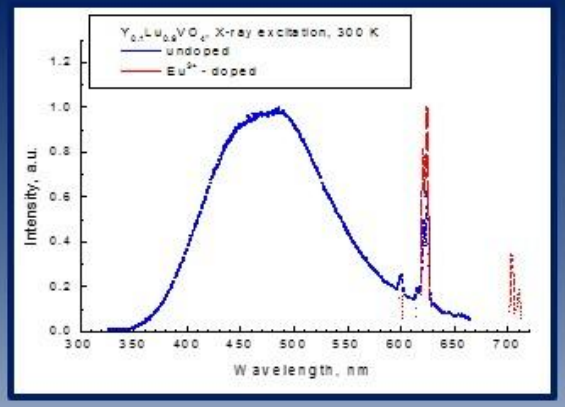
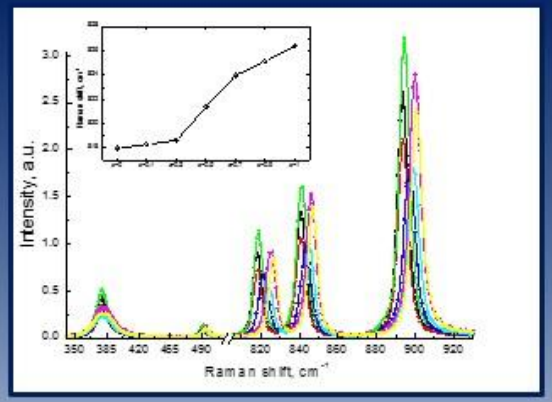
Structural and luminescence properties of vanadates mixed crystal





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Outline

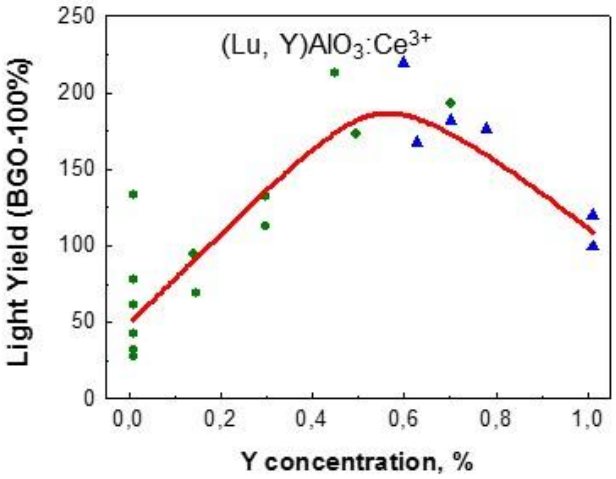
- Motivation
- Crystal structure: - XRD
  - Raman analysis
- Radioluminescence
- Temperature dependencies (TD) of luminescence
- Excitation spectra
- Conclusions

Motivation: mixed crystals

Subject of study: vanadates mixed crystals $Lu_xY_{1-x}VO_4$ undoped and doped with Eu^{3+}

Properties:

Development of mixed crystals based on YVO_4 can improve their luminescent properties due to a non-linear effect of increase of efficiency of excitation energy conversion into luminescence, which also leads to an increase of the scintillation light yield



Solid state method:

$Y_2O_3 + V_2O_5 +$ → Lu_2O_3 → $Lu_xY_{1-x}VO_4$ (1)

$Y_2O_3 + V_2O_5 +$ → $Lu_2O_3 + Eu_2O_3$ → $Lu_xY_{1-x}VO_4:Eu^{3+}$ (2)

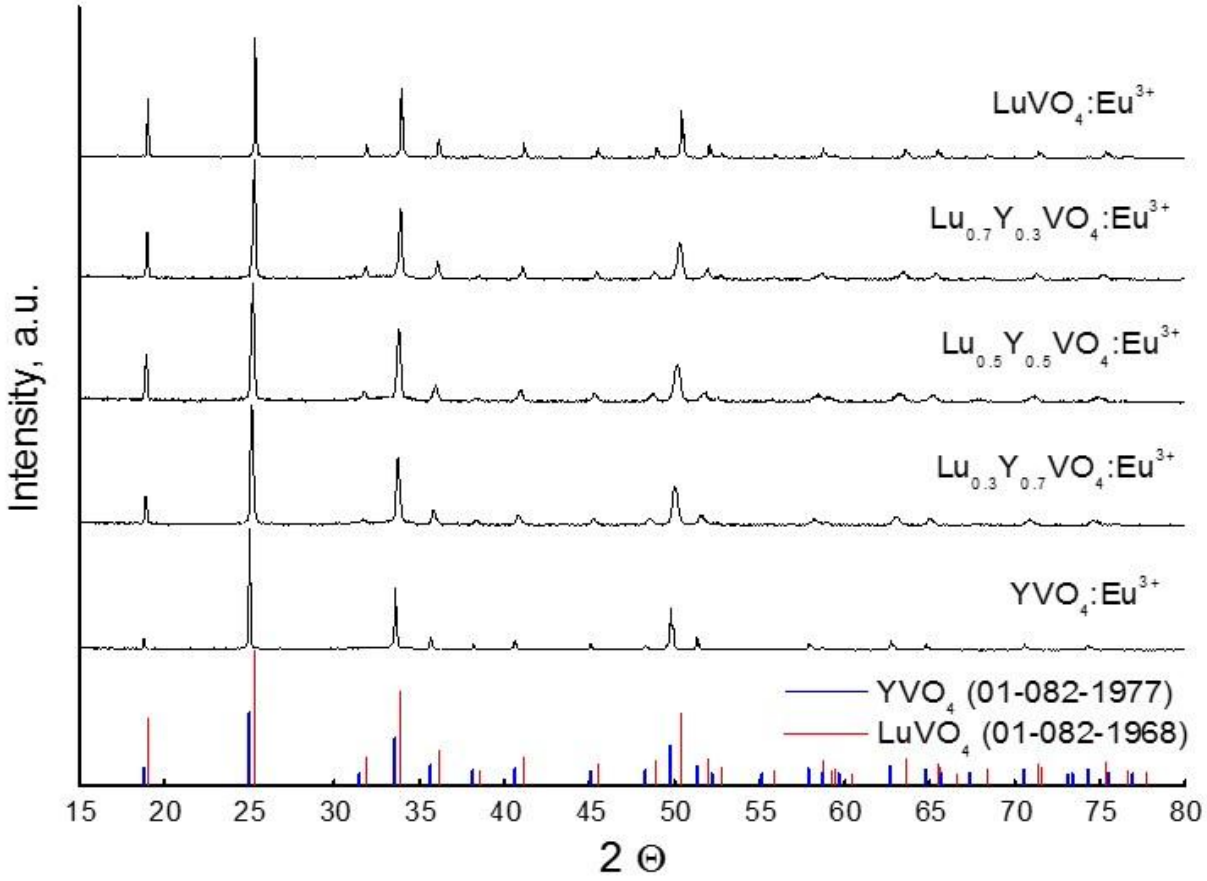
Annealing:

