

# On the luminescence of $\text{Lu}_{3-x}\text{Pr}_x\text{Al}_5\text{O}_{12}$ ceramic bodies

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## Abstract

Luminescent materials are widely applied as converter screens in fluorescent lamps, LEDs, emissive displays, x-ray and high energy particle detectors, and solid state LASERs. In most of the application areas, the luminescent compositions are applied as polycrystalline powders, however, some devices require single crystalline materials, e.g. solid state LASERs or positron emission tomographs.

Since single crystal growth is difficult and rather time consuming, applied crystals are very expensive. Moreover, some application areas require very homogenous and anisotropic optical and thermal properties, which sometimes cannot be sufficiently fulfilled by single crystals due to the inhomogeneous distribution of the cations and peculiarities of the phase diagram. Therefore, the replacement of single crystals by transparent ceramics is of growing interest. An important requirement for the realization of transparent ceramic bodies is the anisotropy of the index of refraction, which is given in cubic materials.

Minerals of the general composition  $\text{A}_3\text{B}_2\text{Si}_3\text{O}_{12}$  (A = Mg, Ca, Fe, Mn; B = Al, Fe, Cr) and ternary oxides according to the formula  $\text{Ln}_3\text{Al}_5\text{O}_{12}$  (Ln = Y, Gd, Lu) crystallize in the cubic garnet structure. The latter compounds are ideal host lattices for the luminescent ions  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Tb}^{3+}$ . Thus the respective luminescent materials have found numerous applications as LED and display phosphors, as gain media in LASERs, and as scintillators in x-ray machines for medical imaging.

This work deals with the preparation and spectroscopic characterization of  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$  ceramic bodies, whereby their optical properties were compared to polycrystalline powders and single crystals. An important finding, in view of their application, is that the decay time of the  $[\text{Xe}]5d^14f^1 - [\text{Xe}]4f^2$  and  $[\text{Xe}]4f^2 - [\text{Xe}]4f^2$  transitions of the  $\text{Pr}^{3+}$  ion in the ceramics is significantly different from the  $\text{Pr}^{3+}$  ion in  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$  powders. With respect to the relation between the internal quantum efficiency of  $\text{Pr}^{3+}$  and the decay constant, possible explanations will be discussed.

**Keywords:** Luminescent materials, optical properties, garnets, sol-gel processes

## CERAMIKA $\text{Lu}_{3-x}\text{Pr}_x\text{Al}_5\text{O}_{12}$ O WŁASNOŚCIACH LUMINESCENCYJNYCH

Materiały luminescencyjne – luminofory znajdują zastosowanie do konwersji promieniowania w lampach świetłówkach, diodach LED, w świecących ekranach, w czujnikach promieniowania wysokoenergetycznego, a także w stałych laserach. W większości zastosowań luminofory używa się w postaci proszków, chociaż w niektórych przypadkach potrzebne są monokryształy, jak to ma miejsce w technice laserowej, czy w tomografach.

Hodowla monokryształów luminoforów jest wyjątkowo trudna i kosztowna. Związczą że w niektórych przypadkach wymagana jest wysoka jednorodność i anizotropia optyczna, jak również termiczna dla materiału luminescencyjnego. Jest to głównie gwarantowane przez monokryształy, przy czym także w tym przypadku mają miejsce niejednorodności w rozproszaniu kationów domieszki, a także występują braki w znajomości układów równowag. Z tego punktu widzenia występuje duże zainteresowanie, żeby zastąpić monokryształy polikrystaliczną ceramiką przezroczystą. Wymaga się przy tym, żeby uzyskiwać materiał jednorodny optycznie, korzystnie o strukturze krystalograficznej regularnej.

Minerały o ogólnym składzie chemicznym  $\text{A}_3\text{B}_2\text{Si}_3\text{O}_{12}$  (A=Mg, Ca, Fe, Mn, i B=Al, Fe, Cr) a także sztuczne związki typu  $\text{Ln}_3\text{Al}_5\text{O}_{12}$  (Ln=Y, Gd, Lu) krystalizują w układzie regularnym i należą do rodziny granatów. Te ostatnie związki uważa się za idealną sieć macierzystą dla aktywatorów typu:  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  i  $\text{Tb}^{3+}$ . Tym sposobem powstały wysoko cenione luminofory znajdujące szerokie zastosowania w diodach LED, w ekranach świecących, jako aktywne media laserowe, a także w scyntylatorach promieniowania X w tomografach.

