

Incorporation of zirconia and germania and ternary compounds of $\text{ZrO}_2\text{--GeO}_2$ into silica sol-gel matrices

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Silica sol-gel glasses were doped with zirconia and germania. Nanoparticles composed from these oxides and the binary oxides Zr–Ge–O were produced within the matrices. XRD, TEM, and XPS studies were used to determine the phase composition and energy of the electronic states of the elements. The optical features of the materials were characterized by UV/Visible absorption and photoluminescence. Nanoparticles of ZrGeO_4 and Zr_3GeO_8 within the solid matrices were fabricated for the first time.

Key words: *zirconia; germania; nanoparticles; sol-gel glasses*

1. Introduction

The most extensively studied nanoparticles are the elemental ones (e.g. Si, Ge, Ag, Cu, Au, etc) and binary compounds like CdS, ZnS, CdSe, etc. [1, 2]. The theory of the size dependence of nanoparticle properties based on the quantum confinement of charge carriers describes observations quite well in many cases, but more complex species which do not belong to direct-band semiconductors or s-metals frequently reveal rather challenging size-dependent features [3–5]. Oxide nanophases (most often studied are: ZnO, TiO_2 , SnO_2 , etc.) fit much worse into the theory of quantum confinement, and in each case special studies are required to investigate the features of small particles of these compounds. The expansion of chemistry of nanoparticles to new compounds is rarely simple. It requires not only the synthesis of nanoparticles,

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but also the fabrication materials to stabilize them for proper characterization. The sol-gel technique possesses powerful potential to expand the chemistry of nanoparticles. In the present work, we address a binary oxide system (and consequently ternary chemical compounds) with zirconium and germanium oxides and report the first results on the synthesis of Zr–Ge–O nanoparticles within the silica matrix.

A great interest exists in the studies of IV-group oxides in composition with silica for the fabrication of nanocomposites doped by isovalent compounds. A number of studies of the binary oxides of silica–germania (e.g., for the waveguide technique [6]) and silica–zirconia (for unique ceramics [7]) have been performed. A combination of both ZrO₂ and GeO₂ [8–10] has rarely been studied. However, it is of interest due to the following reasons: (i) the polymorphism of both compounds with a strong size dependence, in particular ZrO₂ (see, e.g. [11] and Refs.); (ii) various glass-forming abilities, much more GeO₂ than ZrO₂ [12]; (iii) variable coordination numbers of the elements with oxygen in different phases; Zr atoms can have the coordination number of 6–8, while for Ge atoms it can be 4–6; in the latter case this provides easy feasibility of complicated network structures with germanates and polygermanates, which are well known for Ge(IV) chemistry [13]. On the other hand, silica sol-gel matrices open the possibility of controlling the concentration of components, stabilizing nanoparticles and metastable phases, and can be the basis for producing materials with a wide range of applications (optical, catalytic, sensoric, etc.) [14].

Germania is rather rarely used as a dopant in zirconia-based systems, but it works not only due to the effect of the great difference in ionic radii ($R(\text{Zr}^{4+})/R(\text{Ge}^{4+}) \approx 2$) in solid solutions but also due to the formation of stable chemical compounds [8–10] rather than a compensation of oxygen deficiency with usual dopants in ZrO₂ like M(II) and M(III). Zirconia–germania nanocomposites have also been recently synthesized without any matrix [15, 16]. They reveal rather challenging properties, and the formation of new phases was found. Below, we describe nanoparticles of this system within a SiO₂ matrix and investigate them with X-ray diffraction (XRD) and transmission electron microscopy (TEM). The electronic state of the elements has been analysed with X-ray photoelectron spectroscopy (XPS), optical UV/Vis absorption, and photoluminescence, demonstrating that the nanoparticles behave like semiconductors, the band structure of which is affected by their chemical composition and oxygen deficiency rather than their size.

