

# Luminescence of undoped and RE doped $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ under high energy irradiation

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## Motivation

Phosphates with a NASICON type structure such as  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  are known as superionic conductors applied in solid state batteries. Recently it was shown that  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  doped with  $\text{Eu}^{2+}$  demonstrates excellent stability of luminescence in a broad temperature range that makes it promising for lightning applications, e.g. in pLEDs. The processes of the conversion of high energy irradiation into intrinsic or dopant luminescence has not been studied for this compound so far. Actually, in case of high efficiency of energy transfer from the host to emission centers  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  the possible application range of this material could be extended.

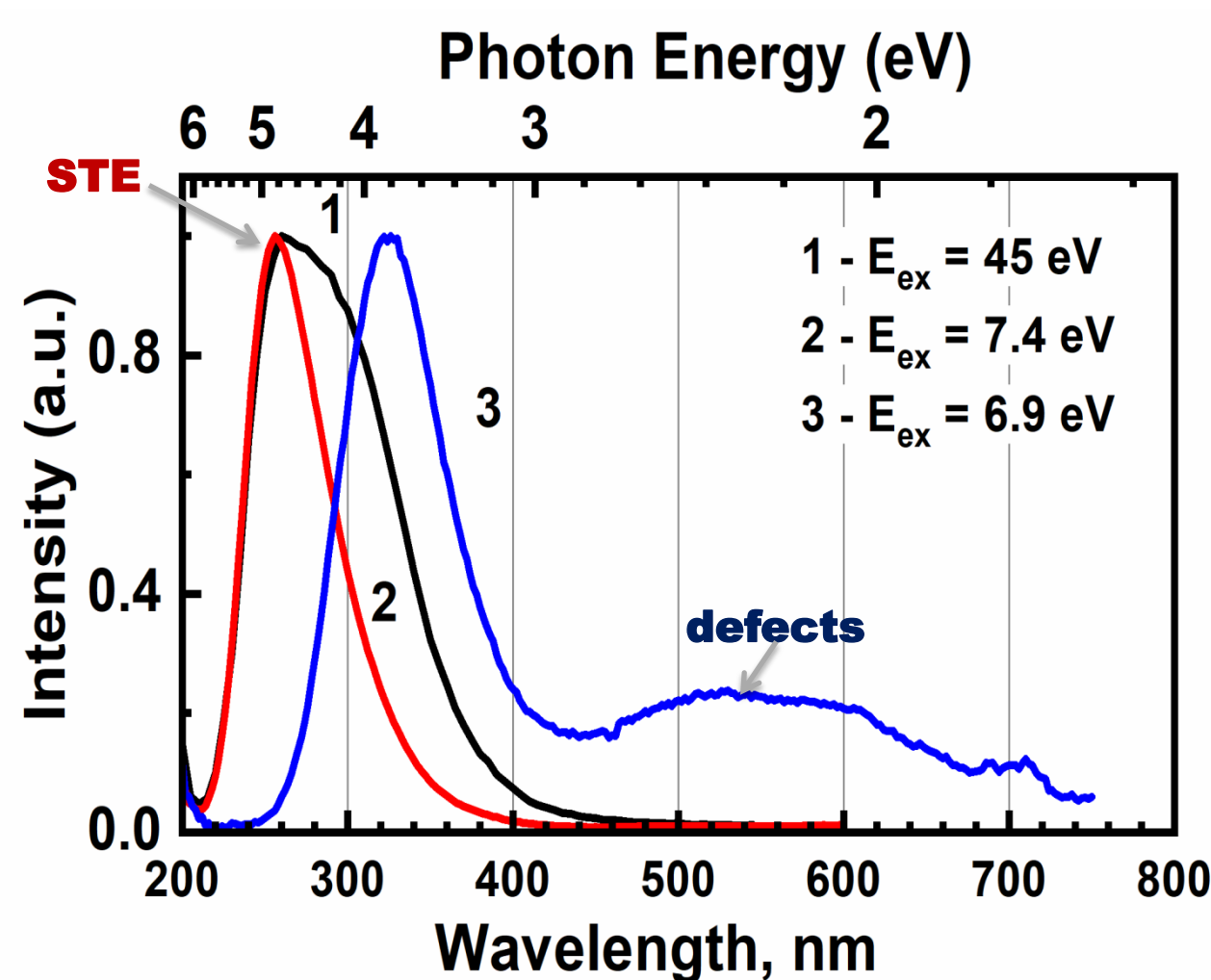
Here we present the results of a study of the luminescent properties of undoped and RE-doped  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  under high energy irradiation.