Powyższa praca przedstawia wyniki syntezy i charakterystyki widmowe uzyskane dla ceramiki  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$ . Dokonano porównania własności materiału proszkowego i ceramiki, a także danych literaturowych dotyczących monokryształu. Jako ważne z punktu widzenia zastosowań pokazano że czasy gaśnięcia dla przejść  $5d, 4f_2-4f_2$  i  $4f_2-4f_2$  dla jonu  $\text{Pr}^{3+}$  w ceramice są różne niż dla proszku.

**Słowa kluczowe:** luminofory, właściwości optyczne, granaty, proces zol-żel

## Introduction

Luminescent materials (phosphors) emit radiation upon excitation by electromagnetic radiation or application of an electrical field beyond thermal equilibrium. The main components of inorganic phosphors are the host lattice and the

dopants, which replace lattice cations at appropriate sites. To obtain materials with high conversion efficiency, ideally close to 100%, absorbed energy must be efficiently transferred to the activator ions, which are in turn promoted to an excited state. Moreover, the excited activator ions must mainly return to the ground state radiatively. In case of pho-

to excitation, a high quantum efficiency of close to 100% is mostly possible, but requires a highly crystalline host lattice with a low defect density and limited energy transfer to the surface. Energy migration to the surface causes often a reduction of quantum efficiency, if the crystallite sizes are in the nanoscale range.

Upon x-ray or high energy particle excitation, the first step in the luminescence process is the thermalisation of the incident particles or photons upon the formation of a large number of excitons. This process goes hand in hand with substantial losses due to the formation of lattice phonons. These excitons show subsequently energy transfer to the activator site, which is another process suspected to losses. Consequently, the energy efficiency or light yield (LY) of an x-ray phosphor (scintillator) is lower than 30% and thus much lower as compared to photoexcitation. The overall light yield of a scintillator upon 1 MeV photon excitation can be written as

$$LY = [10^6/\beta E_g] S \cdot QE$$

where  $\beta$  is a constant,  $E_g$  is the band gap of the host,  $S$  is the transfer efficiency to the activator and  $QE$  is the quantum efficiency of the activator [1].

In many of the application fields of luminescent compositions, the phosphor is applied as a polycrystalline powder in a thick layer, the so-called luminescent screen. Those screens can be found in fluorescent tubes and in emissive displays, such as CRTs, FEDs, and PDPs. Some application areas of luminescent compositions require single crystals due to the necessity to avoid scattering. The loss of spatial information or coherence of radiation must be avoided, e.g. in solid state LASERs or positron emission tomographs. A presently investigated alternative material class to single crystals is transparent ceramic, since this opens up the access to novel material compositions, for which crystal growth is difficult and time consuming. However, even lamps and displays can profit from transparent ceramics. Those ceramics are of particular interest for phosphor converted LEDs, where to much scattering by the conversion layer must be avoided to preserve the beam quality. A good beam quality is of importance for projection purposes and automotive lighting.

Application of luminescent ceramics in solid state LASERs requires completely transparent bodies, whereby other physical parameters, such as thermal conductivity and homogeneity of the refractive index of the ceramic, are important too. Scintillator ceramics must not only be highly transparent, but should also show a fast response to the incident high energy particles or photons and a short decay time. High transparency is here of particular importance, since scattering hampers the transport of the photons to the photomultipliers [2]. Moreover, the optical properties of the scintillator ceramic must be aligned to the sensitivity function of the detector, since this determines the analytical quality of CTs, PETs, and x-ray cameras.

The production of transparent ceramics mostly starts from the respective luminescent powder, which is converted into a ceramic body by several physical treatments. This work deals with LuAG, which is a well investigated host material [3-6] with a band gap of 7.6 eV (165 nm). More particularly, it deals with the synthesis of  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$  (LuAG:Pr) powder, its conversion into transparent ceramics and the optical pro-

perties of the powder and ceramics. Particularly, the effect of the doping concentration on the optical properties of the ceramic was studied.

