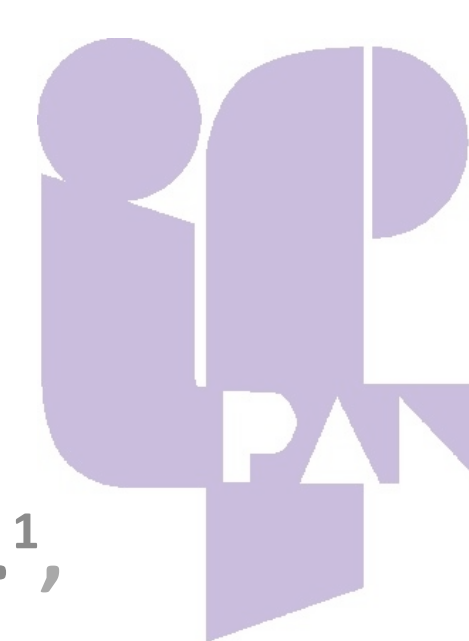


Spectroscopic study of luminescent biphasic $\text{La}_{1-x}\text{Yb}_x\text{VO}_4$ nanoparticles



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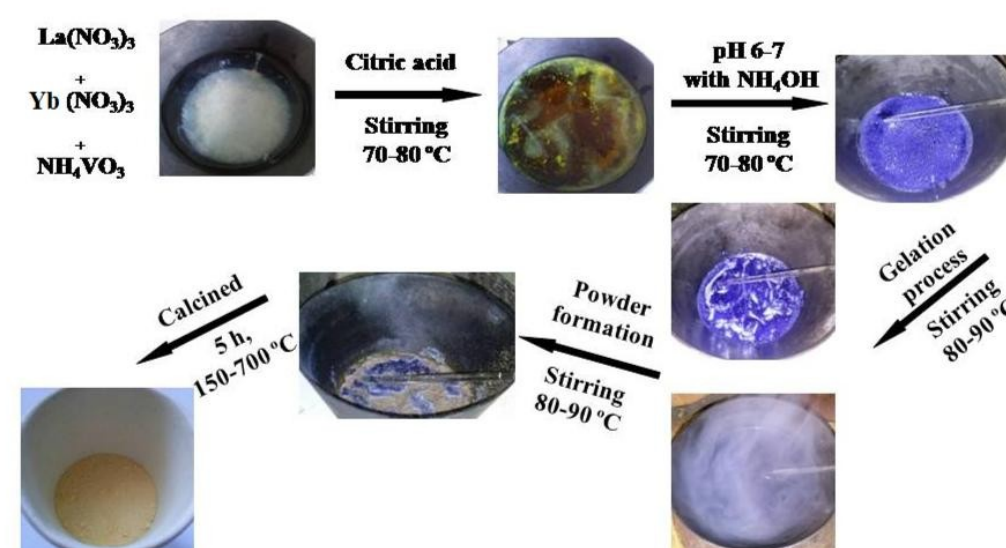
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Introduction

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 $\text{La}_{1-x}\text{RE}_x\text{VO}_4$ nanoparticles are characterized by intensive emission of the RE^{3+} ions that are excited from the wide spectral range including UV diapason. 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 of nanoparticles



