Crystal structure and luminescence properties of $La_{1-x}Sm_xVO_4$ sol-gel nanoparticles doped with hetero valence impurity

Chukova O.[1], Dorofieieva A.[1], Nedilko S.A.[1], Nedilko S.G.[1], Voitenko T.[1], Paszkowicz W.[2], Rahimi Mosafer H.[2], Androulidaki M.[3], Stratakis E.[3]

[1] Taras Shevchenko National University of Kyiv, Volodymyrska Str., 64/13, Kyiv 01601, Ukraine.
E-mail: mdr-23@ukr.net
[2] Institute of Physics, Polish Academy of Sciences, al. Lotników, 32/46, 02-668, Warsaw, Poland
[3] Institute of Electronic Structure & Laser (IESL) of Foundation for Research & Technology Hellas (FORTH), Heraklion 711 10 Crete, Greece.

Introduction

Luminescent materials based on rare earth vanadate matrices are widely used for various science and technology purposes. Luminescent converters are able to convert light from the ultraviolet range to red and thus increase the efficiency of solar panels. Recently, the crystal structure of the vanadate nanoparticles was reported as influences significantly on the efficiency of the luminescent transformation of light from the UV and violet spectral ranges. In particular, the investigated in our previous works $La_{1-x}Sm_xVO_4$ nanoparticles are characterized by intensive emission of the Sm^{3+} ions that are excited from the wide spectral range including UV diapason. [1]. In the present work we carry out an investigation of such compositions and synthesis conditions that give materials with enhanced efficiency of luminescent transformation of UV into visible diapason suitable for application for Si solar cells and blue LEDs.

