TARTU ÜLIKOOL
FÜÜSIKA INSTITUUT

LUMINET

MARIE CURIE ACTIONS

Spectroscopic study of complex oxides solid solution $Lu_xY_{1-x}PO_4:Ce^{3+}$

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ESR conference, 18.09.2014, Augsburg

Properties of phosphates

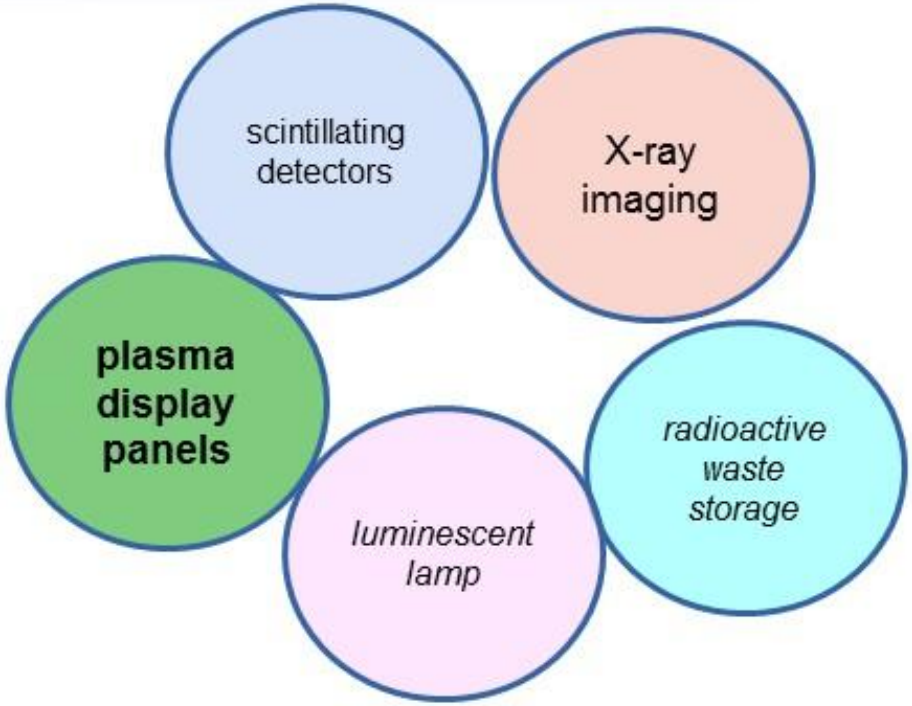
- high thermal stability
- no phase transitions till the melting temperature (*T*m = 2150 C)
- high chemical stability
- a remarkable resistance to radiation damage

+

the luminescence properties of phosphates doped with rare-earth elements

the broad range of applications

Potential application



Properties of solid solution

- A solid solutions may have properties that differ from properties of its components.

- In solid solution of metals increase of resistivity has been observed. This effect is ascribed to the clusterisation.

Clusterisation - a local regulation of the solid solution with creation of the areas with primary content of one of the components.

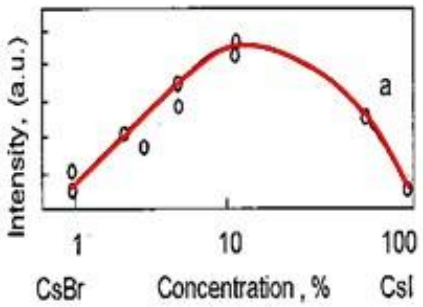
Clusterization of solid solutions

In solid solutions the clusters may appear, which **limits the thermalization length** of hot electrons and holes and therefore influences the energy transfer to the emission centers.

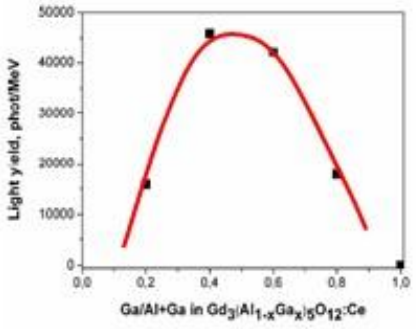
The increase of the light yield

Superior light yield

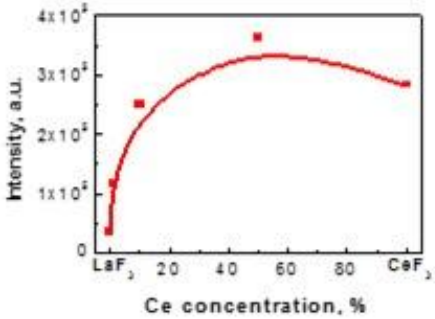
CsI-CsBr



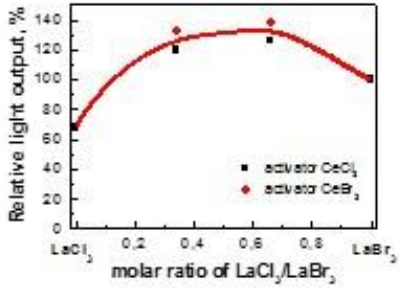
$Gd_2(Al_xGa_{1-x})_5O_{12}$:Ce



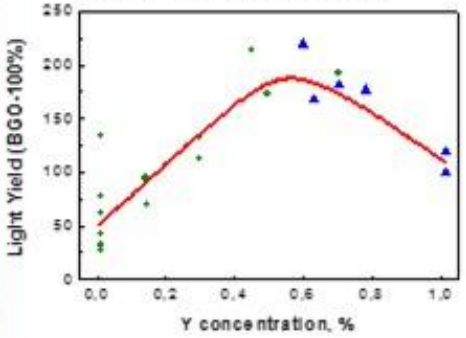
$Ce_xLa_{1-x}F_3$



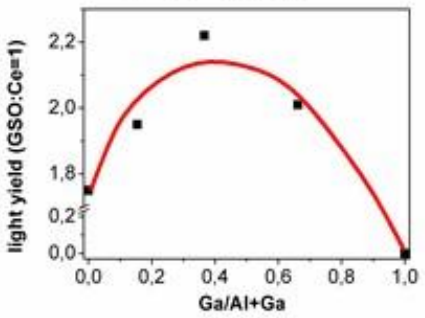
$LaCl_3$-$LaBr_3$



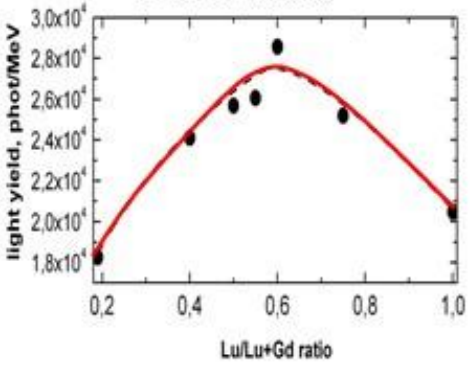
$(Lu, Y)AlO_3$: Ce



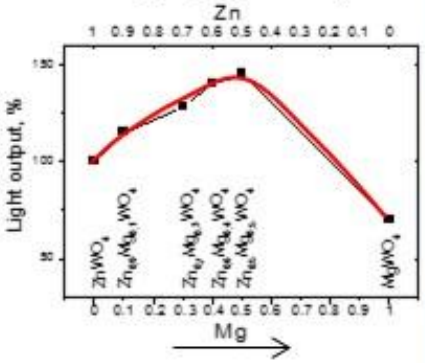
YAGG:Ce



LGSO:Ce



$Zn_xMg_{1-x}WO_4$



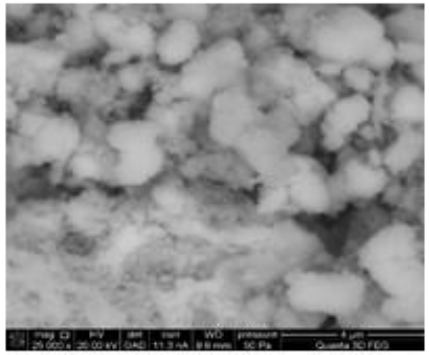
A. Belsky, A. Gektin, A. Vasil'ev, IEEE Trans.Nucl. Sci., vol.61, no.1, pp.262-270, 2014

Aim of research

the spectroscopic investigation of a set of the $Lu_xY_{1-x}PO_4$ (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1) phosphates solid solutions doped with 0,5 mol % Ce^{3+}.