2. Experimental

The samples studied were silica-based glasses with incorporated Zr–Ge–O. The sol-gel derived silica matrix for glass fabrication was obtained by the conventional sol-gel technique [14] with the acid hydrolysis of tetraethoxysilane slightly modified to speed up gelation without strong volume contraction [17], as applied successfully by us for the incorporation of semiconductor nanoparticles into silica glasses [18]. This method resulted in aqueous-alcoholic silica sols mixed with a solid silica filler

(pyrogenic SiO_2 , aerosil, with particle size $\sim 10\text{--}20$ nm) in a mole ratio TEOS/aerosil = 1/1. The sols were neutralized by aqueous ammonia (0.1 M) up to $\text{pH} \approx 6$, and the gels were produced. Drying in air at 60°C and annealing at 800°C lead to porous SiO_2 -matrices, usually named 'xerogels', which are able to incorporate various species by simple impregnation and absorption. Zirconium and 4 germanium were introduced into these xerogels by impregnation in solutions of $\text{ZrO}(\text{NO}_3)_2$ in acetic acid (concentrations varied from saturated down to a 1/10 dilution), in solutions of germania in water, and in ammonia (both saturated at 20°C). These solutions (as sources of Zr and Ge) were used to provide a high amount of incorporated species. The solutions penetrated the matrices for a few minutes, and were kept in this state for about 8 h. In order to get samples containing both Zr and Ge, the impregnation procedures were performed with both solutions, the second element being introduced after drying the sample. The samples were dried and annealed in air by a special temperature–time profile up to a maximum of 1200°C , resulting in the formation of transparent glasses. The samples studied in present paper differ in the sequence of Zr and Ge incorporation and in the concentrations of the precursor solutions. Samples with co-incorporated Zr and Ge are labelled as N11 and N13: for N11 the incorporation of zirconium preceded the incorporation of germanium from an ammonia solution of GeO_2 ; for N13 the first step was the incorporation of zirconium from a doubly diluted saturated acetic acid solution of $\text{ZrO}(\text{NO}_3)_2$ after which germanium was introduced from a saturated aqueous solution.

XRD measurements were done for both powders and glassy samples with a DRON-3 device using CoK_α radiation and a MnO_2 filter. XPS studies were performed with an ES2401 spectrometer (Russia) with MgK_α radiation, and C1s line calibration at 284.6 eV was used.

In order to visualize nanoparticles in the glassy samples with TEM, a 'replica with extraction' method was used. This method consisted of the deposition of a thin carbon film ($10\text{--}20$ nm) onto the surface of the freshly etched glasses, followed by stripping the carbon film upon contact with water. Micrographs were obtained with a UEM-100LM microscope (Russia) in the medium magnification range.

UV/Vis absorption spectra were recorded with a Specord M40 (Carl Zeiss) device in air, and photoluminescence spectra were obtained with a fluorimeter Fluoromax-2 (Jobin-Yvon) under monochromatic excitation from a Xenon lamp.

3. Results and discussion

3.1. TEM

The TEM data presented in Fig. 1 display the structures of a series of glasses prepared with different compositions: glasses doped with ZrO_2 , GeO_2 , and co-doped ones (the two samples described above, N11 and N13). The formation of particles is ob-

served within all types of glasses, however, the morphology of particles is different. The size of particles enters the range of 20–100 nm, but the particles are aggregated in co-doped glasses. Particle concentration cannot be determined unambiguously with the TEM sample preparation method used here. One can state, however, that the order of magnitude is comparable with materials with individual oxides, and rises for binary oxides. Thus, these TEM data in general allow us to consider the synthesized glasses to be nanoparticles-in-matrix systems, and the silica matrix looks like an inert support in a first approximation.

