Luminescent Properties of Transparent Glass-Ceramic Composites Doped with Crystalline Vanadate Nanoparticles

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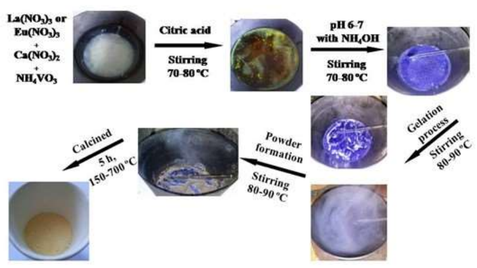
Scope and Goal

Composite materials with oxide nanoparticles have attracted increased research interest in relation with their applications for optical material science needs, in particular, for creation new luminescent coatings for WLEDs.

Oxide micro/nanoscale composite materials, such as activated oxide glass ceramic, are now considered as promising materials for the above noted luminescent coatings because these inorganic systems are usually characterized by high thermal and mechanical stabilities and can give intensive emission.

In a case of activation of glass materials with luminescent nanoparticles, luminescent efficiency of the latter may be decreased due their interaction with a glass matrix with different refractive index.
The aim of this work is to develop and investigate model glass-ceramic composites with luminescent vanadate nanoparticles grown with various concentrations and to study dependencies of their properties on films compositions and growth conditions.

Synthesis of nanoparticles



The initial luminescent $La_{1-x-y}Eu_xCa_yVO_4$ nanoparticles were synthesized by sol-gel method from calculated stoichiometric amounts of $La(NO_3)_3$, $RE(NO_3)_3$, NH_4VO_3, $Ca(NO_3)_2$ 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 meta-vanadate was added.

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

Preparation of glass and composites

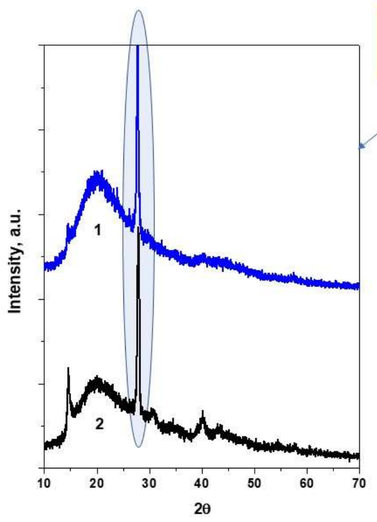
Borate-vanadate glass was synthesized by melt quenching procedure from calculated amounts of vanadium pentoxide and borate acid. The concentration of vanadate component is varied from 3 to 40 mass%. The reagents were grinded, mixed and placed in porcelain crucibles, then melted 2 hours in the air at 700 C in electric muffle furnace. After melting, the samples were quickly quenched using non-magnet metal plates.

The nanoparticles were added to glass composites by two various methods.

In method 1 the nanoparticles were added to powder obtained from crushed and grinded borate-vanadate glass prepared before, mixed and then melted together and quenched as described above.

In method 2 the nanoparticles were added to the initial mixtures of calculated amounts of H_3BO_3 and vanadium oxide V_2O_5, then they were mixed, melted and quenched as described above.

XRD characterization of the synthesized composites

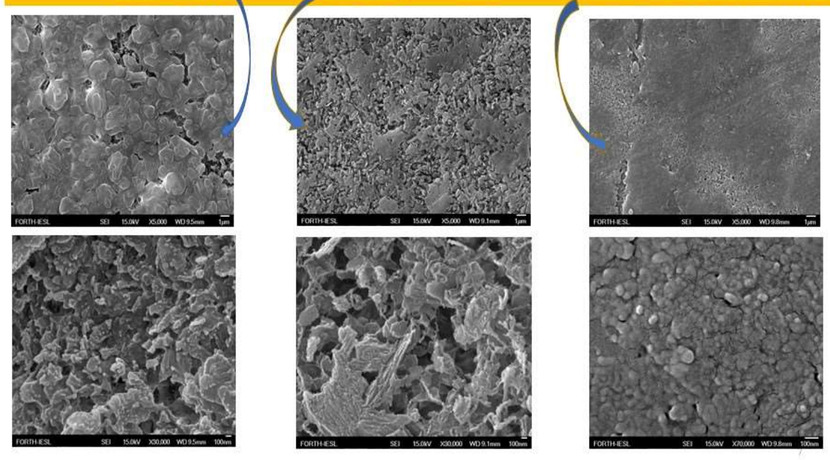


The XRD patterns of the $94B_2O_3$-$3V_2O_5$-$3La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$ composites made by methods 1 (1) and 2 (2)

The XRD patterns of the made samples contain broad bands around 20° and 40°, which clearly indicate that the samples are formed by borate and vanadate glass phases, respectively. The narrow peaks observed on the background of the broad bands are corresponded to the standard monoclinic structure of $LaVO_4$ (JCPDS PDF2 50-0367). Simultaneous manifestation of both glass and crystalline components in the XRD spectra confirms that we really have made borate-vanadate glass-ceramics.