Special attention was paid to the processes of energy transfer to the emission centers in the studied compounds.

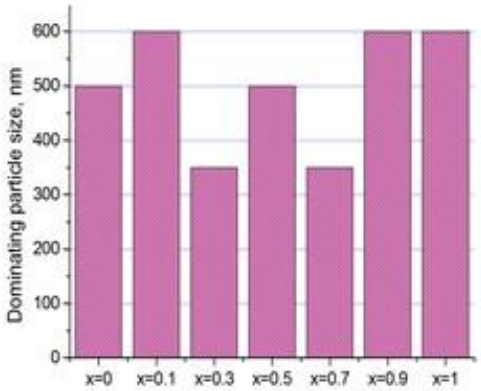
Synthesis and crystal structure



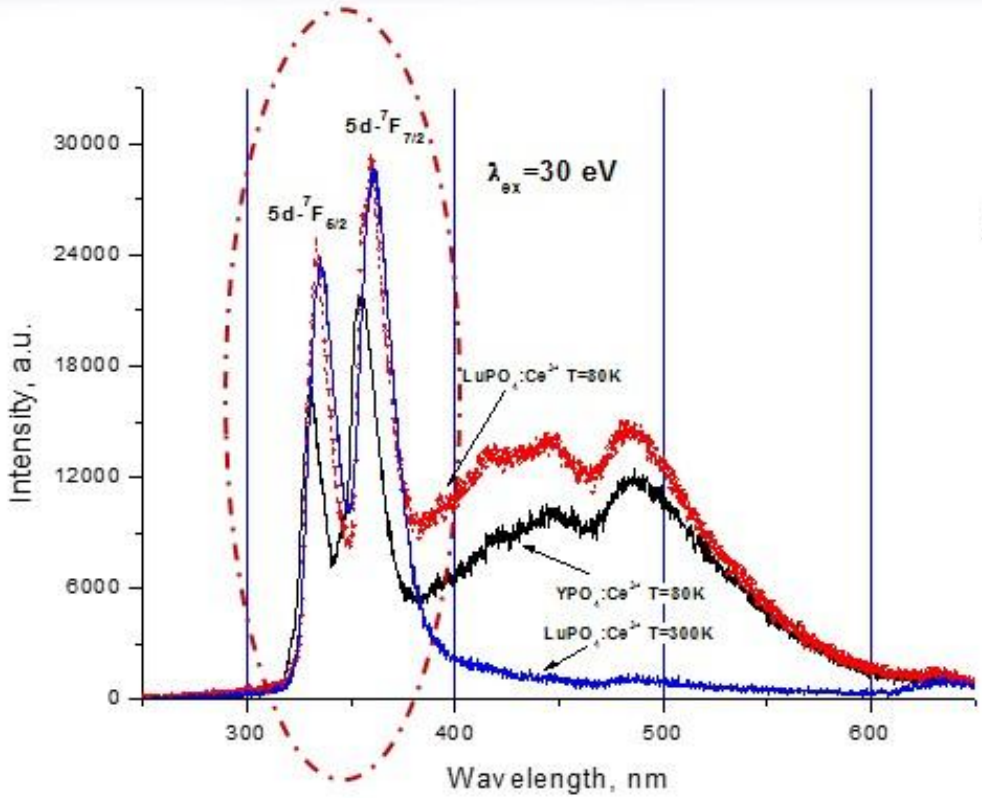
The luminescence properties of a series of phosphate solid solutions with general formula $\mathbf{Lu_xY_{1-x}PO_4}$ were studied (**x** = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1) doped with 0.5 mol % Ce^{3+}.

The samples were synthesized by the **sol-gel method**.

According to the data of the **grain-size analysis,** the dominating size of the particles of all compositions is around **350-600 nm.**

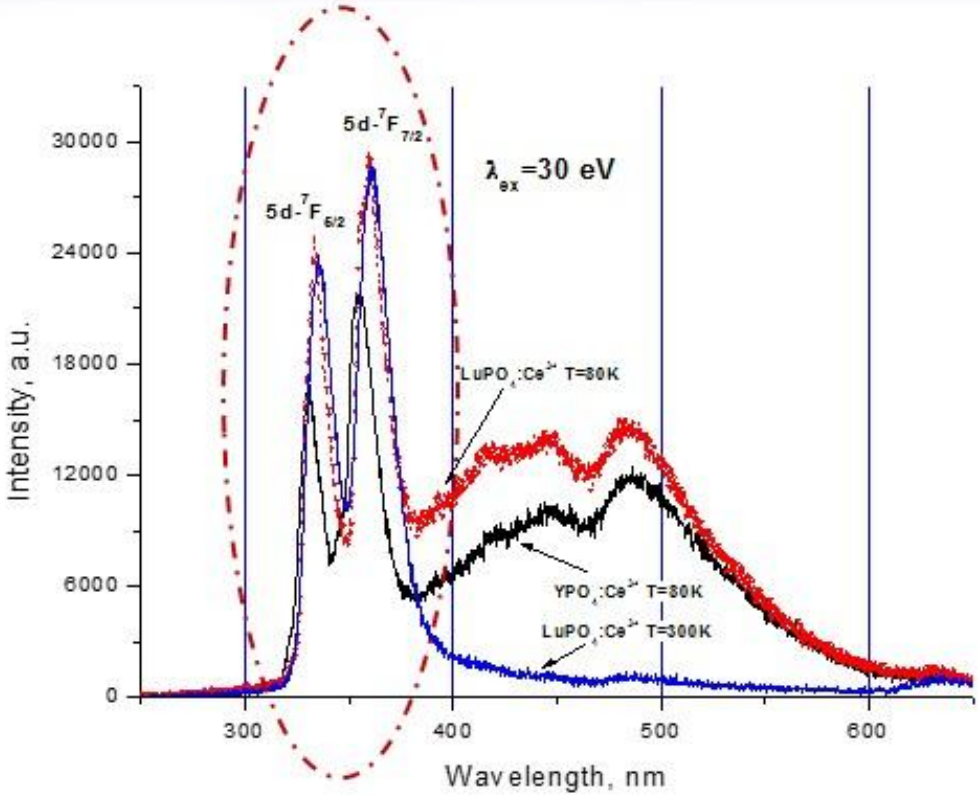


The luminescence spectra



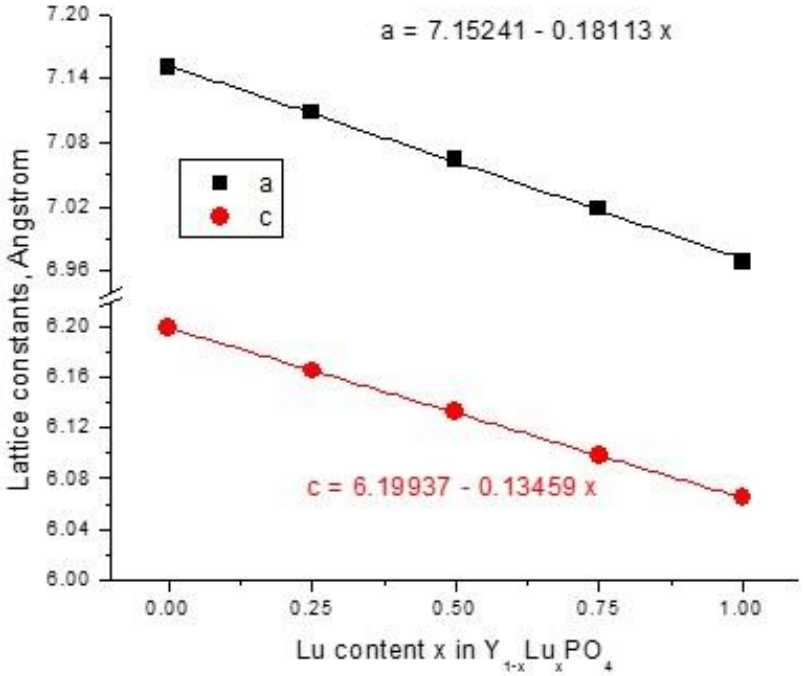
- the pronounced doublet peaking at 335 and 360 nm, which is connected with the 5d-4f transitions of the Ce^{3+} ion