## Experimental Section

### Sample Preparation

All  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}$  samples were synthesized by conventional sol-gel synthesis. To this end,  $\text{Lu}_2\text{O}_3$  was dissolved in  $\text{HNO}_3$  and to this solution appropriate amounts of  $\text{Al}(\text{NO}_3)_3$  and  $\text{Pr}(\text{NO}_3)_3$  were added and subsequently 1 h stirred at 70 - 75 °C. Afterwards, 1,2-ethandiole was added and the solution stirred for further 30 min. Then the solvent was removed at a rotary evaporator and the dry residue was milled to a fine powder. This precursor was calcined at 900 - 1000 °C for 2 h.

To produce ceramics, the obtained powder was blended with a flux ( $\text{BaF}_2$  or  $\text{MgSiO}_3$ ) and further additives (polyethylene glycol, poly acrylic acid, ethyl cellulose), pressed to tablets by an uniaxial press at a pressure of about 300 MPa and the tablets were sintered at 1500 - 1700 °C, whereby the last thermal treatment was done in air or in a CO atmosphere.

### Characterisation

From all powder and ceramic samples powder diffraction diagrams were recorded on a Mini Flex II equipment (Rigaku) using  $\text{Cu K}_\alpha$  radiation. The morphology and micro structure of selected ceramic samples was studied by an optical microscope (Nikon). Optical characterisation was done on a spectrometer set-up based on an Edinburgh Instruments FS 920 equipment.

## Results and Discussion

### a) Powder Samples

All synthesised LuAG:Pr were highly crystalline materials, whereby the reflection spectrum show two strong absorption bands at 240 and 280 nm caused by interconfigurational  $[\text{Xe}]4f^2$  to  $[\text{Xe}]4f^15d^1$  transitions of  $\text{Pr}^{3+}$  and two sets of weak absorption line multiplets centred at 460 and 600 nm due to intraconfigurational  $[\text{Xe}]4f^2 - [\text{Xe}]4f^2$  transitions of  $\text{Pr}^{3+}$  (Fig. 1 right).

### b) Ceramic Samples

Ceramics with the composition  $\text{Lu}_{3-a}\text{Pr}_a\text{Al}_5\text{O}_{12}$  ( $a = 0.003, 0.015$  and  $0.03$ ) were prepared to investigate the effect of the  $\text{Pr}^{3+}$  concentration on the optical properties. Moreover, the effect of the gas atmosphere, i.e. air and CO, on the phase composition and crystalline character was studied. It turned out the gas atmosphere has no influence on the phase composition of the ceramics. However, ceramics annealed in air show a higher crystallinity (Fig.1 left).

Moreover, the grain growth in the ceramics was studied, since grain size has a strong impact on the optical properties of powders/ceramics, as shown by the following reflection spectra (Fig. 2). Reflection spectra of the three samples with different  $\text{Pr}^{3+}$  concentrations show that the intensity of the absorption bands caused by  $\text{Pr}^{3+}$  increases with increasing  $\text{Pr}^{3+}$  concentration.

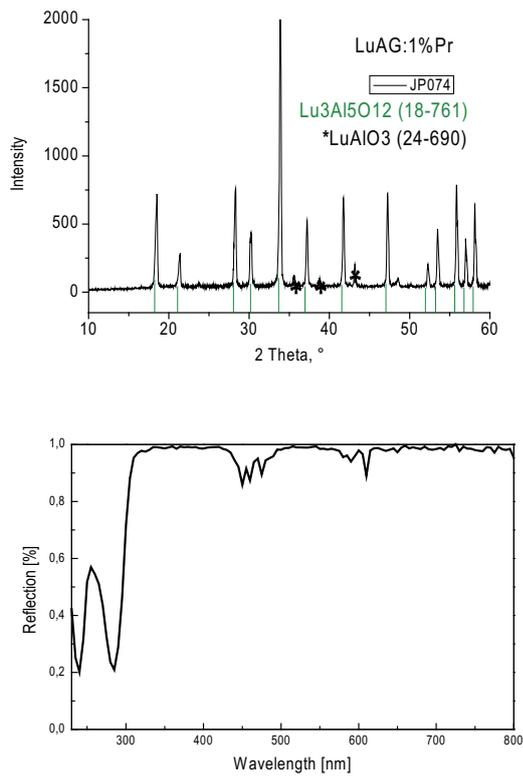


Fig. 1. XRD pattern (up) and reflection spectrum (down) of LuAG:Pr<sup>3+</sup>(1%) powder sintered at 1000°C

