Low-temperature synthesis and the study of nanostructured Co–TiO_2 ferromagnetic compositions

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In recent years nanostructured (1*D*-, 3*D*-dimensional) TiO_2-based materials have become a subject of intense research due to unique physicochemical properties and original morphology [1, 2]. A large ion exchanging capacity combined with high surface area make them attractive for direct applications as magnetooptical, ion-conducting, and spintronic devices, photocatalysts, selective sorbents of radioactive ions, materials absorbing a radiofrequency radiation, as well as high activity participants in fabricating delicate composites. The aim of this work was to study the possibility to produce nanostructured TiO_2-based material with high concentration of Co-containing components via alkaline hydrothermal treatment of TiO_2 and $CoCl_2 \cdot 6H_2O$ powders in the presence of hydrazine.

The properties of hydrothermal products have been studied by Raman and IR spectroscopy, scanning electron (SEM) and transmission (TEM) microscopy, powder X-ray diffraction (XRD), an energy dispersive X-ray (EDX) and magnetic analysis. As a result, optimal conditions for synthesis of nanostructured Co–TiO_2 compositions were determined. It has been found that hydrothermal products are formed in shape of one-dimensional elongated structures Co-doped titanium dioxide and the Co-containing globular nanoparticles (Figure). The elongated nanostructures have lengths exceeding several hundred of nanometers. A higher magnification reveals that one-dimensional structures are characterized by a well-ordered multilayered morphology. The globular nanoparticles are composed of smaller rounded formations having very similar dimensions. After low-temperature air treatment at 60 °C, nanostructured products of hydrothermal synthesis demonstrate abnormally high ferromagnetic properties. An effect of hydrazine on the texture, morphology, and phase composition of products is discussed.

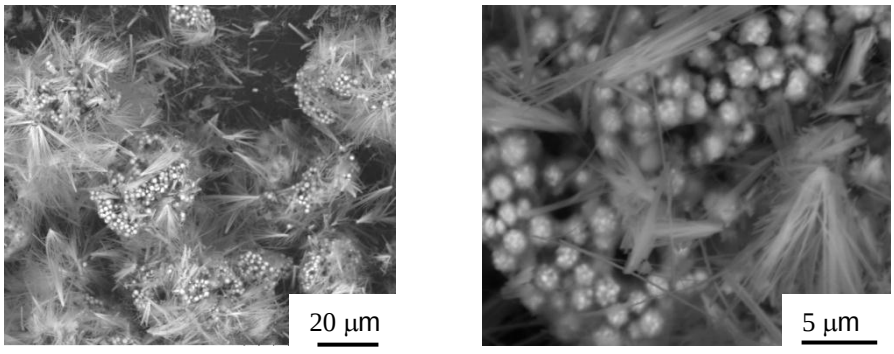

Fig. SEM images of hydrothermal nanostructured Co–TiO_2 product after low-temperature air treatment at 60 °C

References

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Design of new functional materials based on chalcogenide glasses, polymers via modification and nanocomposite techniques

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The purpose of this work is to analyze the ways for design and synthesis of new nanocomposite materials based on chalcogenide glass semiconductor (ChGs) and organic polymers and dyes and overview their optical and principal solid-state properties and some applications. Our research was concentrated within next directions: study the influence of doping on properties of chalcogenide glasses; chalcogenide glasses nanomultilayer structures of various compositions; polymers, composites "polymers – chalcogenide glasses"; and study of their optical, other physical and chemical properties, their properties as recording media and some applications.

Influence of doping with transitional metals and rare-earth elements on properties of chalcogenide glasses was studied. X-ray diffraction measurements confirmed the amorphous structures of doped by transition metals and rare-earth elements chalcogenide glasses. Radial distribution functions have shown no significant changes in distance for nearest neighbourhood with the change of dopant concentration. In Raman spectra the main effect observed under the introduction of dopants was the change in relative concentration of main and non-stoichiometric structural units characteristic for chalcogenide glasses.

Thermal properties (T_g values for undoped and doped glasses) were studied using DSC technique. Activation energy of glass transition was estimated with the use of Kissinger's expression. Optical properties of doped chalcogenide glasses were studied in 700–4000 cm^{-1} spectral region. The observed changes of the vibrational absorption bands were considered to be connected with the interaction of the introduced dopants with the non-stoichiometric structural elements present in glass and inherent impurities of the host glass such as hydrogen and oxygen. The main feature of Raman spectra under the introduction of transitional and rare-earth impurities into chalcogenide glass matrix was the change in relative concentration of the main and non-stoichiometric structural elements typical for initial glasses. Luminescence of chalcogenide glasses doped by transitional metals was studied in 800–1600nm region (T = 77 K, $\lambda_{ex} = 514nm$). Luminescence intensity increased with the metal concentration thus denoting the enlarged level of defects which is in accordance with the modified Tanaka's model. Chalcogenide glasses modified by Yb had two bands of luminescence in near IR region (near 980 and 1060 nm, excitation at 980 nm wavelength, room temperature). In this case transitions were observed characteristic for Yb^{3+} ion. Pure chalcogenide glasses are diamagnetics. Introduction of transitional and rare earth impurities changed the magnetic properties of investigated chalcogenide glasses. In the fields near 5T the M(T) dependence was observed typical for paramagnetics and ferromagnetics in the paramagnetic temperature range.