The luminescence spectra



With increase of x:

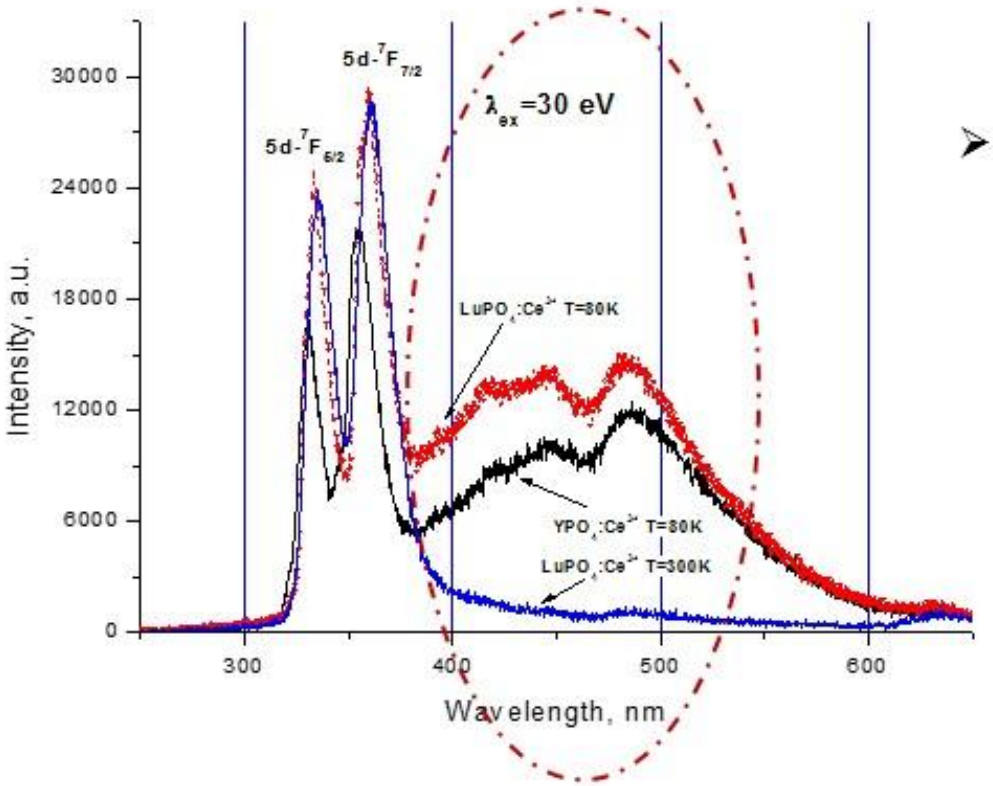
Calculated lattice constants



peaks shift to the longer wavelength region → crystal field strength increases

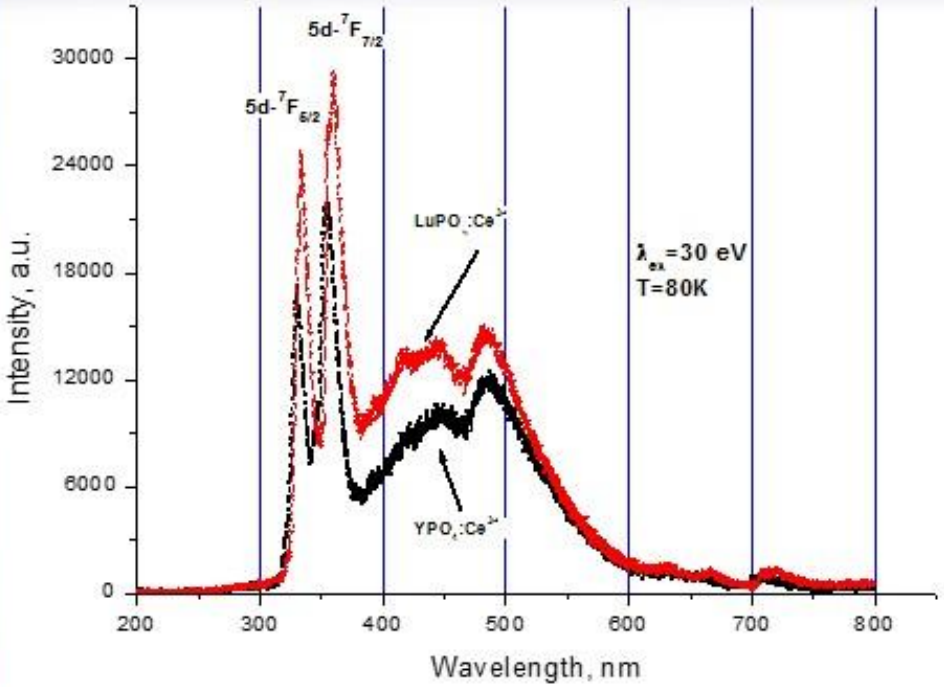
→ the unit cell decreases

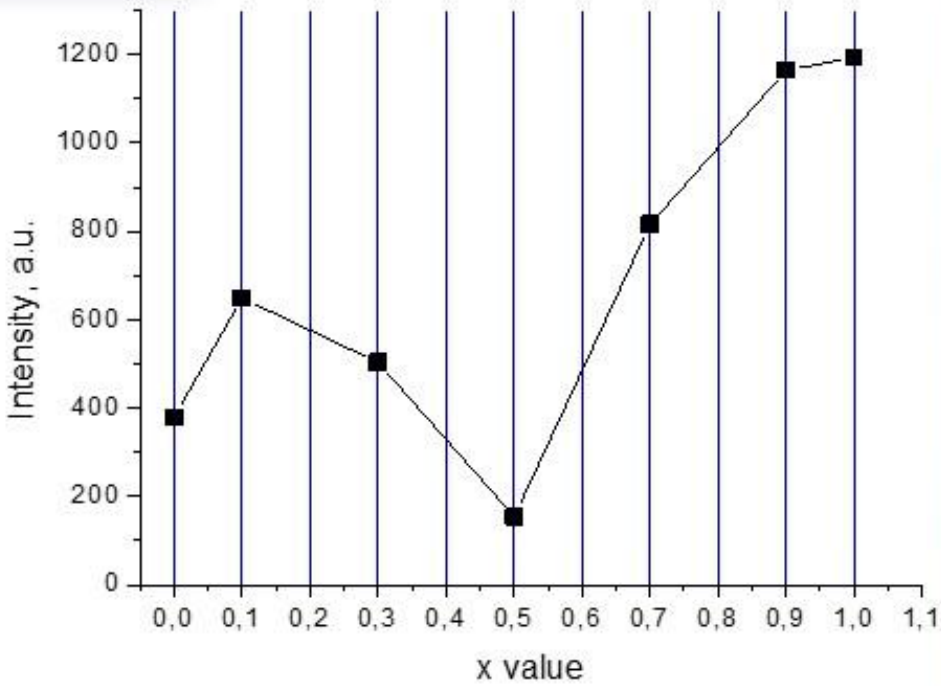
The luminescence spectra



- at T=80K two broad bands detected in the 385 - 600 nm range, which are associated with the defect-related emission.