## Experimental details

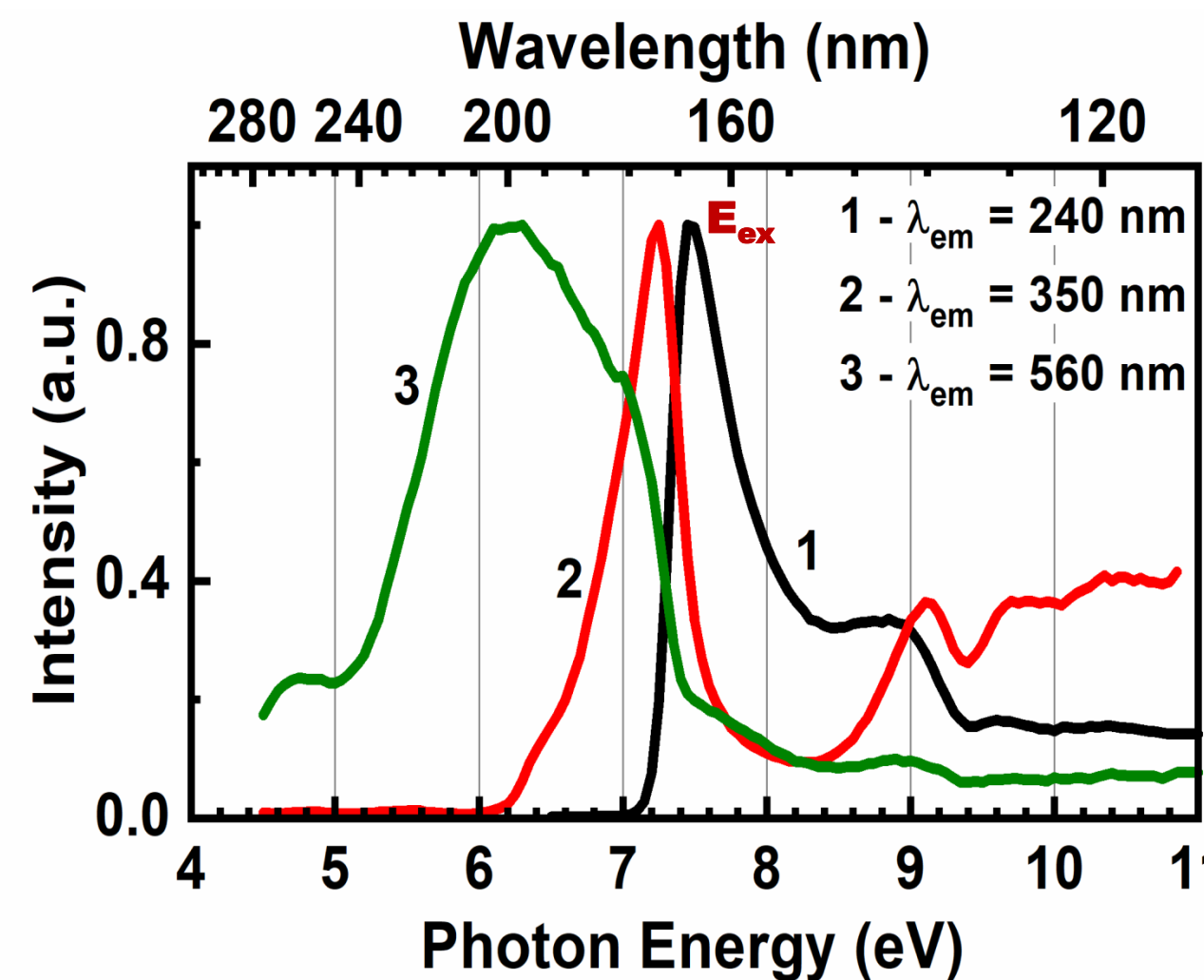
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  (NSP) phosphates, undoped and doped with 0.02 mol%  $\text{Ce}^{3+}$  or 0.01 mol%  $\text{Eu}^{3+}$  were synthesized in the reduction atmosphere using a high-temperature solid-state method. Powder X-ray diffraction study revealed that all synthesized samples were single phased with a NASICON-type structure.

