TARTU ÜLIKOOL

Bandgap engineering of the $Lu_xY_{1-x}PO_4$ mixed crystals

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LUMINET

MARIE CURIE ACTIONS

Complex oxides: phosphates

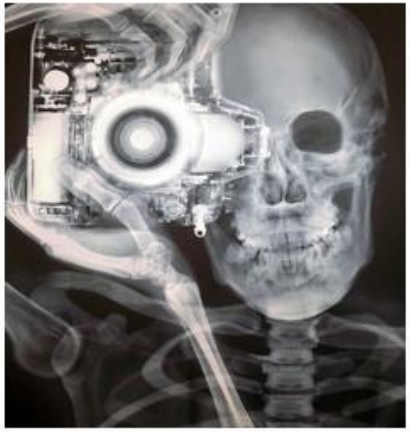
- high thermal stability
- no phase transitions till the melting temperature (T_m = 2150 C)
- high chemical stability
- a remarkable resistance to radiation damage

+

the luminescence properties of phosphates doped with rare-earth elements

the broad range of applications

Potential application of phosphates



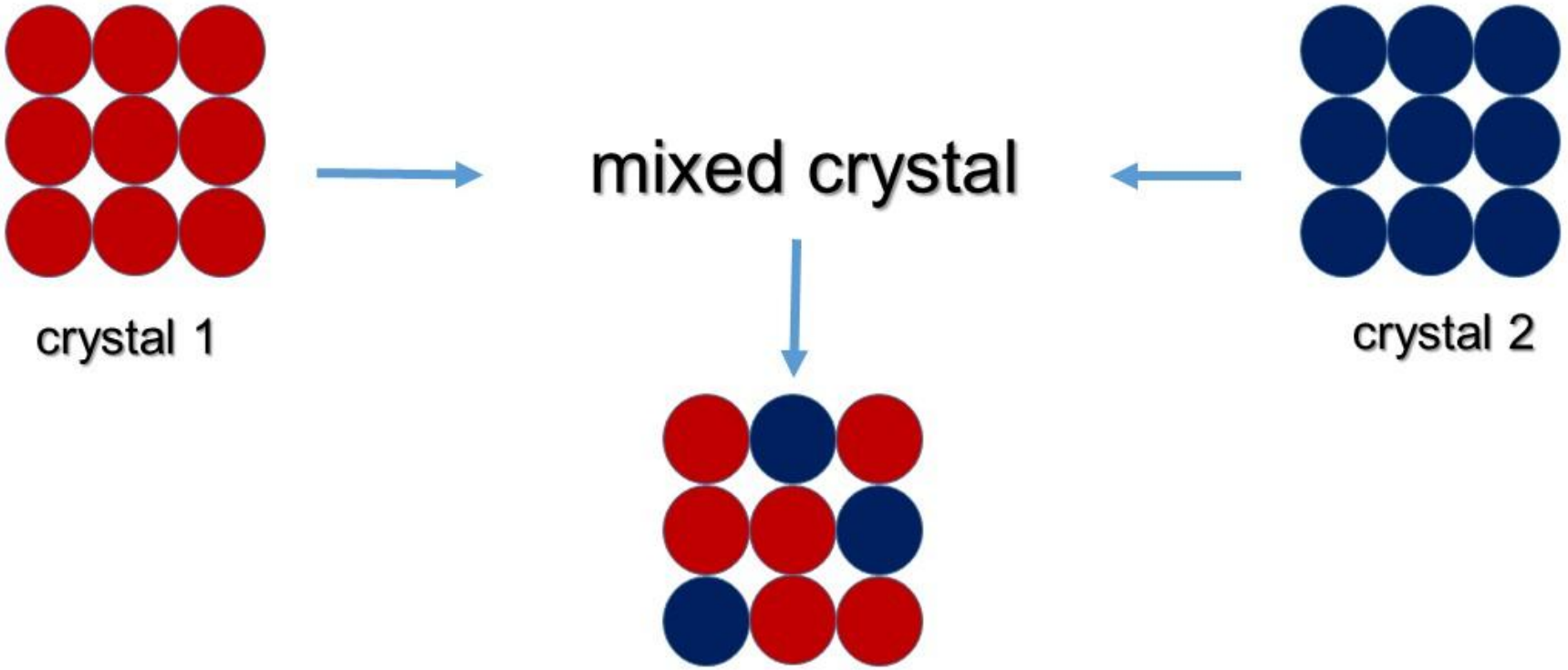
x-ray imaging

luminescent lamp

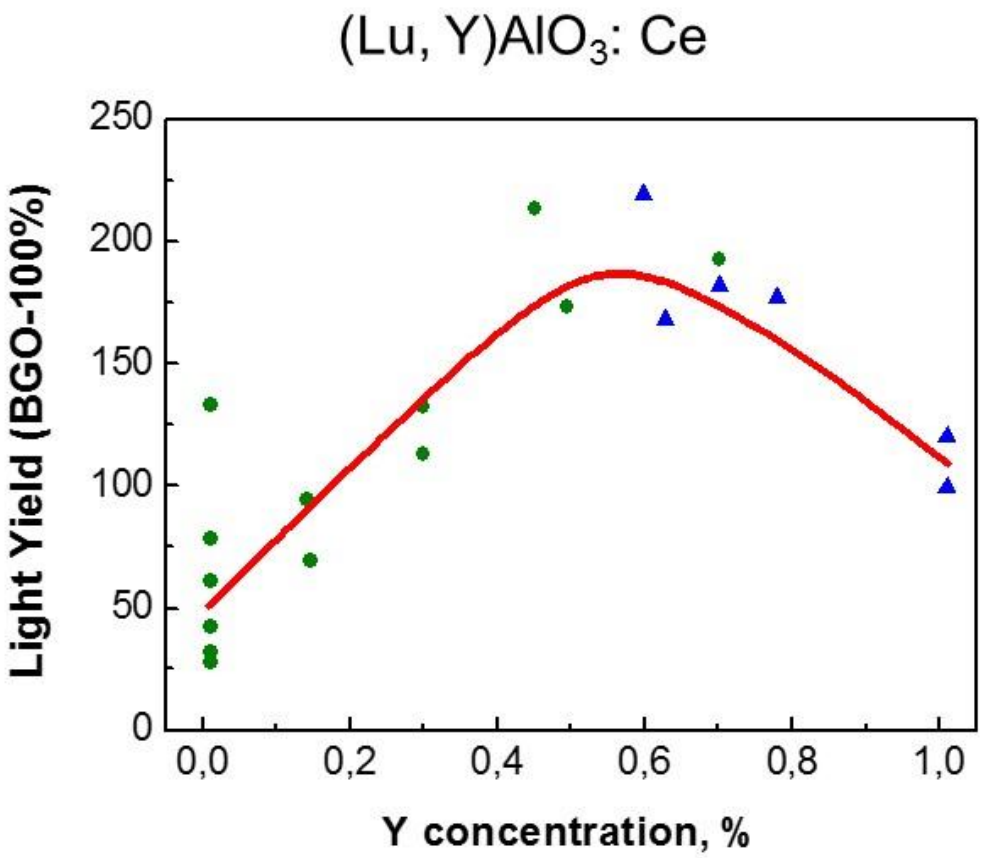
radioactive waste storage

plasma display panels

What is mixed crystal?



Why mixed crystals?



The increase of the light yield

Band gap engineering

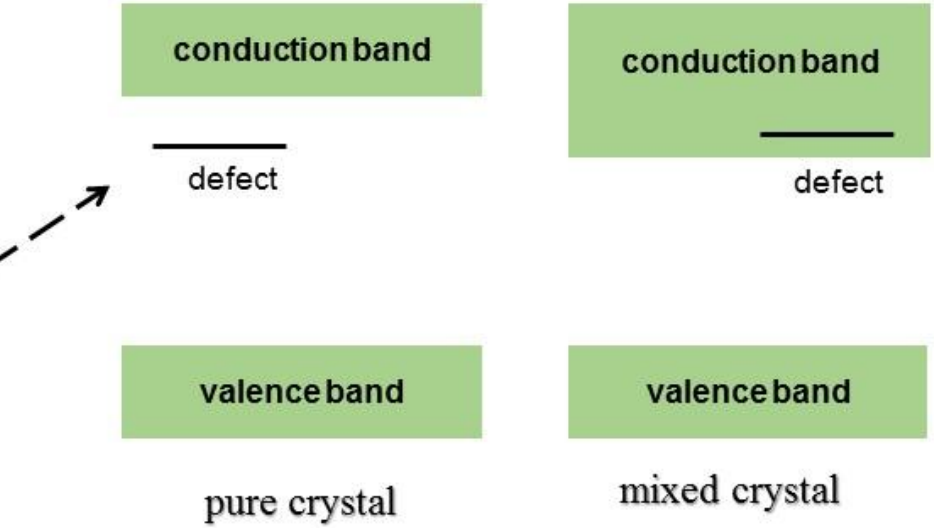
the point defects usually occur in oxides