The luminescence spectra

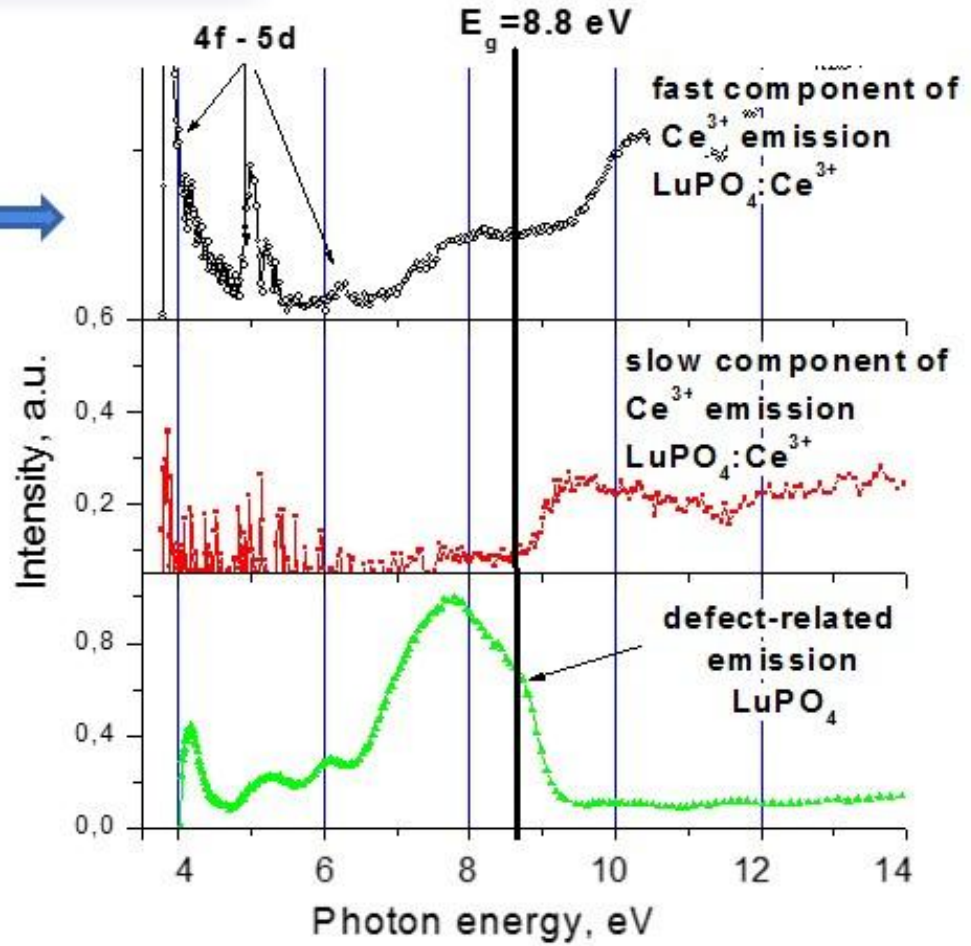




The decrease of the emission intensity for intermediate values of x (opposite effect to the expected one) was detected .

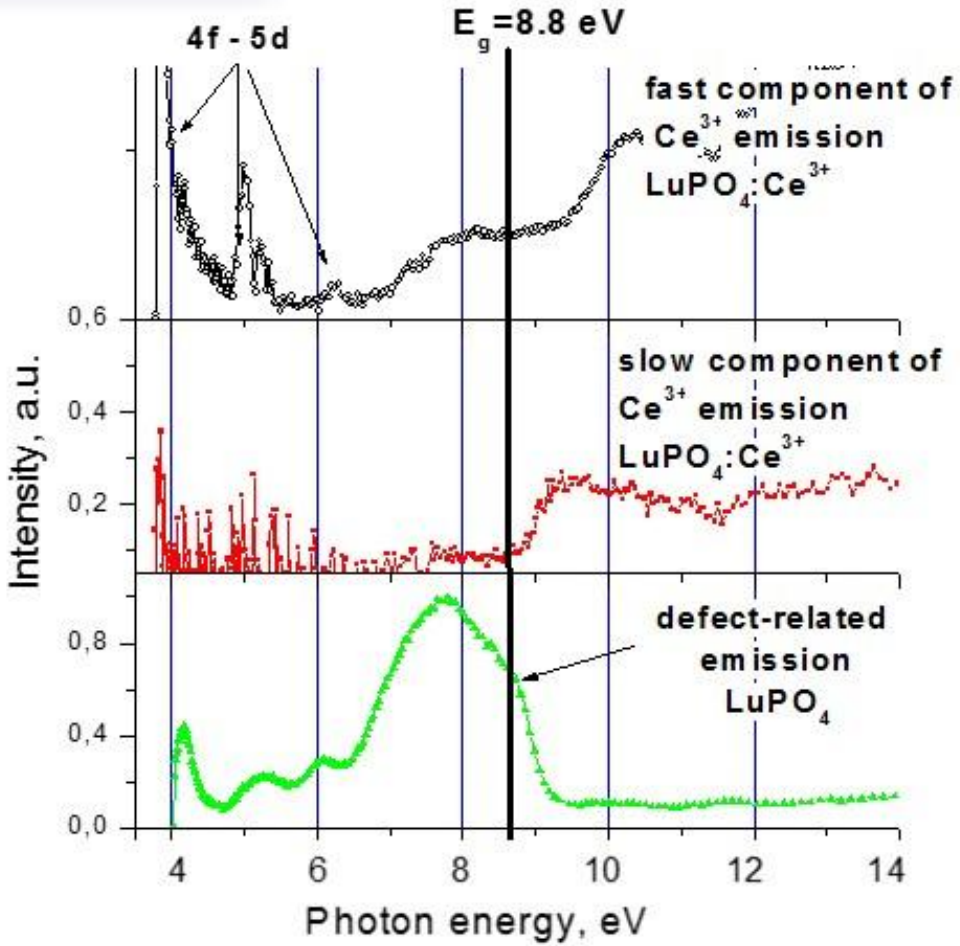
The luminescence excitation spectra

The five bands peaking at 3.9, 4.9, 5.2, 5.5 and 6.1 eV corresponding to 4f-5d intracenter transitions in Ce^{3+} ions.