The studies of luminescence properties in the energy range 2.5 - 9 eV were performed using laboratory set-ups. The studies under higher excitation energies up to 40 eV were performed at photoluminescence endstation of the FinEstBeAMS beamline of the MAX IV synchrotron radiation facility. Luminescence spectra were also measured at the pulsed cathodoluminescence (CL) setup ( $E = 120$  keV, 0-2 ms).

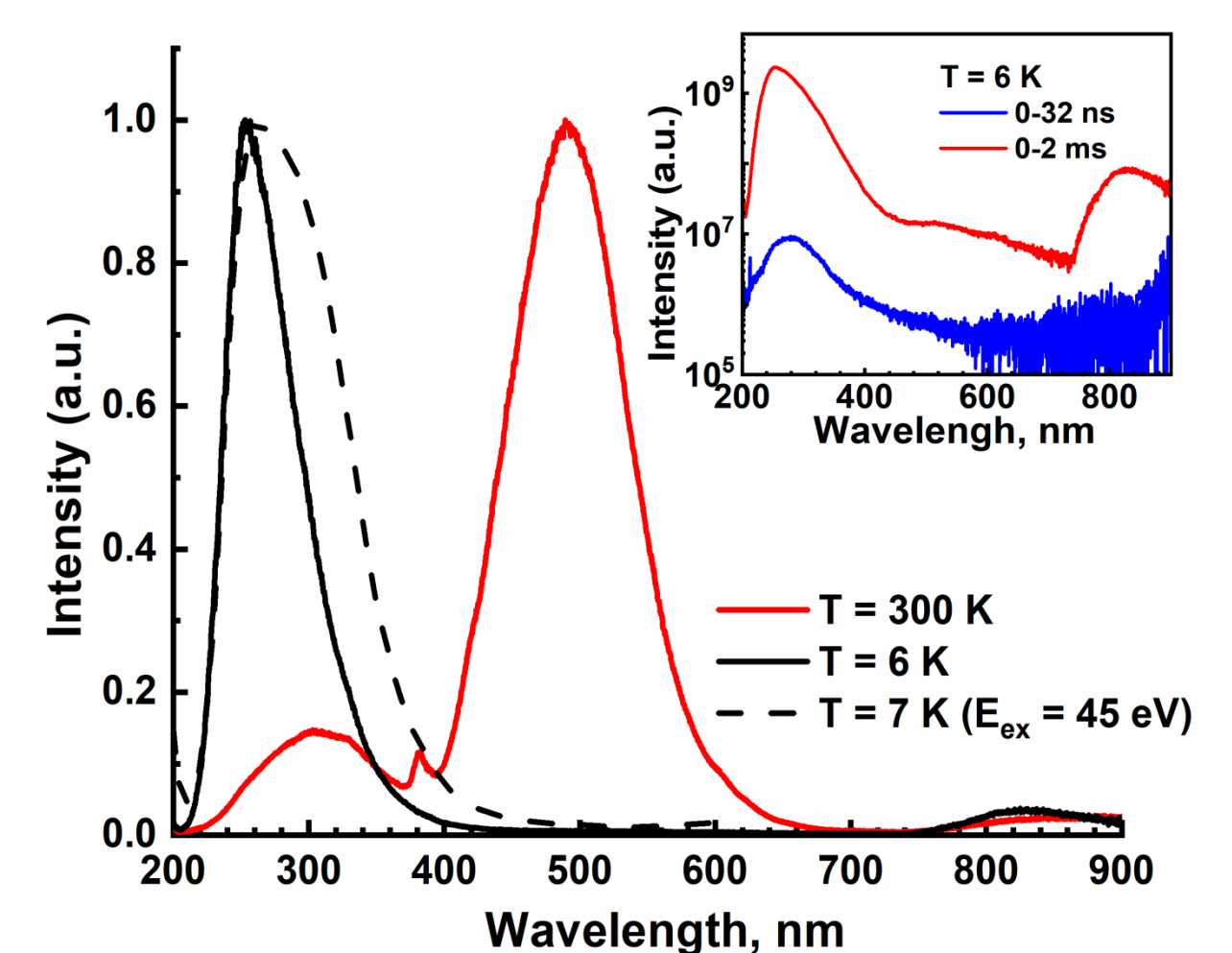
## Luminescence of undoped $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ phosphate



