Energy transfer and luminescence properties of novel $Na_{3.6}Y_{1.8-x}(PO_4)_3:Dy^{3+}$ phosphor


Nataliya Krutyak[1,2*], Dmitry Spassky[2,3], Dina Deyneko[4], Vitali Nagirnyi[2]

* Corresponding author: krutyakn@yahoo.com

Motivation

Inorganic materials with intense luminescence are widely applied in lighting, security systems, medicine, high energy physics, etc. The requirements for their properties depend on the potential application and can differ significantly. However, for the overwhelming majority of phosphors a high light output and temperature stability of luminescence intensity are important. At present thermal quenching is still a main obstacle for phosphor applications in pcLEDs. Dy doped phosphors are attractive for such application because emission spectrum of Dy^{3+} consists of several narrow groups of lines, which covers visible spectral region. In recent years, an active search for novel materials with zero-thermal-quenching has been provided [*Y.H. Kim et al. // Nature Materials. – 2017. – Vol. 16. – 543-550*].

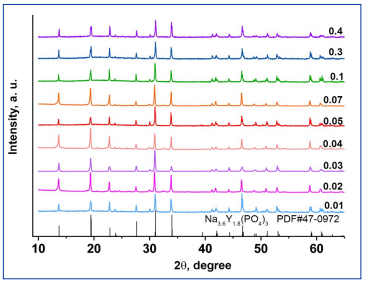
Here we present the results of the study of the luminescence properties of novel $Na_{3.6}Y_{1.8-x}(PO_4)_3:Dy^{3+}$ (NYP:*x*Dy) phosphor.

Experimental details

$Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy^{3+}$ (x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.1, 0.3, 0.4) series were synthesized by high-temperature solid-state route. Characterization of crystal structure has been performed using XRD technique. The Differential Scanning Calorimetry (DSC) was carried out in the temperature range of 273–873 K.

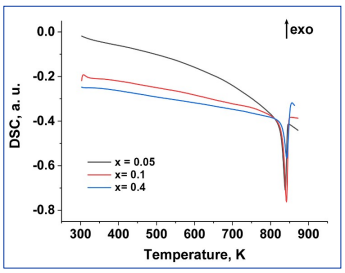
Luminescence excitation and emission spectra under excitation in the UV region were measured using a laboratory setup based on a LOT-Oriel MS-257 spectrograph in the temperature range 77–500 K. Spectra in VUV region were obtained using specialized setup with Shamrock 303i (Andor Technology) monochromator. An optical vacuum cryostat allowed measurements at T = 5–300 K.

Crystal structure



PXRD patterns for $Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy^{3+}$ with x = 0.01-0.4

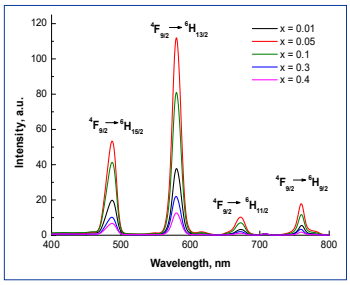
- The samples were single-phased and crystallized in a NASICON-type structure isostructural to $Na_3Sc_2(PO_4)_3$. Refined space group is $R\bar{3}c$.
- There is a maximum at x = 0.04 in the concentration dependence of the unit cell. It can be related to substitution Y^{3+} (r_{VI} = 0.90 Å) by Dy^{3+} (r_{VI} = 0.91 Å) ions. Decrease of the unit cell volumes at x > 0.04 is connected with a changing of the cationic ordering.



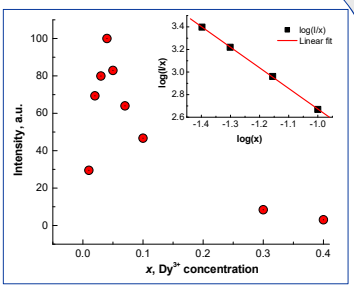
DSC curves for $Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy^{3+}$

- $Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy^{3+}$ undergoes reversible phase transitions. DSC curves reveal reproducible endothermic/exothermic effects for all samples.
- The ΔT hysteresis fluctuates within 1-10 °C and indicates a first-order phase-transition at ~840 K. The location of the peak is not significantly changing with x variations.

UV luminescence spectroscopy

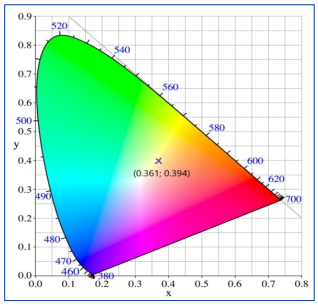


Luminescence spectra of $Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy^{3+}$ phosphates at T = 300 K, λ_{ex} = 350 nm



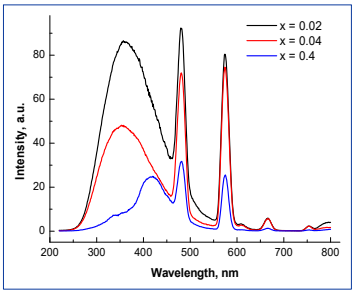
Emission intensity integrated in the spectral region 450-900 nm as a function of the Dy^{3+} content. Inset: log(I/x) to log(x) dependence and its linear fit

- The photoluminescence spectra of $Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy^{3+}$ under UV excitation demonstrate a typical set of Dy^{3+} emission bands corresponding to the intraconfigurational 4f–4f transitions in Dy^{3+} ions.
- The luminescence intensity reaches its maximum at x = 0.04. Decrease of luminescence intensity at x > 0.04 is due to concentration quenching. Linear fit of log(I/x) vs log(x) dependence allowed to determine that the concentration quenching in NYP:xDy^{3+} occurs due to the dipole-dipole interaction between neighbouring Dy^{3+} ions.
- The brightest sample with x = 0.04 is characterized by colour coordinates (0.361, 0.394) and the highest CCT value - 4629 K.