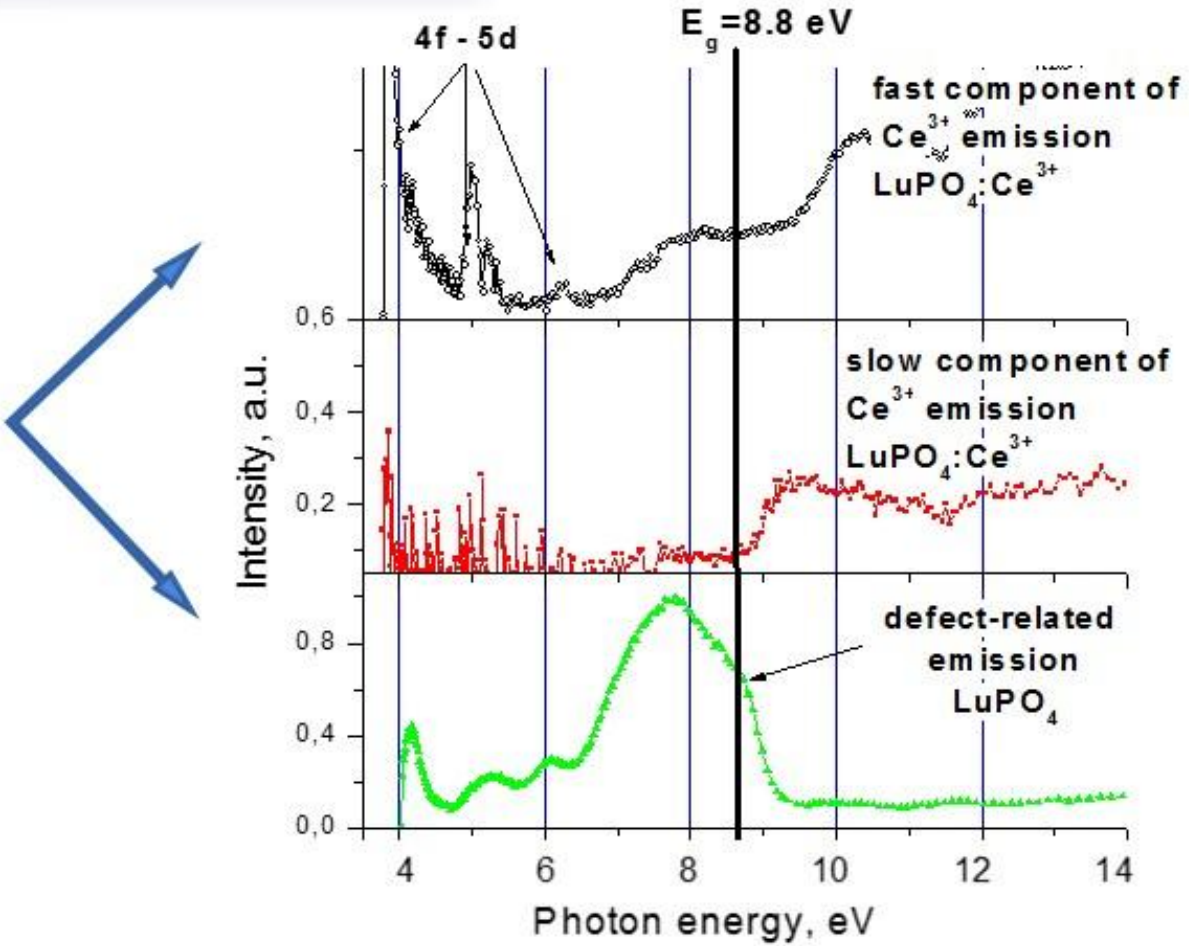
The luminescence excitation spectra

The rise of luminescence in excitation spectrum measured in the "slow" time window starts at E > 8.8 eV. The rise is connected with the creation of separated electrons and holes and can be used for the estimation of bandgap value E_g = 8.8 eV.



The luminescence excitation spectra

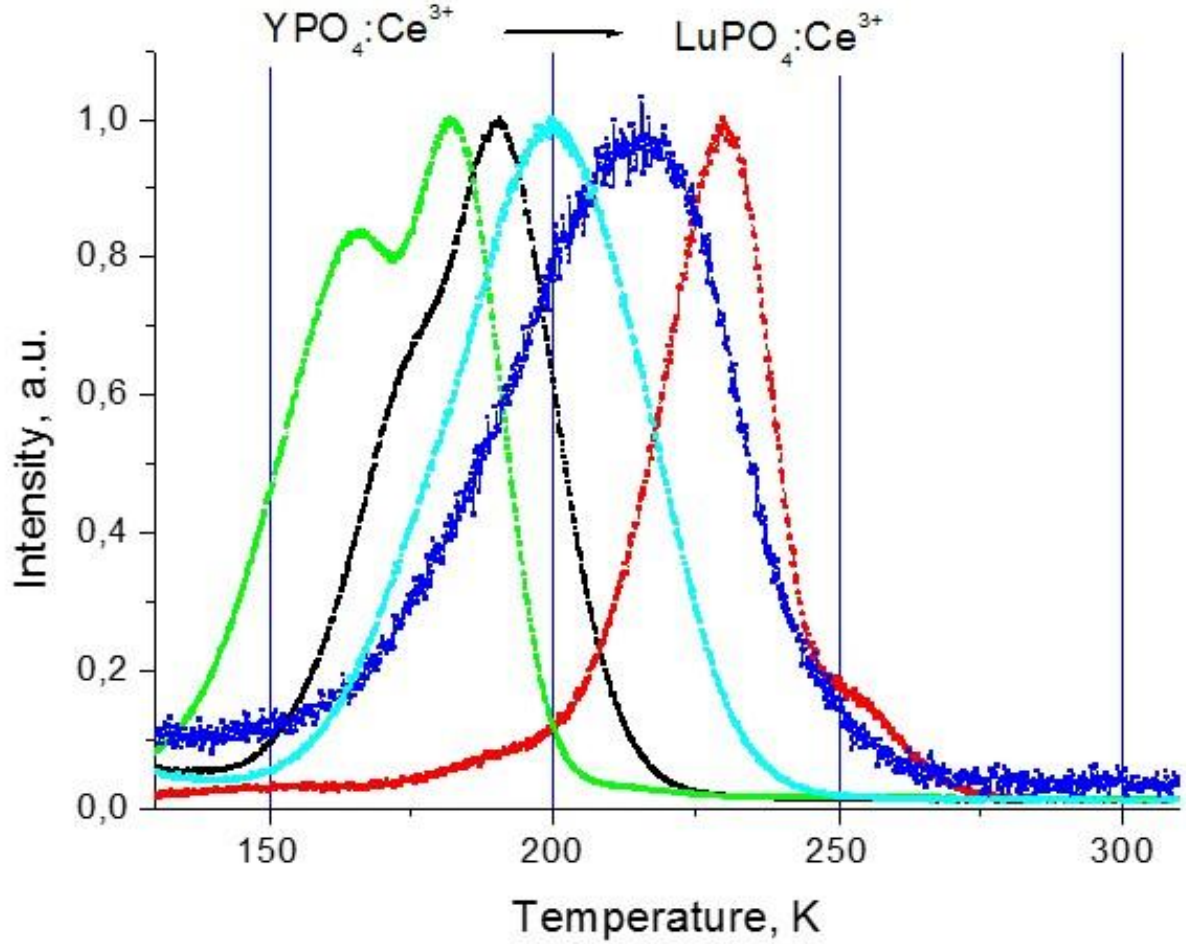
The broad band in the region 7-9 eV is found in the "fast" component of excitation spectra of $Lu_xY_{1-x}PO_4:Ce^{3+}$ as well as in the excitation spectra of defect-related emission in undoped phosphates. The energy transfer from the defect states to Ce^{3+} is proposed to explain the origin of the band in the excitation spectra of $Lu_xY_{1-x}PO_4:Ce^{3+}$.