↓

the discrete energy levels in the host's band gap

↓

negatively affect to recombination proccess



the defect states become buried under the conduction band states

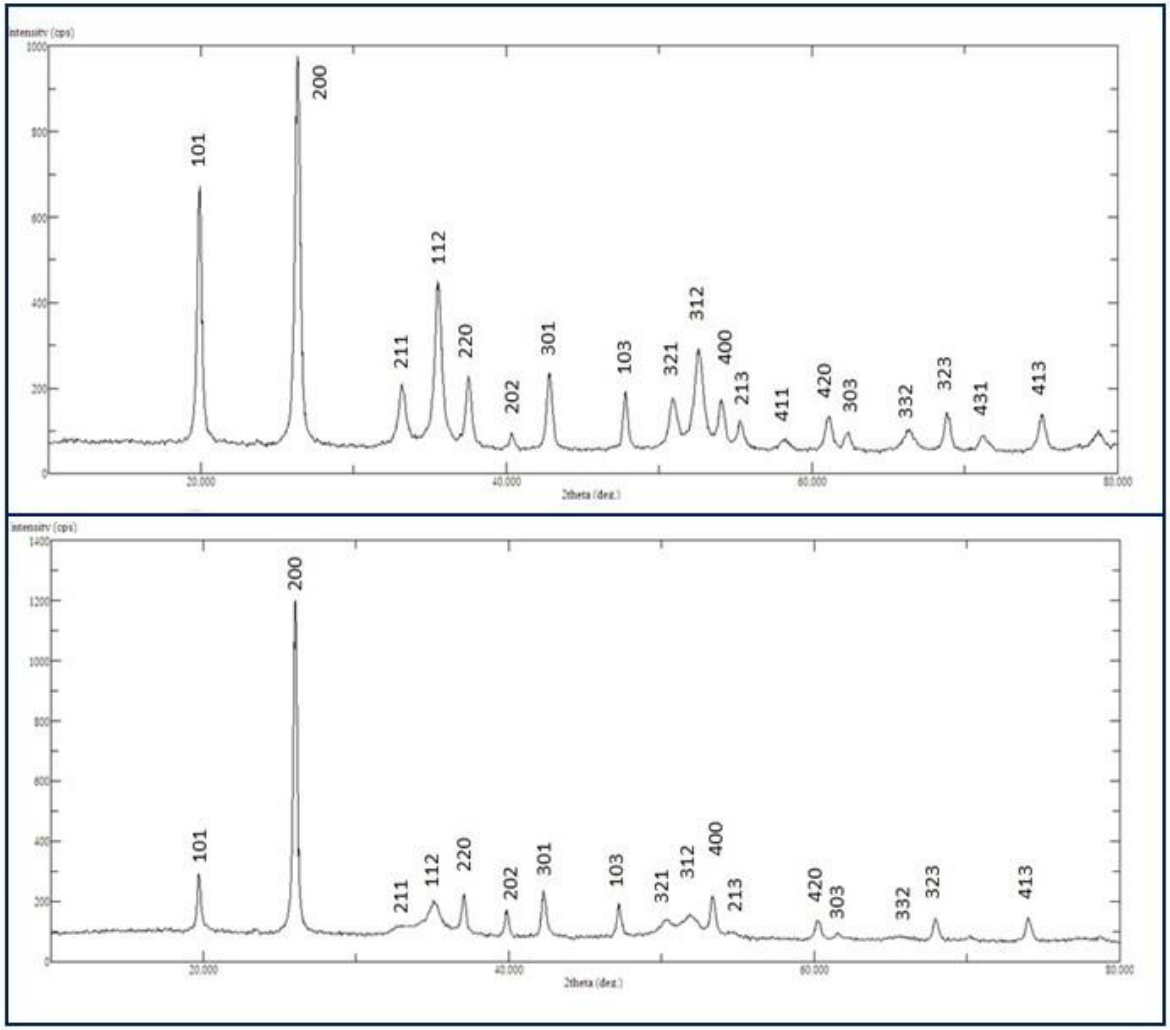
Goal of the investigation

- to study existing electron and hole traps in the $Lu_xY_{1-x}PO_4$
- to study modification of the band structure of the $Lu_xY_{1-x}PO_4$ mixed crystals with the gradual substitution of Y by Lu using thermostimulated luminescence
- to support experimental results by the data of ab-initio calculations

Studied mixed crystals

