

Metaphosphates as surface modifiers for fluoride phosphors

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Conventional fluorescent lamps rely on the very efficient generation of 254 nm radiation excited by a discharge in mercury vapour. This radiation is converted to visible light by luminescent powders with a quantum efficiency close to unity. A non-toxic, but also very efficient alternative to mercury is xenon; however emission from such discharges yields photons with much higher energy (vacuum wavelength of about 170 nm). Luminescent powders with quantum efficiencies higher than unity are needed in order to employ such radiation sources without excessive energy loss.

The quest for suited down-conversion (or cascade) phosphors so far has delivered only fluorides (e.g. $LiYF_4$ or $LiGdF_4$) doped with lanthanoids (see e.g. [1, 2]). There is little hope to find alternative host materials among simple oxides, since charge-transfer absorption by lanthanoid ions and oxygen ligands typically leads to absorption in the spectral region of the discharge emission. Unfortunately, fluorides tend to decompose in contact with water or humidity as well as under particle bombardment in the discharge. Therefore materials (and processes to apply them) are needed that act as protective coatings on fluoride phosphor particles. Suited materials should be oxides for stability reasons and should be transparent down to at least 170 nm.

Among others, phosphates are promising materials for the purpose sketched. They have a large band gap (for orthophosphates lower than 170 nm [3]) and can be synthesized by simple solid state reactions [4, 5], by surface reactions or by sol-gel-methods [6]. Phosphates occur in various polymorphs or in glassy form. Since glass transition temperatures at least for metaphosphates or mixed phosphate glasses are quite low [7], it should be possible to apply thin protecting phosphate coatings on fluoride phosphor particles at comparably low temperature. Once a phosphor particle is covered with a phosphate layer, further modifications by reacting the layer with e.g. fluorides or borates should be possible, opening the way to further modification of the surface.

In order to check the optical data of suited materials, various glassy and crystalline lanthanoid metaphosphates [$Y(PO_3)_3$, $Ce(PO_3)_3$, $Pr(PO_3)_3$, $Nd(PO_3)_3$] have been characterized by means of their reflectivity and excitation spectra (as measures for the absorption behaviour) on the HASY-LAB Superlumi station. Samples were ground, mounted from an ethanolic slurry and then dried in vacuum before measurement.

Fig.1 depicts the absorption of crystalline $Y(PO_3)_3$ from the reflectivity measured at room temperature, recalculated as Kubelka-Munk-function [$F = (1 - R_\infty)^2 / (2 * R_\infty)$], which is proportional to absorption (provided, scattering power is invariant). Fundamental absorption starts at about 160 nm. However, additional absorption is observed in the region around 250 nm; it may be caused by impurities or defects. The onset of absorption is found also in the lanthanoid excitation spectra, but compounded with absorption bands of the lanthanoids themselves. Fig.2 shows the excitation spectrum of $Nd(PO_3)_3$, taken at 9 K and being monitored at 270 nm. Excitation sets in at about 180 nm ($5d \rightarrow 4f$ -transition), convoluted with band gap absorption. Concluding, the optical properties of metaphosphate coatings should be suited to protect fluorides without introducing too much absorption.

Future work will work out preparational routes for the application of phosphates with reproducible stoichiometry; a detailed description of the surface chemistry of fluorides will be a prerequisite.

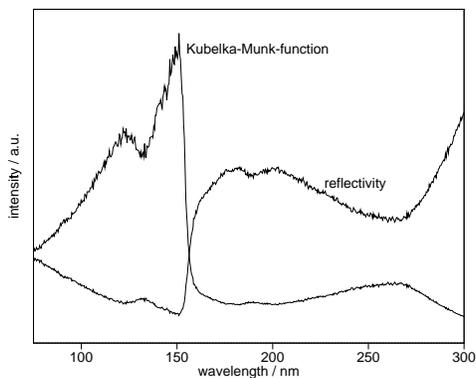


Figure 1: Reflectivity and Kubelka-Munk-function for yttrium metaphosphate

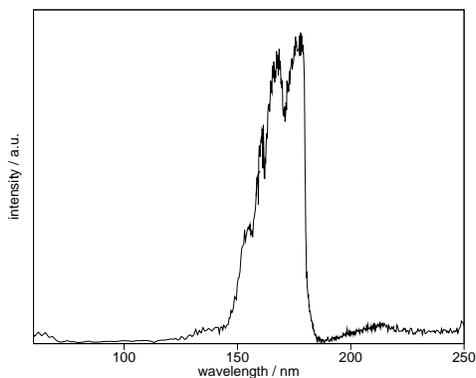


Figure 2: Excitation spectrum (monitor 270nm) for neodymium metaphosphate

This work was funded by *BMBF* in the framework of the project *VUV Leuchtstoffe*.

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