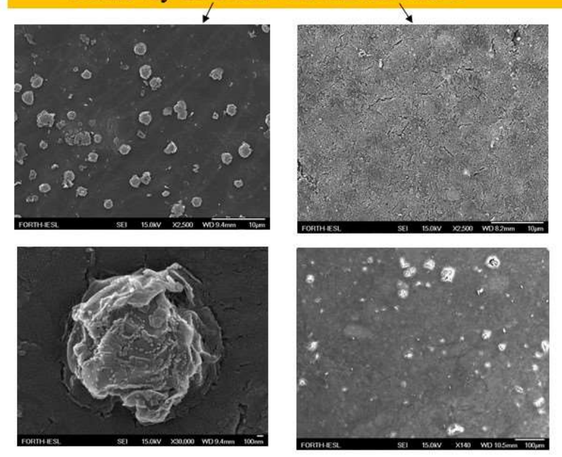
Morphology of the samples. Glass with various components concentrations

SEM images of the B_2O_3-V_2O_5 glass samples containing V_2O_5 oxide with 40, 25, and 4 mass % concentration



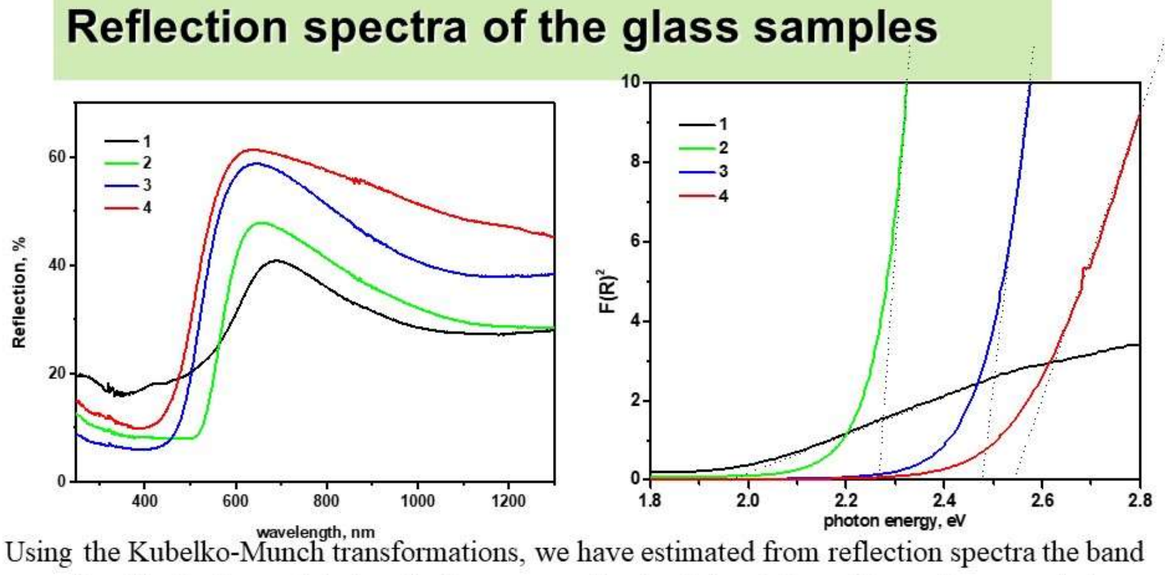
Morphology of the samples. Composites obtained by various methods

SEM images of the $94B_2O_3$-$3V_2O_5$-$3La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$ composites made by method 1 and method 2



In the sample synthesized by method 1, the vanadate nanoparticles are grouped together and arranged in separate islands.
The samples obtained by method 2 are characterized by homogeneous structure.
They do not have filamentous fragments and inclusions of another type. These samples are characterized by a granular structure sometimes with a low pore content. The grain sizes are about 20 nm.

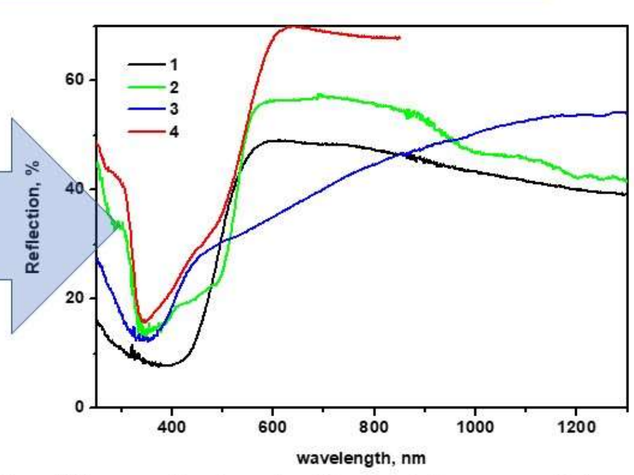
Reflection spectra of the glass samples



Using the Kubelko-Munch transformations, we have estimated from reflection spectra the band gap of synthesized vanadate-borate glass composites by determining of tangent versus photon energy to the F^2 curve, where $F = (1-R)^2/2R$, R is the reflection spectrum.
The obtained band gap values for glass containing 40, 25, 4 and 3% of vanadium oxide are 1.976, 2.265, 2.477 and 2.542 eV, respectively.
Therefore, we consider that samples with 4 and 3% of vanadium should be promising for optical applications. These concentrations of vanadium oxide were used for glass ceramic samples activated by vanadium nanoparticles.