- **$Lu_xY_{1-x}PO_4$** (**x** = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1) doped with 0.5 mol % Ce^{3+} or Eu^{3+}
- the samples were synthesized by the **sol-gel method**.
- the dominating size of the particles is around **350-600 nm.**

All studied mixed crystals crystallize in the tetragonal space group



TSL: $Lu_xY_{1-x}PO_4:Ce^{3+}$

the shift of B,C peaks to high temperature

↓

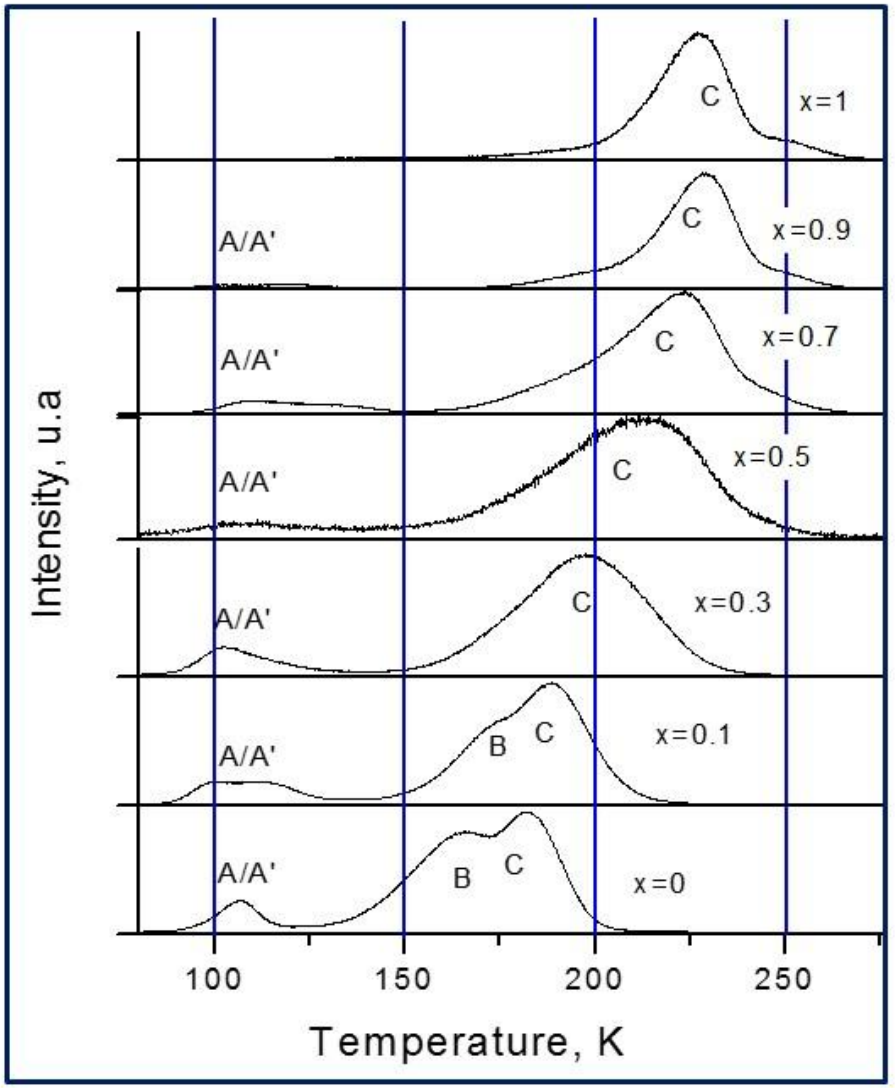
the increase of the activation energy of trap

↓

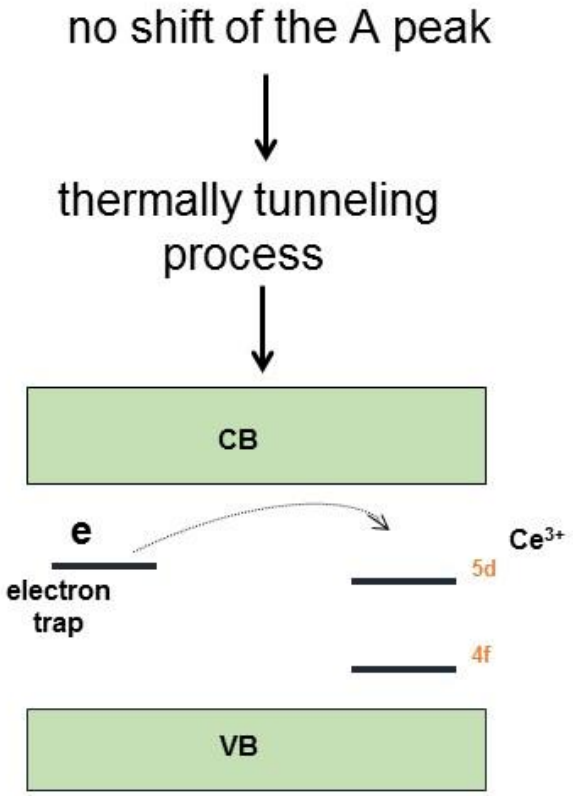
the high-energy shift of the bottom of conduction band