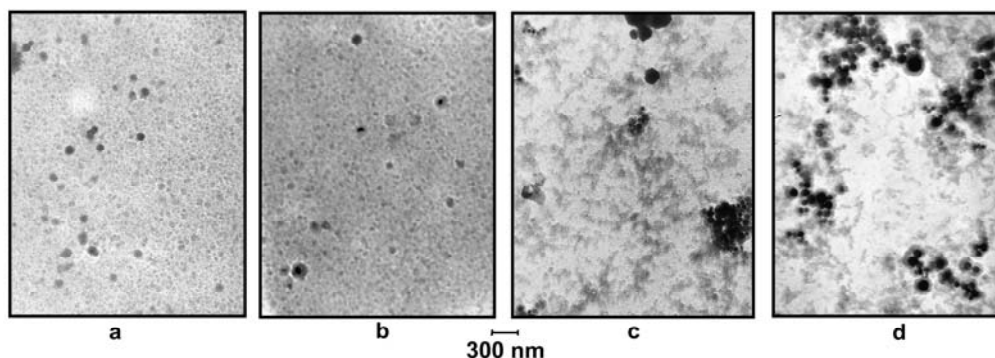


Fig. 1. TEM images of nanoparticles produced in silica glasses by the incorporation of ZrO_2 and GeO_2 : a) ZrO_2 ; b) GeO_2 ; c) ZrO_2 and GeO_2 (N11); d) ZrO_2 and GeO_2 (N13)

This appearance can be explained by nanoparticle formation accompanied by simultaneous matrix annealing. The initial content of zirconia–germania precursors can be rather high in pores within the silica xerogel, and after pore contraction they may form aggregates rather than separated particles. It should be expected that lowering of the amount of precursors would result in the same final products with particles placed separately in the matrix.

3.2. XRD

The XRD patterns presented in Fig. 2 (besides the GeO_2 -doped ones, showing only simple amorphous-type patterns) evidence that the nanoparticles observed by TEM are nanocrystalline phases and that the patterns can be decoded. The picture contains the reference data for three phases suggested: monoclinic zirconia and two compounds common to this binary oxide system, namely the scheelite phase ZrGeO_4 (JCPDS 34-0407) and the compound Zr_3GeO_8 (JCPDS 16-0800). They appear within the annealed glassy silica matrix (the broad halo in the range $2\theta = 15\text{--}30$ deg). The peaks observed are comparatively weak. Keeping in mind that these inclusions are present in the matrix at low concentrations, however, this observation seems to be sufficient for documenting the preparation of this type of material for the first time. The broadening of

the peaks also occurs, and the particle size of both binary oxide phases can be estimated to be 10–30 nm.

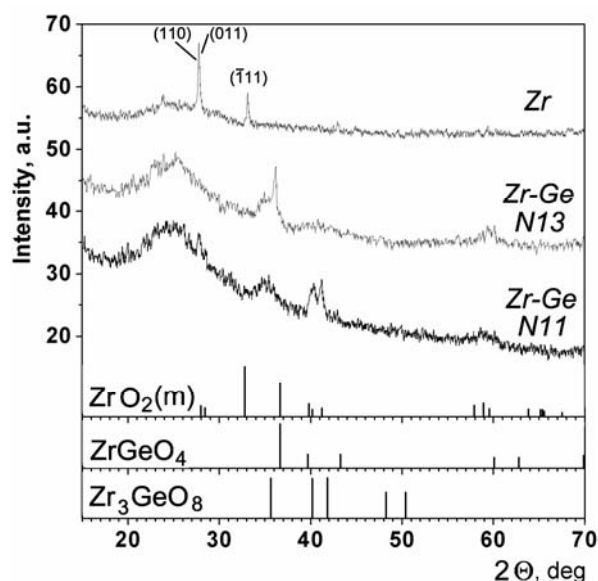


Fig. 2. XRD patterns of silica glasses doped with ZrO_2 and co-doped with ZrO_2 and GeO_2 , referenced to bulk ZrGeO_4 (JCPDS 34-0407), and Zr_3GeO_8 (JCPDS 16-0800)