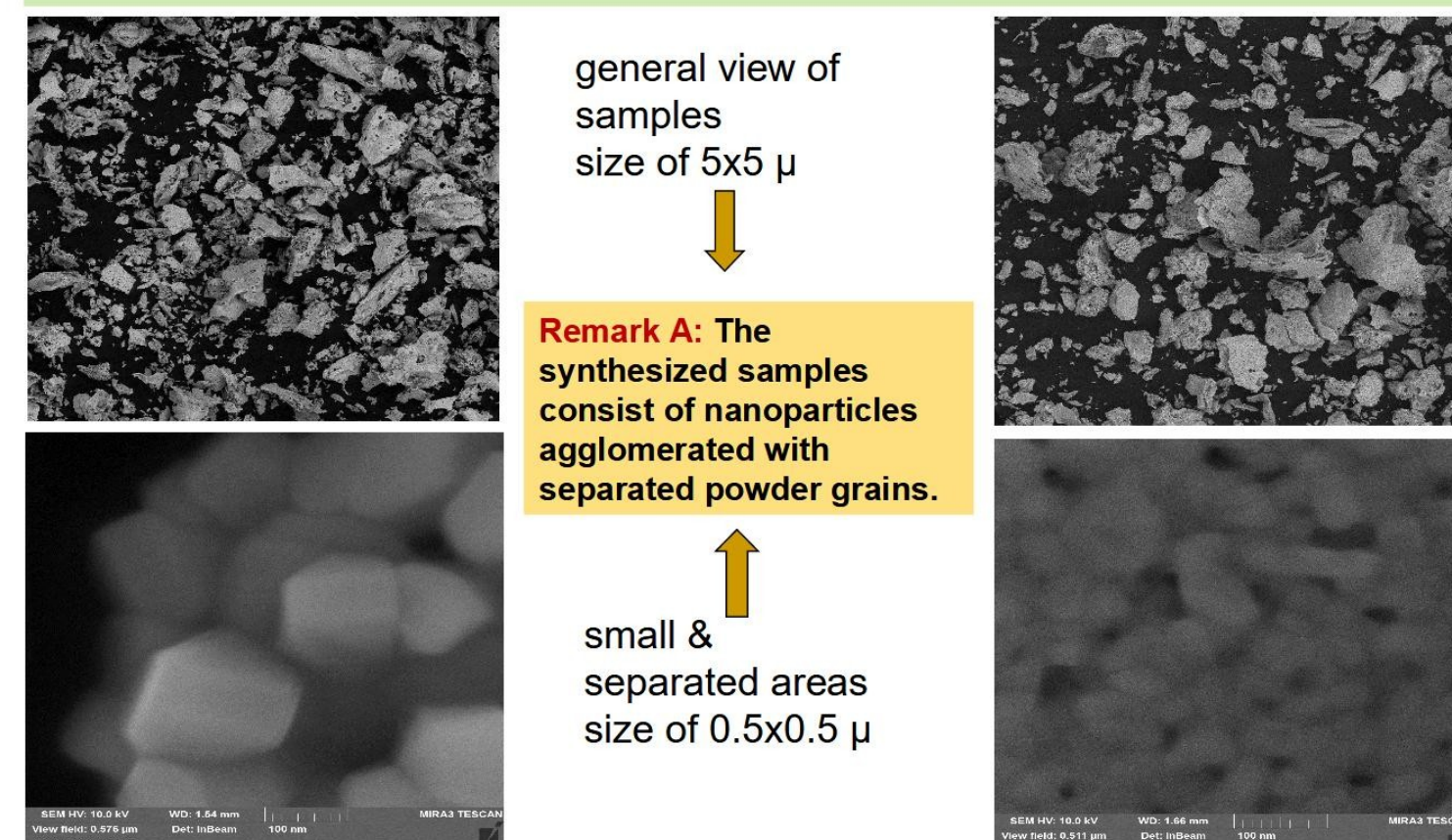
The $\text{La}_{1-x}\text{Yb}_x\text{VO}_4$ nanoparticles were synthesized from calculated stoichiometric amounts of $\text{La}(\text{NO}_3)_3$, $\text{Yb}(\text{NO}_3)_3$, NH_4VO_3 precursors by sol-gel method.

Nitrate solutions of the corresponded metals with a precisely defined concentration were poured into a glass in accordance with the calculated ratios. The pH was adjusted to 7.0-8.0 by ammonia solution. After, solution of ammonium metavanadate was added.

The precipitate was dissolved with a solution of citric acid in the ratio of the starting material. Initially, the solution was concentrated by slow evaporation at 80-90 °C before formation of gel, from which then a fine-grained powder was made and was calcined for 5 hours at 680 ° and carefully homogenized in an agate mortar.