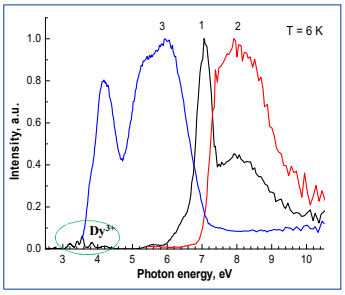


Chromaticity coordinates of the $Na_{3.6}Y_{1.76}(PO_4)_3:0.04Dy^{3+}$ phosphor

VUV luminescence spectroscopy



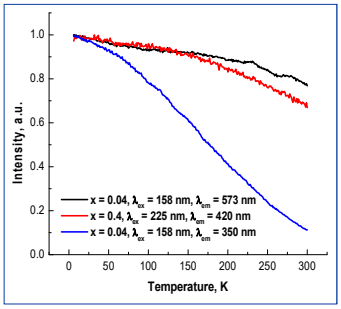
Luminescence spectra of $Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy^{3+}$ phosphors, E_{ex} = 7.85 eV (158 nm) and T = 6



Luminescence excitation spectra of $Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy^{3+}$ phosphors: 1 – x=0.05, λ_{em} = 580 nm; 2 – x=0.05, λ_{em} = 360 nm; 3 – x=0.4, λ_{em} = 420 nm

- Beside the group of narrow bands related to the Dy^{3+} emission, an additional broad non-elementary emission band at ~360 nm is observed. It appears under excitation in the VUV region with the excitation spectrum onset at E_{ex} = 7.1 eV. As this band is excited only at higher energies, it may represent an intrinsic luminescence of the phosphate host, most probably an exciton self-trapped at the PO_4^{3-} group. The appearance of a broad band at 8 eV in excitation spectrum of Dy^{3+} emission provides a strong argument in favour of excitation energy transfer from the host to activator ions.
- In samples with high concentrations of Dy^{3+}, the intrinsic emission is suppressed and the short-wavelength broad emission band is peaked at 420 nm. The excitation spectrum of this band is represented by non-elementary bands at 4.18 and 5.94 eV, i.e., in the transparency region of the crystal. It indicates that the band at 420 nm arises due to the defects of crystal structure.

Temperature dependence of luminescence



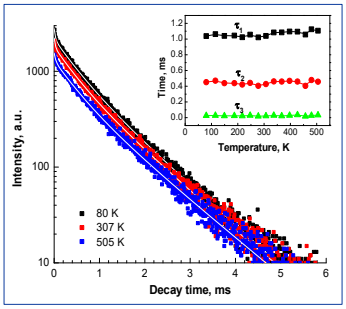
The temperature dependence of the $Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy$ emission intensity

- The temperature dependence of the intensity of the intrinsic emission (350 nm) demonstrates a strong thermal quenching (more than an order of magnitude).
- The intensity of the 420 nm emission from the defect-related center decreases only slightly.
- The intensity of the Dy^{3+} emission (580 nm) decreases by 23% under the interband excitation.
- The absence of thermal stability may be an obstacle for application of NYP:xDy phosphors in lighting.

- All decay curves were fitted by three exponential components using formula:

$$I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + A_3\exp(-t/\tau_3)$$

- The τ value was found to be 1.692 ms. Neither τ_1, τ_2, τ_3 nor τ depend on temperature. Intensity decrease of the Dy^{3+} emission with temperature is due to the decrease of the amplitude values rather than to the reduction of the decay times.
- So the thermal quenching of the Dy^{3+} emission can be connected with excitation energy transfer from non-relaxed excited states of Dy^{3+} to some killer states.



Decay curves of $Na_{3.6}Y_{1.75}(PO_4)_3:0.05Dy^{3+}$, λ_{ex} = 350 nm, λ_{em} = 580 nm. Inset: temperature dependence of decay components τ_1, τ_2, and τ_3

Conclusions

1. A series of $Na_{3.6}Y_{1.8-x}(PO_4)_3:xDy$ (x = 0.01–0.4) phosphors was synthesized by high-temperature solid-state method for the first time. PXRD study reveals that continuous solid solution with NASICON-type structure forms at $0 \le x \le 0.4$.
2. Luminescence properties of the phosphors were studied using the methods of UV and VUV spectroscopy. Narrow emission bands originating from intraconfigurational transitions in Dy^{3+} were detected and optimal concentration of the dopant determined. The concentration quenching of Dy^{3+} emission is shown to be due to dipole-dipole interaction.
3. Two broad bands were detected in the UV and blue spectral regions, which were ascribed to the intrinsic emission of self-trapped excitons and defect-related centers, respectively. Optical bandgap energy of $Na_{3.6}Y_{1.8}(PO_4)_3$ was estimated to E_g ~ 7.1 eV. Influence of temperature on luminescence characteristics was studied.

[1]Physical Department, M.V. Lomonosov Moscow State University, Russia
[2]Institute of Physics, University of Tartu, Estonia
[3]Skobeltsyn Institute of Nuclear Physics, M.V. Lomonosov Moscow State University, Russia
[4]Chemistry Department, M.V. Lomonosov Moscow State University, Russia

The research was performed within the project MOBJD613