This range does not contradict the TEM data (Fig. 1). The TEM images also indicate, however, some coarser particles with sizes up to 100 nm. This can be explained by a tendency to aggregate. Possibly, the coarser particles are the products of secondary processes rather than single particles originally formed within the glass. The XRD pattern for the sample doped with only ZrO_2 , in which the monoclinic zirconia phase has been detected, essentially exhibits less broadened peaks, although the size range in TEM is close to that of the binary oxides. Hence, the broadening effect in the latter case is not only due to size. It could be due to structural disorders, which are known to be specific for these types of compounds [19]. Some authors consider both ZrGeO_4 and Zr_3GeO_8 as solid solutions based on the tetragonal zirconia lattice [10], and a solid solution can possess various degrees of disorder.

On the other hand, a comparison of the reference peaks of zirconia, shown at the bottom axis of Fig. 2, reveals that the case of zirconia is also not simple: the reflexes (111) (shown) and (111) (not shown, since they are absent in the experimental pattern) have much smaller intensity than the (110) and (011) reflexes, and the ratio of intensities is strongly altered from the ones referenced by JCPDS data. We may suppose that the zirconia particles observed in the glasses are oriented nanocrystals as long as the assignment of XRD patterns in the case of glass doped with zirconia is not complicated by any binary phases and compounds from the Zr-Si-O system and other

ZrO_2 patterns are far from the pattern of monoclinic zirconia. A preferred direction is manifested in the glasses investigated by XRD, since flat samples were fabricated in this case. The preparation of samples for TEM includes the removal of particles from the matrix (see Experimental) and any orientational effects are therefore lost. The possibility of orientation of zirconia nanoparticles will be investigated in future studies and is of interest in the context of optical polarization effects.

