Manganese-doped Zn$_2$SiO$_4$ is an old phosphor with a green emission band at 520 nm (α-willemite) or an orange band at 580 nm (β-willemite). In this work the spectroscopic properties of hybrid nanoparticles (NP) with SiO$_2$ core and Zn$_2$SiO$_4$:Mn shell were studied in a framework of a project devoted to the development of photostimulable markers for biomedical applications. These nanoparticles have certain advantages over conventional luminescent markers, as even hours after charging with UV light they can be stimulated with red light to emit the green luminescence of Mn$^{2+}$ (photostimulated luminescence – PSL). During charging, the electrons are stored in traps from where they can be released by long-wavelength light. The conditions of synthesis and codoping affect the defects/traps and need to be optimized to maximize the amount of stored energy and to reduce the role of shallow traps leading to the loss of the PSL capacity through phosphorescence. The effect of codoping Ce$^{3+}$ and Eu$^{3+}$ was studied in microscopic Zn$_2$SiO$_4$ powders.

Spherical silica cores with a diameter of 200 nm were prepared by the modified Stoeber method, and coated with the precursors of the Zn$_2$SiO$_4$:Mn shell by sol-gel process [1]. The doping concentration was 5 mol % referring to Zn. Subsequently, the coated particles were annealed at the temperature of 1100 °C to cause the crystallization of a 5 – 10 nm thick layer of Zn$_2$SiO$_4$:Mn. The silica core serves as the source of Si during the thermal treatment. To ensure redispersability after annealing, the surface of the particles was treated by lyophilization prior to annealing. The microscopic powders of Zn$_2$SiO$_4$:Mn and Zn$_2$SiO$_4$:Mn,RE$^{3+}$ were produced by solid-state synthesis with corresponding oxides as starting materials.

Fig. 1B shows the typical $^4T_1$ – $^6A_1$ emission of Mn$^{2+}$ in α-willemite in the hybrid particles with 5 and 10 nm shell thickness, peaking at 520 nm. The spectral shape of this emission is independent on the excitation wavelength. In the sample with 5 nm shell a considerable fraction of β-willemite is revealed by the presence of the 580 nm PL band. The excitation spectra (PLE), shown in Fig. 1A,
Figure 2. Excitation (A) and photoluminescence (B) spectra of the Zn$_2$SiO$_4$:Mn samples at 300 K.

contain the Mn$^{2+}$-related charge transfer transition around 250 nm (below the band gap) and at least four bands at higher energies. The latter structure differs from that in the excitation spectra of pure Zn$_2$SiO$_4$:Mn$^{2+}$, shown for comparison in Fig. 2A. According to ref. [2] and [3] the 172 nm peak and the 210 nm peak correspond to excitation in the SiO$_4$ cluster. It is possible, that in the hybrid samples energy absorbed in the SiO$_2$ core is partly transferred to the Mn$^{2+}$ ions in the shell, leading to a prevalence of these bands in the excitation spectrum.

In Fig. 3 the spectra of Ce- and Eu-codoped Zn$_2$SiO$_4$:Mn are shown. We have found that especially the codoping with Eu strongly enhances the PSL of the samples. Again, the Mn$^{2+}$ 520 nm band prevails in the PL spectra, codoping with Ce$^{3+}$ results in an additional 400 nm luminescence, while Eu$^{3+}$ is confirmed by the sharp f-f transitions, more clearly seen at low temperatures. In the excitation spectra, the structure seen in the PLE spectrum for the Ce$^{3+}$ luminescence is observed in the PLE spectrum for the Mn$^{2+}$ as well, indicating energy transfer from Ce to Mn. In the case of the Eu$^{3+}$ doped sample, the transfer from Mn$^{2+}$ to Eu$^{3+}$ is observed.

![Figure 3](image-url)

Figure 3. Excitation (A) and luminescence (B) spectra of the Zn$_2$SiO$_4$:Mn,RE$^{3+}$ at 300 K and 10 K.

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References