(i) three times at 1000 °C, 1000 °C and 1200 °C for 2 hours with intermediate grindings

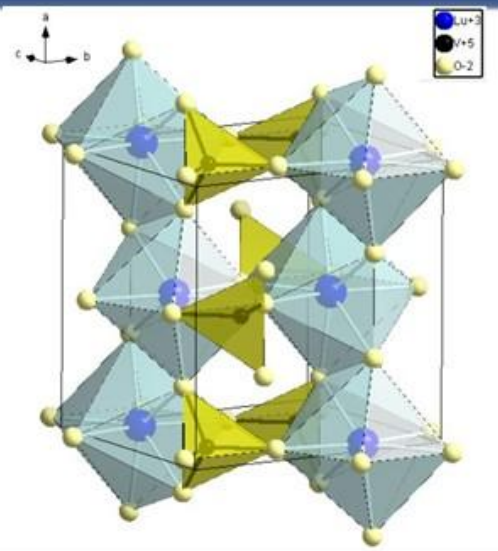
(ii) only once at 1200°C for 2 hours.

(x=0, 0.1, 0.3, 0.5, 0.7, 0.9, 1)

XRD analysis: $Lu_xY_{1-x}VO_4:Eu^{3+}$

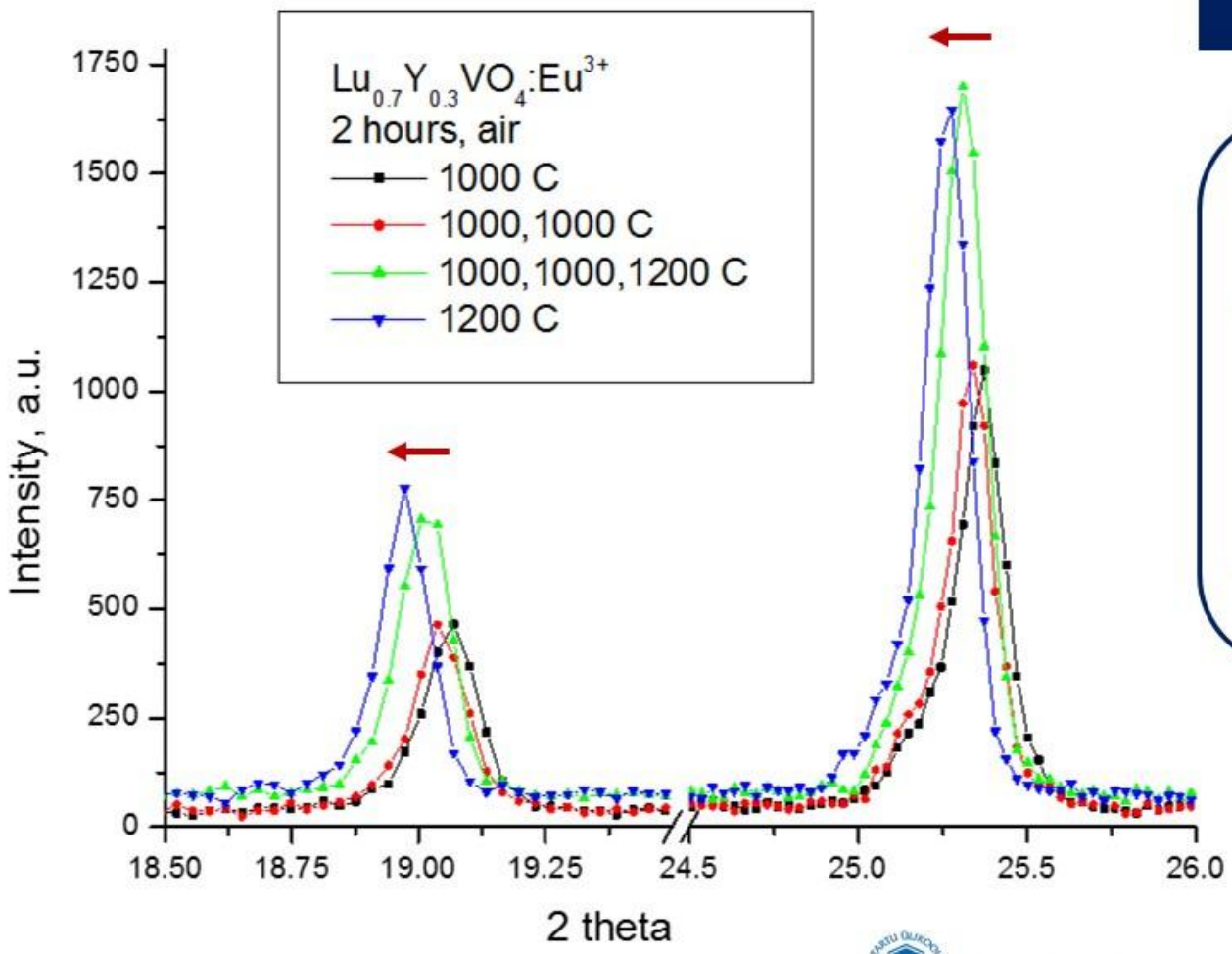


XRD patterns of the $Lu_xY_{1-x}VO_4:Eu^{3+}$ after 1000 °C, 1000 °C , 2 hours, air.