Normalized luminescence spectra of  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  at different excitation energies,  $T = 7$  K.



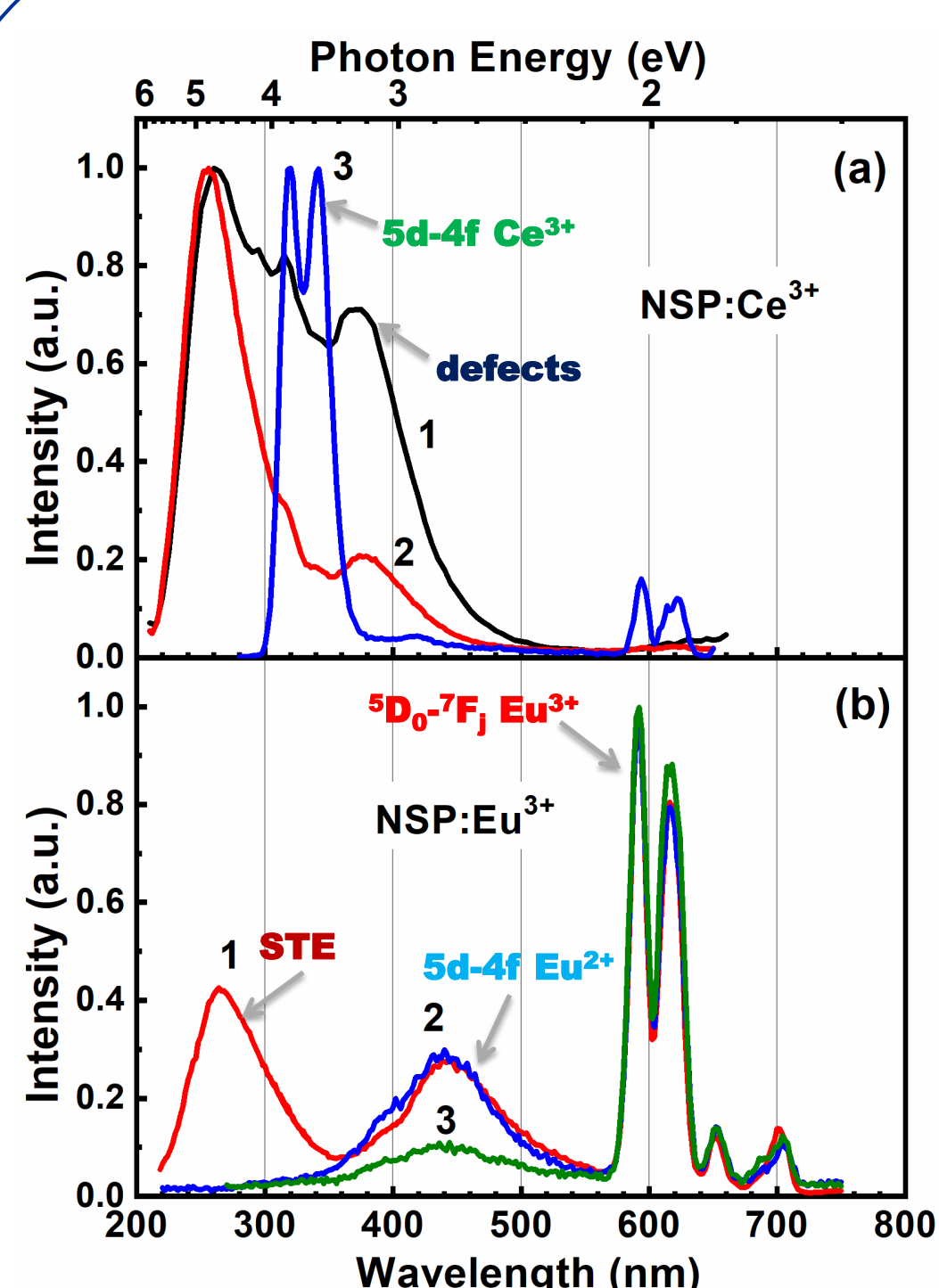
Luminescence excitation spectra of  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  at  $T = 7$  K.