Phase compositions of the synthesized samples were determined using X-ray diffractometer Shimadzu 2000 ($\text{CuK}\alpha$ -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 Yb^{3+} concentration.

SEM characterization of the synthesized samples



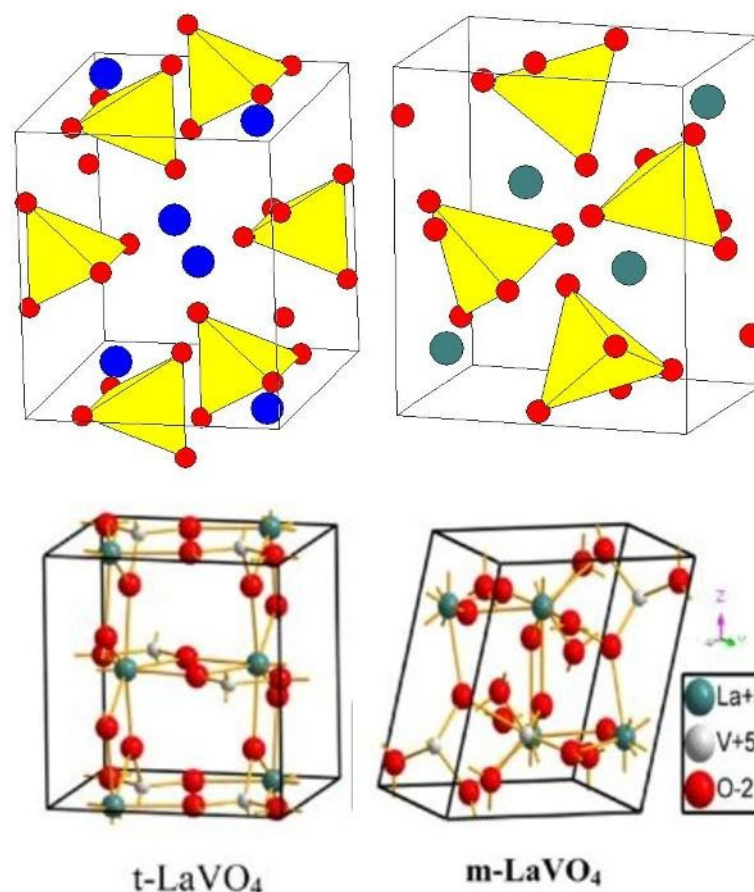
Remark B: Sizes of the nanoparticles decrease with x increasing.

Unique feature of LaVO_4 crystal matrix compared to other rare earth vanadates

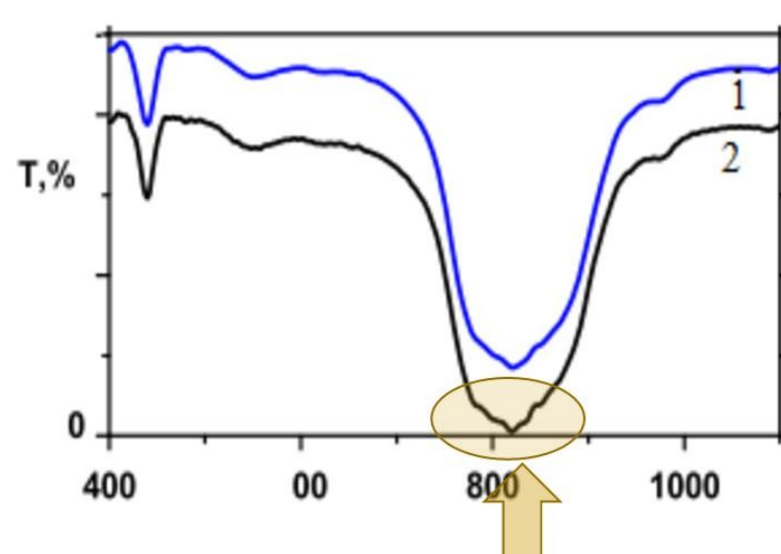
It is known that all the rare-earth orthovanadates (REVO_4) crystal compounds crystallize in the so-called zircon structure. This rule has **one exception** and this exception is lanthanum vanadate (LaVO_4), which is dimorphic and can be stabilized in zircon or monazite crystal structures.

