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New multifunctional zirconia composite nanomaterials – from electronics to ceramics

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Abstract. In the present study the multifunctional composite materials on zirconia based for different applications were synthesized, studied and analyzed. It has been shown that the using of liquid solutions reagents instead of powders mixing allows entering in the matrix material the oxide dopants in supersaturated concentrations. The nanoparticles synthesized during this investigation contain a potential for the formation of various structures. By the controlling of heating regimes during nanopowders firing or sintering processes it become possible to control the diffusion processes on the particles volume and boundaries. In this study was found the decomposition of initial supersaturated solid solution during heat treatment leads to formation of multilevel nanocomposite structure in the ceramic matrix with enhancing mechanical, electrical, optical and catalytic properties. It was established that the modification of zirconia even a slight amount of aluminum oxide, zinc oxide leads to a significant changing in the properties of nanopowders and ceramics.

1. Introduction.

It is known, the properties of nanomaterials are very different from the properties of ordinary materials [1-2]. Consequently, during transformation from nanostructure to microstructure, for example due to heating, the properties of material change. Thus, the controlling of the treatments regimes allows regulating the structural transformations in nanomaterials and adjusts the properties of material to the exploitation conditions. At the same time we continued work in nanomaterials region. This conception is perfectly matched to the conception of multifunctional materials.

The conception of multipurpose materials has been appearing during last several years [3-4]. Multifunctional materials include materials that have the ability to perform multiple functions through judicious combinations of structural properties and at least one additional functional capability as dictated by the system application requirements. This direction is favorably for industry and it is compete with task oriented material.

Zirconia is well known as a multifunctional material with wide range of applications and as a bulk material used many years ago. This material combines the high fracture toughness and biocompatibility, ionic conductivity and chemical stability. It is used in energetic, technical ceramics, optics, catalyst, etc. [5-7]. Zirconia based nanomaterials and nanocomposites are perfect match for demonstration of the universality of material. Electrical conductivity, catalytic and optical properties of zirconia based nanocomposites have due to the peculiarities of nanoparticle formation and surface properties of nanoparticles. So, controlling the structure of composites and their chemical composition

allow demonstrating the different properties of material. We think that the key parameter is the preparation of metastable supersaturated solid solutions in nanodimentional state and its decomposition during heating. This process opens a new possibility in creation of different types of inclusions: clusters, grains, boundary enrichments and interfaces. This diversity of forms can be realized by different physical and chemical synthesis methods (laser and microwave synthesis, CVD and PVD methods) as well as by using the simple wet chemical methods.

Critical factors in the commercialization of advanced materials are the starting powders and the method of their formation. The cheap coarse starting powders and, consequently, high sintering temperature often decrease the level of functional properties of materials, e.g. mechanical strength, density, magnetization, etc. In case of composite materials the amount of critical factors increased in several times, because creation of uniform microstructure of multicomponent composite materials by traditional mixing process is very hard. However now, this method is the most commonly used in the industry. So, we have supposed, there is one way for the cheap improving the properties of composite ceramic materials for the industry at the present time. This is using of mixing of liquid solutions of reagents instead of powders mixing. It is wet chemical methods, for example sol-gel [8-9], colloidal [10], hydrothermal [11] or precipitation [12-13] techniques. In all these techniques the precipitation of insoluble phase is occurs. The using of mixing of reagents liquid solutions instead of powders mixing allows entering in the matrix material the oxide dopants in supersaturated concentrations. The decomposition of initial supersaturated solid solution during heat treatment can lead to formation of multilevel nanocomposite structure in the matrix with enhancing mechanical, electrical, optical and magnetic properties.

In this study we have analyzed the structures and functional properties of different types of zirconia composite materials obtained by precipitation technique and compared these results with structure and properties of materials, obtained by traditional technology. Also we have shown that the traditional ceramic technology processes to impose greater restrictions on the chemical composition of materials and parameters of technological process.