- Tetragonal zircon structure (space group symmetry I41/amd)
- Diffraction lines have shifted due to different radii of the Lu^{3+} (0.98 nm) and Y^{3+} (1.02 nm).
- Doping by 1wt%:Eu^{3+} does not create extra phase

XRD analysis: $Lu_xY_{1-x}VO_4:Eu^{3+}$



After each subsequent annealing (**1000, 1000, 1200 °C**):

- crystal structure does not change
- intensity of the diffraction line increases after annealing at 1200 °C → **crystallinity's enhancement**
- XRD peaks shift → **change of lattice parameters**

Lattice parameters

Position of XRD peaks

+

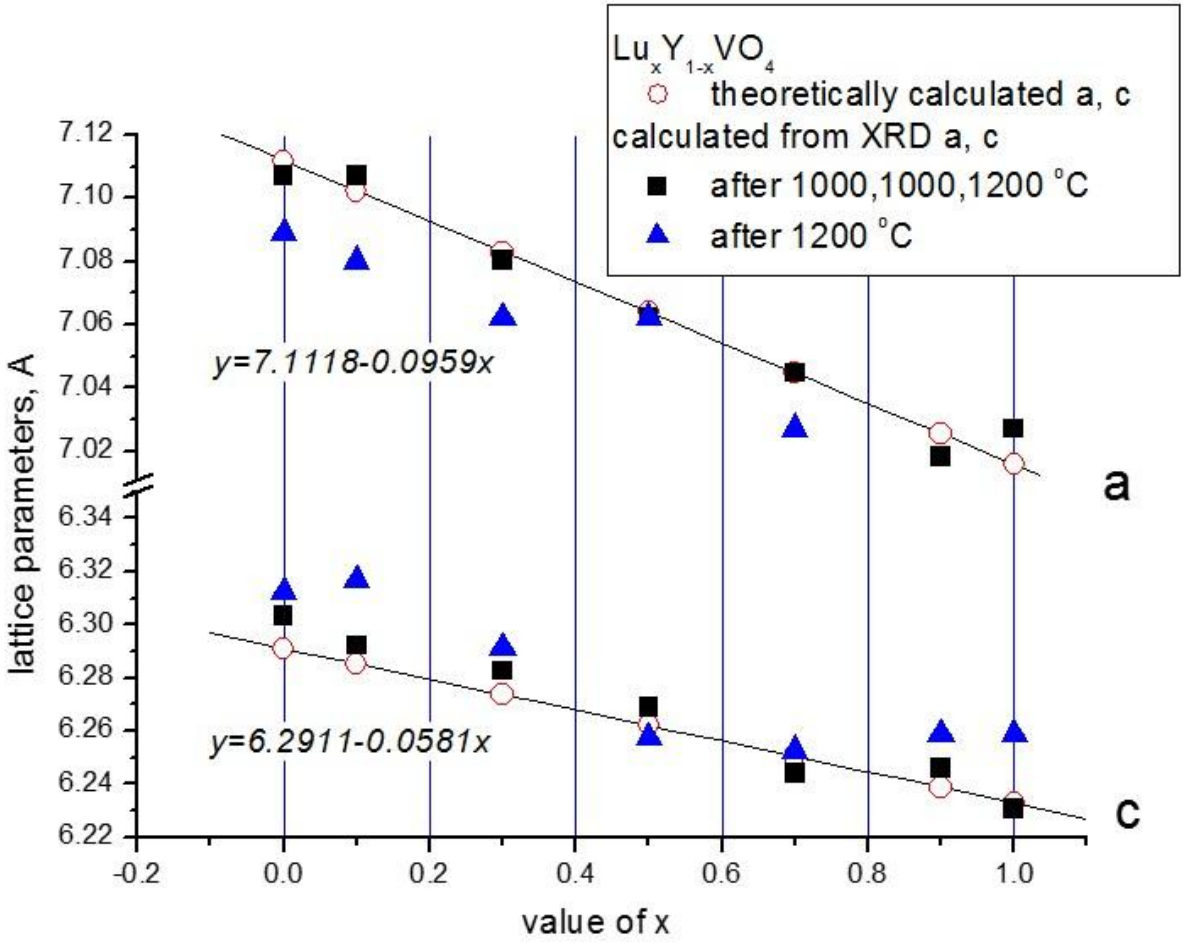
Bragg's Law

$$\lambda = 2d\sin\theta$$

+

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

h,k,l - Miller indices



$$a = 2.13634\ (R_m + R_o) + 0.12351\ (\chi_o - \chi_m) + 0.75521$$

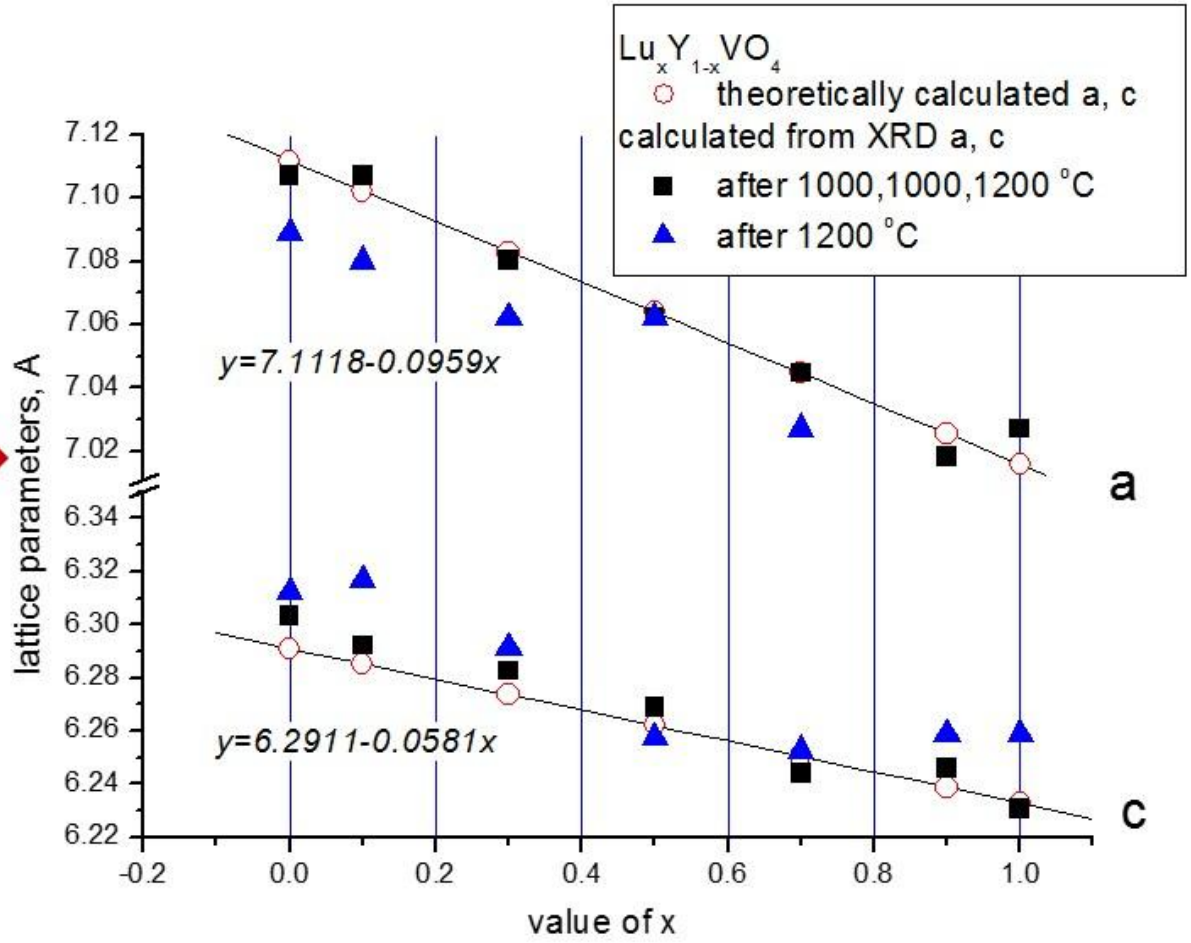
$$c = 1.49644\ (R_m + R_o) - 0.09442\ (\chi_o - \chi_m) + 2.94073$$