The zircon crystal structure is characterized by a tetragonal symmetry with space group $I4_1/amd$ ($Z=4$). In this structure the La and V cations are located at high-symmetry positions those can be described as formed by isolated VO_4 tetrahedral units surrounded by the La atoms forming eight-vertex LaO_9 polyhedrons. Each of V atom is surrounded by four equivalent oxygen atoms forming the perfect VO_4 tetrahedrons with T_d local symmetry of oxygen surrounding and V - O distances near 1.7 Å. In the LaO_9 dodecahedron, the La atoms are coordinated by eight oxygen atoms with identical four short bond lengths (2.2 Å) and four long bond lengths (2.5 Å) with D_{2d} local symmetry of oxygen surrounding. Each VO_4 and LaO_9 polyhedron units are running parallel to the crystallographic c-axis. Each of the chains is joined laterally by edge-sharing LaO_9 dodecahedra.

The monazite structure (space group $P2_1/n$, No. 14, $Z=4$) is another crystal structure adopted by LaVO_4 . At ambient conditions this crystal structure is observed only for LaVO_4 among the REVO_4 family, but can be obtained for several REVO_4 vanadates at high pressure [52]. In the monazite structure, the V and La atoms are four- and nine-fold coordinated, respectively, with C_2 local symmetry of oxygen surrounding for the both cations. The distorted VO_4 tetrahedrons only share corners and edges with the LaO_9 polyhedrons.