2. Experimental

Zirconia (3Y-TZP) and zirconia based composites ZrO_2-3mol%ZnO, ZrO_2 -3mol%Y_2O_3+n%Al_2O_3, ZrO_2+4.4 mol%Y_2O_3 (4.4YZrO_2) doped by $CuCl_2$ and MnS nanopowders were synthesized with a co-precipitation technique using $ZrOCl_2$*nH_2O, $Y(NO_3)_3$*nH_2O, $AlCl_3$*6H_2O and $ZnCl_2$ salts. The amount of alumina was varied from 0.5 to 5 wt%. The amount of ZnO was varied from 3 to 50 wt%. All used chemicals were of high chemical purity. The technological aspects of the precipitation process were described in [14-16]. After washing and filtration, the hydrogel was dried in a microwave furnace with an output power of 700 W and at a frequency of 2.45 GHz. The dried zirconium hydroxides and composites were calcined in a resistive furnace at different temperatures with a dwelling time of 2 h. This variant was named CT and this abbreviation marked in powder name. After the 4.4YZrO_2 powder had been calcined at 700°C for 2 h, it was additionally doped by $CuCl_2$ or MnS (1 wt %) powder and then calcined at 800°C for 120 min in a laboratory furnace again [16].

In order to compare our results with traditional mixing techniques an appropriate amount of commercially available α-Al_2O_3 or ZnO powder was mixed with obtained 3Y-TZP nanopowders in distilled water. The α-Al_2O_3 particle size distribution was wide enough with an average size at 1 μm (manufacturer's data). ZnO powders were synthesized by technique which was mention above and after calcination at 500, 700, 1000°C the average particle size was 45, 80 and 250 nm, respectively. These mixtures were planetary-milled (MSK-SFM-1 MTI Corp., USA) at 400 rpm for 10 h using YSZ milling balls. This variant was named BM and this abbreviation marked in powder name.

The powders and sintered specimens were characterized using XRD analysis (Dron-3) with Cu-Kα radiation for crystallite sizes and quantitative phase analyses with a proven method [17]. Particle sizes of different calcined powders were estimated by transmission electron microscopy (JEM 200, Jeol, Japan).The optical properties of ZrO_2-ZnO nanopowders were measured on Cary 5000 UV-Vis-NIR spectrometer (Agilent Technologies, USA). The chemical composition of synthesized materials was

checked by energy dispersive spectroscopy (EDS) analysis (Oxford Instruments). The fracture toughness values were calculated by Niihara equation for Palmquist type cracks. The microstructures of the ceramics were studied by scanning electron microscopy (JSM 6490LV Jeol) after polishing of the surfaces as well as fractured surfaces.

3. Results and discussion

3.1. Formation of structure and properties in ZrO_2-3mol%ZnO system

The dynamic reflectance spectroscopy (DRS) results of mixed ZrO_2-3mol%ZnO composite have shown the traditional results. The peak near 380 nm is corresponded to ZnO and peak near 220 nm correspond to ZrO_2 (Figure 1). With increasing of calcining temperature and consequently with increasing ZnO particle size, the reflection peak near 380 nm, which was corresponded to ZnO, decreased for all values of ZnO concentrations (Figure 1a).
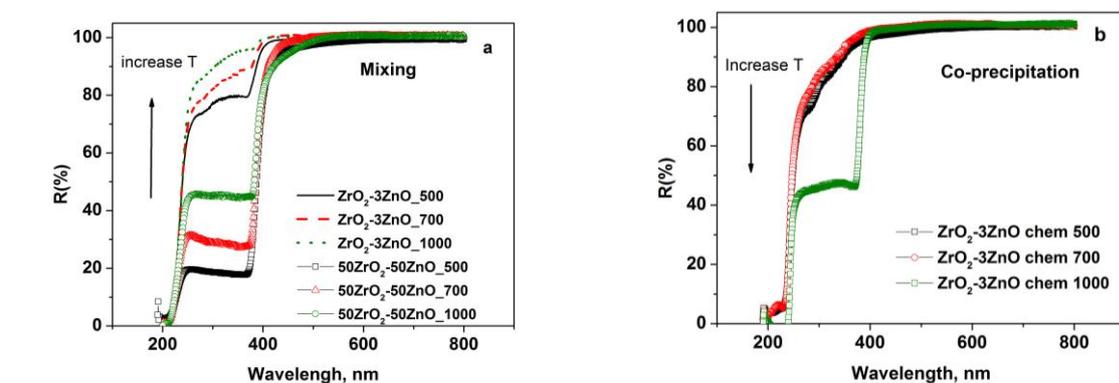
Figure 1. The DRS spectra of ZrO_2-ZnO nanopowders obtained by mixing technique - a) and co-precipitation – b) and calcined at different temperatures: 500 (black), 700 (red) and 1000°C (green).