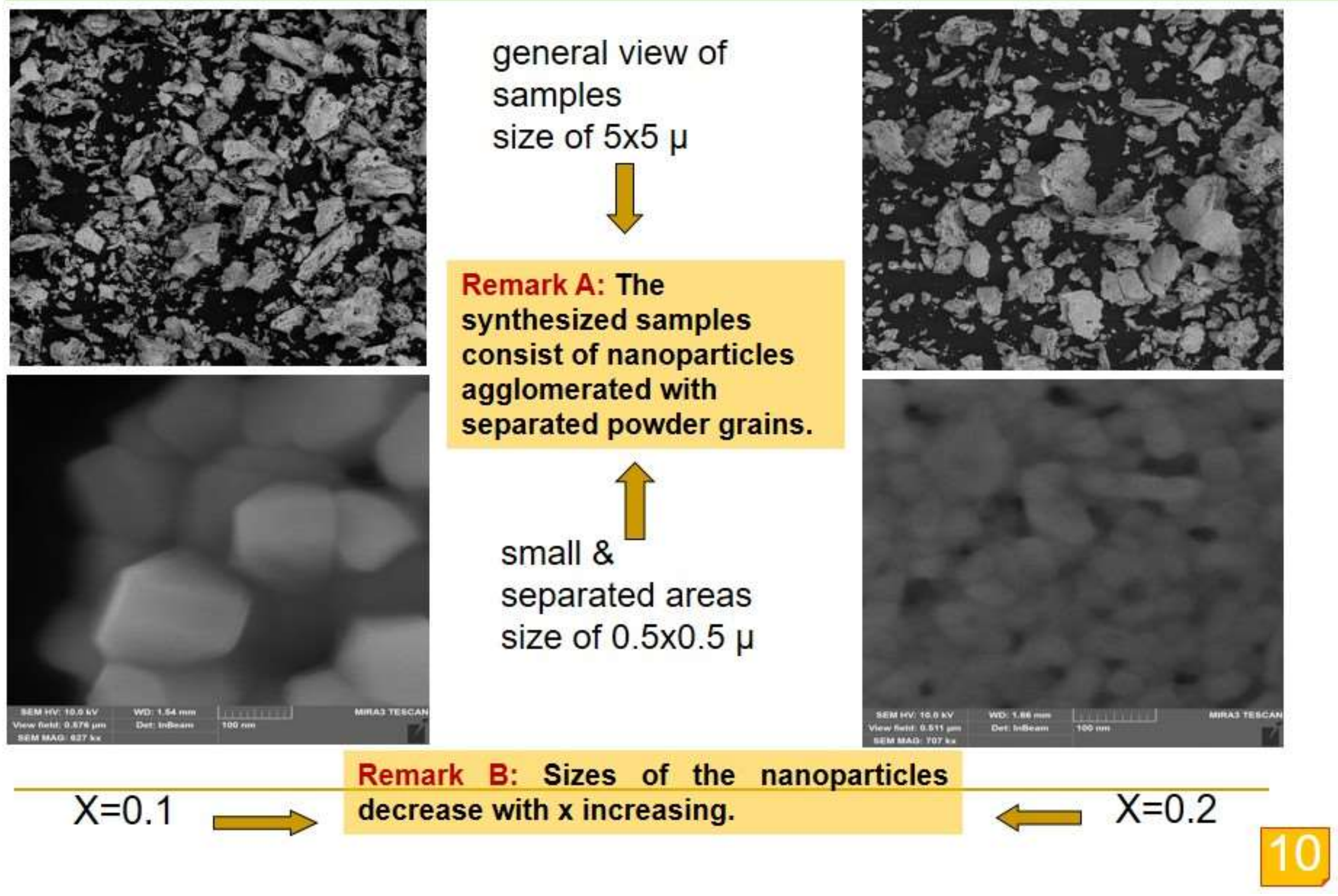
Synthesis and Experimental

Investigated series of the $La_{1-x}RE_xVO_4$ solid solutions were synthesized by the sol-gel method. As initial reagents, a certain amount $Ca(NO_3)_3$, Sm $(NO_3)_3$, and NH_4VO_3 were used. They were taken in the necessary quantities and mixed gradually. Then the solution was poured into a graphite cup and placed on a sand bath. The solution gradually evaporated and turned into a gel, and then to a powder. The fine-grained powder was calcined for 5 hours at with step-by-step heating with 100 °C steps up to 680 °C temperature.

Phase compositions of the synthesized samples were determined using X-ray diffractometer Shimatzu 2000 ($Cu_{K\alpha}$-radiation with a Ni filter). It was found that obtained samples possess multiphase composition with monoclinic and tetragonal crystal structure. Content of the tetragonal $LaVO_4$ phase is increased with increase of Sm^{3+} concentration.

The microstructure of the samples was studied with a scanning electron microscope (SEM) INCA X-max System from Oxford Instruments. Luminescence spectra were excited with 405, 478 and 532 nm lasers or powerful Xenon lamp and were registered using DFS-12 monochromator with grating 600 grooves/mm, slit up to 50 micron and FEU-79 photomultiplier.

SEM characterization of the synthesized samples



general view of samples size of 5x5 μ

Remark A: **The synthesized samples consist of nanoparticles agglomerated with separated powder grains.**

small & separated areas size of 0.5x0.5 μ

X=0.1

Remark B: **Sizes of the nanoparticles decrease with x increasing.**

X=0.2

Emission

Luminescence emission spectra of the synthesized samples consist of four groups of lines in 550 – 725 nm spectral range those are corresponded to well known inner f-f transitions in the Sm^{3+} ions of the incorporated $La_{0.9}Sm_{0.1}VO_4$ luminescent nanoparticles.

Groups of lines located in the 550 – 580, 580 – 620, 625 – 670 and 680 – 725 nm spectral ranges are caused by the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ transitions, respectively.

Distribution of lines in the measured emission spectra depends on the dopants concentrations. This effect is marked by arrows in Fig. below.