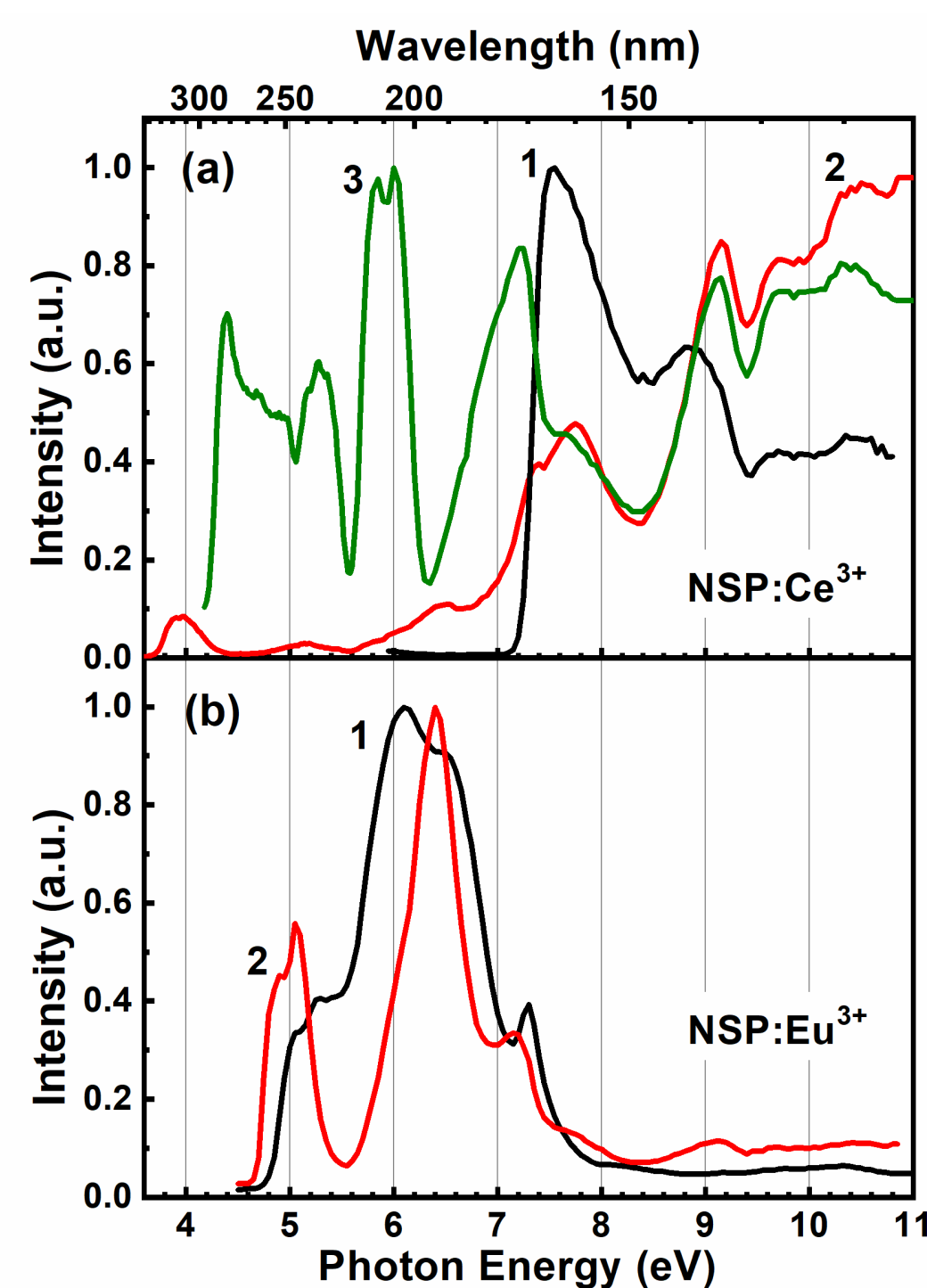
Cathodoluminescence spectra of  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  at different temperatures and time gates (inset).