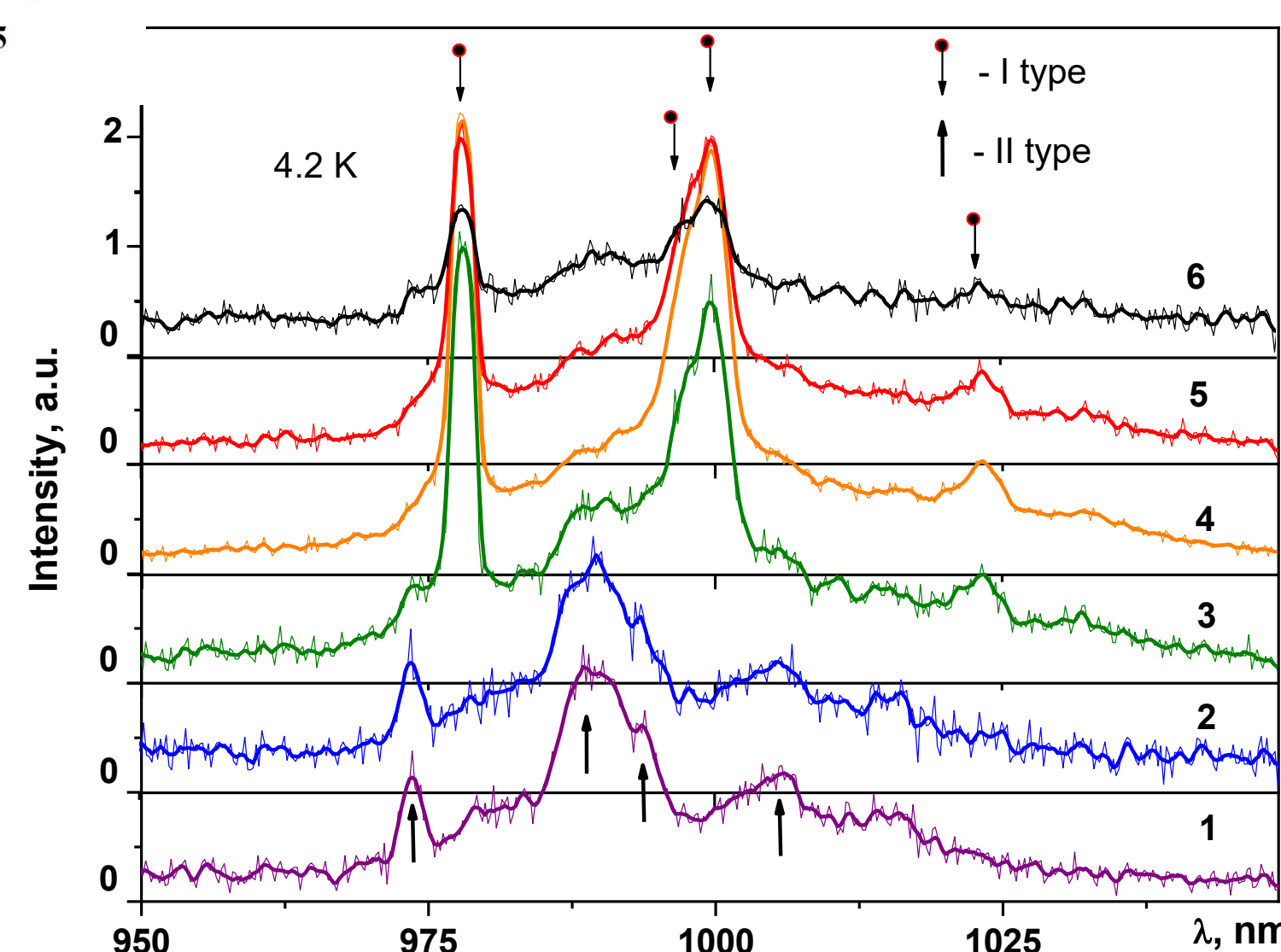
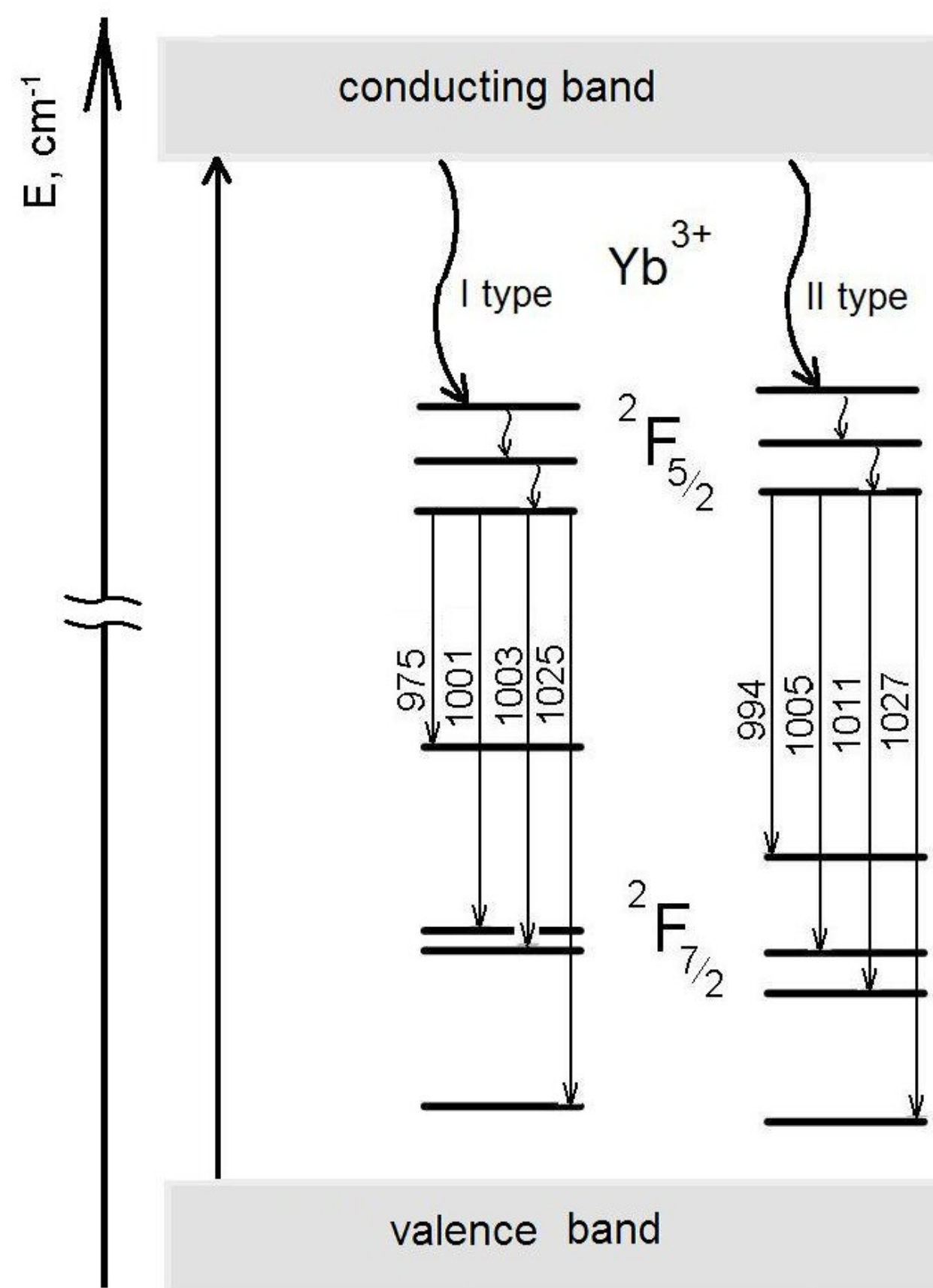