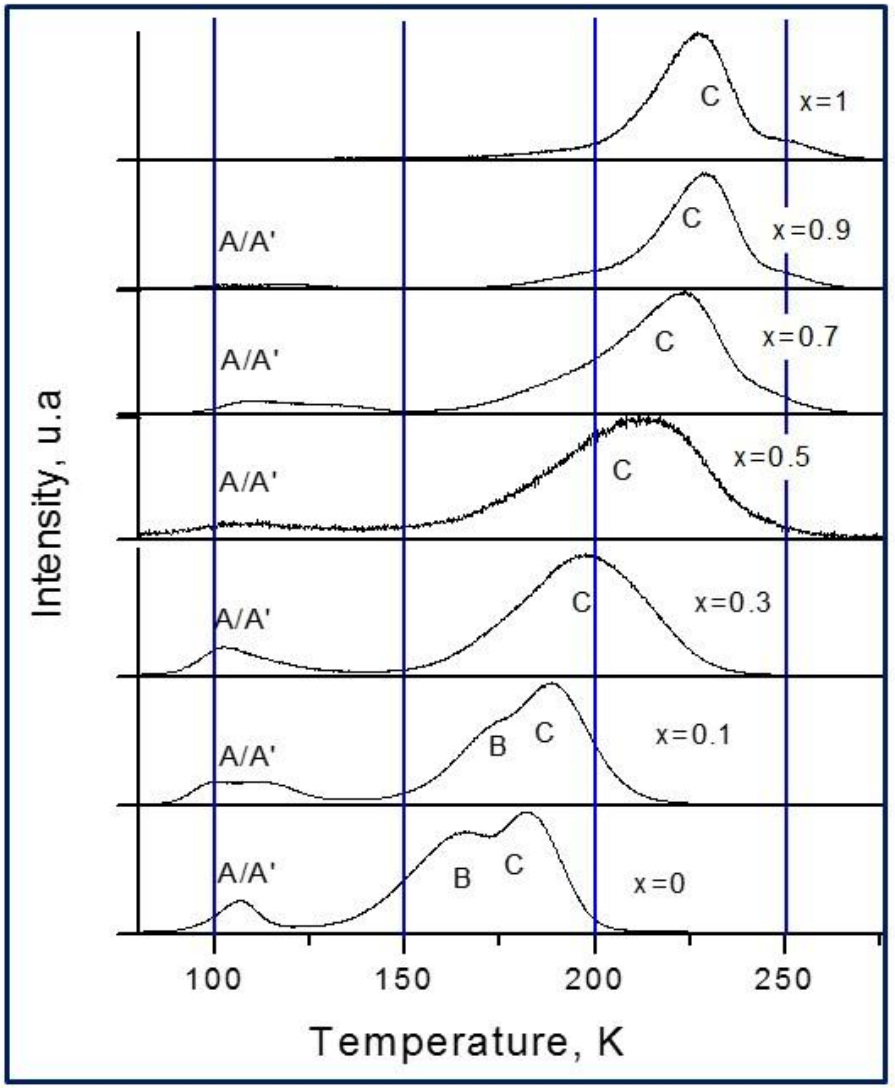
↓

the increase of bandgap's value



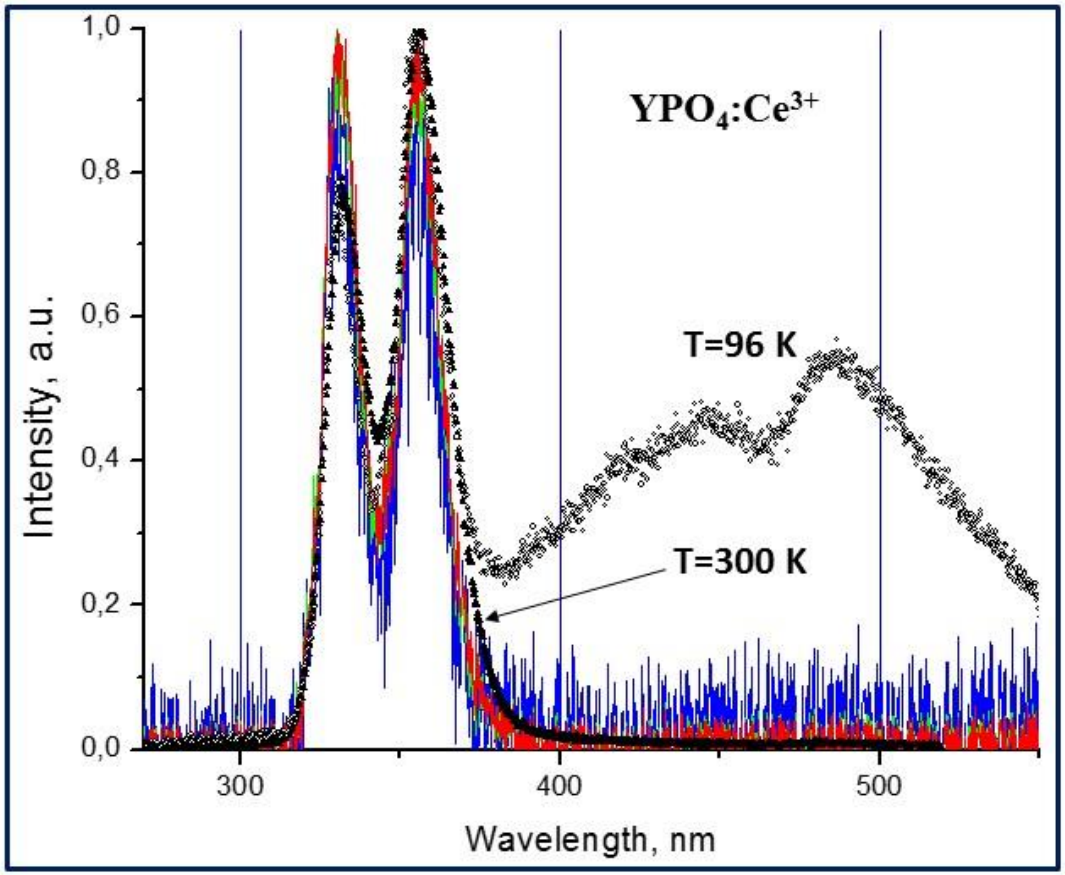
TSL: $Lu_xY_{1-x}PO_4:Ce^{3+}$





Spectral composition of TSL: $Lu_xY_{1-x}PO_4:Ce^{3+}$

- 320-380 nm - 5d-4f transitions on the Ce^{3+}
- 380-600 nm - the defect emission