In case of the ZrO_2-3mol%ZnO powder synthesized by co-precipitation technique the reflection near 380 nm, which correspond to ZnO reflection, did not fixed (Figure 1b) after calcination at temperatures 400-700°C. After calcination at 1000°C the reflectance peak near 380 nm appeared, but the absorption level in this case was in ten times higher than in powders obtained by mixing technique. It is shown the absorption level of 50% ZnO in mixed sample equivalent of 3mol% ZnO in sample obtained by precipitation. So, the opposite behavior of optic properties from method of powder preparation was demonstrated. In case of mixing technique – increasing ZnO particle size leads to decreasing the reflectance level, but in case of co-precipitation technique – increasing of ZnO particle size leads to strong increasing the reflectance level. Consequently, distribution of ZnO in ZrO_2 in this case is different in comparison with powders obtained by mixing technique. The typical TEM images of ZrO_2 - ZnO particles are depicted on Figure 2.
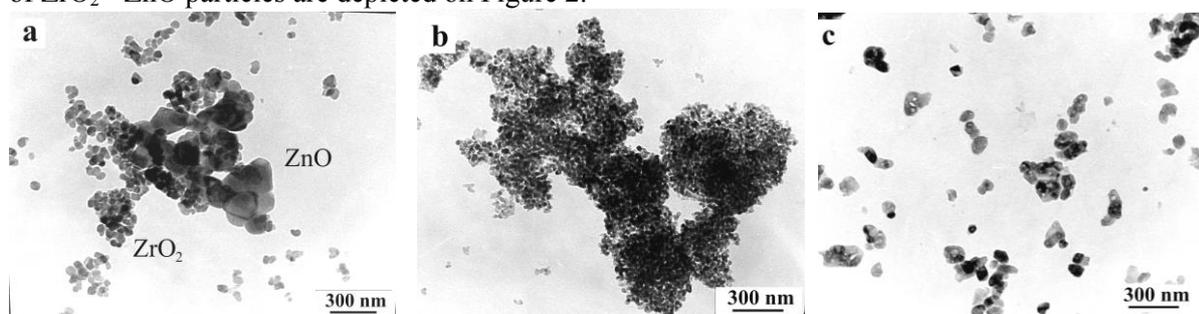
Figure 2. TEM images of ZrO_2-ZnO nanopowders, obtained by mixing - a) and co-precipitation – b, c) techniques and calcined at 700°C – a, b and 1000°C – c).

The mixture of small ZrO_2 particles and big ZnO particles obtained by mixing technology is shown on Figure 2a. The TEM images of powders obtained by co-precipitation technique are shown on Figure 2b and Figure 2c. The nanopowders ZrO_2-ZnO demonstrate the agglomeration but have a uniform structure of ZrO_2-ZnO nanoparticles with average size 20-30 nm after calcination at 700°C. Increasing the calcination temperature up to 1000°C leads to formation of ZrO_2 particles with elliptical shape ZnO inclusions (5-7 nm). The TEM and DRS data can be confirmed and explained by XRD results.