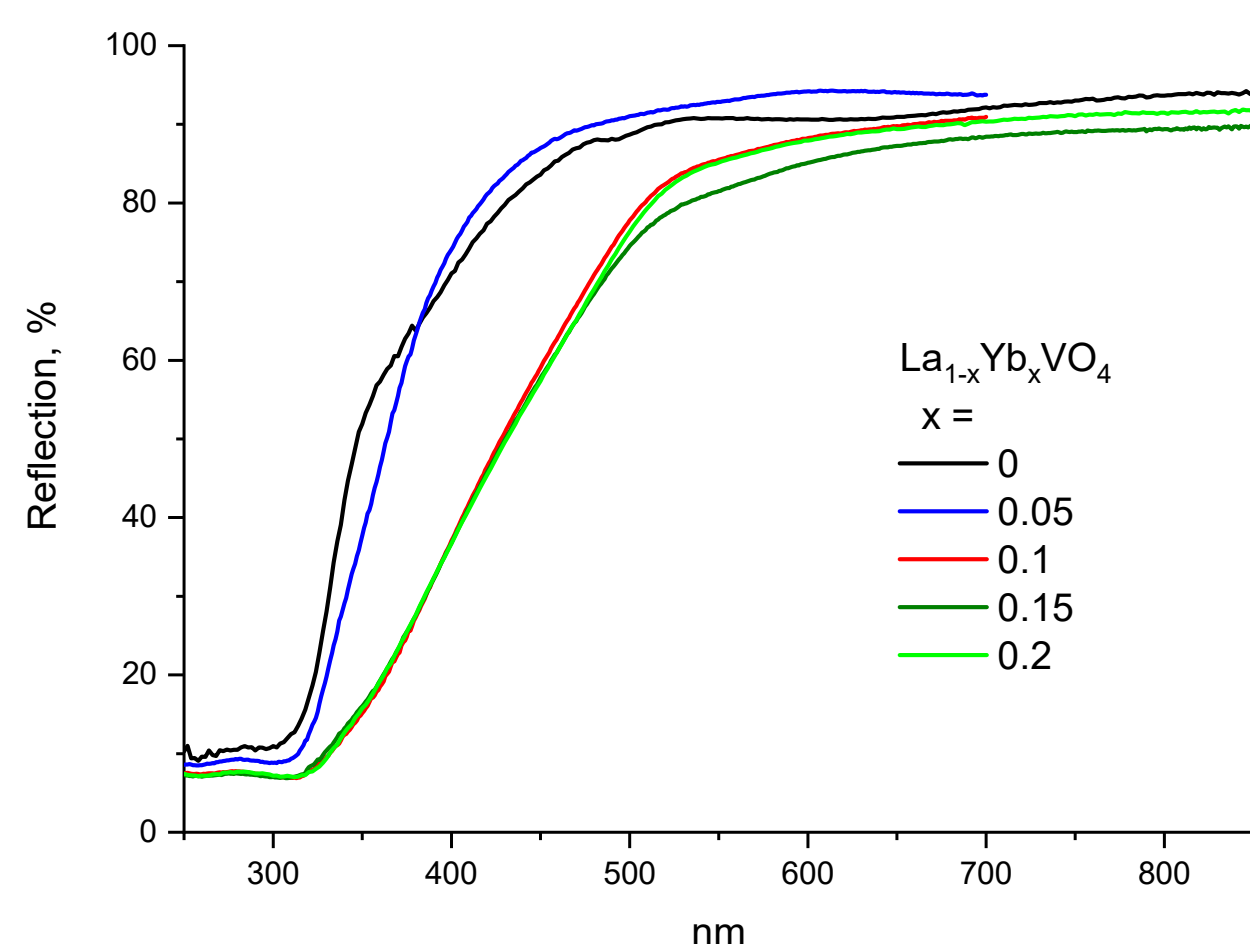
FTIR spectroscopy of the synthesized samples



