Energy transfer in Gd$_2$O$_3$:Er nanoparticles applying as a down-conversion layer for solar cell

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Abstract. The optical properties of Gd$_2$O$_3$:Er (0.25-8 mol%) nanoparticles have been investigated. The observed effect of energy transfer from lattice Gd$^{3+}$ to activator Er$^{3+}$ ions can be used for enhancement of solar cells efficiency. The general scheme showing the principle of operation of down-conversion layer based on Gd$_2$O$_3$:Er was presented. The concentration dependences of emission intensity and energy transfer efficiency were obtained.

1. Introduction
Gadolinium oxide is of interest as host material for functional devices of nanophotonics, optoelectronics, alternative energy and conversion systems because of its low phonon energy, good thermal stability and chemical durability [1]. Among the rare-earth ions, Er$^{3+}$ is one of the most perspective activator. Optical transitions from the Er$^{3+}$ long-lived excited states result in the intensive emission in green and red spectral regions. Moreover, specialties of Er$^{3+}$ energy levels structure provide an opportunity to convert of UV and near infrared radiation to visible light [2].

The efficiency of energy conversion is determined by a number of factors, associated with both the host lattice material (crystal structure, defectiveness, size and surface effects) and properties of activator ions (qualitative and quantitative compositions of donor-acceptor pairs, absorption cross section, quantum yield of luminescence) [3]. Along with the above, the determination of optimal concentrations of dopants is one of the key tasks to achieve the highest energy transfer efficiency [4]. The aim of this work is to investigation the luminescent behavior of nanostructured Gd$_2$O$_3$:Er as a function of different Er$^{3+}$ concentration.

2. Experimental
The nanoparticles of Gd$_2$O$_3$:Er with Er$^{3+}$ concentration from 0.25 to 8 mol% were synthesized by chemical precipitation method. The precursors Gd(NO$_3$)$_2$ and Er(NO$_3$)$_2$ with appropriate molar concentrations were dissolved in aqueous ammonia solution (pH=8.5). After the reaction was completed, obtained Gd(OH)$_3$:Er precipitates were washed with distilled water several times and dried at 120°C. Subsequent calcination at 1000°C during for 2 hours had led to the formation of Gd$_2$O$_3$:Er nanoparticles.

The crystallinity, phase composition and particle size of obtained samples were investigated by X-ray diffraction patterns recorded by the XPertPro MPD diffractometer equpped by the solid state pixel detector for Cu-K$_\alpha$ radiation. Morphology study of prepared nanoparticles was performed by Carl Zeiss SIGMA VP scanning electron microscope in high-vacuum mode with the InLens detector. Photostimulated emission and excitation spectra were measured on a setup assembled with the 400 W

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deuterium lamp, R6358-10 Hamamatsu photomultiplier and two prismatic DMR-4 computer-controlled monochromators.

3. Results and discussion

3.1 Structure and morphology

Figure 1 shows the XRD patterns of undoped as well as Er$^{3+}$-doped Gd$_2$O$_3$ nanoparticles. All peaks are corresponding to the cubic single-phase structure of Gd$_2$O$_3$ with Ia-3 space group (JCPDS No. 65-3181). No impurity peaks and other possible phases were not observed due to the incorporation of Er$^{3+}$ ions. The values of lattice parameter and average crystalline grain size for all samples are listed in table 1. It is seen that increasing of Er$^{3+}$ concentration results in the decreasing of lattice constant and particle size. This fact probably results from smaller radius of Er$^{3+}$ (0.881 Å) in comparison with the Gd$^{3+}$ (0.938 Å) and can indicate the successful doping the activator ions into the host lattice. The SEM images (figure 2 shows the image for sample with 2 mol% of Er$^{3+}$ concentration) reveal that nanoparticles are different in size and shape. In addition, the micrographs clearly indicate the porosity and agglomeration of obtained crystallites.