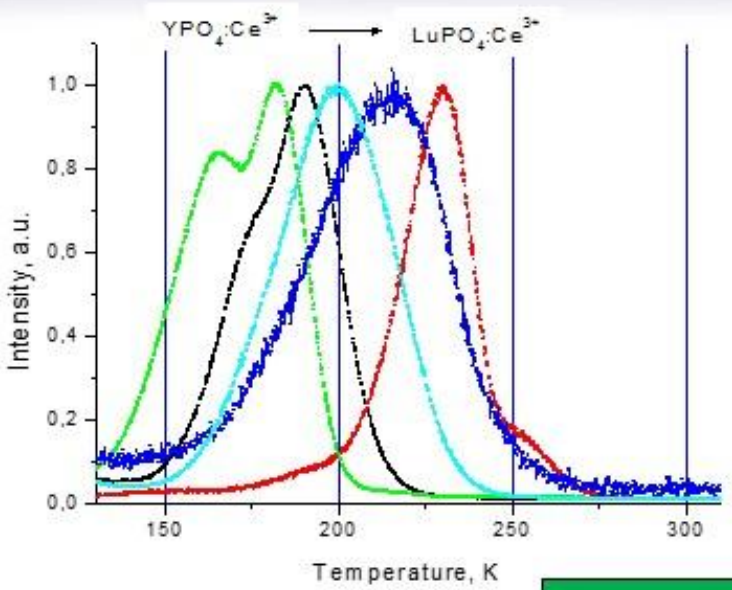
Thermostimulated luminescence

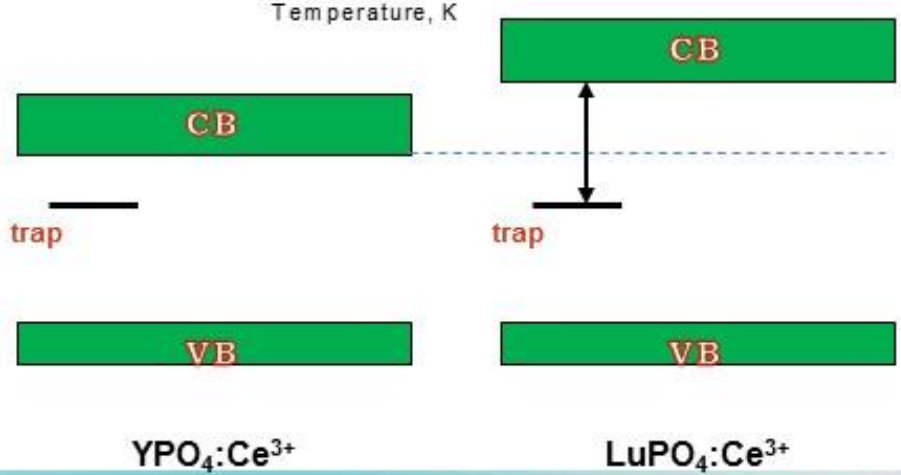
With increase of x:

- the shift of the peak to high temperature with increase of **x**



Thermostimulated luminescence



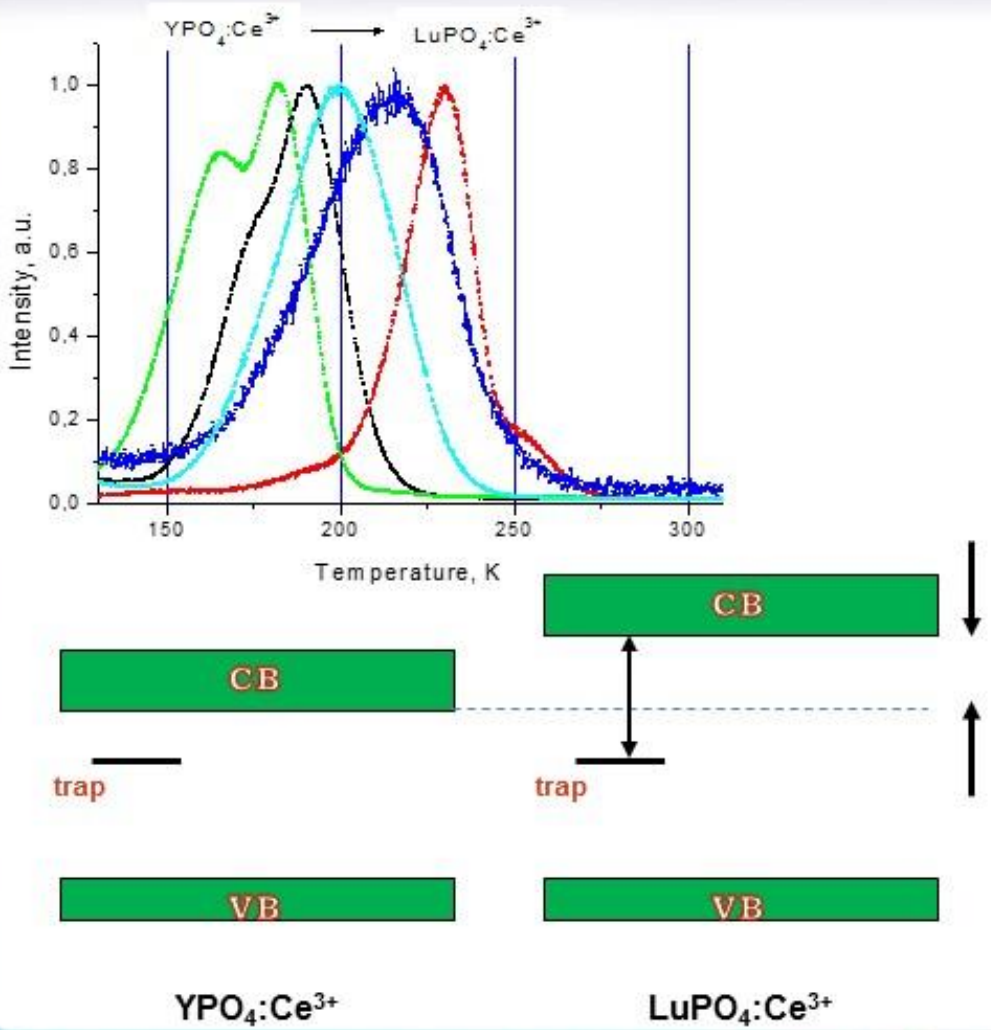


With increase of x:

- the shift of the peak to high temperature

- the increase of depth of the trap

Thermostimulated luminescence



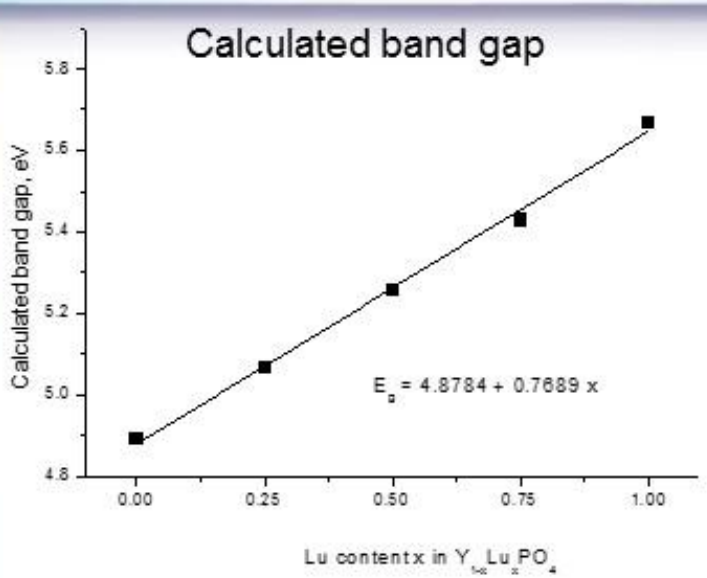
With increase of x:

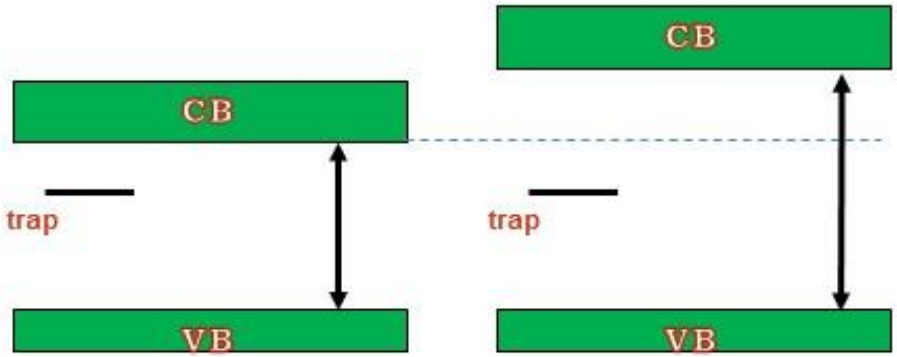
- the shift of the peak to high temperature

- the increase of depth of the trap

- the shift of the conduction band

Bandgap





$YPO_4:Ce^{3+}$ $LuPO_4:Ce^{3+}$

With increase of x:

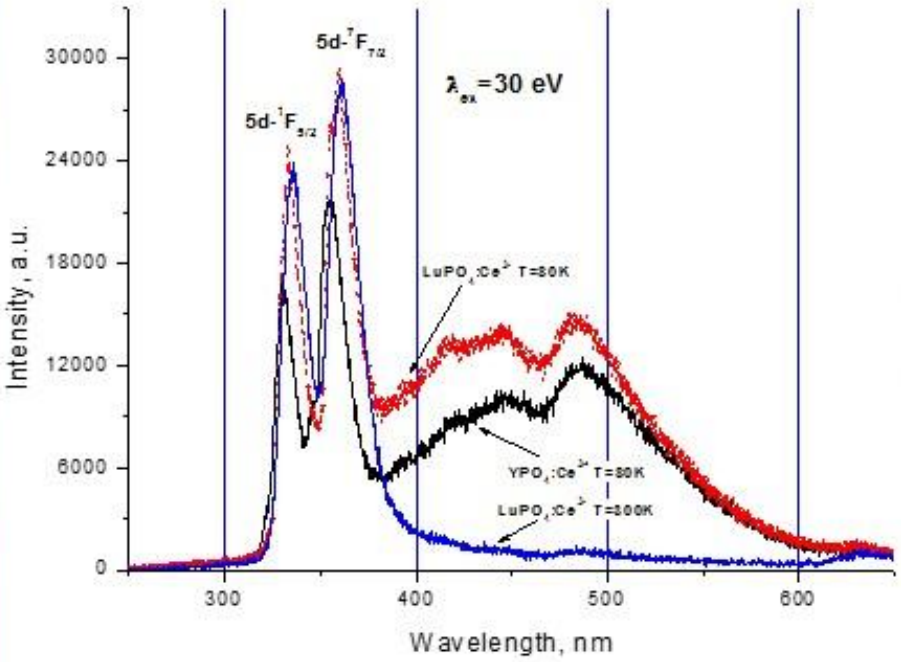
- the shift of the peak to high temperature

