

Luminescence of Eu^{3+} doped $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ and $\text{Na}_{3.6}\text{Y}_{1.8}(\text{PO}_4)_3$ under high energy irradiation



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Motivation

Compounds containing rare earth elements have applications in many technologies, from medicine and telecommunications to solid-state lighting and displays. Among the trivalent lanthanides, Eu^{3+} is well known for its strong emission in the red spectral region and is also a luminescent probe for material structure studies. Phosphates, with their structural features, high chemical and thermal stability over a wide temperature range, are a suitable host type and good candidates for solid-state lighting.

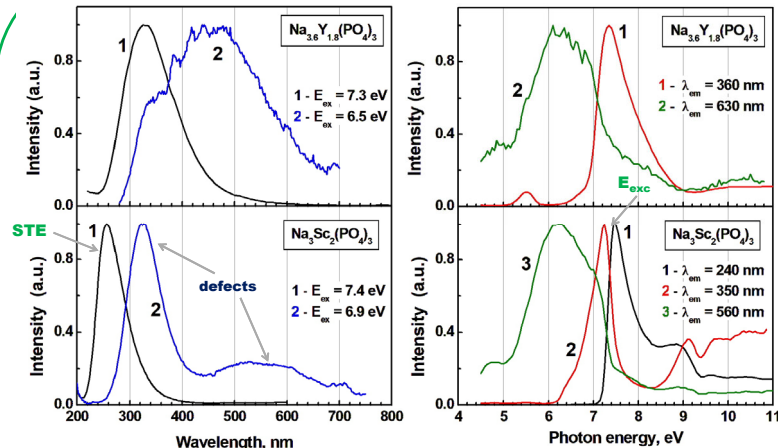
Recently, $\text{Na}_{3.6}\text{Lu}_{1.8-x}(\text{PO}_4)_3$ doped with Eu^{3+} has been shown to improve the thermal stability of europium emission due to the increase in level population with temperature rise [N. Krutyak, D. Spassky et al. Dalton Trans. 51 (2022) 11840]. Here we present the results of the study of the luminescence properties of Eu -doped $\text{Na}_{3.6}\text{Y}_{1.8-x}(\text{PO}_4)_3$ and $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ under high-energy irradiation.

Experimental details

$\text{Na}_{3.6}\text{Y}_{1.8-x}(\text{PO}_4)_3$ (NYP) and $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ (NSP) phosphates doped with 0.7 and 0.01 mol% Eu^{3+} , respectively, were synthesised in a reduction atmosphere by a high-temperature solid-state method. Powder X-ray diffraction study revealed that the obtained compounds were single-phase with a NASICON-type structure.

Photoluminescence (PL) studies in the energy range 2.5 – 9 eV were carried out using a laboratory setup. The studies at higher excitation energies up to 40 eV were performed at the photoluminescence endstation of the FinEstBeAMS beamline of the MAX IV synchrotron radiation facility. Luminescence spectra and emission decay curves were also recorded at the laboratory pulsed cathodoluminescence (CL) setup.

$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ and $\text{Na}_{3.6}\text{Y}_{1.8}(\text{PO}_4)_3$ phosphates



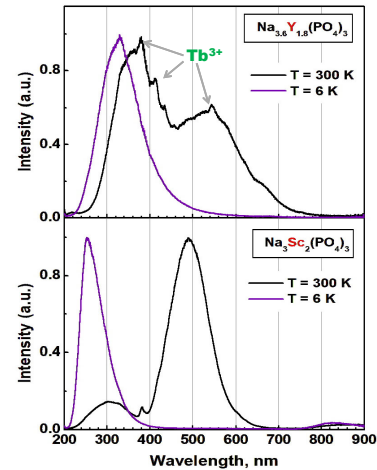
Photoluminescence (left) and excitation (right) spectra of NYP and NSP phosphates, $T = 7$ K.

> Y and Sc-containing sodium-based phosphates with NASICON structure have different luminescence properties.

> A good correlation is observed between the PL ($E_{\text{ex}} = 7.3/7.4$ eV) and CL ($E = 120$ keV) spectra at low temperature.

