

^{151}Eu Mössbauer study of luminescent $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ core-shell nanoparticles

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Abstract ^{151}Eu Mössbauer spectroscopy was applied to distinguish among different Eu microenvironments and phases in spherical $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and core-shell $\text{Y}_2\text{O}_3@\text{Eu}^{3+}$ phosphor nanoparticles prepared by using homogeneous precipitation method. ^{151}Eu isomer shift revealed that Eu atoms exist only in oxidation state Eu^{3+} in all spherical and core-shell phosphors. Significant differences have been found between the Mössbauer parameters (isomer shift, principal component of EFG and linewidth) characteristic of spherical $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and core-shell $\text{Y}_2\text{O}_3@\text{Eu}^{3+}$ phosphor nanoparticles. The Mössbauer parameters of spherical $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ were associated with Eu substituting Y in the Y_2O_3 , while Mössbauer parameters of core-shell $\text{Y}_2\text{O}_3@\text{Eu}^{3+}$ phosphor were attributed to Eu being in the Eu_2O_3 shell, proving the structural model and the successful preparation of these phosphors.

Keywords Phosphors · Eu doped yttrium oxides · Core-shell nanoparticles · Spherical nanoparticles · ^{151}Eu Mössbauer spectroscopy

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1 Introduction

More and more industrial interest was focused on semiconductor-based light-emitting diodes (LEDs). In their preparation the phosphors play a very important role. Among the phosphors Eu doped Y_2O_3 is one of the best luminophors regarding the emission efficiency of a red light. For the flat-panel display industry it became necessary to obtain nanoparticles with regular morphology and narrow size distribution [1]. Spherical morphology of phosphors is needed to achieve high brightness and high resolution. Spherical nanoparticles can be prepared by solvothermal synthesis [2], spray pyrolysis [3], and homogeneous precipitation [4] method. By forming core-shell particles spherical particles can also be produced [5]. In our recent work [6] we prepared spherical $Y_2O_3:Eu^{3+}$ and core-shell $Y_2O_3@Eu^{3+}$ nanoparticles using homogeneous precipitation. The structure model of these phosphor nanoparticles are shown in Fig. 1. Eu incorporation into the yttrium oxide is supposed in the case of the spherical $Y_2O_3:Eu^{3+}$ nanoparticles with average diameter of 106 nm (Fig. 1 (I)), while Eu is expected to be a constituent of Eu_2O_3 which forms a shell around the Y_2O_3 core in the case core-shell $Y_2O_3@Eu^{3+}$ nanoparticles (Fig. 1 (II)). However, XRD of both spherical $Y_2O_3:Eu^{3+}$ and core-shell $Y_2O_3@Eu^{3+}$ nanoparticles showed solely the cubic structure of Y_2O_3 , without any information about the effect of Eu doping on the structure. Therefore the aim of this study was to elucidate the location and microenvironments of Eu atom incorporated both in spherical $Y_2O_3:Eu^{3+}$ and in core-shell $Y_2O_3@Eu^{3+}$ phosphor nanoparticles prepared by homogeneous precipitation method. For this study we have used ^{151}Eu Mössbauer spectroscopy which has been already applied to investigate different europium (II) and (III)-activated phosphors even many years ago [7].