The XRD data of pure ZrO_2 and ZrO_2 – ZnO mixes are typical and commonly known [12, 18]. The pure ZrO_2 was presented by monoclinic structure $P2_1/c$, ZnO by wurtzite structure $P6_3mc$. The XRD spectra of ZrO_2 – ZnO mixes were presented by the monoclinic phase of ZrO_2 and ZnO wurtzite phase for all samples (Figure 3a). Thus, it was not found the formation of solid solution ZnO in ZrO_2 for all ZnO concentrations, which were used in this study. The increasing of intensity peaks is due to the increasing of particles size during heating. In case of the ZrO_2-ZnO powder synthesized by co-precipitation technique and calcined at temperatures 400-700°C XRD analysis was not found peaks which correspond to ZnO. After calcinations at 1000°C the absorption peak appeared and ZnO was fixed by XRD (Figure 3b). At the same time the tetragonal phase of ZrO_2, which was formed at low firing temperatures transforms to monoclinic phase at 1000°C.
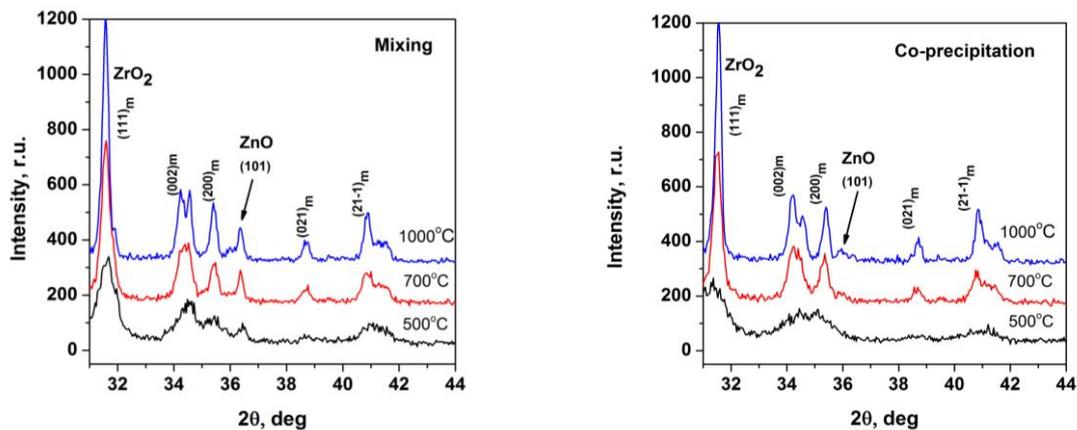
Figure 3. The XRD spectra of ZrO_2 – ZnO powders synthesized by mixing - a) and co-precipitation – b) technique.
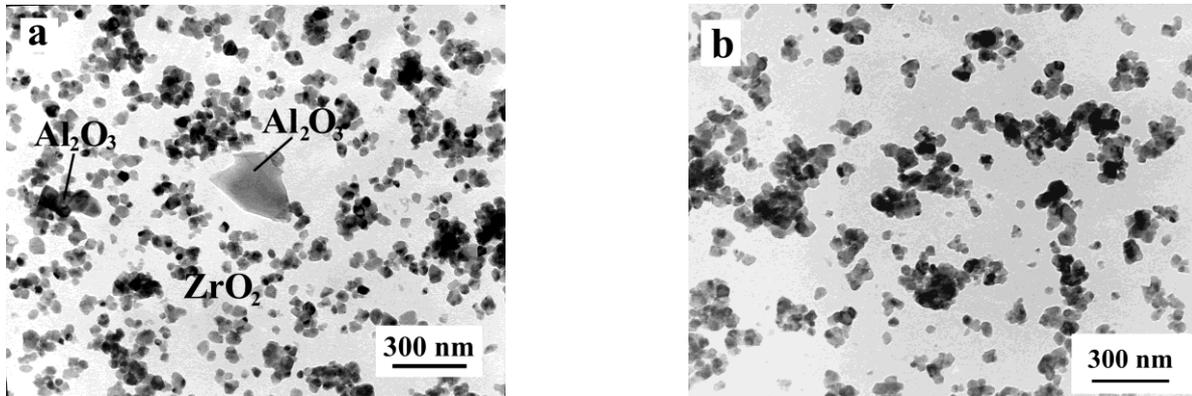
In case using the co-precipitation technique it is possible to create conditions (at low firing temperatures) when the nonequilibrum supersaturated solid solutions exists. We have supposed the ZnO concentration was low (near 3-5 wt%) and Zn atoms were located in nonequilibrium solid solution in ZrO_2 lattice and the absorption spectrum was determined by ZrO_2, the reflection, which conforms to ZnO was not fixed and ZnO can influence on changing in long wave tails in absorption spectra only. When the firing temperature increased the ZnO diffused from ZrO_2 particles the absorption which was corresponded to ZnO appeared. The XRD analysis data detected the changing of phase composition and lattice parameters ZrO_2 and ZnO lattices in composites with low ZnO amount during increasing firing temperature. During heating at low temperatures the tetragonal phase of ZrO_2 was formed. After increasing the firing temperatures up to 800-1000°C the tetragonal phase transformed to monoclinic phase and XRD analyses fixed ZnO as separated phase.

3.2. Formation of structure and properties in ZrO_2-3mol%Y_2O_3 – Al_2O_3 system

The analogical situation in formation of supersaturated solid solutions of Al^{3+} ions in ZrO_2 lattice was found in ZrO_2-3mol%Y_2O_3–Al_2O_3 composite system. In this case the formation of complex structure of composite was demonstrated not only in structure of nanopowders but in the structure and properties of sintered ceramics. The formation of complex structure of Al_2O_3 inclusions in zirconia

matrix during sintering leads to increasing the K_{1C} and wear resistance of zirconia ceramics in 1.5-2 times [19]. At the same time the density and strength values remains at the same level.