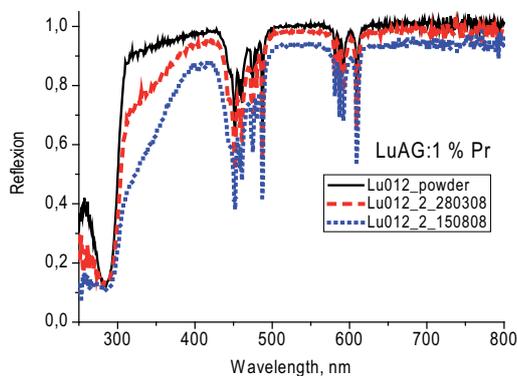


Fig. 2. Reflection spectra of LuAG:Pr<sup>3+</sup>(1%) powder and two respective ceramic bodies sintered at 1750 °C and subsequently at 1650°C

From emission spectra upon excitation by a blue LED (465 nm), the optimal concentration of Pr<sup>3+</sup> in the LuAG:Pr ceramics can be estimated. The following graph show that the concentration should be adjusted between 0.5 and 1.0% Pr<sup>3+</sup> (Fig. 3). The transmission grade of all tablets having a thickness of 1.2 mm was around 15%.

The emission spectra recorded in transmission mode show the LED spectrum superimposed by the LuAG:Pr<sup>3+</sup> emission spectrum. In contrast, emission spectra measured in reflective mode, solely show the LuAG:Pr<sup>3+</sup> emission spectrum, which comprises a large number of emission lines between 480 and 680 nm due to the  $[\text{Xe}]4f^2 - [\text{Xe}]4f^2$  transitions of Pr<sup>3+</sup> (Fig. 4).

The excitation spectrum of the ceramics monitored for the red 610 nm line demonstrate that LuAG:Pr ceramics can be efficiently excited by blue diodes.

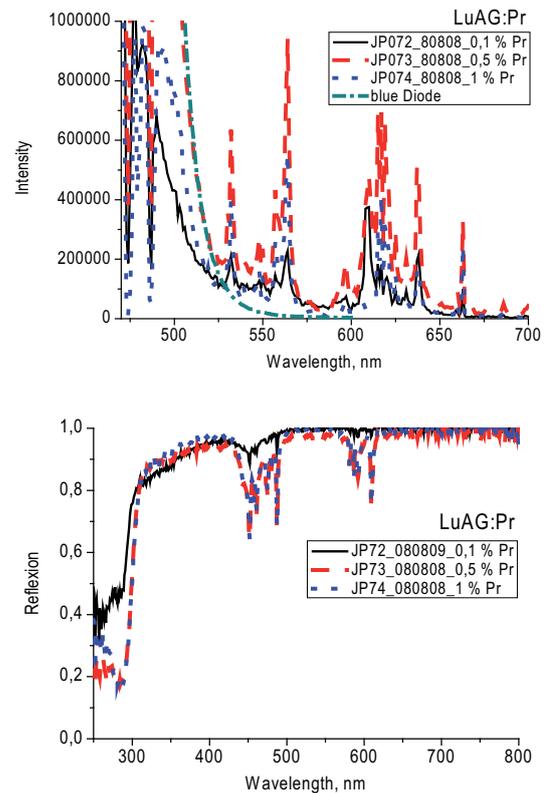


Fig. 3. Emission spectra in transmission (up) and the reflection spectra (down) of LuAG:Pr<sup>3+</sup> ceramics with a Pr<sup>3+</sup> concentration of 0.1, 0.5, or 1% (thickness of the tablets ~ 1.2 mm)