The measured IR absorption spectra in the range of 400–1100 cm^{-1} is typical for the LaVO_4 compound. It is well known that the bending and stretching vibrations of O–V–O bonds of the VO_4^{3-} anion form IR absorption spectra of various orthovanadates in the range 400 – 500 and 700 – 1100 cm^{-1} . In fact, measured by us, spectrum of the undoped LaVO_4 contains separated peaks located near 440 cm^{-1} , those should be assigned to ν_4 vibration mode of the VO_4^{3-} anion. The stronger wide band in the range 700–1000 cm^{-1} contain peaks around 820 and 875 cm^{-1} those should be assigned to ν_3 and ν_1 vibration modes, respectively.

It possible to see from curve 2 that ν_3 mode is split on three weakly separated components for the $\text{La}_{0.9}\text{Yb}_{0.1}\text{VO}_4$ samples. These observation described above confirms results of the XRD study of the samples about a mainly monoclinic and a mainly tetragonal structures of the $\text{La}_{0.9}\text{Yb}_{0.1}\text{VO}_4$ and $\text{La}_{0.8}\text{Yb}_{0.2}\text{VO}_4$ samples, respectively.

Diffuse reflection spectra



The emission spectra consist of spectral lines appeared in the 970 – 1040 nm range which are caused by the $f-f$ electron transitions in the Yb^{3+} ions. Structure of the spectra depends on the Yb^{3+} concentration. The carried out analysis has revealed that Yb^{3+} ions form at least two different types of emission centers in the studied materials. Correlations between crystalline structure, morphology of the nanoparticles, reflection spectra and luminescence properties of the samples were analyzed and discussed. The assumption was made that changes of the samples morphology are caused by changes of nanoparticles crystal structure, as well as appearance of two types of emission centers are related with the Yb^{3+} ions located in the nanoparticles of different crystal structure.

Acknowledgments:

This work has received funding from Ministry of Education and Science of Ukraine through the Research in Universities Program, Polish Academy of Sciences through the Institute of Physics grants and from the EU-H2020 research and innovation program under grant agreement No 654360 having benefited from the access provided by the Institute of Electronic Structure and Laser IESL-FORTH, Crete, Greece within the framework of the NFFA-Europe Transnational Access Activity.



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