$$R_m = xR_{Lu} + (1-x)R_Y$$

$$\chi_m = x\,\chi_{Lu} + (1-x)\,\chi_Y$$

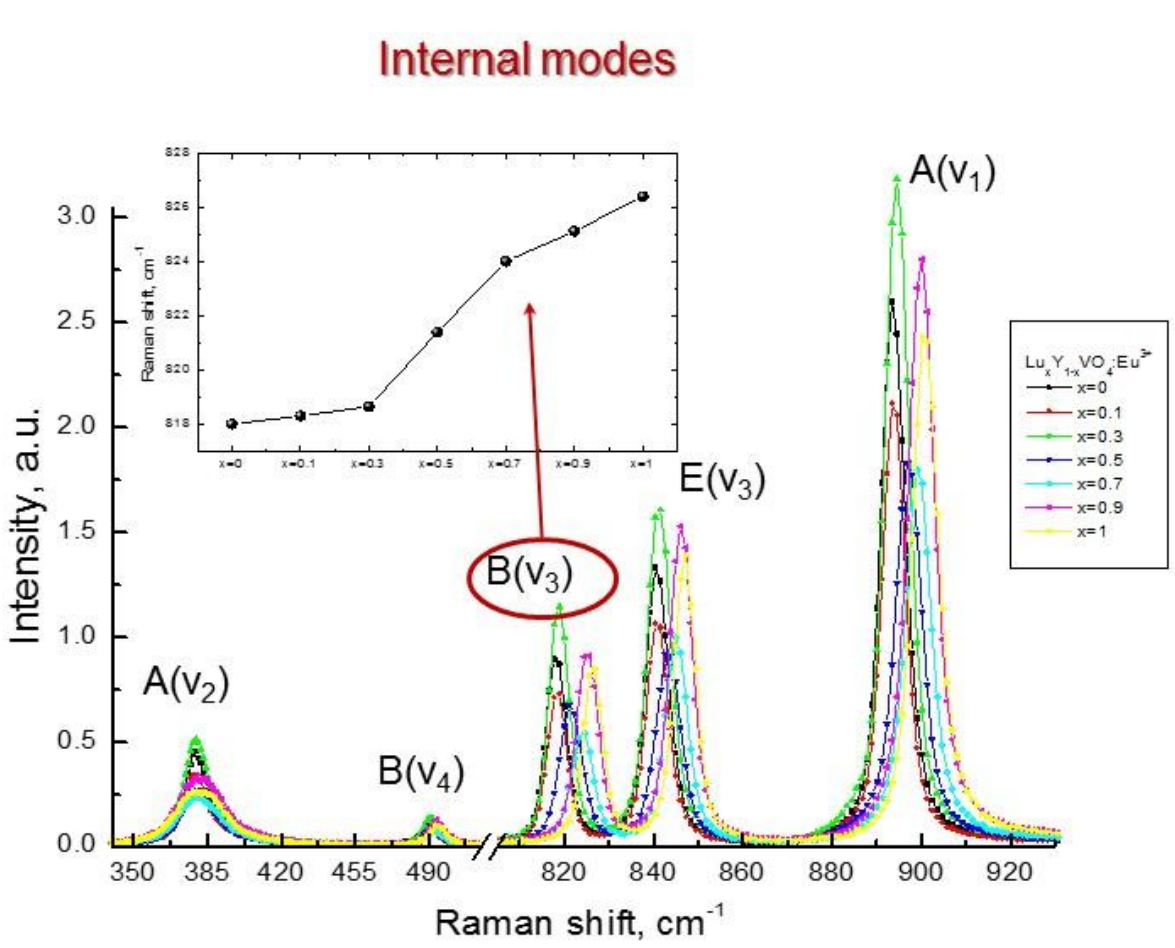
χ - electronegativity

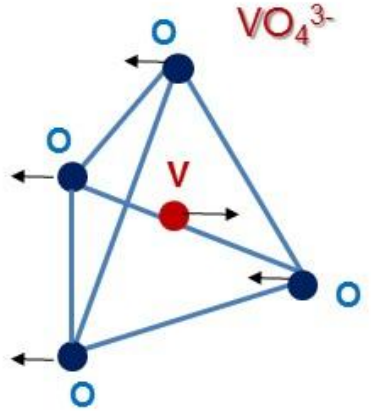
R - ionic radius



M.G. Brik, M.Bettinelli , E.Cavalli, J. Sol. St. Chem. 230 (2015) 49–55

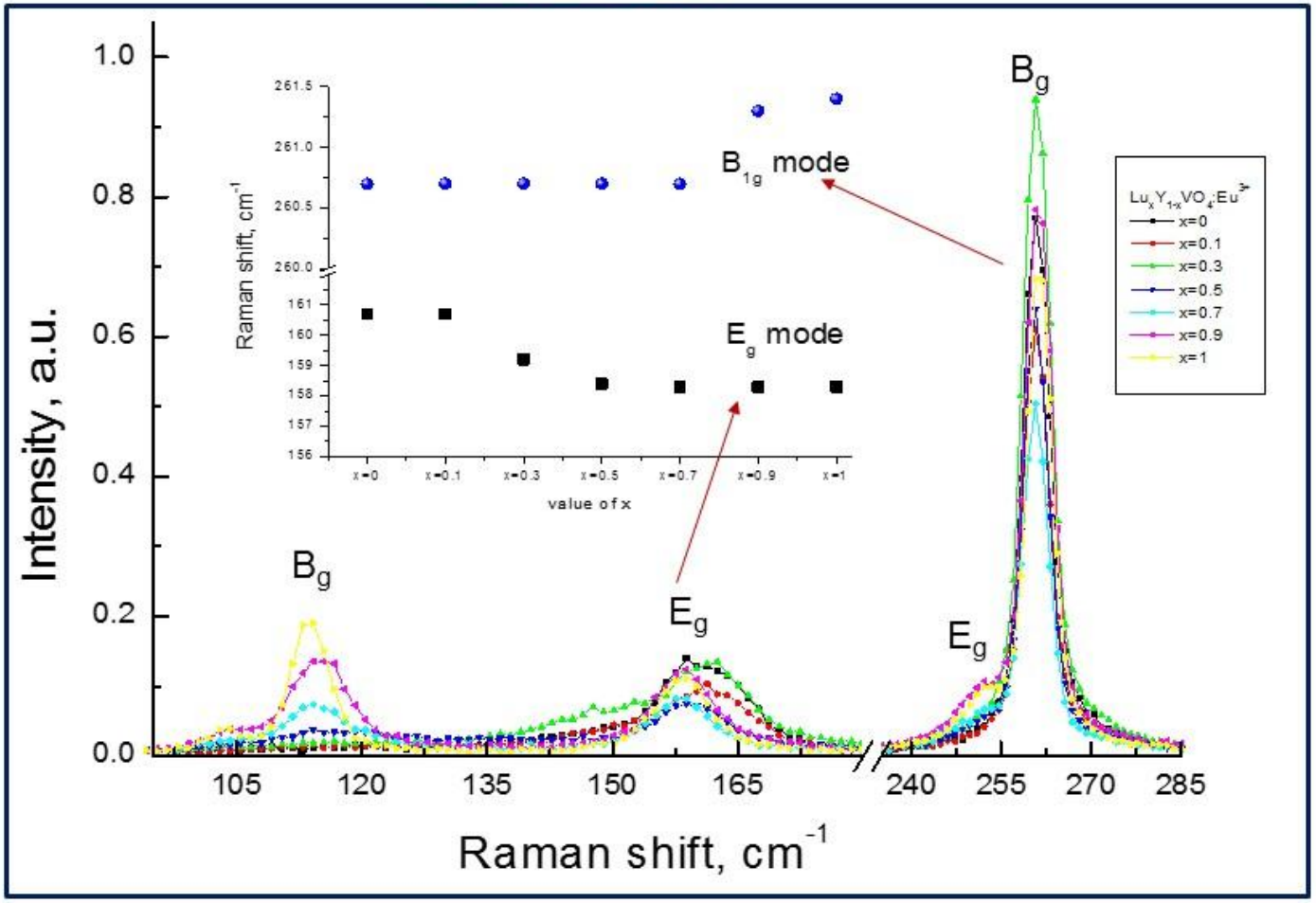
Raman analysis

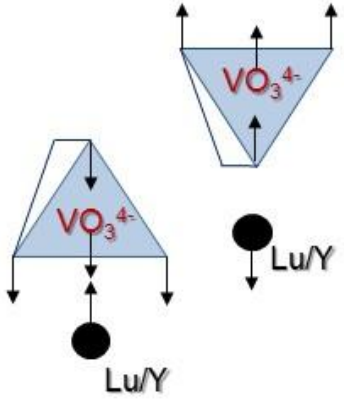




- Raman-active modes confirm tetragonal D_{4h} structure
- The increase of frequencies of internal modes is due to increasing crystal field effect on the VO_4 tetrahedron, as a result of the replacement of Y by Lu.