- The intrinsic emission is represented with a broad band peaking at 260 nm related to radiative annihilation of self-trapped excitons (STE) with electron components belonging to 3d Sc. Additional broad emission bands peaking at 325 and 530 nm were ascribed to the defects of crystal structure, presumably to the complexes with oxygen vacancies.
- The onset at 7.1 eV in the excitation spectrum of 260-nm emission band coincides with the fundamental absorption band, while the first peak at 7.45 eV is related to the exciton creation energy. The excitation spectrum of the emission band at 325 nm is represented by a peak at 7.24 eV and a shoulder at 6.4 eV. Its excitation efficiency decreases towards excitonic and fundamental absorption energy region that is related to the competition in energy transfer with the emission centres responsible for the 260-nm band. The intensity in the excitation spectrum of 530-nm emission band drops almost to zero at  $E_{\text{ex}} > 7.5$  eV indicating poor energy transfer from the host to this defect emission centre.
- At low temperature a correlation between cathodo- and photoluminescence ( $E_{\text{ex}} = 45$  eV) spectra is observed, while at room temperature the defect-related band at ~490 nm dominates in CL spectrum of NSP phosphate. The time-resolved CL spectra shown in the inset indicate the prevalence of slow emission components.

## Luminescence of $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3:\text{Ce}^{3+}$ and $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3:\text{Eu}^{3+}$ phosphates



Luminescence spectra of  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  doped with 0.02  $\text{Ce}^{3+}$  (a) at  $E_{\text{ex}} = 45$  eV (1), 7.8 eV (2) and 6.0 eV (3) and 0.01  $\text{Eu}^{3+}$  (b) at  $E_{\text{ex}} = 7.7$  eV (1), 6.4 eV (2) and 5.3 eV (3),  $T = 7$  K.

