Вісник ХНУ, серія «Фізика», вип. 24, 2016. с. 41-44

UDC: 546.284-31-022.532+539.1.074.3
PACS: 81.07.Bc,78.55.-m

Nano-porous SiO_2-matrices for development of new optical materials

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Nano-porous transparent SiO_2-matrices obtained by sol-gel techniques and organic phosphors PPO, o-POPOP, p-Tp are produced, and their optical, luminescent, and scintillation characteristics are studied. It is shown that these simples generate an intense photoluminescence signal, possess a nanosecond decay time. The absolute light yield of the composites was determined to be 4400 photon/MeV for SiO_2:PPO, 5100 photon/MeV for SiO_2:o-POPOP, and 1800 photon/MeV for SiO_2:pTh.
Keywords: SiO_2-matrice, organic phosphors, scintillation characteristics.

Описан метод получения нанопористых прозрачных SiO_2-матриц, содержащих органические фосфоры PPO, o-POPOP, p-Tp, изучены их оптические, люминесцентные и сцинтилляционные характеристики. Показано, что такие материалы имеют интенсивный сигнал фотолюминесценции и обладают наносекундными временами затухания. Величина абсолютного световыхода при возбуждении альфа-излучением с энергией 5.46MeV составила 1800−5100 фотон/MeV, амплитудное разрешение лежит в диапазоне 27−67%.
Ключевые слова: SiO_2-матрица, органические фосфоры, сцинтилляционные характеристики.

Описано метод отримання нанопористих прозорих SiO_2-матриць, які містять органічні фосфори PPO, o-POPOP, p-Tp, досліджено їх оптичні, люмінесцентні і сцинтиляційні характеристики. Показано, що такі матеріали мають інтенсивний сигнал фотолюмінесценції і володіють наносекундним часом загасання. Величина абсолютного світловиходу при збудженні альфа-випромінюванням з енергією 5.46MeV складає 1800-5100 фотон/MeV, амплітудне розширення лежить у діапазоні 27-67%.
Ключові слова: SiO_2-матриця, органічні фосфори, сцинтиляційні характеристики.

Nowadays, highly porous materials obtained by different techniques have attracted a lot of attention as materials for the development of new nanoscale objects with unusual and unique properties [1, 2]. There are a number of properties such as the strict ordering of pores at large surface areas, the narrow dispersion of pore diameters and intervals between them, the controlled pore diameter allowing to create new materials based on the nanosized matrices.

Different polymers, silica-gels, xerogels, ormosils and composite glasses were used as matrices, and are of great potential for technical application in the fields of optics, electronics, mechanics and environment protection [2].

Nano-porous silica matrices are unique materials with high specific surface area, high porosity (order 50-75%) and low index of refraction [3, 4]. The sol-gel technique is the primary method used to prepare nano-porous SiO_2-matrices. For the synthesis of materials by a sol-gel technique organic metal compounds are usually used such as metal alkoxides [$M(OR)_n$], where M represents a network forming element (Al, Si, Ti, Zr, etc.), and R is usually an alkyl group [2, 5]. The hydrolysis and polycondensation of the metal alkoxide precursor lead to the transition from a colloidal solution to a solid phase. The characteristics of the materials synthesized via the sol-gel technique are influenced by many parameters, such as the nature of the reagents, the molar ratios used, the type of solvents and catalysts, the reaction temperature and the rate of removal of solvents. In particular, the choice of catalyst influences the properties of the material. Hydrolysis is favored by acidic catalysis and, therefore, in such conditions the formation of linear Si-O-Si polymers is favored. This causes the formation of more compact material (with small pores) compared with that obtained using basic catalysis [2, 6].

Due of their unique properties, SiO_2-matrices have been extensively studied as inter-metal dielectric materials, for optical and acoustic applications [1, 2]. The introduction of various organic phosphors into nano-porous SiO_2-matrices makes possible to produce composite luminescent materials with required properties. Such SiO_2-matrices can be used as fluorescent screens or scintillator materials [1, 7, 8].

In this work, we report our experimental results on the structural properties of pure nano-porous SiO_2-matrices and optical properties of SiO_2-matrices doped by organic phosphors. As organic phosphors 2,5-diphenyloxazole (PPO), 1,2-bis(5-phenyloxazolyl-2)benzene (o-POPOP) and 1,4-diphenyl benzene (p-Tp) were used.

Experimental techniques

Optical transmission spectra were measured using a SPECORD 200 spectrophotometer (Analytik Jena, Germany). Luminescence spectra were recorded using an automated spectrofluorimeter based on a grating monochromator. Luminescence was excited by the radiation of a He-Cd laser with a wavelength of 325 nm. Luminescence decay curves were measured using a FluoTime 200 picosecond spectrofluorimeter (PicoQuant, Germany) with a semiconductor laser with a wavelength of 330 nm as the excitation source and a setup instrument function of 0.5 ns.

Pulse amplitude spectra were measured using a spectrometric circuit consisted of a BUS2-94 preamplifier, a BUI-3K spectrometric amplifier, and an AMA-03-F multichannel amplitude analyzer (Tenzor Co., Russia). An R1307 photoelectric multiplier (Hamamatsu Co., Japan) was used as the photodetector; scintillations were excited by α particles with energy of 5.46 MeV emitted from a 238Pu radioactive source.

