

Spherical phosphors $\text{Lu}_2\text{O}_3:\text{Eu}$ coated with SiO_2 shells

Yu.V.Yermolayeva

Institute for Single Crystals, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

Received October 9, 2009

Amorphous SiO_2 coatings of controlled thickness ranging from 10 to 100 nm have been fixed onto submicron-sized $\text{Lu}_2\text{O}_3:\text{Eu}$ spheres for a first time by Stober method. The morphology, nanostructure, and chemical composition of the resultant $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ core-shell heteroparticles have been studied. A considerable luminescence decrease was observed for $\text{Lu}_2\text{O}_3:\text{Eu}$ spheres coated with SiO_2 shell as compared to the uncoated phosphors, due to the features of $\text{Lu}_2\text{O}_3:\text{Eu}$ sphere crystallization in a volume bounded by the SiO_2 shell.

Впервые аморфные покрытия SiO_2 контролируемой толщины в пределах 10–100 нм получены на сферических субмикрочастицах $\text{Lu}_2\text{O}_3:\text{Eu}$ методом Штобера. Исследованы морфология, наноструктура и химический состав полученных гетерочастиц "ядро-оболочка" $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$. Значительное снижение интенсивности люминесценции наблюдалось в $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ гетерочастицах по сравнению с исходными $\text{Lu}_2\text{O}_3:\text{Eu}$ частицами, что связано с особенностями кристаллизации $\text{Lu}_2\text{O}_3:\text{Eu}$ сфер в ограниченном оболочкой SiO_2 объеме.

Nowadays, lutetium oxide (Lu_2O_3) doped with trivalent europium (Eu^{3+}) ions is considered as one of the most promising materials for X-ray detection and imaging due to excellent set of physicochemical properties and high luminescence efficiency as well as high effective atomic number ($Z_{eff} = 67$) and density ($\rho = 9.4 \text{ g/cm}^3$) [1, 2]. Moreover, $\text{Lu}_2\text{O}_3:\text{Eu}$ submicron-sized monodisperse spherical particles are extremely promising as structural units of the close-packed functional films and photonic crystals, which can be prepared by the self-assembly procedure from the solutions. However, to make it possible to self-assembly along with the high monodispersity, ideal spherical shape, and non-agglomeration in the solutions of the structural units, it is necessary to provide its specified surface properties, namely, a surface charge, wettability in the chosen solvent and sufficient sliding one particle with respect to other ones. The assortment of the materials satisfying the above requirements is rather

scant. Thus, the additional surface modification is used, for example, silica coating formation, taking into account the possibility of the silica spheres to self-assembly into close-packed ordered opaline structures in nature [3]. A wide variety of silica-coating procedures have been developed for some types of the nano- and micrometer-sized particles (CdTe , Fe_3O_4 , ZnS) during the past decade [4, 5], with a significant progress particularly in metal nanocrystals such as Au and Ag [6–8]. The literature data concerning SiO_2 shell formation onto other types of particles, for example rare-earth oxides, are absent till now. Opal-like photonic crystals on the basis of core-shell particles with the SiO_2 shells (Au/SiO_2 , ZnS/SiO_2) have been formed by the self-assembly procedure from the solutions [9, 10]; at the same time, it was shown that the uncoated particles are not suitable for this purpose. Moreover, silica coating provides controlling of the minimal distance between the functional cores in the close-packed or-

dered structure through varying of the SiO_2 shell thickness.

The aim of this study is the preparation of the controlled thickness SiO_2 shells on the spherical $\text{Lu}_2\text{O}_3:\text{Eu}$ particles and also the detailed characterization of the morphology, structure, and composition of the resultant core-shell $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ particles as well as examination of the SiO_2 layer effect on the luminescence properties of $\text{Lu}_2\text{O}_3:\text{Eu}$ spheres.

Europium-doped lutetium basic carbonate $\text{Lu}(\text{OH})\text{CO}_3:\text{Eu}$ spherical particles (150 nm average diameter) previously prepared by the UBHP technique [11] were used as a core material for the silica coating procedure. The as-prepared and dried $\text{Lu}(\text{OH})\text{CO}_3:\text{Eu}$ powders (0.02 g) were dispersed in 100 mL isopropanol/water (4/1) mixture, then ammonia NH_3 (2.5 mL, 25 %) was added to the dispersion under vigorous mixing, followed by addition of tetraethoxysilane (TEOS, concentration range 0.1–1 g/L), and resultant solution stirred during 2 h at room temperature. The resulting core-shell particles were separated by centrifugation, washed several times with isopropanol and water, dried and annealed for 2 h at 900°C in air.