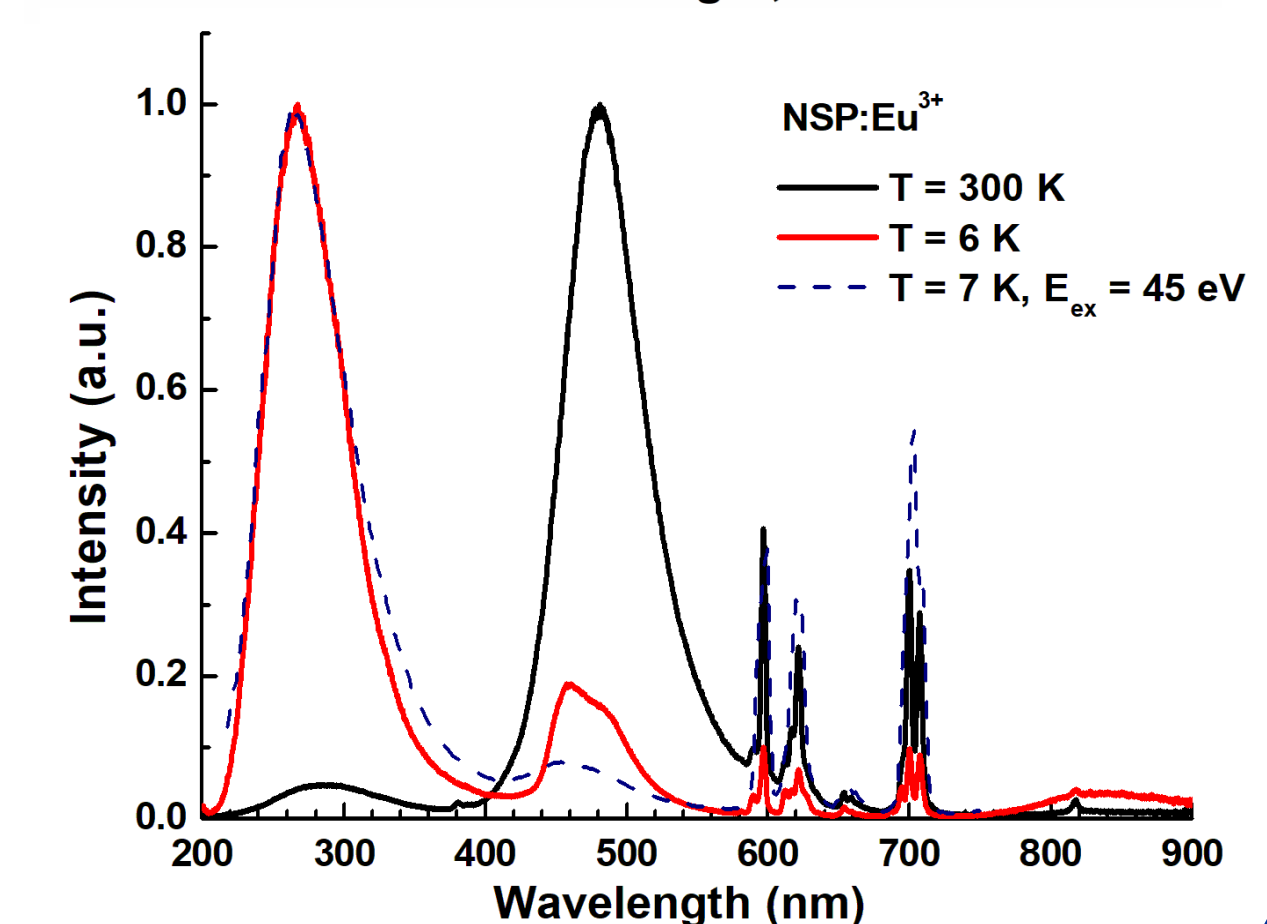
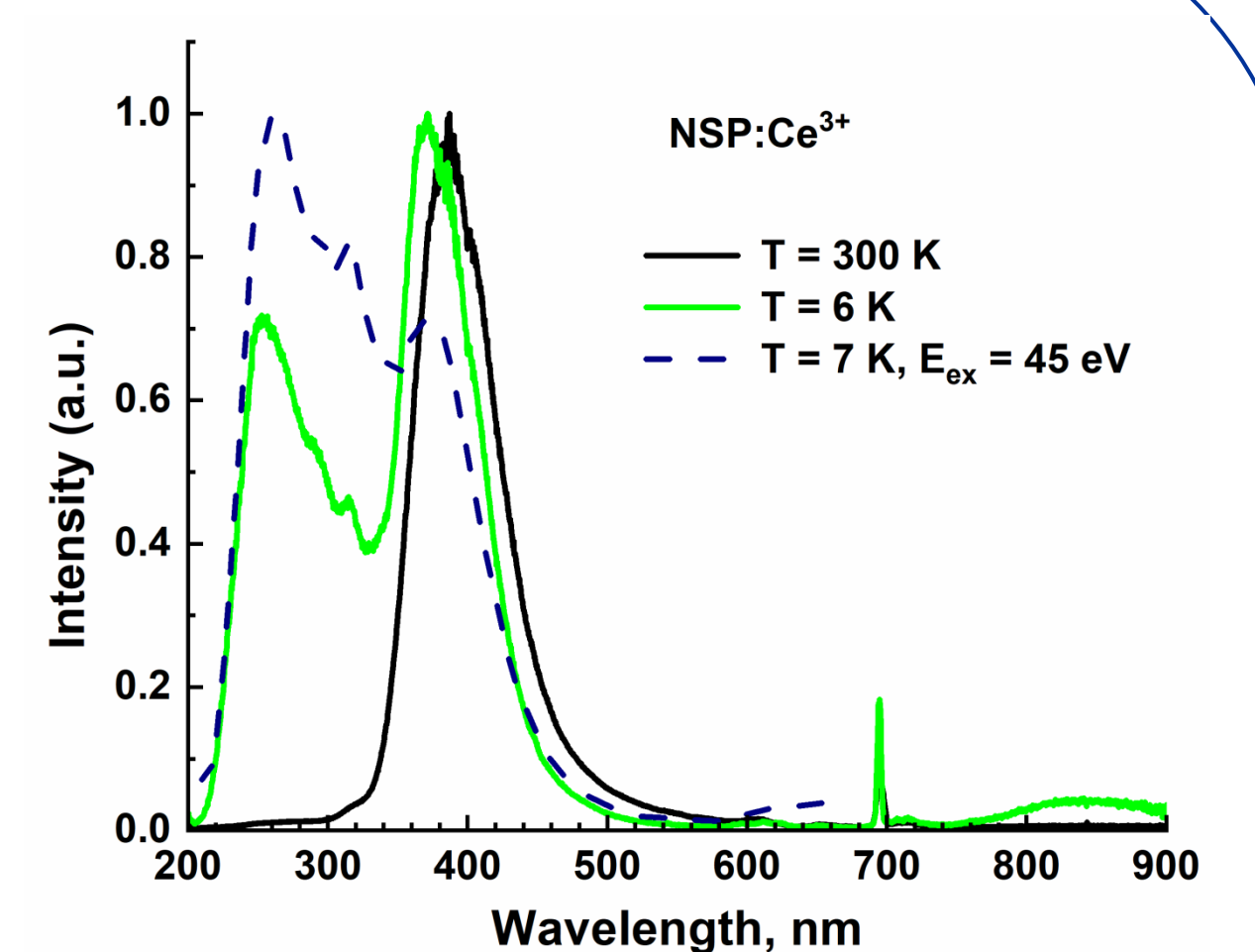