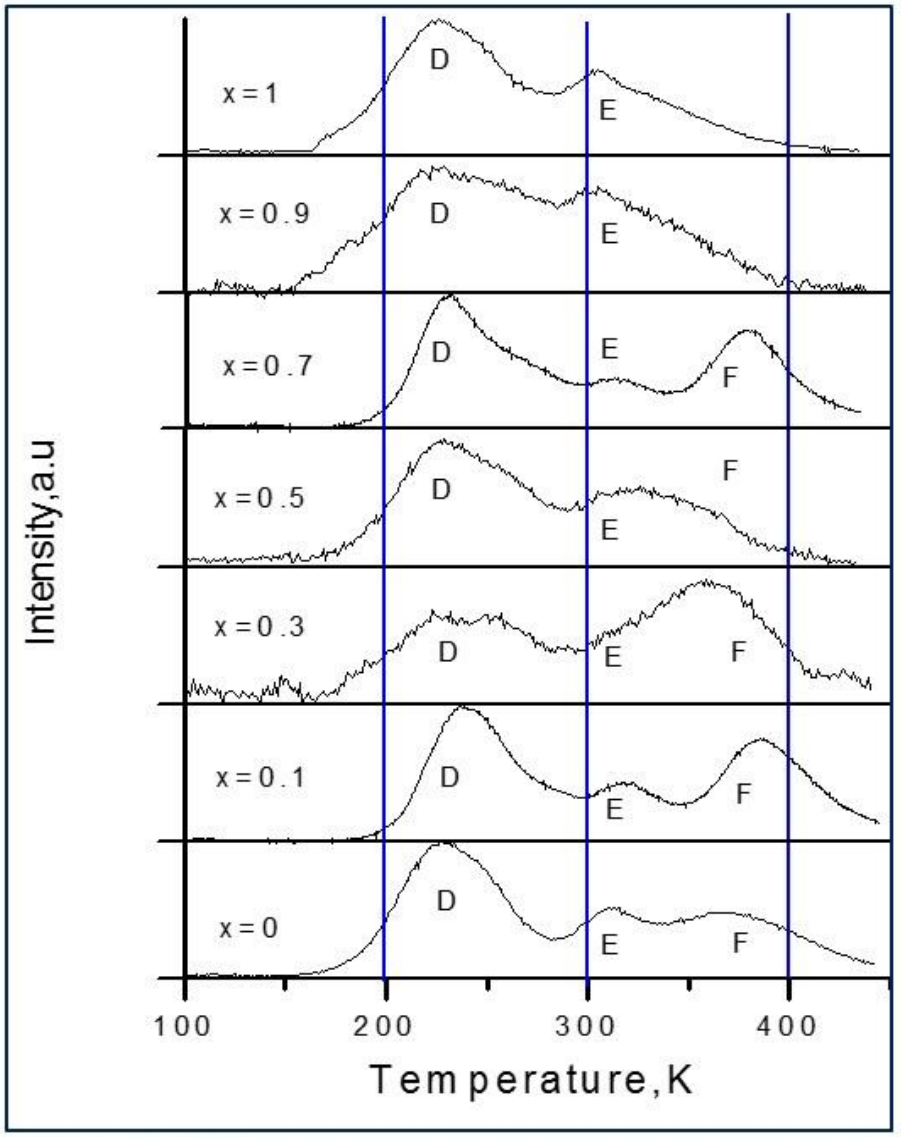
TSL: $Lu_xY_{1-x}PO_4:Eu^{3+}$

no shift of the peaks

redistribution of intensity in case of high temperature peaks

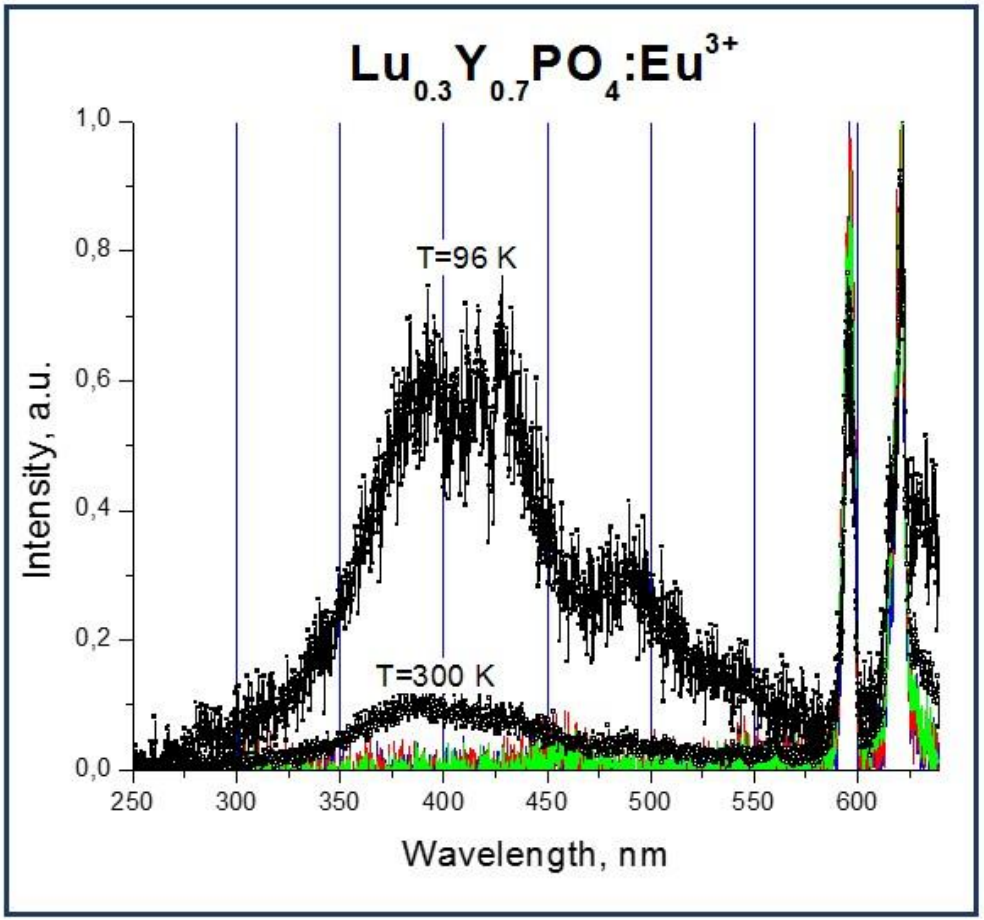
↓