Synthesis and characterization

The method of obtaining of SiO_2-matrices is based on the widely known sol-gel method, which proceeds through the steps of hydrolysis and polycondensation of organic silicon compounds in an alcohol solution containing acid or base catalyst.

Briefly, tetramethoxysilane ($Si(OCH_3)_4$, 98,0% "Merck" (Germany), TMOS), anhydrous methanol and water with volume ratios of 1:0,84:1,2 were used as precursors for the silica and nitric acid (HNO_3, 65%) used as a catalyst. All components were mixed for about 5 min until the transparency appear. The mixture was poured in plastic Petri dishes (D=35 mm) and held for 24 h at room temperature until a gel was formed, which was then dried in the oven at 45°C for several days. The heat-treatment was executed at increasing temperature up to 500°C for 10 h and held for 2 h. The samples of SiO_2-matrices were transparent colorless disks with D = 20 mm and H = 1 mm (Fig.1.).

The organic phosphors were introduced by

Fig. 1. Photographic of SiO_2-matrices.

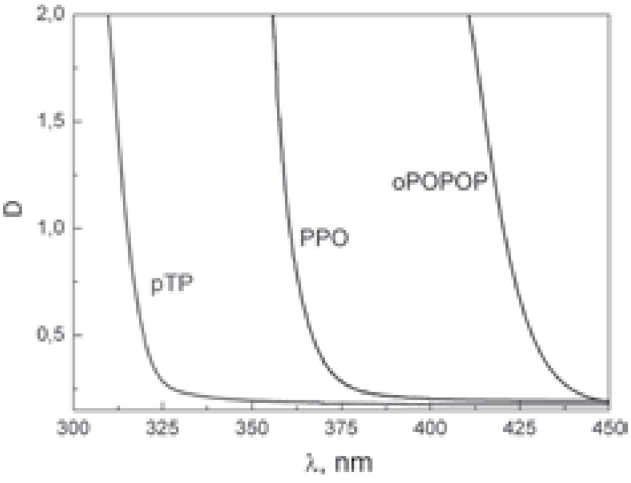
impregnating the SiO_2-matrices into the compositions of the solutions PPO, o-POPOP and p-Tp in toluene with optimal concentrations of 1,0 wt % [9]. SiO_2-matrices were held in these solutions for 5-48 h and then dried at 50°C until constant weight. It has been found experimentally that the samples of SiO_2-matrices with a concentrations of the dopant of 1-10 wt % possess the most intensive luminescence.

According to X-ray phase analysis SiO_2-matrices have an amorphous structure. Studying the surface of the matrices by AFM revealed open pores with the diameters about 20 nm. TEM images of the samples reveal that matrices consist of silica nanoparticles with average sizes of about 30 nm. Pore distribution, and specific surface areas were calculated from the nitrogen adsorption isotherms, via the BET method. The specific surface area of the samples of SiO_2-matrices is 800 m^2/g with corresponding total pore volume of 0,55 cm^3/g. The density and porosity of the matrices determined using the hydrostatic weighing method [8] are 1.40 g/cm^3 and 54 vol %, respectively. The average microhardness of the matrices is 170 kg/mm^2, which is practically twice as high as the values reported by the other authors [1, 10].

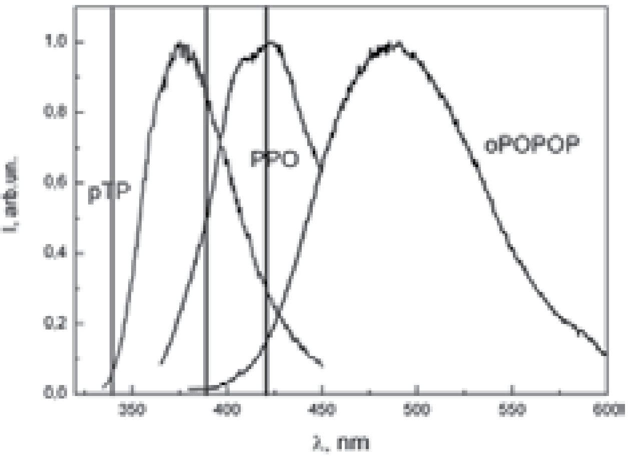
Optical properties

Luminescence and scintillation properties of obtained materials were investigated. In Fig. 2 the absorption and luminescence spectra of SiO_2-matrice with incorporated PPO, o-POPOP and p-Tp organic phosphors are shown. Both the edge of fundamental absorption and maxima of luminescence of organic phosphors in the matrix are shifted (~40 nm) to long-wavelength region as compared with the spectra of corresponding solutions indicating a strong interaction of phosphor molecules with pores of SiO_2-matrices.