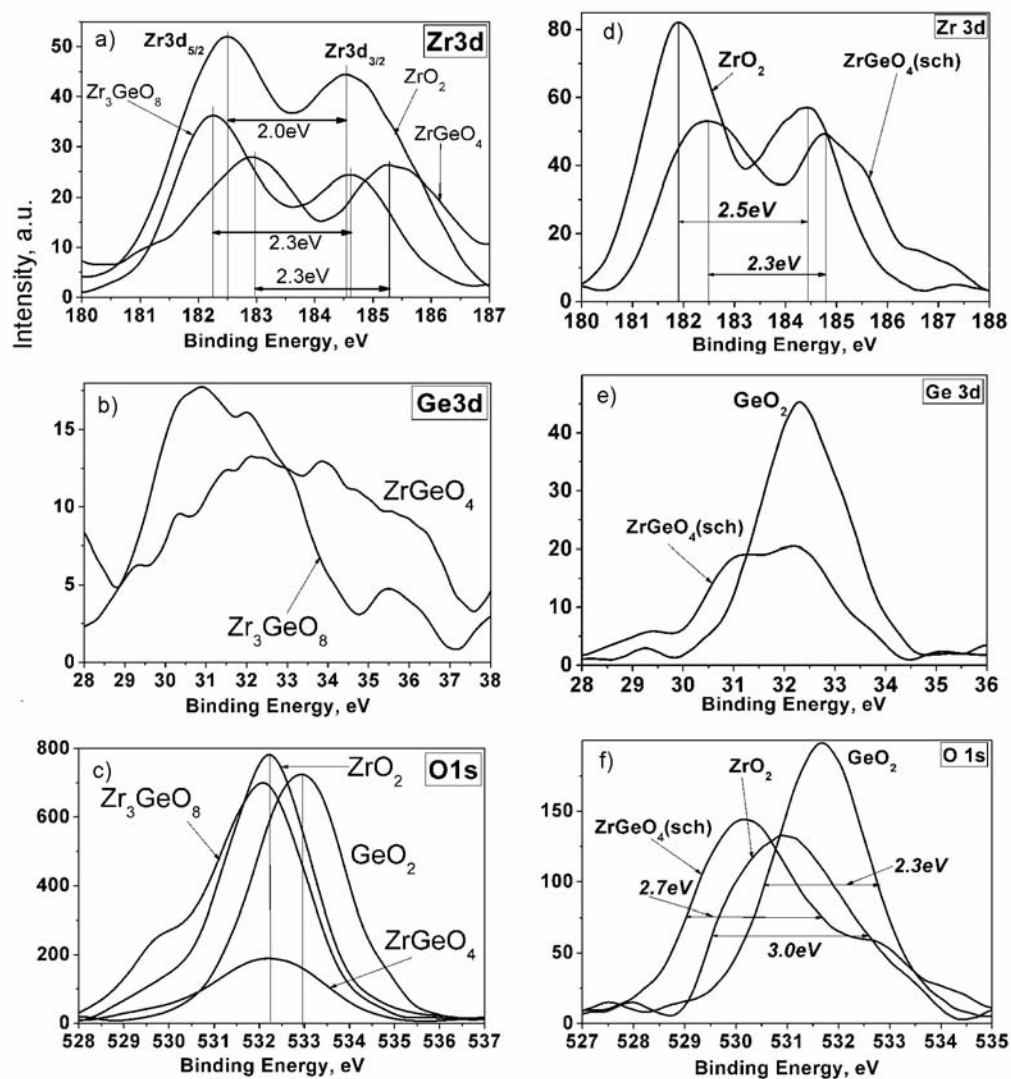


Fig. 3. XPS data for silica glasses doped with ZrO_2 and co-doped with ZrO_2 and GeO_2 in comparison to the data for ZrO_2 , GeO_2 (commercial pure chemicals), and ZrGeO_4 prepared by high-temperature sintering of ZrO_2 and GeO_2

The silica glasses fabricated with zirconia- and zirconia–germania dopants exhibit nanoparticles of mono-oxides or binary oxides from the two known compounds of the Zr–Ge–O system. The phase composition depends on the sequence of zirconia and germania incorporation. The electronic state of the elements in the samples of different composition was studied with XPS and compared to the data available for the corresponding compounds without matrix (Fig. 3).

3.3. XPS

The XPS spectra of four types of glasses doped with zirconia and germania and two co-doped versions are presented in Figs. 3a–c. The elements in all the compounds considered in the system present formally the same oxidation degrees for the series of samples of Zr^{4+} and Ge^{4+} . The XPS data, however, reveal strong differences in the positions of the photoemission lines and in the intensities for the same compounds in the corresponding samples. Variations in intensity can be associated with the inhomogeneous localization of nanoparticles throughout the sample volume. A noticeable range of binding energy of the core electrons of all elements under consideration also exists for the reference samples (Figs. 3d–f). We have used a commercial zirconia (a monoclinic modification stable at room temperature) and polycrystalline ZrGeO_4 synthesized from ZrO_2 and GeO_2 by the high-temperature sintering in a sealed ampoule followed by the XRD confirmation. ZrO_2 formed within glasses gives the Zr doublet signal (the usual 5/2 and 3/2 components) shifted to higher energies by about 0.6 eV with respect to the reference ZrO_2 . ZrGeO_4 has a much larger shift, while the shift for the glass with Zr_3GeO_8 is, in contrast, less than for ZrO_2 , but still positive (Fig. 3a).

A positive shift in the binding energy of the Zr_{3d} doublet also occurs for ZrGeO_4 in glass as compared to the bulk polycrystalline compound. The interval between the doublet components is observed in the range of 2.3–2.5 eV for all except ZrO_2 nanoparticles in glass, for which it equals 2.0 eV. The general width of the latter is larger, however, and it could possibly be deconvoluted into two components with close binding energies. These may be, for example, contributions due to surface and interior atoms. For these reasons, we can draw some conclusions from the above variations in the interval between the 5/2 and 3/2 components of the Zr_{3d} core levels.

