, hydroxo-, and aqua complexes of the corresponding elements.
Table 2. Local elemental composition of samples of multicomponent oxide systems after drying (experimental)

| Series number | Type of the multicomponent system | Content of elements, at. % |
|---------------|-----------------------------------|--------------------------|
|               | Silicon  | Titanium | Zirconium | Oxygen  |
| Series 1      |          |          |           |         |
| SiO₂-TiO₂     |          |          |           |         |
| 26.27         | 2.66     | –        | 71.01     |         |
| 23.78         | 4.64     | –        | 71.58     |         |
| 21.94         | 6.59     | –        | 71.47     |         |
| 18.52         | 9.41     | –        | 72.07     |         |
| 15.58         | 13.02    | –        | 71.40     |         |
| 12.75         | 15.39    | –        | 71.86     |         |
| 10.99         | 17.08    | –        | 71.93     |         |
| 8.01          | 19.12    | –        | 72.87     |         |
| 4.28          | 23.02    | –        | 72.70     |         |
| -             | 28.40    | –        | 71.60     |         |
| Series 2      | TiO₂-ZrO₂|          |           |         |
| -             | 28.13    | 0.01     | 71.86     |         |
| -             | 28.57    | 0.05     | 71.38     |         |
| Series 3      | SiO₂-ZrO₂|          |           |         |
| -             | 28.56    | 0.13     | 71.31     |         |
| -             | 27.89    | 0.28     | 71.83     |         |
| -             | 27.98    | 0.45     | 71.57     |         |
| Series 4      | SiO₂-TiO₂-ZrO₂|       |           |         |
| -             | 30.19    | –        | 0.01      | 69.80   |
| -             | 26.78    | –        | 0.06      | 73.16   |
| Series 3      | SiO₂-ZrO₂|          |           |         |
| -             | 30.81    | –        | 0.12      | 69.07   |
| -             | 30.09    | –        | 0.21      | 69.70   |
| -             | 30.34    | –        | 0.41      | 69.25   |
| Series 4      | SiO₂-TiO₂-ZrO₂|        |           |         |
| -             | 24.67    | 2.69     | 0.01      | 72.63   |
| -             | 22.6     | 1.96     | 0.03      | 75.41   |

The results of studying the microstructure of multicomponent oxide systems of various series by scanning electron microscopy, are presented in the figures 4-7: SiO₂-TiO₂ with titanium dioxide content from 10 to 90%; TiO₂-ZrO₂ with a zirconium dioxide content of 0.1 to 3%; SiO₂-ZrO₂ with a zirconium dioxide content of 0.1 to 3%; SiO₂-TiO₂-ZrO₂ with titanium dioxide content from 7 to 10% and zirconium dioxide from 0.1 to 3%.
Figure 4. SEM-micrographs of SiO$_2$-TiO$_2$ samples containing: a) 30.76 at. % Si and 2.57 at. % Ti, b) 28.06 at. % Si and 5.27 at. % Ti, c) 25.21 at. % Si and 8.12 at. % Ti, d) 22.20 at. % Si and 11.13 at. % Ti.

The analysis of the micrographs showed that the SiO$_2$-TiO$_2$ samples containing from 2.57 at. % up to 8.12 at. % Ti, consist of spherical particles, that is, the shape and structure of particles are determined by the component that is prevailing in the system. With an increase in the Ti content to 29.05 at. % the structure of the samples changes - there is a transition from spherical particles to large aggregates of a non-spherical shape. Micrographs of samples of multicomponent SiO$_2$-ZrO$_2$ system are shown in Figure 5.
Figure 5. SEM-micrographs of SiO$_2$-ZrO$_2$ samples, containing 0.01 at. % Zr (a), 0.08 at. % (b) Zr, 0.17 at. % Zr (c) and 0.33 at. % (d) Zr

Analysis of micrographs of the SiO$_2$-ZrO$_2$ multicomponent system showed that the concentration of introduced zirconium dioxide affects the microstructure of silicon dioxide. So the introduction of 0.01 at. % zirconium in the system leads to the formation of spherical particles with a diameter of 50 to 200 nm. An increase in the concentration of zirconium leads to a halving of the particle diameter. This may be due to the fact that zirconium compounds have significantly lower solubility product values than...
silicon compounds. With the co-precipitation of silicon and zirconium oxides from aqueous-alcoholic solutions, zirconium compounds begin to crystallize, which serve as crystallization centers for silicon oxide. The higher the initial concentration of zirconium in the solution, the more zirconium crystallization centers are formed in the multicomponent system and the smaller the diameter of the particles formed on their basis. Micrographs of the TiO$_2$-ZrO$_2$ samples with different component contents are shown in Figure 6.

**Figure 6.** SEM-micrographs of TiO$_2$-ZrO$_2$ samples, containing 0.02 at. % Zr (a), 0.11 at. % Zr, 0.44 at. % Zr (c) and 0.66 at. % (d) Zr
The micrographs of the TiO$_2$-ZrO$_2$ samples show that the structure of the multicomponent system is represented by large faceted aggregates of various shapes and spherical particles of smaller sizes. An analysis of the relevant works [19, 20] showed that during the co-precipitation of titanium and zirconium compounds from aqueous-alcoholic solutions, nucleation is the limiting stage of phase formation in the TiO$_2$-ZrO$_2$ system. The absence of nucleating complexes affects both the structure and the size distribution of the resulting multicomponent particles. The process of co-precipitation of titanium and zirconium compounds is complicated by the possibility of chemical interaction between them with the formation of complex salt systems. At a zirconium dioxide concentration of 0.02 - 0.11 at.%, These aggregates consist of nanoparticles with a diameter of 50 - 170 nm. It is important to note that an increase in the ZrO$_2$ concentration in a multicomponent system leads to an increase in the polydispersity of TiO$_2$-ZrO$_2$ nanoparticles - the structure becomes more inhomogeneous. Micrographs of the SiO$_2$-TiO$_2$-ZrO$_2$ three-component system are shown in Figure 7.

**Figure 7.** SEM-micrographs of SiO$_2$- TiO$_2$-ZrO$_2$ samples, containing (a) 0.02 at. % Zr and 2.54 at. % Ti, (b) 0.08 at. % Zr and 2.45 at.% Ti (c) 0.17 at. % Zr and 2.31 at. % Ti, (d) 0.51 at. % Zr and 1.82 % Ti
As a result of the analysis of SiO$_2$-TiO$_2$-ZrO$_2$ nanocomposite micrographs, it has been established that the structure of the three-component system is represented by aggregates of various shapes, which are enclosed in a silicon dioxide matrix. Moreover, the highest polydispersity is observed in the sample containing 0.33 at. % Zr and 2.07 at. % Ti, which contains spheres with a diameter of 1 - 2 μm.

4. Conclusion
As a result of the studies carried out, it was found that multicomponent systems based on silicon, titanium and zirconium dioxides obtained by the sol-gel method have an amorphous structure. In samples of two and three-component systems, after drying, a deviation from stoichiometry towards an increase in the oxygen content was observed. This suggests that the composition of multicomponent systems after drying includes complex oxo-, hydroxo-, and aqua complexes of the corresponding elements in addition to silicon, titanium and zirconium dioxides. First of all, the structure and shape of multicomponent oxide particles is determined by the component that is prevail in the system. The presence of additional components and possible chemical interactions between them determines the process of nucleation, which in turn affects the particles size and polydispersity of the composites.

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