As_2S_3–Se and $Ge_5As_{37}S_{58}$–Se nanomultilayers were studied as recording media. Optical constants of nanomultilayers, thickness and optical band-gap energy were obtained from transmission using Swanepoel method. Optical properties of nanomultilayer structures were analysed within the frames of single-oscillator model.

Diffraction gratings were recorded using DPSS green laser (λ = 532 nm and power 100 mW) with synchronous diffraction efficiency measurement at λ = 650 nm in the first diffraction order. Atomic force microscopy (AFM) studies of the surface of holographic gratings with a period Λ = 1 μm recorded on nanomultilayers As_2S_3 –Se and $Ge_5As_{37}S_{58}$–Se have shown high optical quality of the obtained relief. Diffraction efficiency η values of the gratings was ~ 20–30 % in

transmission mode at wavelength $\lambda = 0.65$ μm. Due to the changes in transmission, reflection, and in thickness under the influence of laser irradiation, As_2S_3–Se and $Ge_5As_{37}S_{58}$ –Se multilayers can be used for effective amplitude-phase optical information recording, for the production of surface-relief optical elements.

Two-component nanocomposites based on chalcogenide glass semiconductor (ChGS) and metal phtalocyanine were obtained by simultaneous condensation of the two components on the surface of substrates in vacuum. Surface morphology of the samples was investigated using AFM. In the optical absorption spectra of composites characteristic bands of phtalocyanine were present. Comparison of Raman spectra of nanocomposite films and ChGS or Me–ChGS allowed us to identify the main structural bounds. Metal atom formed additional coordinating bonds with chalcogen atoms in nearby ChGS matrix.

Layers of polyepoxypropilcarbazole (PEPC) were studied as a media for holographic recording. The polymer was synthesized as the host polymer matrix and iodoform CHI_3 was used as the photosensitizing dye. As the pure polymer material was sensitive only in the UV spectral range its sensitivity had to be shifted to the type of recording laser region. To shift the spectral sensitivity to the blue region of spectrum the sensitizing dye such as iodoform CHI_3 has been introduced into the samples. The dependence of photosensitivity of the deposited films on the content of iodoform CHI_3 was studied earlier, where it was established that the optimal concentration of the iodoform was ~10 wh. %. Thin polymer films with thickness ~ 1.3 μm were prepared from homogeneous polymer solution in toluene by spin coating procedure using programmable spin-coater "SGS Spincoat G3P-8". For the determination of film thickness in this work the modified interferometric PC measurement based on MII-4 interference microscope was applied.

With the purpose of firmly assessing the nature of the synthesized material, a detailed characterization by IR and UV-VIS spectroscope was applied. 473 nm 100 mW DPSS laser was used for holographic characterization. Diffraction gratings were recorded on these films by keeping the beam ratio as 1 : 1 and spatial frequency 1000 lines/mm. On exposing to the interference pattern, the CHI_3 molecules get excited and electron transfer takes place between carbazole ring and CHI_3. Carbazole radical is produced in the reaction and this radical initiates the polymerization reaction. Polymerization takes place at the region of constructive interference and, as a result of this polymerization (crosslinking), contributes to the structurization of co-polymer. This structurization takes place without significant change in the refractive index and transmittance of film which leads to the hidden grating formation. After recording the wet chemical treatment was applied for the surface relief formation. Etching treatment was controlled by measuring the diffraction efficiency of the gratings in transmission mode at the 633 nm wavelength within the equal time interval. The carbon tetrachloride was chosen as etching agent. Evolution of diffraction efficiency of the gratings in dependence on recording and etching time was studied. After the recording the diffraction efficiency (η) of all samples was less than 0.1 %. After chemical etching due to surface relief formation the diffraction efficiency value was grown up to 18 %. Diffraction efficiency of gratings in dependence on the etching time of polymer films was studied.

Obtained results show that optical, thermal, luminescent and magnetic properties of chalcogenide glasses can be changed by doping of transitional and rare-earth metals. Chalcogenide glasses can be a host for rare-earth metals that provides the possibility of simultaneous change both in luminescent and magnetic properties of glasses.

Nanomultilayer composites based on chalcogenide glasses and inorganic (chalcogenide glass) – organic (polymers, dyes) composites are perspective as holographic recording media. Direct surface recording or recording with consequent selective etching can be realized. New functional materials based on chalcogenide glasses, polymers and produced via modification and nanocomposite techniques are perspective for the applications in optics, optoelectronics and integrated optics.