Thus, two main observations can be established from the XPS data of Zr: (i) a pronounced difference between ZrGeO_4 and Zr_3GeO_8 , the first showing a more positive position, 0.7–0.8 eV; (ii) significant positive shifts for compounds within the glasses as compared to those in a matrix-free polycrystalline form, amounting to about 0.5 eV for both ZrGeO_4 and ZrO_2 . The latter conclusion indicates that nanocrystallines formed (being close to their macroscopic counterparts in the long-range ordering as shown the XRD patterns) are essentially different in their local structures. We expect, that one of the factors in this difference can be the oxygen deficiency effect, which can get stronger at the nanoscale level due to larger surface contribution and due to

effects of the silica matrix. Naturally, the oxygen deficiencies of ZrGeO_4 and Zr_3GeO_8 can be different, since the Zr/O ratio is different for these compounds, and the coordination number of Zr atoms for oxygen in the structure of Zr_3GeO_8 is larger than that for ZrGeO_4 . Oxygen deficiency should diminish the positive shift in the binding energy with respect to the zero-valent state of Zr. Thus, in the glasses studied the compounds include less oxygen vacancies than their bulk counterparts. The matrix can be a stabilizing factor, keeping the structures closer to the stoichiometric ones.

The XPS data for the germanium core level are shown only for the binary oxides, and have low intensity. Ge levels used in this analysis display weaker photoemission signals. Moreover, conclusions concerning the shifts in this case are rather disputable due to the possible contribution of Zr_{4p} states to these signals (they also appear at 30 eV [20]). By comparing the data in Fig. 3b with that in Fig. 3e, we may see that the germanium state is different from that of GeO_2 , and is very smooth both in bulk and nanoparticles. There is a clear tendency for a lower binding energy than in the stoichiometric oxide GeO_2 . The spectra for O_{1s} core levels (Figs. 3c, f) in the glasses based on silica have a big contribution from the oxygen in the matrix. We have observed, however, that a noticeable difference exists for glasses with the oxide phases studied. Without the matrix we attain reasonable differences both in the maxima position and width of the lines (Fig. 3f). The less ionic oxide, GeO_2 , has the most positive position, and ZrGeO_4 looks like a sum of two or more components. The complicated profiles of the lines, in particular that of ZrO_2 and ZrGeO_4 , can be explained by the contribution of adsorbed oxygen and hydroxyl from air. The spectra of O_{1s} levels of the compounds in the glass appeared to be closer one to another, which can be explained by the dominance of oxygen in the silica matrix of the same composition, and a noticeable difference exists nevertheless. It corresponds to the reference samples without the matrix. The spectrum for Zr_3GeO_8 is similar to that of ZrO_2 with an additional shoulder on the lower-energy side (probably the adsorbed or non-bridging oxygen). Thus, the data for oxygen photoemission confirms the formation of different nanophases within glasses.

3.4. Optical studies

Figure 4 presents the optical absorption spectra and photoluminescence spectra of a series of glasses. Absorption spectra show that binary Zr–Ge oxides reveal semiconductor-like behaviour with rather sharp edges, 5.0 eV and 4.6 eV for ZrGeO_4 and Zr_3GeO_8 , respectively. The features at ~220 nm in the spectra are not discussed here since the silica matrix begins to absorb in this range. The spectra of glasses with ZrO_2 and GeO_2 nanoparticles display similar behaviour, but have larger slopes. According to the known values of the band gaps for these oxides, namely ~5.2 eV [21, 22] and ~5.6 eV [23, 24], respectively, and to the referenced view of spectra, we would expect more pronounced absorption edges. The broad rise for ZrO_2 at $\lambda < 400$ nm and the feature at $\lambda = 270$ nm for GeO_2 can be due to structure defects developing as a result

of high-temperature treatment in contact with the silica matrix during the annealing of the glasses with nanoparticles. The range of absorption of both oxides is in accordance with the above reference data, but details (including the minor features observed) depend strongly on the history of the oxides (heating, storage, atmosphere, impurities).