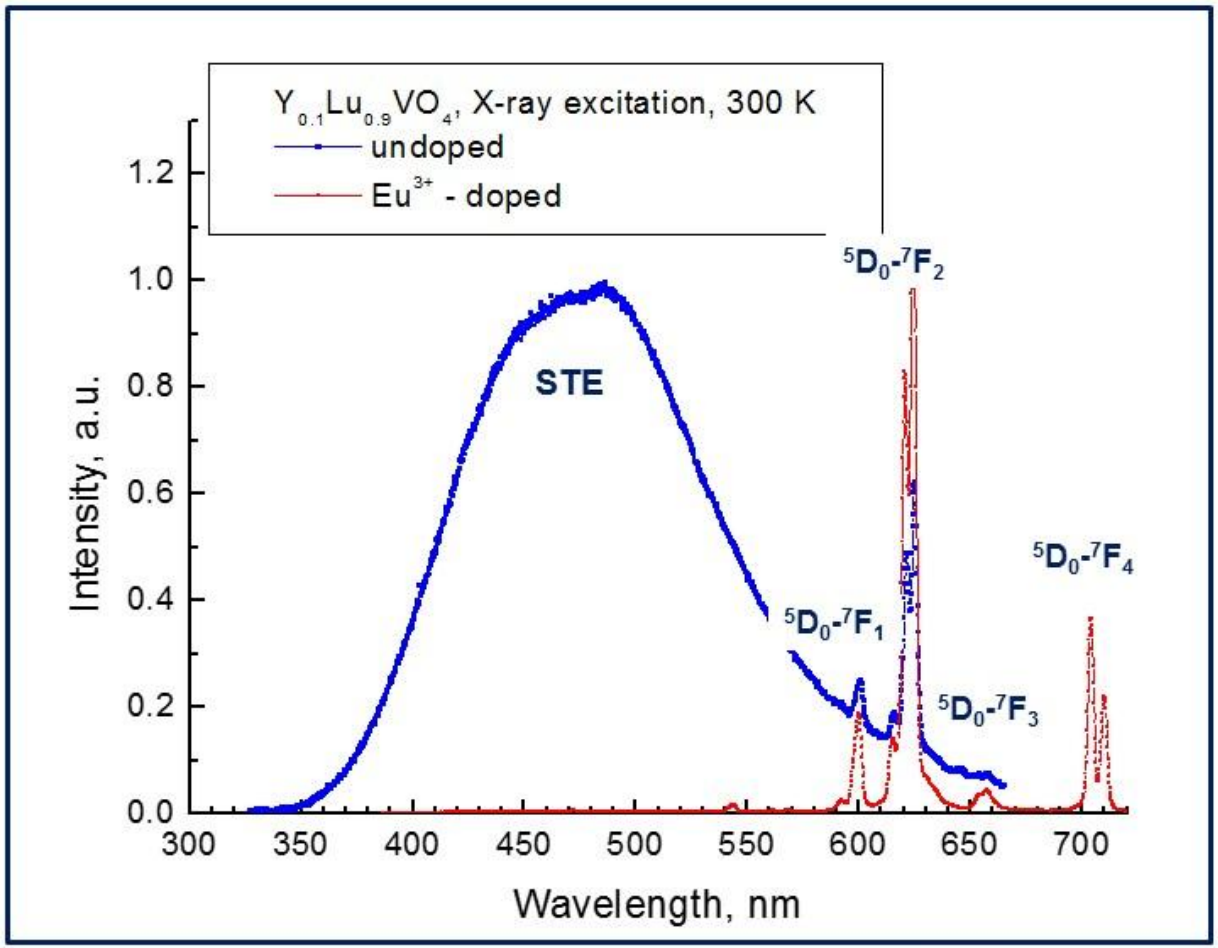
External modes





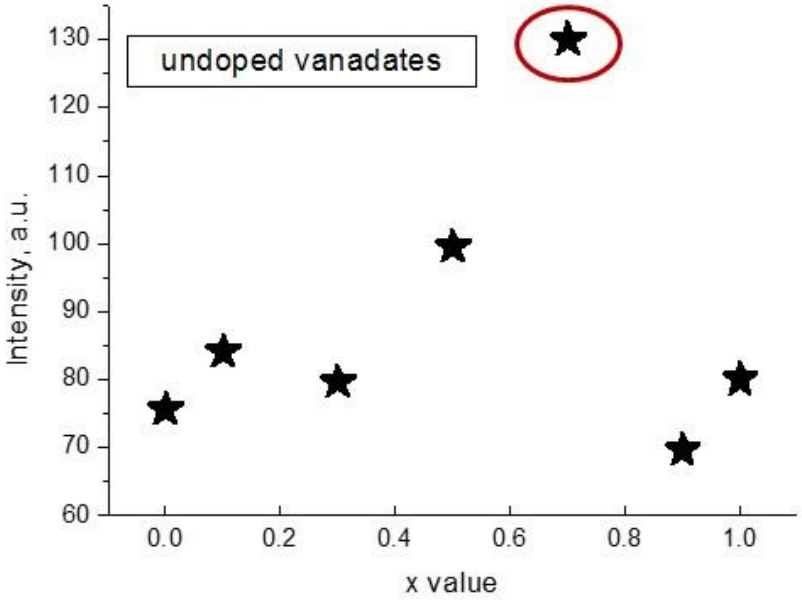
- External modes (translation and rotation) involve both Lu/Y and VO_4 ions.
- Modes around 252 cm^{-1} (E_g) and 115 cm^{-1} (B_g) are probably related to Y motion.

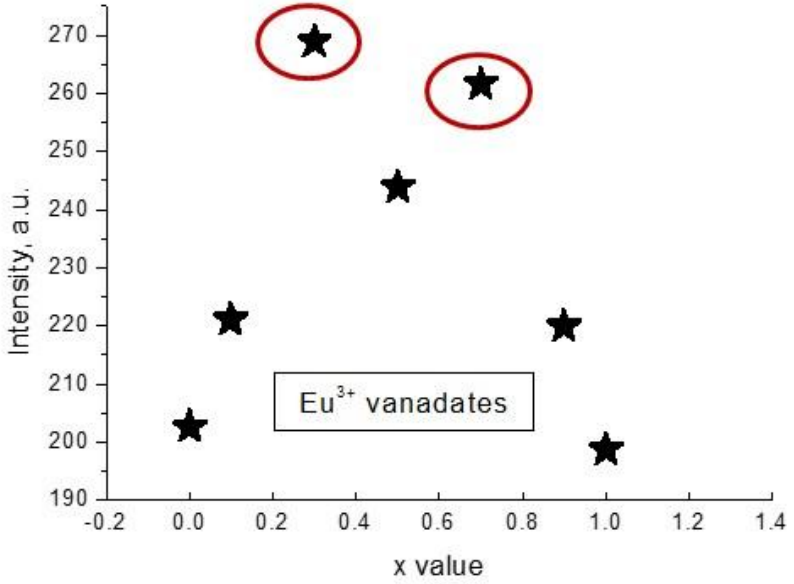
Luminescence of the mixed vanadates



- Single emission band at 485 nm is attributed to STE. Traces of contaminating Eu^{3+} ions in luminescence are observed as well.
- Only emission of Eu^{3+} is observed in doped vanadates.
- Intrinsic emission in doped vanadates is quenched at room temperature.