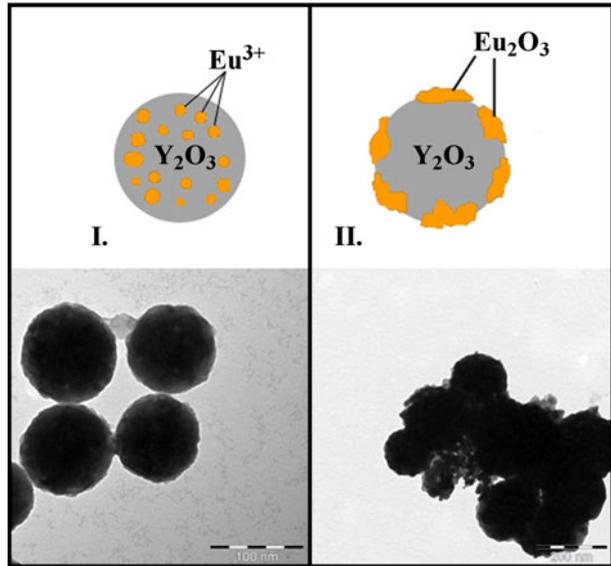
2 Experimental

The spherical $Y_2O_3:Eu^{3+}$ nanoparticles were prepared by homogeneous precipitation according to Gai et al. method [4]. $Y(NO_3)_3$ and $Eu(NO_3)_3$ and urea were dissolved in deionized water. The solution was stirred at 90 °C for 4 h and the precipitate appeared. The suspension was separated by centrifugation. The product was washed with deionized water and dried in air at 80 °C for 24 h. The sample was calcined at 800 °C for 3 h.

Preparation of $Y_2O_3@Eu^{3+}$ core shell nanoparticles: spherical Y_2O_3 nanoparticles were prepared the same way as above and was dispersed in deionized water creating a suspension. $Eu(NO_3)_3$ and urea was given to this suspension separately. The suspension was stirred at 90 °C for 4 h so the Eu_2O_3 could precipitate onto the surface of the Y_2O_3 nanoparticles. The suspension was separated by centrifugation. The product was washed with deionized water and dried in air at 80 °C for 24 h. The sample was calcined at 800 °C for 3 h. The doping concentrations of the Eu^{3+} were 2.5, 5, 10, 15 mol%.

^{151}Eu Mössbauer spectra of powdered samples were recorded in transmission geometry with a conventional Mössbauer spectrometers (WISSEL, RANGER) working in constant acceleration mode. The γ -rays were provided by a 1×10^{10} Bq $^{151}SmF_3$ source. The measurements were performed at 300 K. Isomer shifts are given

Fig. 1 Structural model and TEM micrograph of spherical $\text{Y}_2\text{O}_3\cdot\text{Eu}^{3+}$ (I) and core-shell $\text{Y}_2\text{O}_3\text{@Eu}^{3+}$ (II) phosphor nanoparticles



relative to EuF_3 . The Mössbauer spectra were analyzed by least-square fitting of Lorentzian lines by the help of the MOSSWINN code [8].

3 Results and discussion

Typical room temperature ^{151}Eu Mössbauer spectra of spherical $\text{Y}_2\text{O}_3\cdot\text{Eu}^{3+}$ and core-shell $\text{Y}_2\text{O}_3\text{@Eu}^{3+}$ nanoparticles prepared with different Eu content can be seen in Fig. 2. A lower signal to noise ratio obtained for spectra in Fig. 2a and c is due to the lower Eu concentration of samples compared to those of the corresponding ones (Fig. 2b and d). These spectra were also recorded in high velocity scale, one of the typical spectrum is depicted in Fig. 3. The ^{151}Eu Mössbauer spectra were evaluated by using the full Hamiltonian of the excited $I_e = 7/2$ and ground $I_g = 5/2$ nuclear spin states. The quadrupole moments of the excited and the ground state were fixed to $Q_e = 1.5 \times 10^{-28} \text{ m}^2$ and $Q_g = 1.14 \times 10^{-28} \text{ m}^2$. The Mössbauer parameters derived from the evaluation are shown in Table 1.

The ^{151}Eu isomer shift of all spherical $\text{Y}_2\text{O}_3\cdot\text{Eu}^{3+}$ and core-shell $\text{Y}_2\text{O}_3\text{@Eu}^{3+}$ nanoparticles were found in the interval corresponding solely to Eu^{3+} states [9, 10]. The occurrence of Eu^{2+} in these samples is ruled out according to the result of evaluation of spectra recorded at high velocity interval. ^{151}Eu Mössbauer spectroscopy evidence only Eu^{3+} valence state in all spherical $\text{Y}_2\text{O}_3\cdot\text{Eu}^{3+}$ and core-shell $\text{Y}_2\text{O}_3\text{@Eu}^{3+}$ phosphor nanoparticles prepared by homogeneous precipitation method.