The morphology of the samples obtained was studied by scanning electron microscopy (SEM) using a JSM-6490 LV (JEOL, Japan) system and transmission electron microscopy (TEM) using a TEM-125, 100 kV (Selmi, Ukraine). The X-ray diffraction (XRD) of the powder samples was examined using a DRON-3M diffractometer in CoK_α radiation ($\lambda = 1.79021 \text{ \AA}$). Fourier transformed infrared spectroscopy (FT-IR) spectra of the samples were measured on a FT-IR spectrometer SPECTRUM ONE (Perkin-Elmer) using the KBr pellet technique. X-ray luminescence spectra of the samples in the form of pellets were obtained using

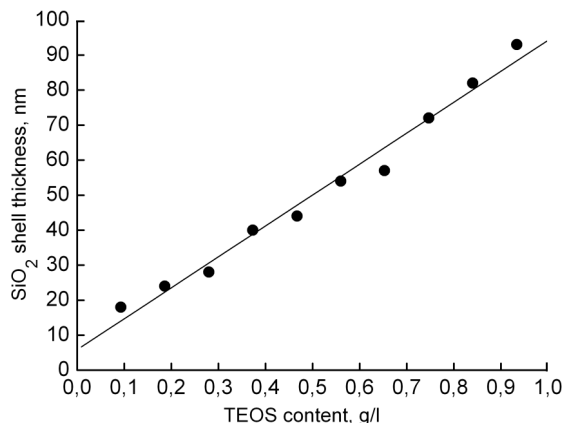


Fig. 1. SiO_2 shell thickness depending on the TEOS concentration in the reaction solutions.

an SDL-2 (LOMO, Russia) automated complex. X-ray luminescence was excited by REIS-E X-ray source (Cu anticathode, deceleration radiation with $E \sim 30 \text{ keV}$), operated at $U = 30 \text{ kV}$ and $I = 50 \text{ mA}$.

In this study, the controlled thickness SiO_2 shells were formed on the amorphous $\text{Lu}(\text{OH})\text{CO}_3:\text{Eu}$ spheres by the Stober method using TEOS as the starting agent [12]. Subsequent annealing of the $\text{Lu}(\text{OH})\text{CO}_3:\text{Eu}/\text{SiO}_2$ core-shell particles was used for the core crystallization at 900°C, which is below the point of solid-state reaction between Lu_2O_3 and SiO_2 components [13]. As a result, stable suspensions of $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ core-shell particles in aqueous medium were prepared. The surface charge of the silica shell due to presence of OH groups provided the particle stabilization. It is to note that the use of crystalline $\text{Lu}_2\text{O}_3:\text{Eu}$ particles as a core material resulted in inhomogeneous silica shell growth along with the additional separate silica formation in the reaction mixture. Such effect could be connected with the reduced adsorption of the silica precursor molecules on the crystal surface in compari-

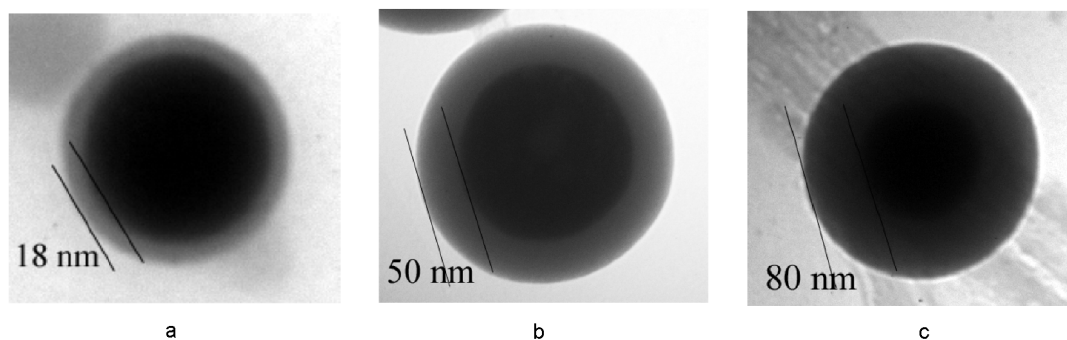


Fig. 2. TEM images of the individual silica-coated $\text{Lu}_2\text{O}_3:\text{Eu}$ spheres with the thickness of the silica shell: 18 nm (a), 50 nm (b), 80 nm (c).