the absence of changes in position of the top of valence band



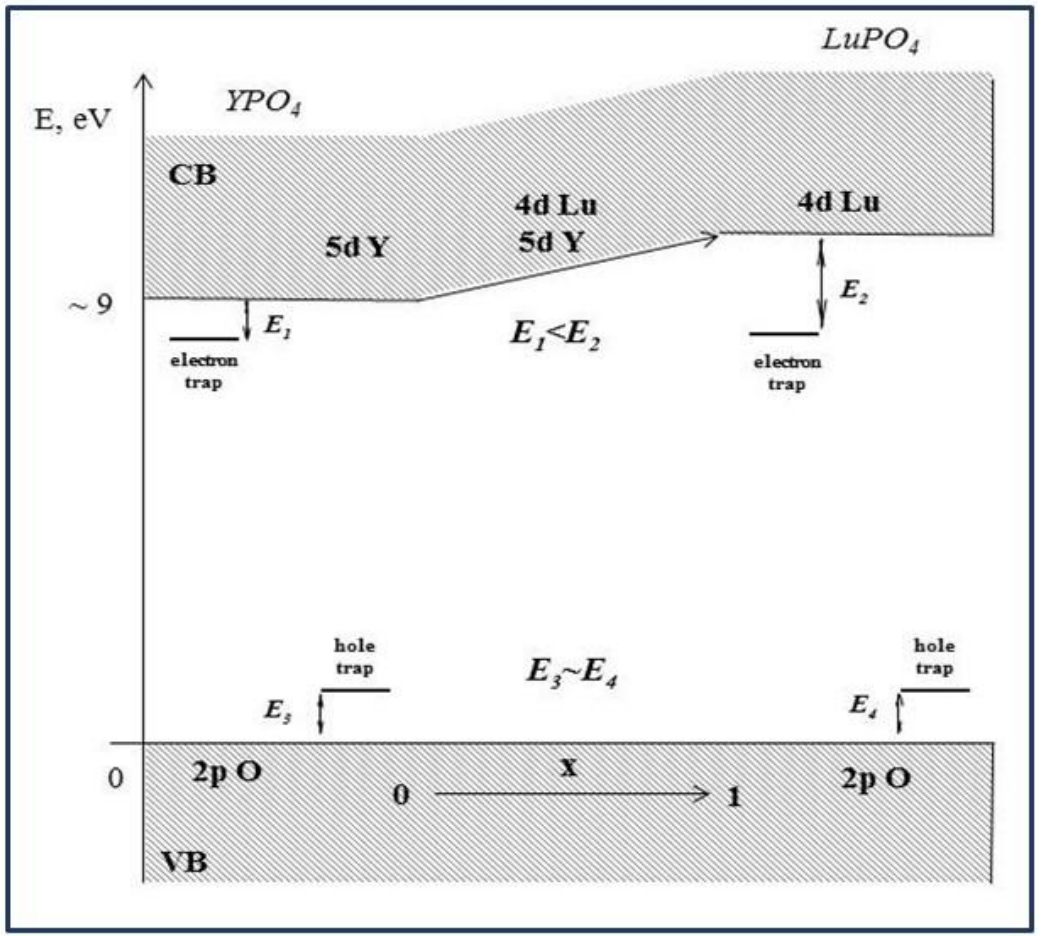
Spectral composition of TSL: $Lu_xY_{1-x}PO_4:Eu^{3+}$

- 580-650 nm – 4f-4f transitions on the Eu^{3+}
- 300-550 nm - the defect emission