Table 1 shows that significantly different Mössbauer parameters are obtained for spherical $\text{Y}_2\text{O}_3\cdot\text{Eu}^{3+}$ phosphors than those characteristic of core-shell $\text{Y}_2\text{O}_3\text{@Eu}^{3+}$ phosphor nanoparticles. The isomer shift and the V_{zz} belonging to spherical nanoparticles is higher than the corresponding parameters found for core-shell

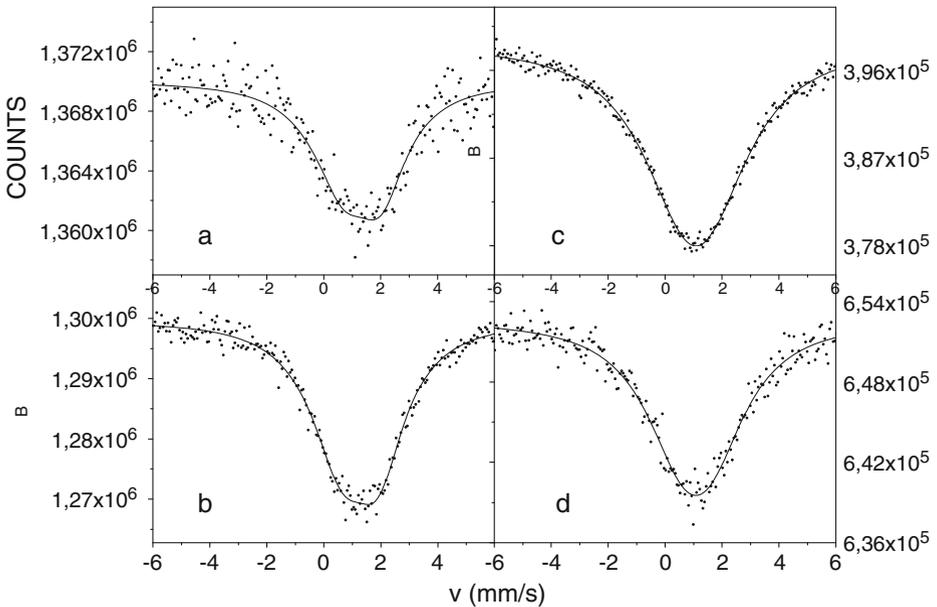
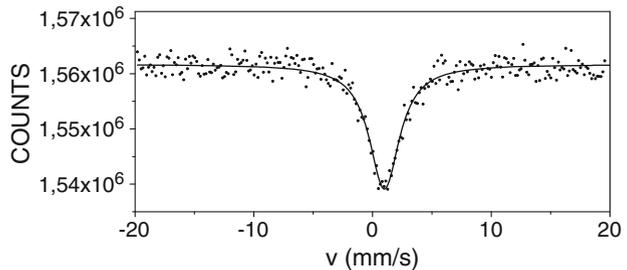


Fig. 2 Typical room temperature ^{151}Eu Mössbauer spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Y}_2\text{O}_3@\text{Eu}^{3+}$ nanoparticles **a** $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ containing 2.5 % Eu^{3+} , **b** $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ containing 10 % Eu^{3+} , **c** $\text{Y}_2\text{O}_3@\text{Eu}^{3+}$ with 10 % Eu^{3+} and **d** $\text{Y}_2\text{O}_3@\text{Eu}^{3+}$ with 75:25 of $\text{Y}_2\text{O}_3:\text{Eu}_2\text{O}_3$

Fig. 3 ^{57}Fe Mössbauer spectra, recorded in a high velocity scale at room temperature, of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor nanoparticles



nanoparticles. On the other hand, smaller linewidth is characteristic of spherical phosphors than that of core-shell ones.

The isomer shift observed for spherical $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ sample with 2.5 % Eu content is close to that found for Eu occupying Y site in Y_2O_3 compound in a previous work [11]. Consequently, we assign the spectra of spherical $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ samples to Eu substituting Y site in Y_2O_3 in these spherical nanoparticles. This is consistent well with the XRD results which show no structural changes in the crystal lattice of Y_2O_3 at the relatively low concentration of the doped Eu, which is our case. Our site assignment is also supported by the relatively narrow linewidth indicating a well defined Eu microenvironment which is expected at the Y site. In the case of spherical $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ samples the V_{zz} value, higher than that characteristic of Eu_2O_3 , can be understood by the distortion of the local environment of Eu doped into the Y_2O_3 lattice at low Eu content. The differences found in the Mössbauer parameters of