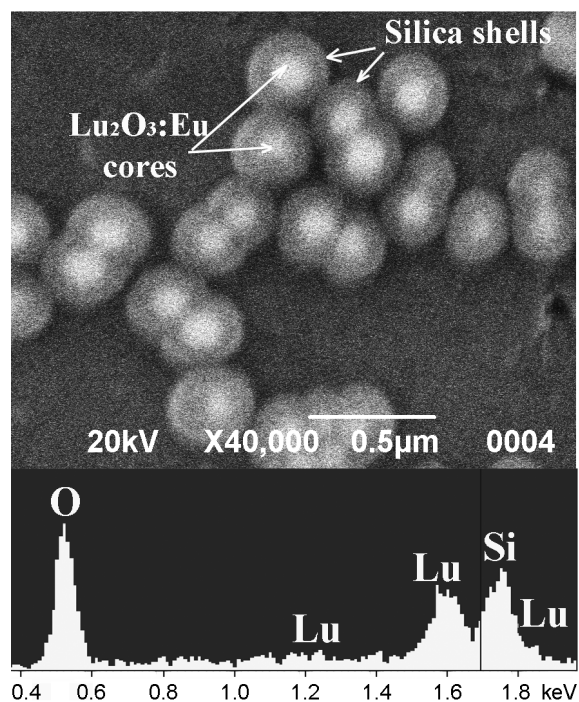


Fig. 3. SEM image and EDS analysis of the $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ core-shell particles.

son with amorphous basic carbonate particles. The silica shell thickness can be easily controlled within limits of 10 to 100 nm by changing the TEOS amount. Fig. 1 shows the influence of the TEOS concentration in the reaction solution on the silica shell thickness.

TEM was used to examine the core-shell structure and to measure the shell thickness. The TEM images of the $\text{Lu}(\text{OH})\text{CO}_3:\text{Eu}/\text{SiO}_2$ core-shell particles before annealing with the different SiO_2 shell thickness are presented in Fig. 2. The TEM images testify that the $\text{Lu}_2\text{O}_3:\text{Eu}$ cores are

coated with uniform silica shells with the keeping of the particle sphericity. The SEM image of the annealed $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ particles is presented in Fig. 3. It is seen clearly that after the sample annealing, the particles keep their spherical morphology and core-shell structure. Energy dispersive X-ray (EDS) spectrum measured for $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ particles includes the peaks attributed to Si and O elements together with Lu peaks, and the atomic ratio of elements agrees well with the expected stoichiometry. Europium dopant was not determined because its concentration in the sample was below the detection limit.

The FT-IR spectra recorded for the $\text{Lu}(\text{OH})\text{CO}_3:\text{Eu}/\text{SiO}_2$ core-shell spheres and annealed $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ ones are shown in Fig. 4a. The FT-IR spectrum 1 for $\text{Lu}(\text{OH})\text{CO}_3:\text{Eu}/\text{SiO}_2$ particles includes intense bands of C–O in CO_3^{2-} groups (ν_{as} 1530 cm^{-1} and 1403 cm^{-1} ; ν_s 1092 cm^{-1} ; δ 40 cm^{-1}) [14] and the absorption bands corresponding to Si–O–Si (ν_s 1106 cm^{-1} ; ν_{as} 804 cm^{-1}), Si–O–H (ν_s 952 cm^{-1}), Si–O (δ 472 cm^{-1}) groups, where ν_s represents symmetric stretching, ν_{as} -asymmetric stretching, and δ -bending [15]. The group of absorption bands related to SiO_2 are still observed after the samples annealing, however, the C–O bands disappeared because of the core decomposition and crystallization in Lu_2O_3 , which is established by characteristic Lu–O bands (491 cm^{-1} and 575 cm^{-1}), Fig. 4a, spectrum 2. FT-IR spectra contain an absorption band near 3435 cm^{-1} , which is assigned to stretching vibration of O–H bonds.