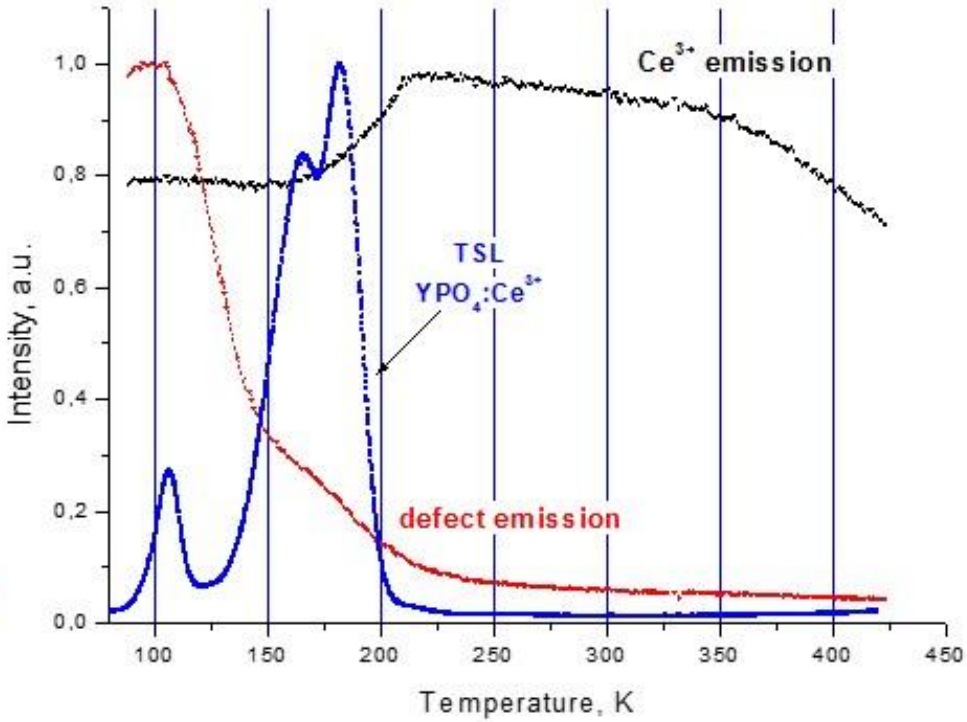
- the the rise of depth of the trap

- the shift of the CB

- the increase of bandgap

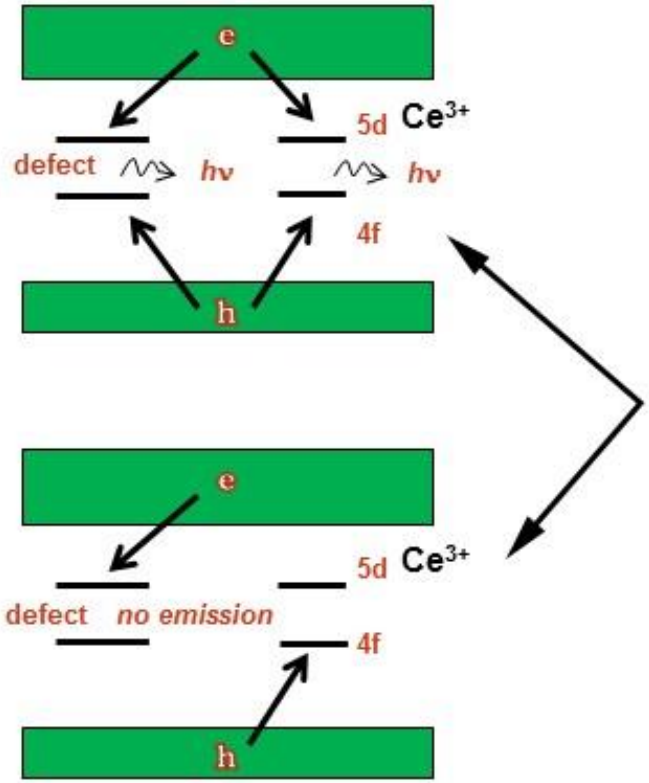
Temperature dependence of luminescence

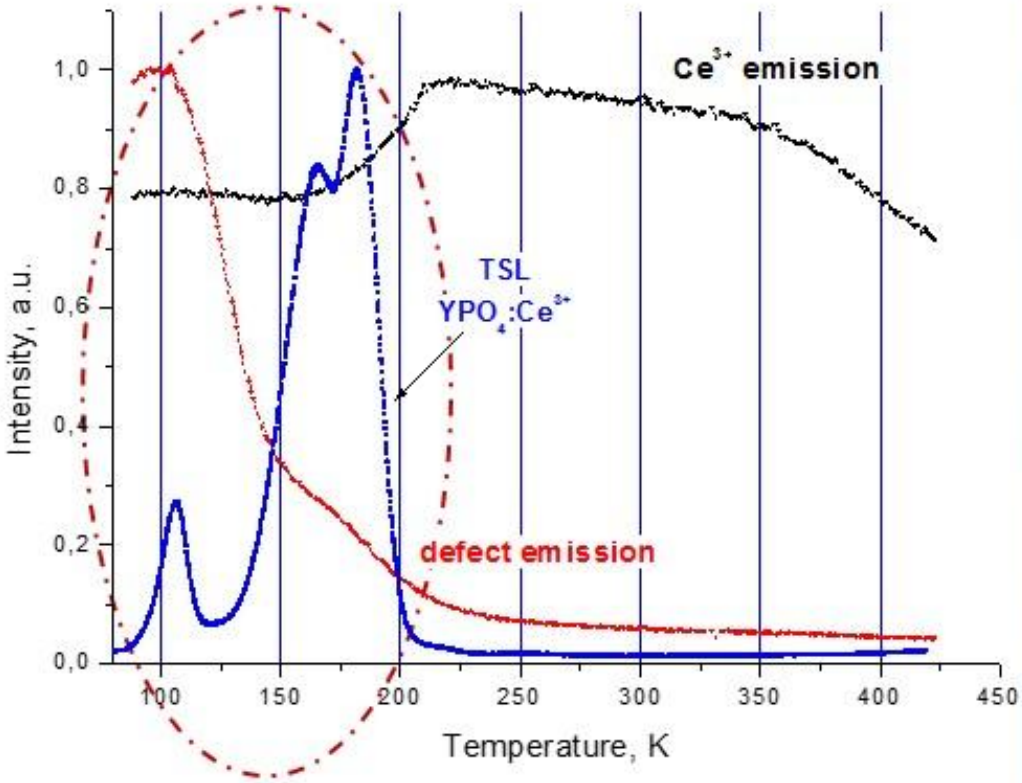




Temperature dependence of luminescence

T < 200 K : the electron can be trapped by the defect

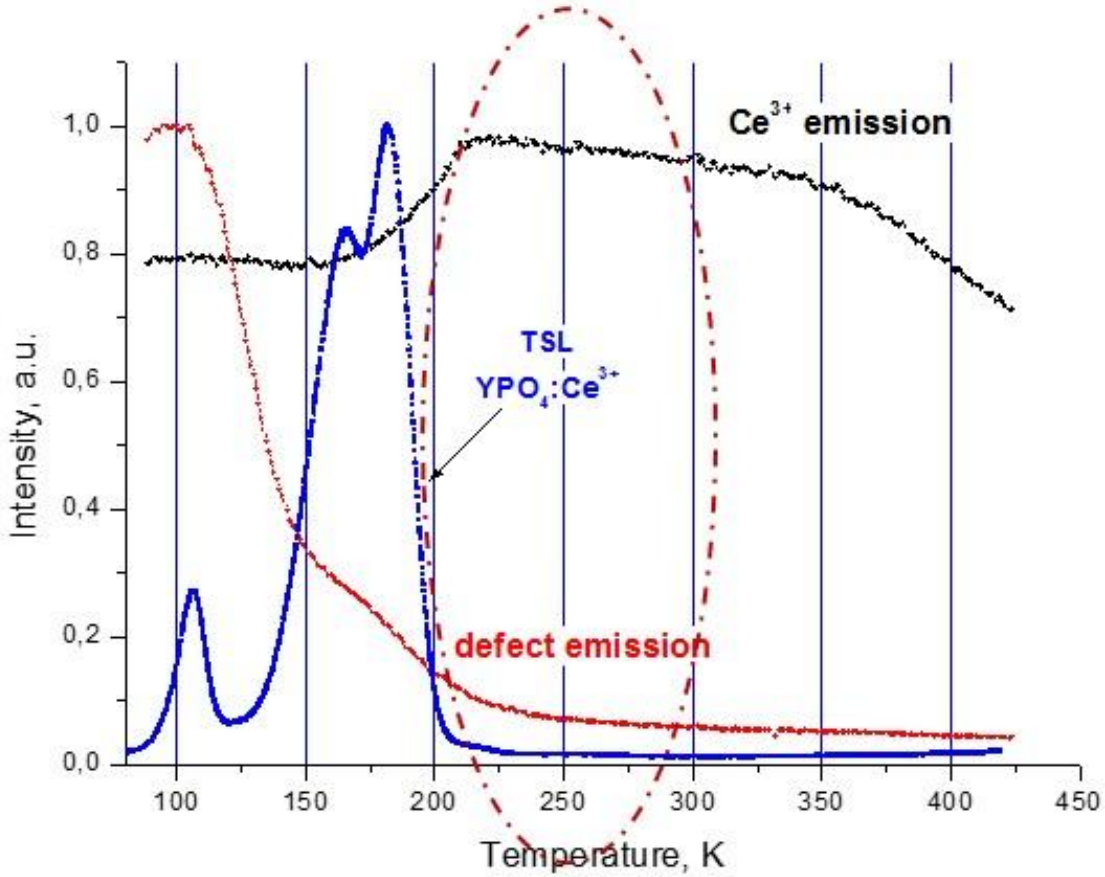




Ce^{3+} emission reduces by 20 %

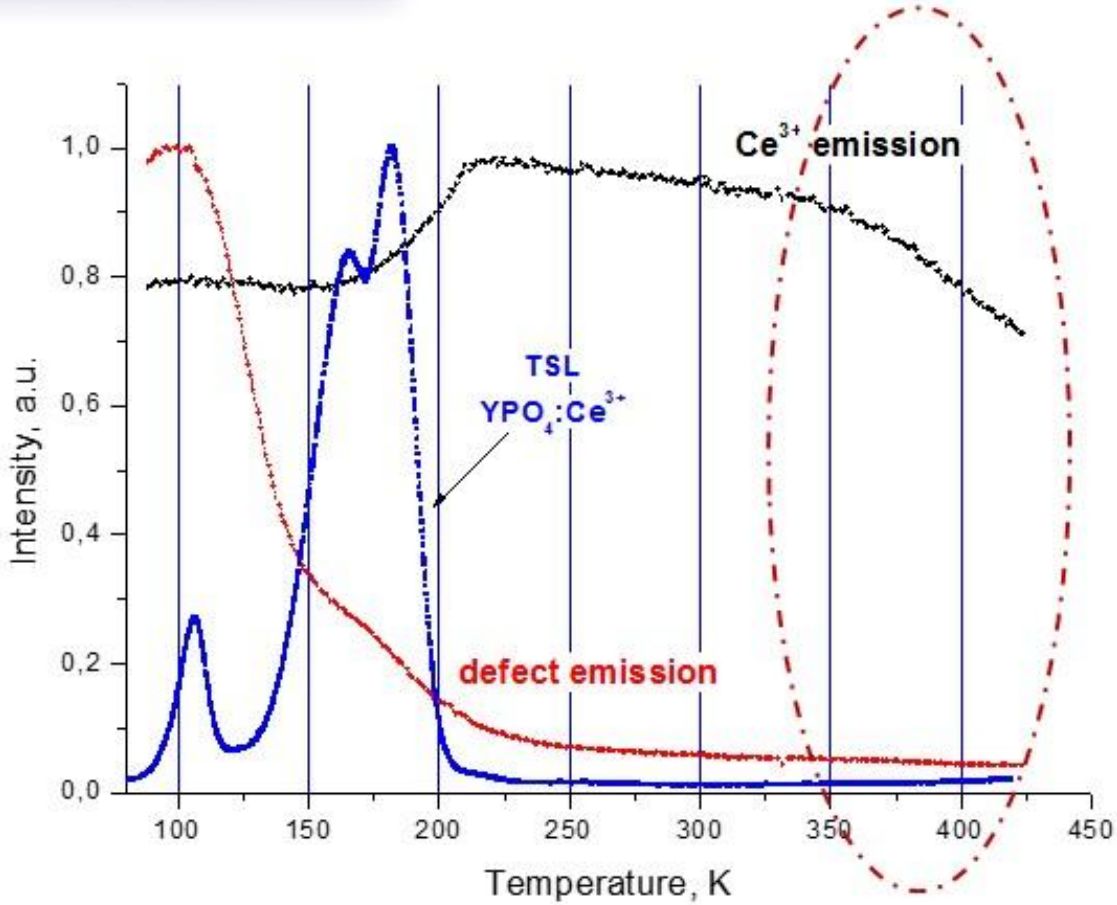
Temperature dependence of luminescence

200 < T < 350 K:
insignificant change of Ce^{3+} emission



Temperature dependence of luminescence

T > 350 K:
temperature quenching of the Ce^{3+} emission



Conclusions

- Luminescence properties of the set of phosphates solid solutions were investigated. The decrease of the emission intensity for intermediate values of x (opposite effect to the expected one) was detected .

- The luminescence excitation spectra have been analyzed. Time-resolved spectroscopy allowed to separate the slow processes of luminescence excitation connected with sequential capture of separated charge carriers on Ce^{3+} ion and the fast processes connected with the direct excitation of luminescence center.

Conclusions

- The temperature dependence of both the Ce^{3+} and defect emission were studied. The competition between emission from Ce^{3+} ions and defect-related emission occurs at T < 200 K and is attended by the trapping of electrons in vicinity of the defect-related states.

- The values of the bandgap were calculated. The calculations shows the increase of Eg and the result is further confirmed experimentally by the shift of the peaks of the TSL curves.

Thank you for attention