Table 1 ¹⁵¹Eu Mössbauer parameters of Y₂O₃:Eu³⁺ and Y₂O₃@Eu³⁺ nanoparticles

	δ (mm/s)	V_{ZZ} (EFG) (10 ²¹ V/m ²)	η (EFG)	W (mm/s)
Spherical Y ₂ O ₃ :Eu ³⁺ 2.5 % Eu ³⁺	1.28 (0.05)	4.78 (0.52)	0.98 (0.22)	2.10 (0.23)
Spherical Y ₂ O ₃ :Eu ³⁺ 10 % Eu ³⁺	1.19 (0.02)	4.77 (0.17)	0.98 (0.08)	2.10 (0.08)
Core-shell Y ₂ O ₃ @Eu ³⁺ 75:25 Y ₂ O ₃ :Eu ₂ O ₃	1.03 (0.02)	2.89 (0.82)	0.99 (0.39)	3.70 (0.27)
Core-shell Y ₂ O ₃ @Eu ³⁺ 10 % Eu ³⁺	1.02 (0.03)	3.53 (0.96)	0.98 (0.35)	3.02 (0.40)

spherical Y₂O₃:Eu³⁺ nanoparticles with different Eu content may be explained by the effect of some Eu incorporation into the second coordination shell in the case of higher Eu concentration. Our results confirm the structural model suggested for spherical Y₂O₃:Eu³⁺ nanoparticles (Fig. 1 (I)), i.e. Eu incorporates into Y₂O₃ by substituting Y sites in these spherical Y₂O₃:Eu³⁺ phosphors.

The ¹⁵¹Eu isomer shift we found for core-shell Y₂O₃@Eu³⁺ phosphor nanoparticles agrees resonantly with the literature data of Eu₂O₃ [9, 10, 12]. Consequently, we assign the spectra of core-shell phosphor samples to Eu being in Eu₂O₃. Thus ¹⁵¹Eu Mössbauer spectroscopy reveal the occurrence Eu₂O₃ in the core-shell samples, in contrast to the results of XRD which method was not able to detect Eu₂O₃ probable due to the occurrence of Eu₂O₃ in highly defected or amorphous-like state. The very high linewidth observed for the core-shell phosphors also strongly support that highly defected Eu₂O₃ are present in the shell of these nanoparticles. The difference in the linewidth between the spectra of core-shell samples can be consistent with the change mainly in the Eu content. Our results confirm the structural model suggested for core-shell Y₂O₃@Eu³⁺ nanoparticles (Fig. 1 (II)), i.e. Eu locates in the Eu₂O₃ shell in these core-shell Y₂O₃@Eu³⁺ phosphors.

Fluorescence intensity of the spherical Y₂O₃:Eu³⁺ samples are much higher than in the Y₂O₃@Eu³⁺ core-shell nanoparticles because the Eu³⁺ ions are situated in the matrix of the Y₂O₃ lattice and they occupy C₂ sites where the ⁵D₀-⁷F₂ transition is not forbidden. In the spherical Y₂O₃:Eu³⁺ nanoparticles the intensity increases with the amount of the Eu³⁺ ions until the concentration reaches 5 mol%. At higher concentrations the emission decreases due to quenching. In the Y₂O₃@Eu³⁺ core-shell nanoparticles have a lower intensity than spherical Y₂O₃:Eu³⁺ nanoparticles but it slightly increases with the amount of the Eu₂O₃.

4 Conclusion

¹⁵¹Eu Mössbauer spectroscopy was able to distinguish and assign the Eu microenvironments in spherical Y₂O₃:Eu³⁺ and Y₂O₃@Eu³⁺ core-shell nanoparticles and confirmed their structural models. Eu occupies the Y site in Y₂O₃ in the spherical Y₂O₃:Eu³⁺ nanoparticles, while Eu locates in Eu₂O₃ in the core-shell samples. It was confirmed that phosphors of both spherical Y₂O₃:Eu³⁺ and core-shell Y₂O₃@Eu³⁺ nanoparticles and were successfully prepared by homogeneous precipitation.

Acknowledgements The authors are very thankful for the financial support of the Hungarian Scientific Fund (OTKA) Nr. K 73307 and of the Project named “TÁMOP-4.2.1/B-09/1/KONV-2010-0005”.

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