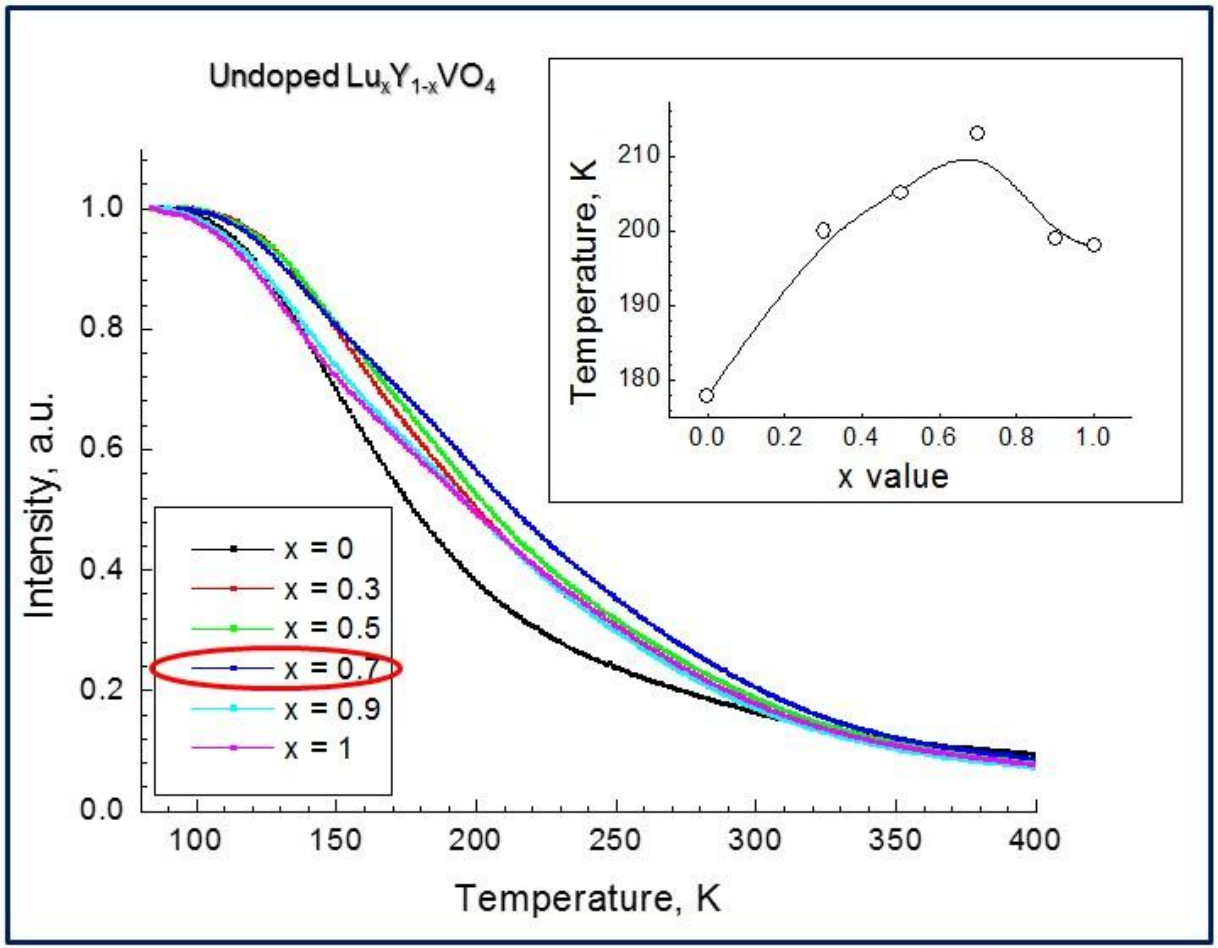
Relative intensity of radioluminescence





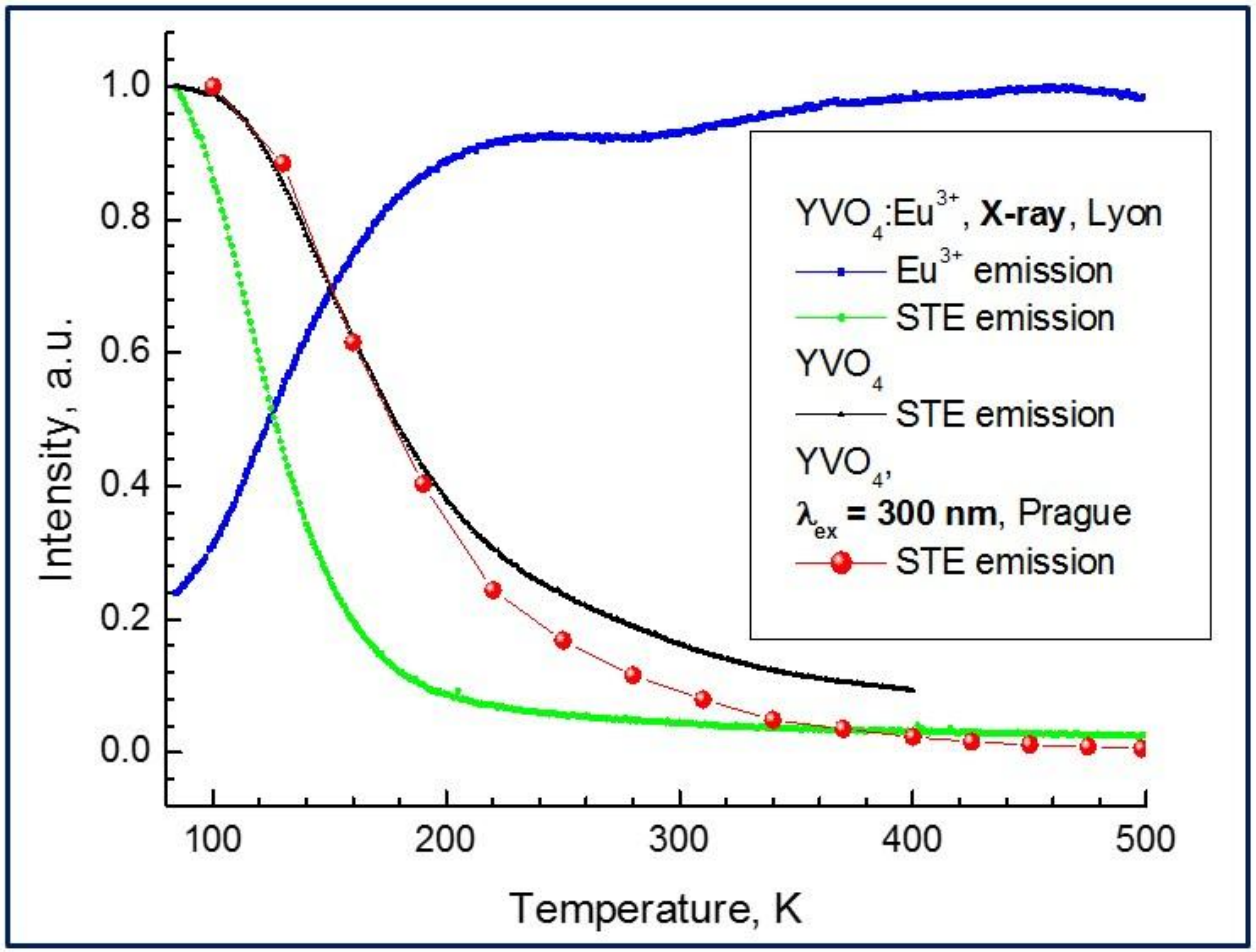
- Considerable influence of STE thermal quenching at T = 300 K does not allow to estimate dependence of the modification of light yield on the thermalization length for the undoped mixed vanadates. The most intensive emission is observed for x = 0.7 and is connected with less quenched emission in this crystal.
- For the doped mixed vanadates the emission is not quenched and the considerable enhancement of luminescence intensity is observed for the intermediate values of x.

