

Optical Materials Activated with CeO₂:Ln³⁺ Nanoparticles

G.E. Malashkevich^{1,*}, T.G. Khottchenkova¹, V.V. Kouhar¹, V.N. Sigaev², E.V. Pestryakov³

¹ *B.I. Stepanov Institute of Physics, NAS of Belarus, 68, Nezalezhnastsi Av., 220072 Minsk, Belarus*

² *D.I. Mendeleev University of Chemical Technology, 9, Miusskaya Sq., 125047 Moscow, Russia*

³ *Institute of Laser Physics, SB RAS, 13/3, Acad. Lavrent'ev Av., Novosibirsk, 630090, Russia*

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Silica glasses and siliceous powders activated with CeO₂:Ln³⁺ (Ln ≠ Ce) nanoparticles were synthesized by the sol-gel method and their structural and spectral-luminescent properties were investigated. It is shown that the main features of the Ln³⁺ ions are a high relative intensity of magnetic dipole transitions and sufficiently effective sensitization of their luminescence with labile photoreduced (Ce⁴⁺)⁻ ions by means of superexchange mechanism or/and by transfer of electron.

Keywords: Oxide nanoparticles, Luminescence, Structure of optical centers, Transfer of electron excitations.

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1. INTRODUCTION

In the middle of the 90th years, we discovered that quantum yield of Ce³⁺ ions luminescence in the silica gel-glasses containing triply and quadruply charged cerium ions can exceed up to some times the fraction of exciting radiation quanta absorbed by Ce³⁺ [1]. The effect stimulated us to more intimate investigation of the cerium optical centers in the glasses. As a result of the fulfilled work we discovered that this effect is caused by transfer of excitation in conditions of exchange-resonance interaction from the labile photoreduced (Ce⁴⁺)⁻ ions to the stable Ce³⁺ ions in the CeO₂ nanoparticles whose Ce⁴⁺ ions are partially substituted by Ce³⁺ ions. It opens wide possibilities for creation of optical materials with the nanoparticles as the Ce³⁺ ions can be substituted by another Ln³⁺ ions as well as a number of other luminescent ions. Therefore, the aim of the report is to show the "spectroscopic and photo-physical potentials" of CeO₂-nanoparticles formed in silica glasses and siliceous powders with partial substitution of the cerium ions by other rare earth ions.

2. MATERIALS AND EXPERIMENTAL

The glass samples were prepared by known sol-gel method [2]. Activation of the glass samples was carried out by impregnation of the obtained xerogels with the water-alcohol solution of cerium and other rare earth salts. In some cases, solution of alkaline or alkaline-earth elements salts was similarly doped for compensation of the local charge. Then, the dehydrated samples were vitrified in oxygen or in air to a state of transparent glass. The powder samples were prepared by entering of the salts solutions into the sol, grinding of the xerogel obtained to the ultradispersed state and their heat-treatment in the corresponding redox conditions. At necessity, the samples were additionally heat-treated in hydrogen to reduce the Ln⁴⁺ ions.

The investigation of samples was carried out by an X-ray diffraction, small-angle neutron scattering, scan-

ning electron microscope and spectral-luminescent methods.

3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of transparent oxygen-vitrified silica glass doped with Ce and Ho in concentrations of 3×10²⁰ and 4×10¹⁹ ions/cm⁻³ (a) and air-annealed siliceous powder including the dopes in concentrations of 2×10²¹ and 2×10²⁰ cm⁻³ (b) respectively. Comparison of locations and relative intensities of the main displayed Bragg reflections with the data of the JCPDS-1998 Powder Diffraction File testify that they correspond to the CeO₂ cubic lattice with space group of symmetry $O_h^5 - Fm\bar{3}m$. Additional doping of the samples with Cs or Mg for the local charge compensation practically doesn't influence on the diffraction patterns. As small-angle neutron scattering investigation showed, the mean sizes of the nanoparticles are close to 10 nm for the glass. At that, entering of the local charge compensator leads to the limitation of the

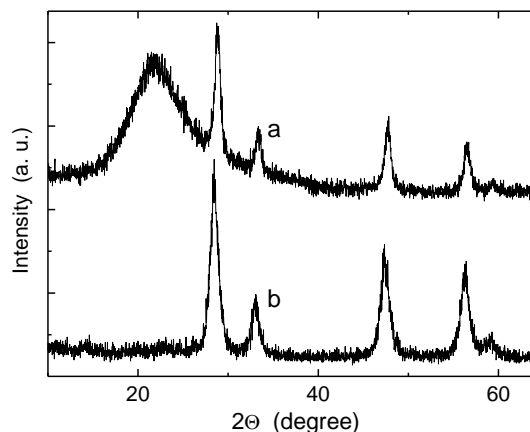


Fig. 1 – X-ray diffraction patterns of (a) silica glass and (b) siliceous powder containing nanoparticles CeO₂:Ho. $\lambda = 0.154184$ nm

* g.malashkevich@ifanbel.bas-net.by

nanoparticles sizes. As for the powder obtained, the microscopic analysis showed that it represents agglomerates with sizes about 1 μm including individual spherical particles with sizes about 50 nm. It should be noted that due to the presence of significant share of SiO_2 , we suppose that the individual particles are surrounded by the SiO_2 shell, the powder relatively easily vitrifies to the ceramics.