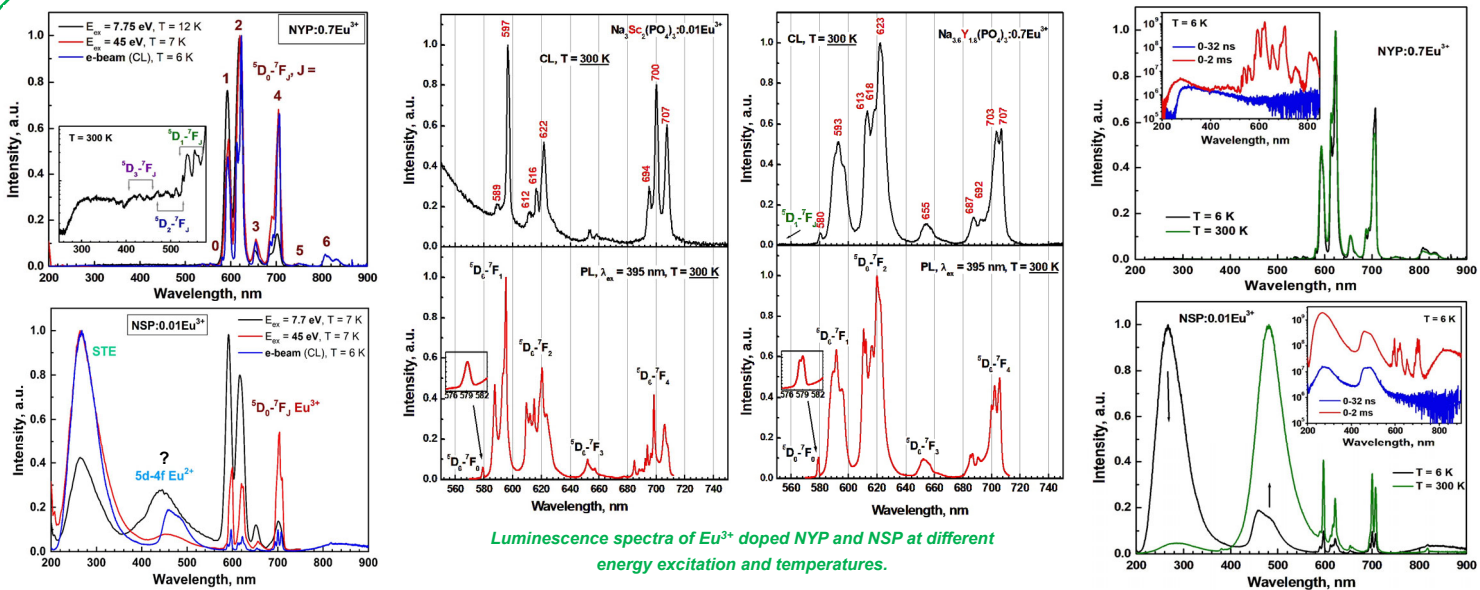
> At room temperature, the CL band shifts to the long-wavelength region, and traces of Tb^{3+} uncontrolled impurity are present in NYP. A defect-related band at ~ 490 nm dominates in the CL spectrum of NSP phosphate.

Cathodoluminescence spectra of NYP and NSP at different temperatures.



- > The intrinsic emission band at 260 nm is observed only for the $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ compound. This band is related to self-trapped excitons (STE) with an electron component belonging to 3d Sc, which explains the absence of this band in $\text{Na}_{3.6}\text{Y}_{1.8-x}(\text{PO}_4)_3$.
- > Broad emission bands at 325 and 530 nm were ascribed to the defects of NSP crystal structure, presumably to the complexes with oxygen vacancies.
- > The NYP luminescence is characterised by bands at 330 and around 480 nm, which are related to the emission of structural defects. These emission centers can be excited at energies below the energy of the exciton peak ($E_{\text{exc}} = 7.45$ eV).

$\text{Na}_3\text{Sc}_{1.99}(\text{PO}_4)_3:0.01\text{Eu}^{3+}$ and $\text{Na}_{3.6}\text{Y}_{1.1}(\text{PO}_4)_3:0.7\text{Eu}^{3+}$ phosphates



Luminescence spectra of Eu^{3+} doped NYP and NSP at different energy excitation and temperatures.

> For $\text{Na}_{3.6}\text{Y}_{1.8-x}(\text{PO}_4)_3:0.7\text{Eu}^{3+}$ phosphate, only the Eu^{3+} emission with domination of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition at 623 nm is observed, independently of temperature or excitation energy. On CL spectra, bands related to the transitions from the ${}^5\text{D}_3$, ${}^5\text{D}_2$ and ${}^5\text{D}_1$ levels in Eu^{3+} ions are also detected. The low site symmetry of the Eu^{3+} environment in the host and location of Eu^{3+} ions in non-inversion sites have been established.

> For $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3:0.01\text{Eu}^{3+}$ phosphate, the intrinsic emission dominates at high energy excitation and low temperature, whereas the Eu^{3+} emission is more intense at $E_{\text{ex}} = 7.7$ eV. A broad band in the region 350–550 nm is also detected, which dominates in the CL spectrum at $T = 300$ K and can be ascribed to the 5d-4f transitions in Eu^{2+} . Competition between all emission centers takes place.

Conclusions

The luminescent properties of NASICON-type $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ and $\text{Na}_{3.6}\text{Y}_{1.8-x}(\text{PO}_4)_3$, undoped and doped with Eu^{3+} ions, were studied in a wide energy range for the first time. Intrinsic emission originating from self-trapped excitons was detected only in $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$. The behaviour of the Eu^{3+} emission in both phosphates was studied. The influence of temperature on luminescence properties, particularly energy transfer between the host and dopant, has also been analysed.

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