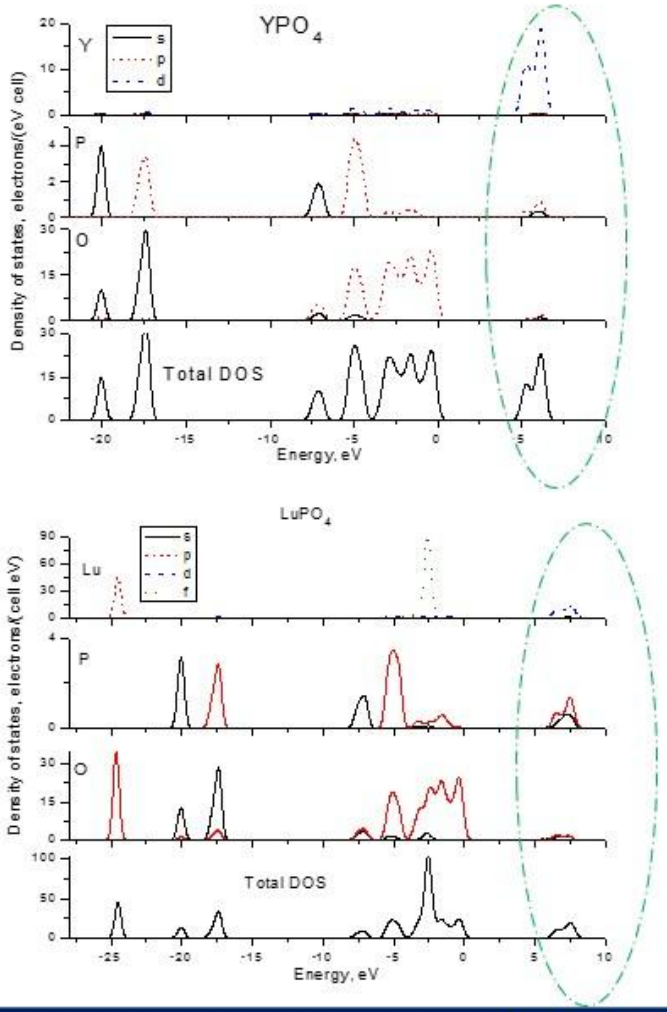


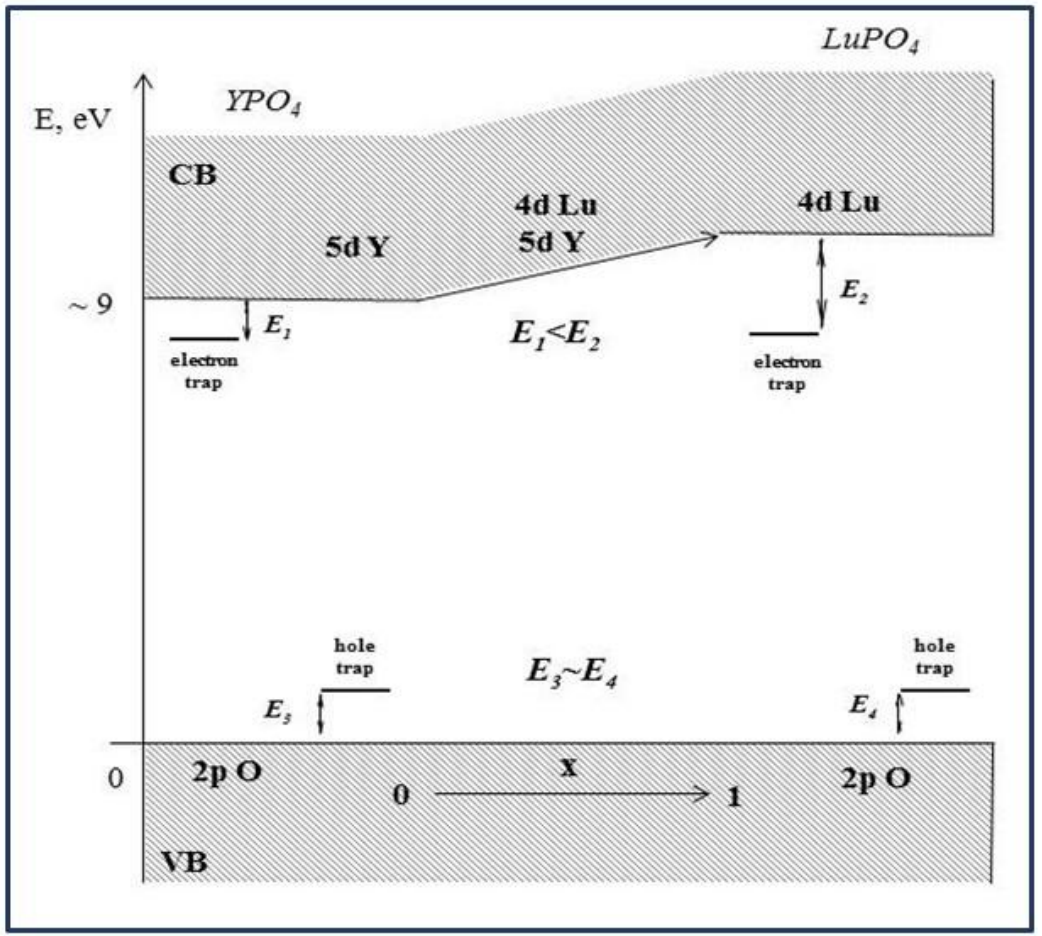
Band gap's modification

The band gap increases from YPO_4 to the $LuPO_4$ due to the change of the position of bottom of CB