The composite powders obtained by ball-milling 3Y-TZP nanopowder (particle size 32 nm) with commercial α-Al_2O_3 powder and ZrO_2-3mol%Y_2O_3 – Al_2O_3 nanopowder are shown on Figure 4.

Figure 4. TEM structure of the ball-milled 32 nm 3Y-TZP powder with 2w% a-Al_2O_3 – a) and 3Y-TZP-2w% Al_2O_3 obtained by the co-precipitation technique – b). Calcination temperature was 1000°C.

After milling, the particle sizes of ZrO_2 did not change. From XRD data (peak on 43.36°) was identified the α-Al_2O_3 in the composite powder that was obtained with the ball-milling technique (Figure 5). According TEM and XRD data the mean particle size of ZrO_2-3mol%Y_2O_3 – Al_2O_3 nanopowders obtained by the co-precipitation technique decreased from 32 to 19.3 nm with increasing concentrations of Al_2O_3 from 0 to 5 wt%, respectively. In contrast with previous data, in the nanocomposite powder obtained by the co-precipitation technique, the (101) α-Al_2O_3 reflex has not been found during powder characterization (Figure 4). The XRD investigation also determined that the lattice parameters (a, c) and lattice volume (V) of T-ZrO_2 changed from a = 0.50934nm, c = 0.51682 nm, V = 0.13408 nm^3 for matrix 3Y-TZP powder to a = 0.509162 nm, c = 0.516377 nm, V = 0.13386 nm^3, for 3Y-TZP-2wt% Al_2O_3, in powders obtained by co-precipitation technique. In case of 3Y-TZP-2wt% Al_2O_3, obtained by ball-milling technique such changes have not been found.
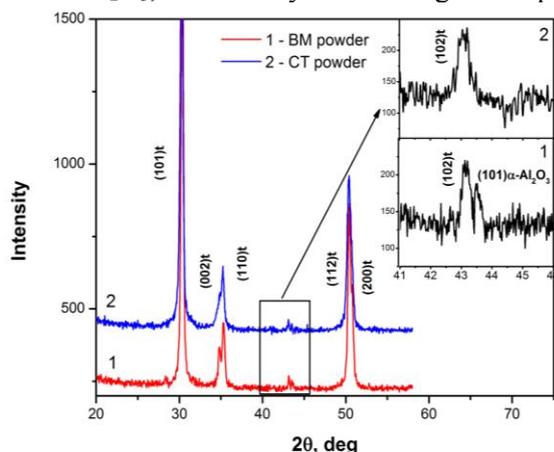
Figure 5. XRD data of 3Y-TZP-2wt% Al_2O_3 powders. 3Y-TZP-2wt% Al_2O_3 composite obtained by the ball-milling technique – 1 and co-precipitation technique – 2). In the inserts, the regions 40 – 46° are shown.

In case of using co-precipitation method, Al^{3+} ion are located in zirconia lattice. Al^{3+} solubility in zirconia is very low, and the active diffusion of ions Al^{3+} from the volume to the grain boundary or triple junctions takes place during sintering. The process of grain growth during sintering of co-precipitated nanopowders is competing with Al^{3+} segregation. Some inclusions can be captured by growing grains and turn into intertype inclusions. An amount of alumina can remain on sub-grains and grains boundaries. The final structure consists of matrix grains and sub-grains with or without alumina

segregations, inter- and intratypes of inclusions. The crack propagation from such a structure should be hampered. In the case of ball-milling powder preparation method, the initial Al_2O_3 particles are located only on zirconia grain surfaces and structure changes took place near the its starting location, so intragranular alumina inclusions in zirconia grains during sintering could not be formed in appropriate amount as well as Al^{3+} segregations, because the solubility of Al^{3+} ions in ZrO_2 is too low.

Thus, the increase in the K_{1C} value of zirconia ceramics with a small amount of alumina sintered from nanopowders obtained using co-precipitation techniques can be conditioned through a series of processes for composite structure formation during precipitation, crystallization, and sintering of nanopowders. These processes strongly differ from structure formation processes in composites produced from ball-milled powders.