Luminescence excitation spectra of  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  doped with 0.02  $\text{Ce}^{3+}$  (a) at  $\lambda_{\text{em}} = 240$  (1), 340 (2) and 400 (3) nm and 0.01  $\text{Eu}^{3+}$  (b) at  $\lambda_{\text{em}} = 600$  (1) and 450 (2) nm,  $T = 7$  K.

- At low temperature a correlation between cathodo- and photoluminescence ( $E_{\text{ex}} = 45$  eV) spectra is observed with redistribution of bands intensities for both phosphates. At room temperature only defect-related band at ~385 nm takes place in CL spectrum of NSP: $\text{Ce}^{3+}$ , while the band tentatively related to  $\text{Eu}^{2+}$  emission dominates in case of NSP: $\text{Eu}^{3+}$  compound.

- The emission spectra of  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  doped by  $\text{Ce}^{3+}$  or  $\text{Eu}^{3+}$  ions, demonstrate intense dopant emission only under intraband excitation. However, dopant emission is weak under the excitation above the fundamental absorption edge ( $E_{\text{ex}} > 7.1$  eV) that is related to the low efficiency of energy transfer from the host to these centers as well as the presence of competitive radiative relaxation channels such as intrinsic and defect-related emission centers.

- A broad structured band in the region of 4.8–7.3 eV in the excitation spectra of NSP: $\text{Eu}^{3+}$  is related to charge transfer from the 2p O to 4f  $\text{Eu}^{3+}$  states. The dips at 5.1 and 6.4 eV – consequence of the competition with the excitation of  $\text{Eu}^{2+}$  ions.



Cathodoluminescence spectra of  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  doped with 0.02  $\text{Ce}^{3+}$  and 0.01  $\text{Eu}^{3+}$  at different temperatures.

## Conclusions

The luminescent properties of NASICON-type  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  phosphates, undoped and doped with  $\text{Ce}^{3+}$  or  $\text{Eu}^{3+}$ , were studied under high-energy excitation for the first time. The origin of the emission bands was determined. Intrinsic emission originating from self-trapped excitons with electron component localized at the 3d Sc states was detected in all compounds. The factors determining the energy transfer efficiency from the host to emission centers were elucidated. The bandgap value was estimated on the basis of excitation spectra analysis to ~8 eV.