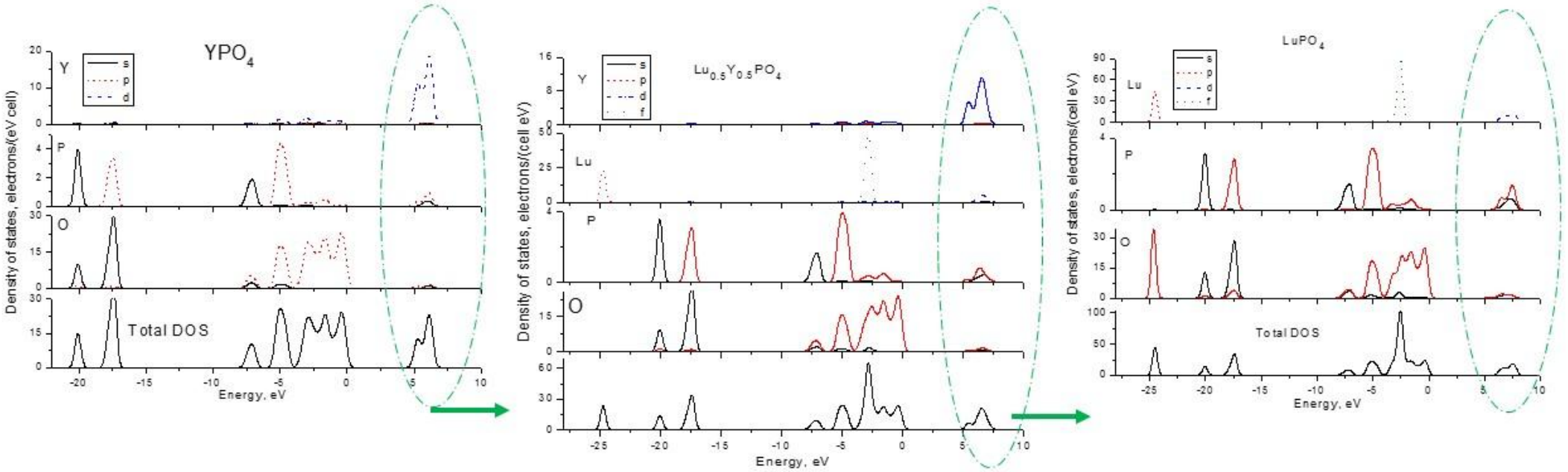


Band structure



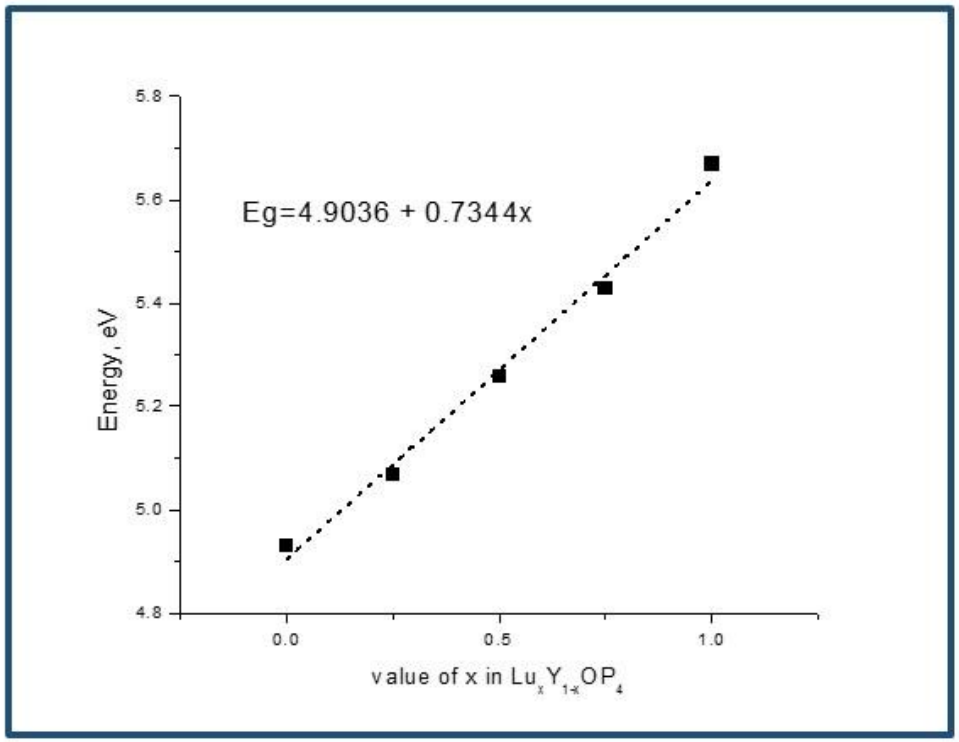


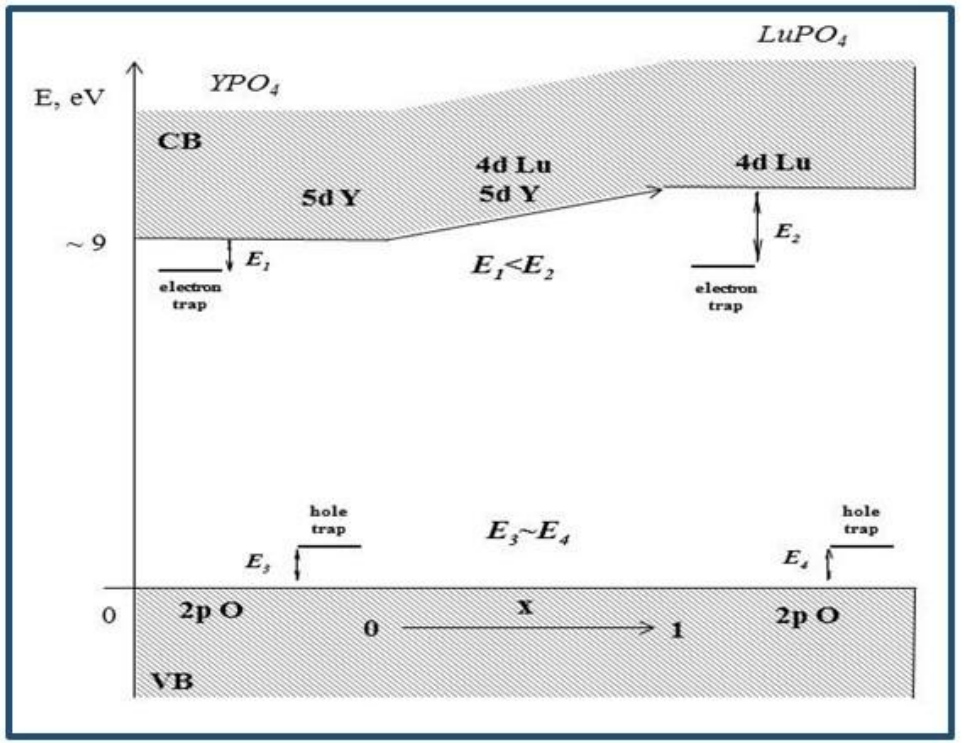
Band structure



- The top of the VB is formed by the 2p states of O with a minor contribution of the 3p and 3s states of P.
- The bottom of the conduction band is formed with the 4d and 5d states of substituted cations (Y and Lu).
- The gradual substitution of cations is responsible for the bandgap shift.

Change of band gap's value





The modification of the CB is confirmed by the band structure calculations of $Lu_XY_{1-X}PO_4$

Conclusions

- the gradual shift of the position of the TSL peaks in case of $Lu_xY_{1-x}PO_4:Ce^{3+}$ to high-temperature with the increase of **x** value indicates the high-energy shift of the bottom of CB.

- the absence of considerable shift of TSL peaks in case of $Lu_xY_{1-x}PO_4:Eu^{3+}$ points out that the position of the top of VB does not depend on the relative concentration of Lu and Y.

- the band gap gradually increases from YPO_4 to the $LuPO_4$ due to the change of the position of bottom of CB only.

- the calculations of the energy bands structure confirm the experimental results and demonstrate a similar trend in the modified band gaps.