The XRD patterns of the annealed SiO_2 -coated $\text{Lu}_2\text{O}_3:\text{Eu}$ spheres include diffraction

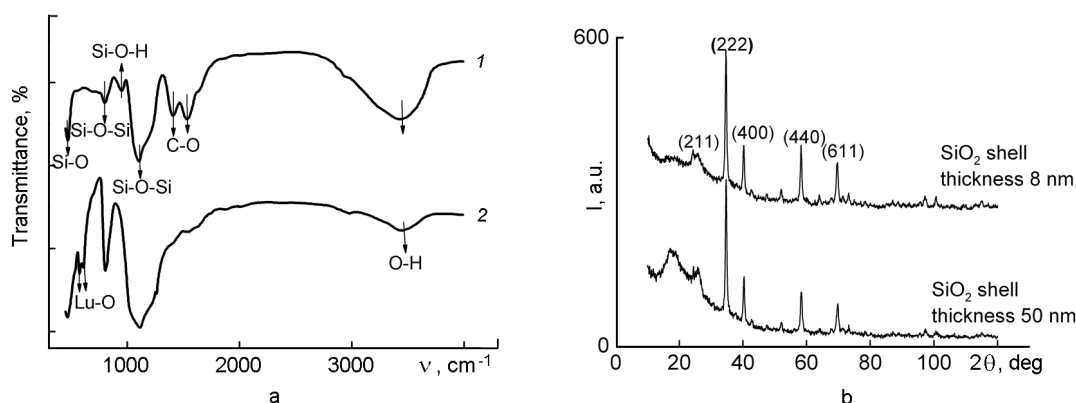


Fig. 4. FT-IR spectra of core-shell particles prior to (1) and after annealing (2) (a), X-ray diffraction patterns of the samples with the SiO_2 shell thickness 8 nm and 50 nm (b).

peaks belonging to crystalline cubic Lu_2O_3 structure and also a broad peak of small 2θ value, related to amorphous silica. The coherent scattering region (or the average size of the $\text{Lu}_2\text{O}_3\text{:Eu}$ crystallites) calculated according to Scherrer formula is near 35–40 nm.

Fig. 5 presents the normalized radioluminescence spectra of the bare $\text{Lu}_2\text{O}_3\text{:Eu}$ spherical particles and those coated with the SiO_2 shell of various thickness. All the radioluminescence spectra consist of a group of lines in the $\lambda = 575\text{--}725$ nm spectral region corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions ($J = 0\text{--}4$) of Eu^{3+} ions and conforms well to emission of Eu^{3+} ions in the Lu_2O_3 host lattice [1]. The high luminescence intensity of the $\text{Lu}_2\text{O}_3\text{:Eu}$ spheres under X-ray excitation evidences the presence of an efficient energy transfer channel from matrix to the Eu^{3+} emission centers according to a recombination mechanism [2]. The luminescence intensity for the SiO_2 -coated particles decreases almost by one decimal order in comparison with bare $\text{Lu}_2\text{O}_3\text{:Eu}$ spheres, moreover, such a reduction was observed at the silica shell rising. Such effect could be explained by possible features of the sphere crystallization in the space bounded by silica shell. The continuous SiO_2 shell presence may inhibit the removal of decomposition products, which can favor the defect formation and also the stabilization of impurities in the sphere volume as well, resulting in a nonradiative recombination in the relaxation processes of dopant ions located in the defect positions. However, a more detailed investigation has to be done to explain this phenomenon.

Thus, the following conclusions have been made in this study. The amorphous SiO_2 shells of controlled thickness (10–100 nm) on the $\text{Lu}_2\text{O}_3\text{:Eu}$ polycrystalline spherical particles have been formed by the Stober method followed by annealing. The SiO_2 shell thickness was varied by changing of the TEOS concentration in the reaction solution. The heteroparticles prepared demonstrate the core-shell nanostructure, ideal sphericity, and stability in the solutions. The luminescence intensity decrease of the $\text{Lu}_2\text{O}_3\text{:Eu/SiO}_2$ core-shell heteroparticles was observed in comparison with the uncoated ones due to some features of the sphere crystallization in the volume bounded by silica shell.