Fig. 2 shows luminescence spectra of oxygen-vitrified silica glasses activated with $\text{CeO}_2\text{:Ln}$ nanoparticles (curves 1 and 3) where Ln = (a) Eu, (b) Nd, (c) Ho and (d) Sm and Ln^{3+} ions (curve 2) These spectra are corrected with regard to the spectral sensitivity of the recording system and normalized by reducing their maximum to unity. As it is seen, the luminescence

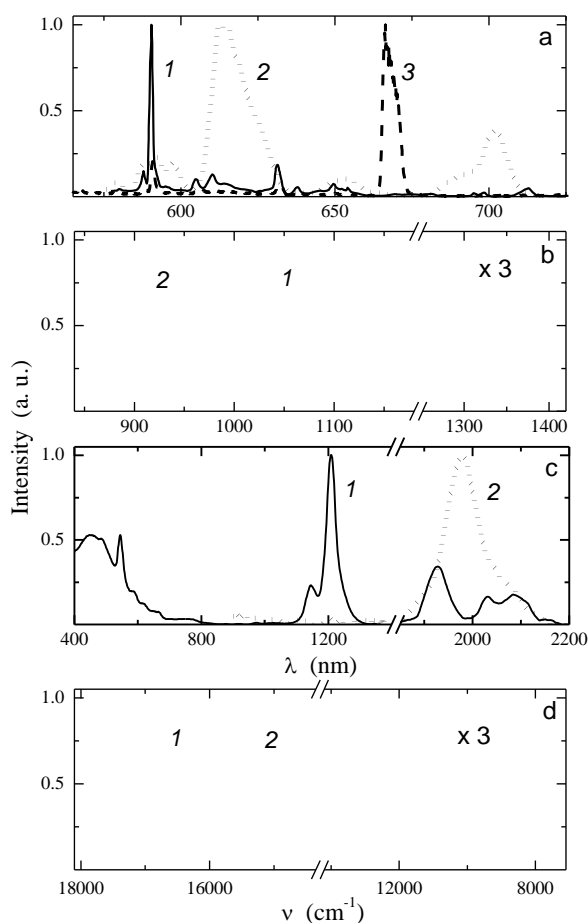


Fig. 2 – Corrected luminescence spectra of silica glasses activated with (1, 3) $\text{CeO}_2\text{:Ln}$ nanoparticles and (2) isolated Ln^{3+} ions Ln = (a) Eu, (b) Nd, (c) Ho and (d) Sm. λ_{exc} (nm): 266 (1a, 3a); 320 (1c, 1d); 370 (1b); 395 (2a); 400 (2d); 450 (2c); 580 (2b). $T = 30\text{K}$ (1a, 3a) and 298K for all other curves

caused by Ln^{3+} ions incorporated in the nanoparticles is characterized by structural spectra typical for the crystals in contrast to the spectra caused by isolated Ln^{3+}

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ions. At that, the share of quanta radiated by the first indicated ions in the magnetic-dipole transitions significantly higher than radiated in the electric-dipole transitions (cf. curves 1 and 2 in Fig. 2a and Fig. 2d). Given feature testifies to the possibility to increase the quantity of laser channels for account of the magnetic-dipole transitions for the materials activated with the $\text{CeO}_2\text{:Ln}^{3+}$ nanoparticles. Similar luminescence spectra are character for the corresponding powders too.

Comparison of luminescence intensity of the Ln^{3+} ions in the nanoparticles at excitation through the above indicated sensitizer at decreasing of temperature from 298 to 77K shows that the intensity decreases for the Sm^{3+} and Eu^{3+} significantly larger than for the Nd^{3+} and Ho^{3+} ions. As the samarium and europium ions can relatively easily reduce to the double-charged state, the indicated fact permits us to conclude about essential role of charge transfer in the processes of the ions luminescence sensitization. Moreover, the luminescence of highly-symmetric photoreduced (Eu^{3+}) ions is characterized by narrow band centered at 666 nm that can be observed at low temperatures ($\approx 30\text{K}$) as it is confirmed by Fig. 2a, curve 3.

A reduction of quadruply charged cerium to triply charged state in the nanoparticles by saturation of the glasses and powders with hydrogen permits to reach an efficiency of sensitization of their Ln^{3+} ions luminescence by the stable Ce^{3+} ions close to 100 % in some cases. However, the luminescence spectra of Ln^{3+} ions in the nanoparticles with stable reduced Ce^{3+} ions can significantly differ from their spectra in the initial nanoparticles.

Here it should be noted that at co-existence in the glasses of isolated $\text{Ce}^{4+}\text{-Ln}^{3+}$ and Ln^{3+} -centers besides of the $\text{CeO}_2\text{:Ln}^{3+}$ nanoparticles such glasses possess by strong dependence of their luminescence spectrum on excitation wavelength.

4. CONCLUSION

In a process of the sol-gel synthesis of silica glasses and siliceous powders co-doped with Ce and $\text{Ln} \neq \text{Ce}$, the formation of the $\text{CeO}_2\text{:Ln}^{3+}$ nanoparticles with the $O_h^5\text{-Fm}3m$ space group symmetry is possible. It can operate by sizes of the nanoparticles with the help of extrinsic compensators of local charge. Due to the spherical shape and presence of such binding agent as SiO_2 the powders may be promising precursors for obtaining of laser ceramics able to stimulated radiation in the magnetic-dipole transitions of rare earth ions.

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