Temperature dependence of luminescence



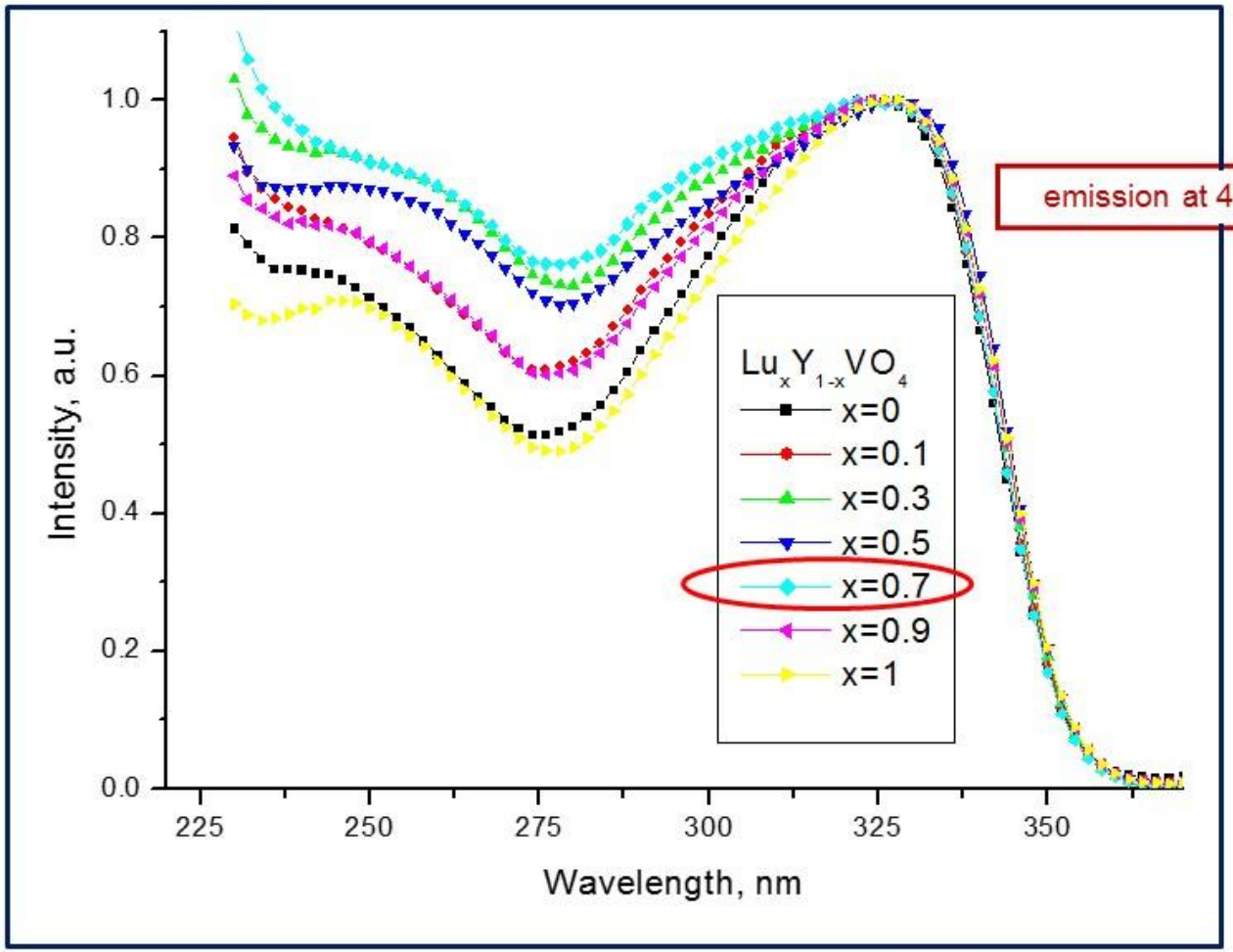
- Enhancement of the thermal stability of STE in the mixed crystals is observed (see the inset for quenching temperature dependence)
- Decrease of thermalization length explains the observed tendency

Temperature dependence of luminescence



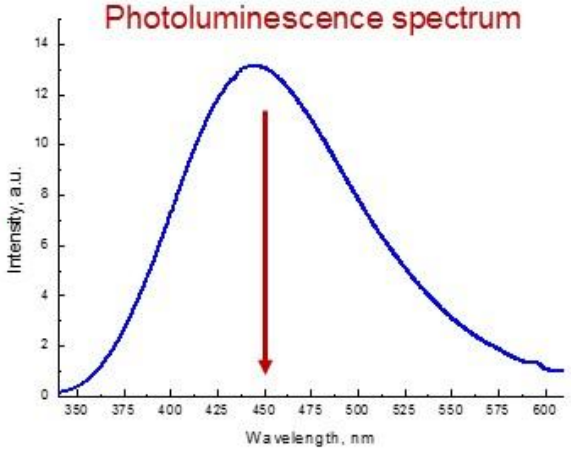
- At T = 300 K the STE luminescence is partially quenched
- Thermal quenching may be connected with:
  - Non-radiative transitions within emission center (STE non-radiative relaxation)
  - Exciton migration to non-radiative center (defect, impurity)
  - Non radiative relaxation of separated e-h pairs
- The presented result demonstrates that at T > 100 K excitons migrate in the crystal and can be captured by Eu^{3+} ions

Excitation photoluminescence spectra



emission at 450 nm

Photoluminescence spectrum



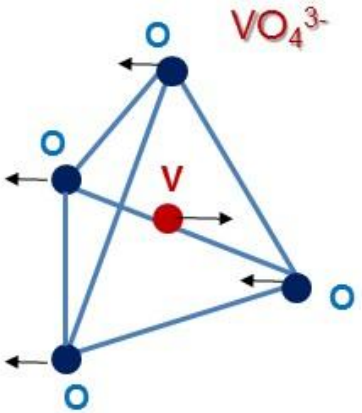
Efficiency of energy transfer to luminescence centers increases for mixed crystals (in the energy range of e-h pairs' creation).

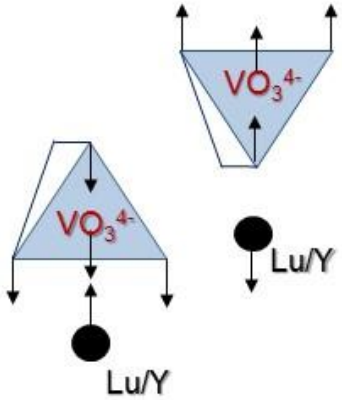
Decrease of thermalization length explains the observed tendency

Conclusions

- Lattice parameters of the $Lu_xY_{1-x}VO_4$ mixed crystals, which were annealed 3 times at 1000 °C, 1000 °C, and 1200 °C, are close to calculated ones.
- XRD and Raman spectroscopy have confirmed tetragonal D_{4h} structure of the vanadates mixed crystals.
- For the Eu^{3+} doped mixed vanadates considerable enhancement of luminescence intensity is observed for the intermediate values of x at 300 K. In the undoped crystals the relative luminescence intensity at 300 K is determined by thermal quenching.
- Proposed decrease of the thermalization length in the undoped mixed vanadates reveals itself in the enhancement of thermal stability of STEs and in the increase of STE creation probability from separated e-h pairs in the excitation spectra.

Thank you for attention!





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