Author is grateful to Dr. V.F.Tkachenko for the help in testing of the experimental samples by XRD technique and also to Dr. O.M.Vovk and

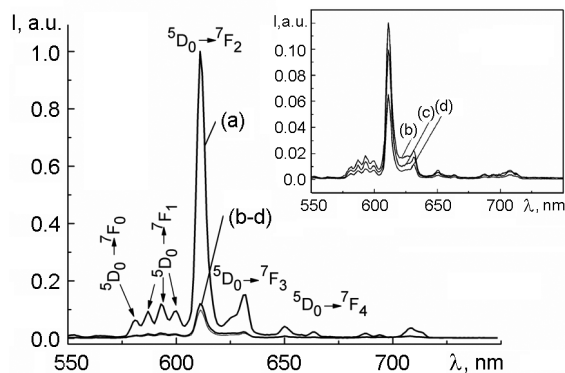


Fig. 5. Room-temperature X-ray luminescence spectra of bare $\text{Lu}_2\text{O}_3\text{:Eu}$ spherical particles (a) and $\text{Lu}_2\text{O}_3\text{:Eu/SiO}_2$ core-shell particles (b–d) with the SiO_2 shell thickness 8 nm (b), 30 nm (c), 50 nm (d). Eu concentration in all samples 5 at.%.

P.V.Mateychenko for the testing of the samples by electron microscopy.

References

1. E.Zych, *J.Phys.:Condens.Matter.*, **14**, 5637 (2002).
2. E.Zych, J.Trojan-Piegza, *Chem.Mater.*, **18**, 2194 (2006).
3. R.K.Iler, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica*, Wiley-Interscience, New-York (1979).
4. Yu.Lu, Y.Yin, Z.-Y.Li, Y.Xia, *Nanolett.*, **2**, 785 (2002).
5. S.Santra, D.Dutta, G.A.Walter, B.M.Moudgil, *Technology in Cancer Research & Treatment*, **4**, 593 (2005).
6. N.A.Matveevskaya, Yu.V.Yermolayeva, Yu.I.Pazura et al., *Nanosystemy, Nanomaterialy, Nanotechnologii*, **7**, 517 (2009).
7. Y.Qi, M.Chen, S.Liang et al., *Appl. Surf. Sci.*, **254**, 1684 (2008).
8. J.-L.Gong, J.-H.Jiang, Y.Liang et al., *J. Colloid Interface Sci.*, **298**, 752 (2006).
9. C.Graf, A.Blaaderen, *Langmuir*, **18**, 524 (2002).
10. K.P.Velikov, A.Moroz, A.Blaaderen, *Appl. Phys. Lett.*, **80**, 49 (2002).
11. H.Giesche, E.J.Matijevic, *Mater. Res.*, **9**, 436 (1994).
12. W.Stober, A.Fink, *J. Colloid Interface Sci.*, **26**, 62 (1968).
13. Yu.V.Yermolayeva, A.V.Tolmachev, T.I.Korshikova et al., *Nanotechnology*, **20**, 325601 (2009).
14. Q.Chen, Y.Shi, L.An et al., *J.Europ.Ceram. Soc.*, **27**, 191 (2007).
15. M.Yu, H.Wang, C.K.Lin et al., *Nanotechnology*, **17**, 3245 (2006).

Сферичні фосфори $\text{Lu}_2\text{O}_3:\text{Eu}$ з оболонкою SiO_2

Ю.В.Єрмолаєва

Вперше аморфні покриття SiO_2 різної товщини у межах 10–100 нм отримано на сферичних субмікрочастинках $\text{Lu}_2\text{O}_3:\text{Eu}$ методом Штобера. Досліджено морфологію, наноструктуру та хімічний склад отриманих гетерочастинок $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ типу "ядро-оболонка". Значне зниження інтенсивності люмінесценції спостерігалось у гетерочастинках $\text{Lu}_2\text{O}_3:\text{Eu}/\text{SiO}_2$ у порівнянні з вихідними частинками $\text{Lu}_2\text{O}_3:\text{Eu}$, що пов'язано з особливостями кристалізації сфер $\text{Lu}_2\text{O}_3:\text{Eu}$ в обмеженому оболонкою SiO_2 об'ємі.