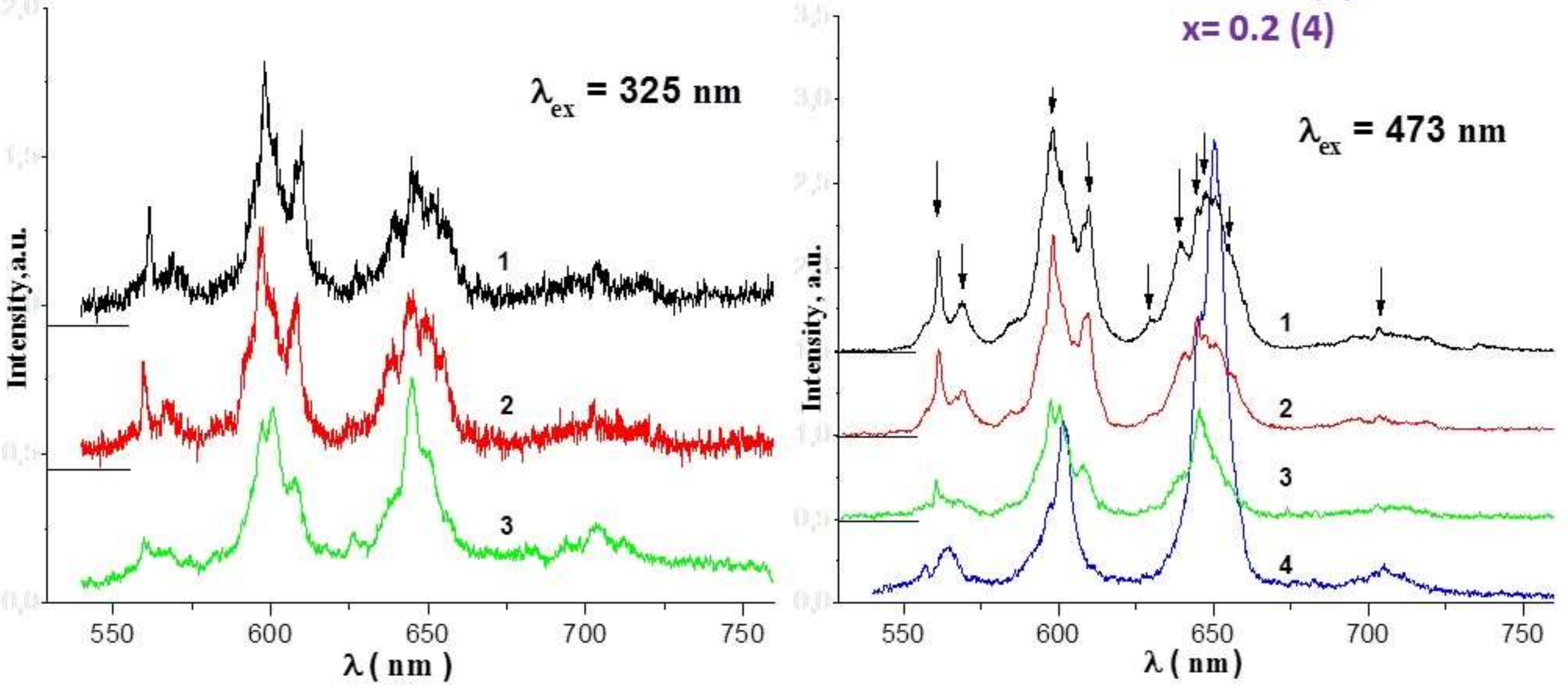
Excitation

The observed excitation bands correspond to different types of transitions.

- The broadband in 300 – 350 nm spectral range should be assigned to transitions in the VO_4^{3-} groups
- The band at 325 nm is in the region of transitions in defects.
- Differences between relative contributions of these bands can be caused by the influence of features of crystal microstructures and neighbor surroundings of the Sm3+ ions on efficiency of energy transfer to the impurity ions from a matrix in general and vanadate anion in particular.