![Figure 1. XRD patterns of undoped and Er$^{3+}$-doped (0.5-8 mol%) Gd$_2$O$_3$ nanoparticles.](image1)

![Figure 2. SEM image of Gd$_2$O$_3$:Er nanoparticles with 2 mol% of Er$^{3+}$ concentration.](image2)

Table 1. Average particle size and lattice parameter of Gd$_2$O$_3$:Er nanoparticles with different Er$^{3+}$ concentrations.

| Concentration of Er$^{3+}$ ions (mol%) | 0  | 0.5 | 1  | 2  | 4  | 8  |
|--------------------------------------|----|-----|----|----|----|----|
| Average particle size (nm)           | 57 | 56  | 54 | 53 | 50 | 48 |
| Lattice parameter (Å)                | 10.813 | 10.812 | 10.810 | 10.808 | 10.804 | 10.793 |

3.2 Luminescent properties and energy conversion parameters

The excitation spectrum of Gd$_2$O$_3$:Er (2 mol%) shown at figure 3 was recorded under the monitoring of the most intensive emission of Er$^{3+}$ at 540 nm. The three bands with maximums at 232, 275 and 310 nm correspond to the 4f-4f optical transitions of Gd$^{3+}$ ion that indicates the realization of energy transfer between lattice cations and activator ions [5,6]. Optically-active Gd$^{3+}$ ions provide the absorption of near UV radiation followed with the energy transfer to Er$^{3+}$ ions that in turn emit in the visible spectral range, so we observe down-conversion process [7].
Figure 3. The explaining scheme of the operating principle of Gd\(_2\)O\(_3\):Er additional layer on the top of silicon solar cell in accordance with the down-conversion mechanism that is realized due to the Gd\(^{3+}\)-Er\(^{3+}\) energy transfer.

This mechanism of radiation conversion is applicable for special additional layer that is placed in the front surface of traditional silicon solar cells in order to enhancement of their efficiency. Down-conversion layer is intended to reduce the thermalization losses that arise due to the absorption of photons with energy higher than the Si band-gap [8].

In order to determine the influence of Er\(^{3+}\) concentration on luminescent behavior of Gd\(_2\)O\(_3\):Er nanoparticles as well as to obtain the information about energy transfer efficiency in Gd\(^{3+}\)-Er\(^{3+}\) ion pair we have performed the photoluminescence measurements for all samples from the Gd\(_2\)O\(_3\):Er (0.25-8 mol\%) concentration series (figure 4 and figure 5). It was observed that the intrinsic emission of Gd\(^{3+}\) ions acting as donors of excitation continuously decreases with Er\(^{3+}\) concentration increases. This fact points out the growth of Gd\(^{3+}\)-Er\(^{3+}\) energy transfer efficiency under the increasing of acceptor concentration (table 2). Herewith the intensity of Er\(^{3+}\) emission under the indirect excitation (energy transfer from Gd\(^{3+}\)) increases up to the 2 mol\% of Er\(^{3+}\) concentration at which it reaches a maximum. A decrease in the luminescence intensity with a further increase of Er\(^{3+}\) concentration can be explained by the non-radiative losses related with the energy migration of excitation along a chain of Er\(^{3+}\) ions (so-called concentration quenching effect) [9,10]. In other words, for concentrations of acceptor ions greater than 2 mol\% the efficiency of Er\(^{3+}\)-Er\(^{3+}\) energy migration process begins to prevail over the efficiency of Gd\(^{3+}\)-Er\(^{3+}\) energy transfer.

Table 2. Energy transfer efficiency in Gd\(^{3+}\)-Er\(^{3+}\) pair as function of Er\(^{3+}\) concentration.

| Concentration of Er\(^{3+}\) ions (mol\%) | 0  | 0.5 | 1  | 2  | 4  | 8  |
|-----------------------------------------|----|-----|----|----|----|----|
| Energy transfer efficiency (%)           | 25 | 41  | 50 | 59 | 50 | 76 |
Figure 4. Emission spectra of Gd$_2$O$_3$:Er (0.5-8 mol%) in the region of 450-600 nm. Bands at 525 and 540 nm correspond to the optical transitions in Er$^{3+}$ ions under the indirect excitation by the energy transfer from Gd$^{3+}$ ions.

Figure 5. Emission spectra of Gd$_2$O$_3$:Er (0.5-8 mol%) in the region of 290-350 nm. Band at 315 nm corresponds to the optical transition in Gd$^{3+}$ ions under the direct intracenter excitation.

4. Conclusion
The Gd$_2$O$_3$:Er (0.5-8 mol%) nanoparticles with cubic crystalline structure and average particle sizes of 48-57 nm were obtained by the chemical precipitation method and characterized by XRD and SEM techniques. The emission and excitation spectra reveal the energy transfer from Gd$^{3+}$ to Er$^{3+}$ ions that can be applicable for improvement of solar cells efficiency. The structural scheme demonstrating the applying Gd$_2$O$_3$:Er as a down-conversion layer is presented. It was established that the intensity of Er$^{3+}$ emission achieves maximum at concentration of 2 mol% while the efficiency of Gd$^{3+}$-Er$^{3+}$ energy transfer is 50%.

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