Incorporation of organic phosphors into SiO_2-matrices leads not only to strong interaction between phosphor molecules and pores of SiO_2-matrices, but also to increase of interaction between molecules themselves that can be



a



b

Fig.2. Absorption spectra of SiO_2-matrices with different phosphors (a). Luminescence spectra of SiO_2-matrices with different phosphors (b).

seen from the modification of kinetics of excitation energy relaxation. Decay curves of PPO in solution and in the SiO_2-matrice at different concentrations of phosphor molecules are shown in Fig. 3 (λ_{exc}= 377 nm). Decay curves of phosphors are sufficiently modified with their incorporation into SiO_2-matrices. At the initial stage of luminescence decay (0-15 ns) shortening of decay time is observed, most likely due to luminescence quenching due to decrease of the distance between PPO molecules. Meanwhile, in the range of 15-50 ns, the second component is observed, which may be determined by migration of excitation energy between the phosphor molecules.

In the Fig.4 the pulse height spectra of SiO_2-matrices with different phosphors under excitation by alpha-radiation are shown. It can be seen that spectra are symmetric and well fitted by Gaussian function that indicate the uniform distribution of the dopant molecules within the matrix volume. The pulse height resolution R is 27% for SiO_2:PPO, 32 % for SiO_2:o-POPOP and 67% for p-Tp. The absolute light yiel d of the composites was determined to be 4400 photon/MeV for SiO_2:PPO, 5100 photon/MeV for SiO_2:o-

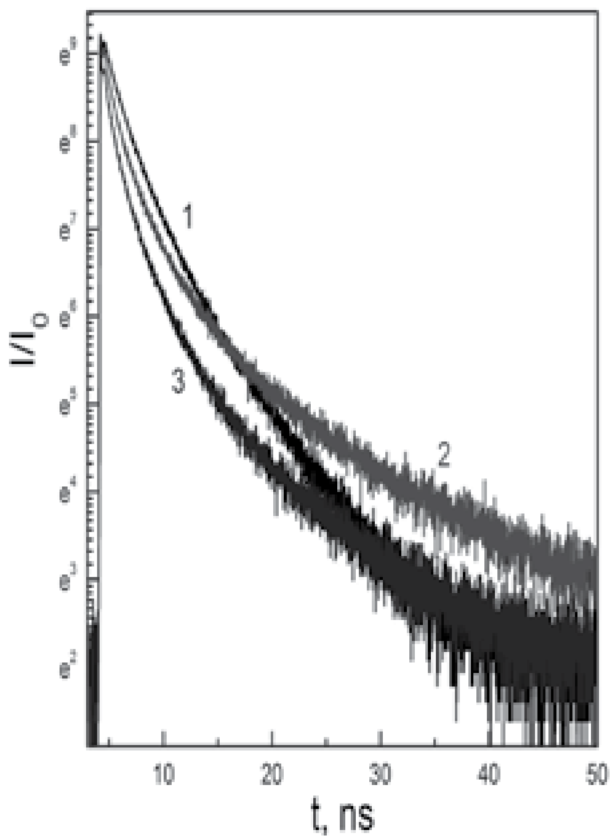


Fig. 3. Decay curves of PPO luminescence (λ_{exc}= 377 nm). 1 – in solution, 1 mass.%; 2 – in SiO_2-matrice, 1 mass.%;3 – in SiO_2-matrice, 10 mass.%.

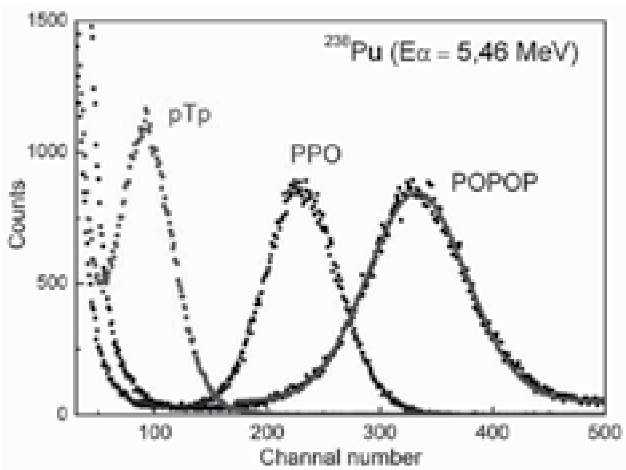


Fig. 4. Pulse height spectra of SiO_2-matrices with different phosphors under α-excitation (excitation source - ^{238}Pu).

POPOP, and 1800 photon/MeV for SiO_2:p-Tp. These values of light yield are rather low, but comparable to the light yield of. the BC416 commercial plastic scintillator based on polyvinyl toluene (Saint Gobain Co.), equal to 6000–7000 photon/MeV.

Conclusions

Highly-porous transparent SiO_2-matrices obtained by sol-gel techniques are perspective materials for creation of new luminescence and scintillation materials on their base. These matrices have high porosity (54 vol. %) with average pore diameter equal to 10 nm. Impregnation of SiO_2-matrices by phosphor molecules (such as PPO, o-POPOP, p-Tp) allows to obtaining luminescent and scintillation materials with properties quite different from those observed in corresponding phosphor solutions. Obtained materials have moderate scintillation properties; however their light yield is comparable with the one of commercial plastic scintillators.

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