Reflection spectra of the composites

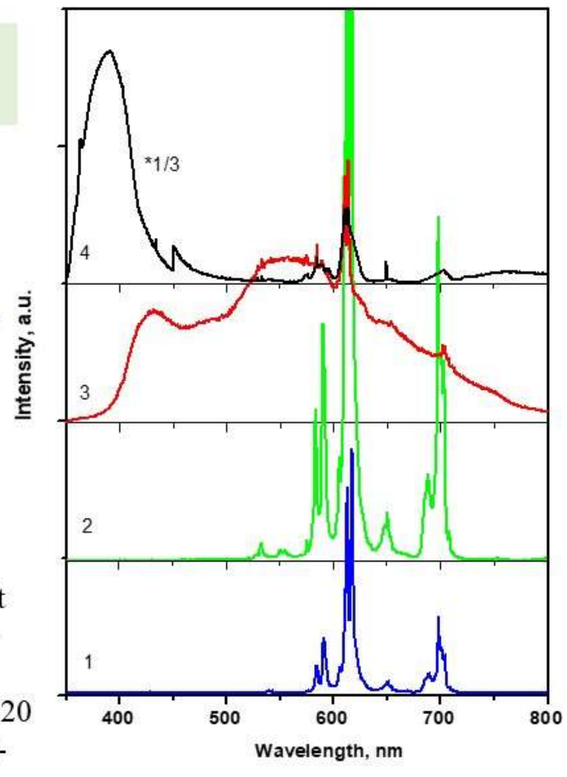
Reflection spectra of the the $94B_2O_3$-$3V_2O_5$-$3La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$ glass composites synthesized by method 1 (1) and method 2 (2); $90B_2O_3$-$3V_2O_5$-$3La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$-4ZnO glass composites synthesized by method 2 (3) and of the initial $La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$ nanoparticles



Described features of the reflection spectra of the samples doped with vanadate nanoparticles are related with the reported previously properties of vanadate nanoparticles those have been used for doping the synthesized composites.
In particular, the 340 and 475 nm bands in the reflection spectra of the glass composites doped with vanadate nanoparticles should be assigned to transitions in the VO_4^{3-} groups and Ca-induced defect centers in the $La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$ nanoparticles, respectively

Luminescence

Luminescence emission spectra of of the $94B_2O_3$-$3V_2O_5$-$3La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$ glass composites synthesized by method 1 (1) and method 2 (2); $90B_2O_3$-$3V_2O_5$-$3La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$-4ZnO glass composites synthesized by method 2 (3, 4) taken in two different points .



Luminescence emission of the B_2O_3-V_2O_5 glass composites at room temperature is very weak and it will not be considered here. Spectra of the $94B_2O_3$-$3V_2O_5$-$3La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$ glass composites are characterized by narrow spectral lines in the 580 -720 nm spectral range, those should be ascribed to well-known f-f electron transitions in the Eu^{3+} ions. Intensity of this emission is higher in 5 times for the samples synthesized by method 2.

Narrow line Eu^{3+} emission is strongly suppressed for the $90B_2O_3$-$3V_2O_5$-$3La_{0.8}Eu_{0.1}Ca_{0.1}VO_4$-4ZnO samples.

Conclusions

The vanadate-borate glass samples were synthesized by melt quenching method and investigated. The glass compositions with the best optical characteristics were additionally incorporated with luminescent vanadate nanoparticles. Simultaneous manifestations of both glass and crystalline components in the XRD patterns of the samples activated with vanadate nanoparticles have confirmed creation of vanadate-borate glass-ceramic materials.

Dependencies of band gap energy values on concentration of the vanadate and borate components are studied using Kubelko-Munk transformations. Luminescence properties of the synthesized samples are investigated. Spectra of the 94B2O3-3V2O5-3La0.8Eu0.1Ca0.1VO4 composites contain narrow spectral lines in the 580 -720 nm spectral range, those should be ascribed to well-known f-f electron transitions in the Eu3+ ions. Intensity of this emission is dependent on method of incorporation of luminescent nanoparticles in the glass basis. It is in 5 times higher for the samples synthesized with adding of luminescent nanoparticles to starting glass-forming components before glass synthesis comparing to the samples obtained by sintering of the synthesized glass and nanoparticles.

Influence of conditions of synthesis and optimal ratios of the components those allow obtaining of samples promising for practical applications as luminescent materials are discussed.

Acknowledgments

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