### 3.3. Other examples of application of ZrO_2 NPs

The formation of different states on NPs surfaces during heating of nanopowders in presence of impurities is one of the promising methods for creation of selective properties of nanopowders. For example the sensitivity of ZrO_2 nanoparticles to humidity increased with increasing of calcination temperature up to $700^{\circ}C$ (Figure 6).
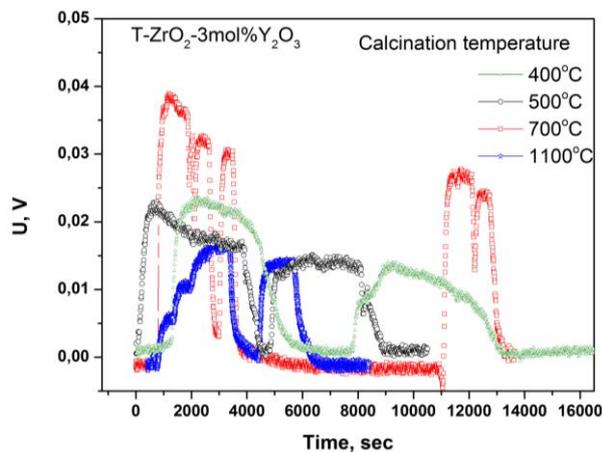
Figure 6. The electric potential of ZrO_2 samples, prepared from different type of nanopowders.

The electric potential is generated on zirconia NPs surface according to processes adsorption of water molecules and its decomposition on NPs surface. In this process the crucial point is the formation of surface centers of certain type. It was found that the calcination in the presence of residual Cl^- atmosphere leads to formation of basic Bronsted type surface centers. Increasing of calcining temperature up to $700^{\circ}C$ leads to removing Cl^- ions from NPs surface and formation of basic Bronsted centers. Further increasing of calcining temperature results in annealing of defects and decreasing the effectiveness the conversion humidity to electricity.

The analogical influence of annealing of ZrO_2 nanopowders with small amounts of $CuCl_2$ or MnS leads to the changing in optical properties of matrix material (Figure 7).
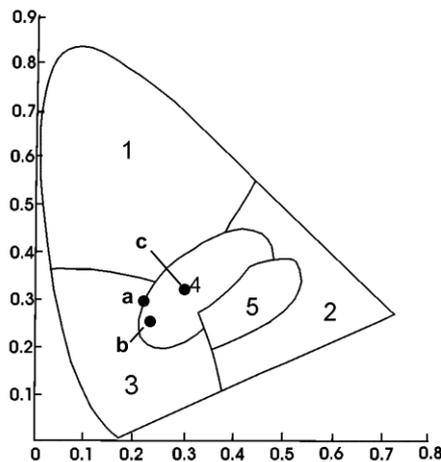
Figure 7. Representation of the PL spectrum of the 4.4Y-ZrO$_2$ powder in color coordinates: (1) green, (2) red, (3) blue, (4) white, and (5) pink. (a) 4.4Y-ZrO$_2$: 1% CuCl$_2$, (b) 4.4Y-ZrO$_2$: 3% CuCl$_2$, and (c) 4.4Y-ZrO$_2$: 1% MnS. Figure was taken from [8].

The annealing of ZrO$_2$+4.4mol%Y$_2$O$_3$ with CuCl$_2$ or MnS leads to an increase in the intensity of the photoluminescence (PL) spectrum in the range 350–550 nm, where this spectrum is likely to be a superposition of individual PL bands with $\lambda_{max} \approx$ 388, 420, 455, and 497 nm. The appearance of PL in the 4.4YZrO$_2$ nanopowder may be due to the temperature-induced changes in its oxygen sublattice. These results demonstrate that 4.4Y-ZrO$_2$:(1%)MnS can be used to producing a single-component nanophosphor with a continuous radiation spectrum and with color coordinates (X = 0.3, Y = 0.31) corresponding to white radiation.

4. Conclusions

In the present study has been shown that zirconia materials in nanostructured state has a wide spectrum of properties, which was impossible to achieve in traditional microscopic state. This technology approaches lead to creation of nonequilibrum supersaturated solid solutions, which were partially or fully destroyed during calcination and sintering process. The process of dopant migration from grain volume to the grain surface leads to creation of complex multilevel composite structures such as ion segregation on zirconia grain boundaries, clusters, intra- and intercrystalline inclusions in zirconia grains. These processes strongly differ from structure formation processes in composites produced from industrial ball-milled powder.

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