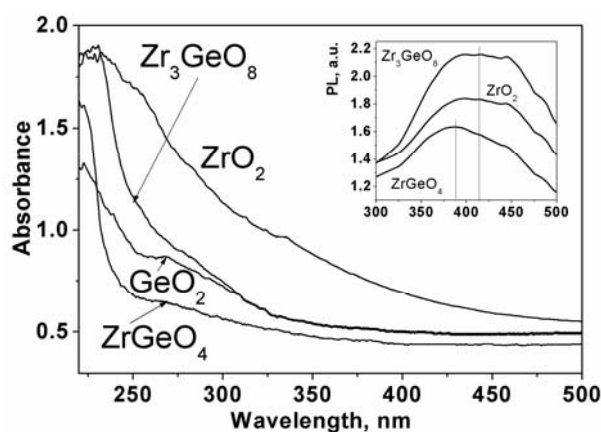


Fig. 4. UV/Vis absorption spectra of silica glasses with nanoparticles of different compositions (indicated). The inset contains photoluminescence spectra obtained with a 280 nm excitation

The optics of glassy GeO_2 has been studied [25], and the absorption features, like those presented by us in Fig. 4 for GeO_2 , have been reported for the heated glasses. They are associated to paramagnetic defect centres observed simultaneously by ESR. The nanoparticles of binary oxides show sharper edges in the absorption spectra. This suggests that they are more stable with respect to structure defect formation, which in oxides like ZrO_2 and GeO_2 occurs easily due to the high mobility of oxygen ions. Taking into account the above XPS data, we may not propose that higher oxygen deficiency provides additional absorption. Hence, oxygen defects can take the form of some absorption positions at the particle–matrix interface or uneven nanocrystal sites.

Preliminary electron spin resonance data were obtained for these samples and no ESR signals for the nanoparticles of ZrGeO_4 and Zr_3GeO_8 were detected (to be published elsewhere). The photoluminescence spectra presented in the inset of Fig. 4 show significant signals for the glasses containing nanoparticles of ZrGeO_4 , Zr_3GeO_8 , and ZrO_2 . The glass with GeO_2 showed no photoluminescence above the background. An observable intensity cannot be considered to be an essential factor, since it varies in the range of double enhancement for one sample with respect to another due to little differences in size and thickness. The positions of the band maxima, however, are shifted about 50 nm to the right for glasses with ZrO_2 and Zr_3GeO_8 as compared to ZrGeO_4 . Note that the absorption of the first pair also enters higher wavelengths. The excitation wavelength was chosen to get the most intense spectrum without contribution from matrix luminescence (a relatively low concentration of nanoparticles in the samples

necessitates the separation of background from the matrix also showing a luminescence signal, though this is much weaker than for glasses with Zr-containing particles).

Similar emission spectra and Stock's shifts of the photoluminescence signal, about 100 nm for ZrGeO_4 and 150 nm for ZrO_2 and Zr_3GeO_8 , can point to a similar photoluminescence mechanism: light with $\lambda=280$ nm only partially corresponds to the inter-band excitation of the semiconductors. The emission bands are rather broad and multiple centres can be responsible for their appearance. It should be noticed that the detailed nature of photoluminescence in materials of this type can be rather complicated. A formation of various oxygen-deficient centres is strongly inherent to metal oxides with high oxygen content like ZrO_2 and GeO_2 (and compounds derived from them), without a reduction in the oxidation degrees of the elements.