Emission spectra

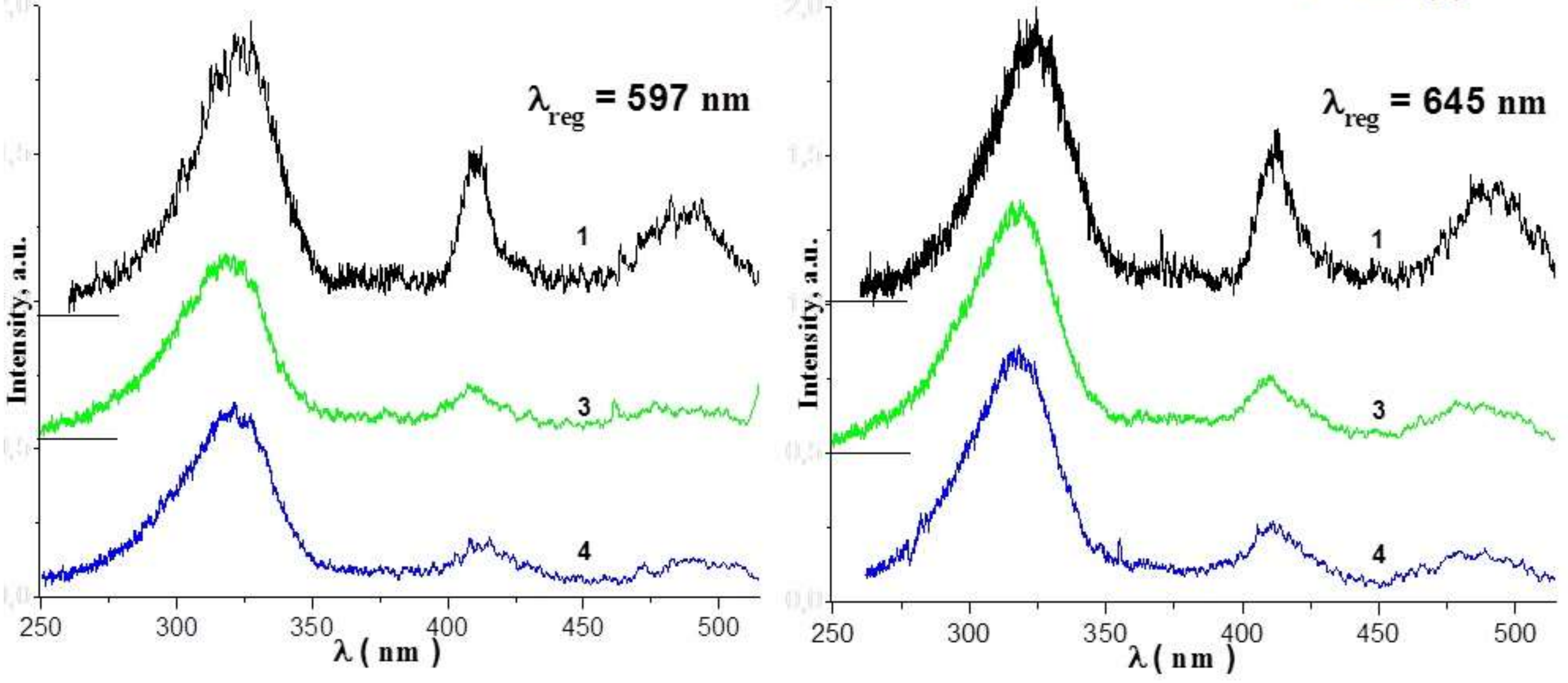
$La_{1-x}Sm_xVO_4$: Ca
x= 0.05 (1)
x= 0.1 (2)
x= 0.15 (3)
x= 0.2 (4)



The relative luminosity intensity in the region of 625 - 670 nm increases in relation to the luminescence intensity in the region of 580 - 620 nm with increasing concentration of Ca^{2+} impurities, and there is a redistribution of intensities between individual peaks within each of the regions. Lines whose intensity decreases with increasing Ca2 + content are indicated by arrows in the figure.

Excitation spectra

$La_{1-x}Sm_xVO_4$: Ca
x = 0.05 (1)
x = 0.15 (3)
x = 0.2 (4)



The wide excitation band in the spectrum corresponds to the electronic transitions in the vanadate anion VO_4^{3-}, and the narrow lines correspond to the transitions in the inner f^m shell of Sm^{3+} ions. The relative intensity of the narrower lines decreases with increasing concentration of Ca^{2+} impurities.

Conclusions

- The $La_{1-x}Sm_xVO_4$:Ca (from x = 0.05 to x = 0.2) nanoparticles were synthesized by sol-gel method and investigated.

- In emission spectra of the $La_{1-x}Sm_xVO_4$:Ca compounds with increasing concentration of Ca^{2+} impurities, a redistribution of intensities between different maxima in the radiation spectra is observed. In the lexcitation spectra of the investigated compounds, the relative intensity of the narrower lines corresponding to the transitions in the inner shell of La^{3+} and Sm^{3+} ions decreases with increasing concentration of the Ca^{2+} impurities.

- It was found that changes in crystal phases influence on fine structure of the emission and excitation spectra of the $La_{1-x}Sm_xVO_4$:Ca nanoparticles, whereas Ca-doping leads to formation of additional Ca-induced centers of luminescence. It is assumed that the introduction of the Ca^{2+} impurities into the composition of the $La_{1-x-y}Sm_{1-x}Ca_yVO_4$ nanoparticles lead to the formation in their crystal structure of additional complex defect centers.

References

1. O.V. Chukova, S.A. Nedilko, A. Papadopoulos, S.G. Nedilko, A.A. Slepets, E.I. Stratakis, T.A. Voitenko, Structure and spectroscopy characterization of La1-xSmxVO4 luminescent nanoparticles synthesized co-precipitation and sol-gel methods Optical Materials, 2019, vol. 95, pp. 109248-10.doi:10.1016/j.optmat.2019.109248

2. Oksana V. Chukova, Sergiy A.Nedilko, Sergiy G. Nedilko, Alina A. Slepets, and Tetiana A. Voitenko, Synthesis and Investigation of La,Ca -Doped EuVO4 Nanoparticles with Enhanced Excitation by Near Violet Light Phys. Status Solidi A 2018, article number 1700894