At deeper steps, this process can lead to some amount of low valence states (Zr^{3+} [26] and Ge^{2+} , Ge–Ge–bonds [27]), which appear usually as active luminescence centres. The latter phenomenon is probably not of great importance in our case, since we do not observe these states in the XPS analysis. As long as the glasses with GeO_2 do not show luminescence signals and only Zr-containing compounds have visible bands, it is worthwhile to associate the nature of luminescence centres with zirconia. Moreover, the intensity of the band is higher when the atomic ratio of $\text{Zr}/\text{Ge} = 3$, and for $\text{Zr}/\text{Ge} = 1$ the band is weaker (Fig. 4, inset). The luminescence band in the range of 380–450 nm is typical of ZrO_2 . The centres responsible for the emission can be oxygen vacancies, F-centres, surface defects, or impurities of foreign ions [28, 29]. They have been extensively studied from the point of view of the thermoluminescent behaviour of zirconia [30, 31].

Our interpretation of the luminescence bands is based on the most common item that can be expected in both Zr–Ge compounds studied and in ZrO_2 created in an oxidative environment (air, 1200 °C) and in contact with silica matrix. The latter is not an active oxygen-transferable medium and is chemically active at high temperatures with respect to many metal oxides that could be present as uncontrollable impurities. On the other hand, silica is inert with respect to zirconia under these conditions, since we did not detect any zirconia silicate phase. We suppose that a small amount of oxygen vacancies are formed, and their concentration is variable depending on the type of compound, but is too small to shift any XPS lines or change lattice parameters in the XRD data within experimental error. A large tendency to produce oxygen vacancies occurs in zirconia synthesized from hydrous forms [32, 33] by heat treatment in air or vacuum. The silica matrix in our case, however, can be a stabilizing agent. A more detailed study of the nanoparticles in the materials fabricated will be presented in future publications, after more data is obtained.

4. Conclusions

A novel approach to the fabrication of composite optical materials containing nanoparticles of binary oxide semiconductors is offered in this work. The selection of

dopants has been motivated by a search for oxide compounds that exhibit polymorphic transformation at ambient pressure and interesting features in their optics, catalysis, ionic conduction, etc. In contrast to chalcogenide compounds, which are the most frequently studied among semiconductor nanoparticles, oxides are more compatible with the silica matrix and more stable under heating in air. Zirconia and germania (oxides from the IV group) and silica can exist in several crystalline forms. Furthermore, germania is capable of amorphisation. The compounds in the system, ZrO_2 and GeO_2 , have been studied rather scarcely. We have produced them within a solid matrix by a simple method of co-impregnating porous silica, followed by thermal treatment with simultaneous annealing at the silica matrix to the glass state. The composition of the final products is determined by several factors that are easily controlled during the developed procedure: (i) the concentration of dopants and solvent used for impregnation; (ii) the order of the sequential introduction of Zr- and Ge-containing precursors; (iii) the properties of the silica matrix used (porosity, hydroxyl groups, etc). Other ways to control the final state will be elaborated with further research.

ZrO_2 and GeO_2 possess a limited homogeneity region to form solid solutions with a structure based on one of the components. Three known compounds have been reported in this system to date. In our materials, however, we have detected only two, with the compositions ZrGeO_4 and Zr_3GeO_8 (a third phase has been reported recently [34] and has a zircon-like structure). Their features have been revealed by TEM, XRD, XPS, UV/Vis absorption, and photoluminescence measurements. The nanoparticles are aggregated within the matrix, and the mean size range is tens of nanometers. XPS data have shown a chemical shift for zirconium (with respect to the bulk counterparts) probably due to diminishing oxygen deficiencies stabilized by the matrix. The optical data correspond to the formation of a wide-gap semiconductor with blue luminescence.

Promising applications of glasses with Zr-Ge-oxide nanoparticles offer silica-based optical materials with a low content of wide-band gap semiconductors (ZrO_2 , ZrGeO_4 , and Zr_3GeO_8) and media with lower valence states of germanium (including Ge nanoparticles and clusters) that are tuneable by reducing the chemical treatment of

the glasses presented above. Preliminary results have been obtained, showing the appearance of new and intense luminescence bands.

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