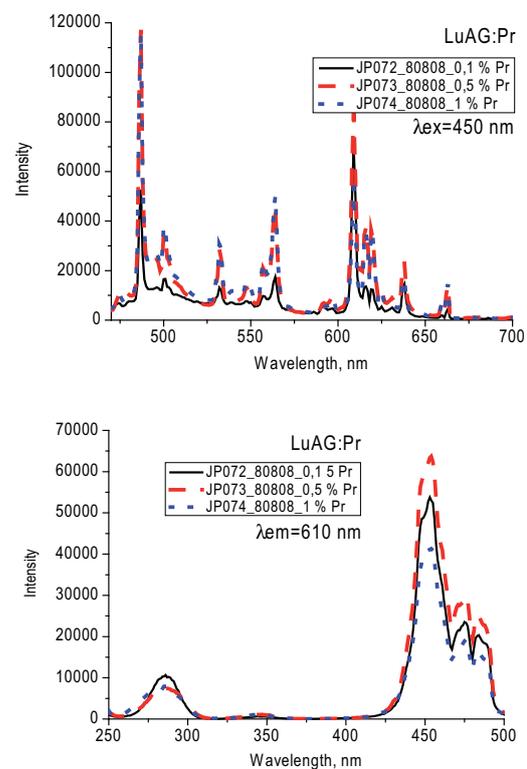


Fig. 4. Emission spectra (up) upon 450 nm excitation and excitation spectra (down) monitored at 610 nm of LuAG:Pr<sup>3+</sup> ceramics with a Pr<sup>3+</sup> concentration of 0.1, 0.5, or 1% (thickness of the tablets ~ 1.2 mm), measured in a reflective mode

Since LuAG:Pr show strong absorption bands in the UV range due  $[\text{Xe}]4f^2 - [\text{Xe}]4f^15d^1$  transitions at 230 and 280 nm and due to band gap excitation at around 160 nm (Fig.

5), the emission spectra of the ceramics upon UV excitation were also studied. This is of particular interest for the application of LuAG:Pr ceramics as a scintillator, since band gap excitation is the final result of excitation by high energy particles or photons.

All LuAG:Pr samples, i.e. powders and ceramics, show several strong and overlapping emission bands upon 160 nm excitation, whereby the peak intensity is at 310 nm. These bands are due to the interconfigurational  $[Xe]4f^15d^1$  to  $[Xe]4f^2$  ( $^3H_{4,5,6}$  and  $^3F_2$ ) transitions.

Thus,  $Pr^{3+}$  doped LuAG powders and ceramics exhibit strong UV and visible emission, whereby the emission spectra upon 160 and 450 nm excitation can be explained by a simplified Dieke diagram (Fig. 8) including the expected position of the lowest crystal-field component of the  $[Xe]4f^15d^1$  configuration.

The emission spectrum upon 160 nm excitation thus fits to the sensitivity range of GaN photodiodes. However, the application of LuAG:Pr ceramics as a scintillator requires highly transparent ceramics. Therefore, the impact of additives on the optical properties of the LuAG:Pr ceramic was studied too, since fluxes and sinter additives promote the grain growth and thus can enhance the transparency of resulting ceramic bodies.

It turned out, that grain growth, which will result in samples with less scattering, can be promoted by extending the annealing time and/or the application of  $MgSiO_3$  as a flux (Fig. 6).

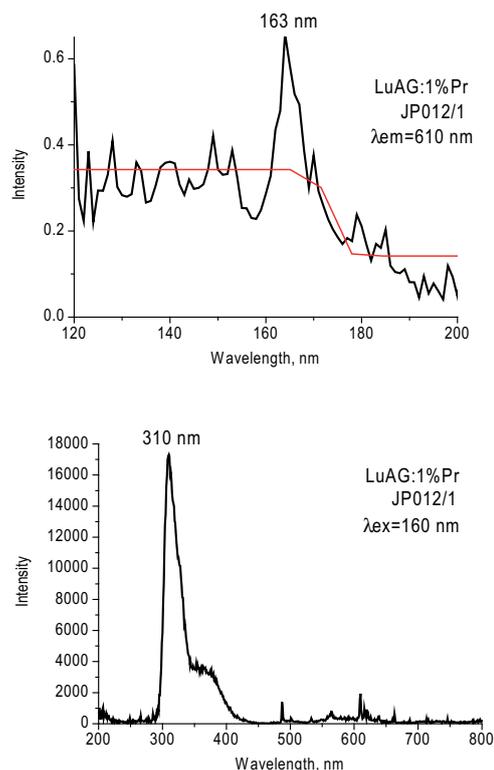


Fig. 5. Excitation spectrum (up) monitored at 610 nm and emission spectrum (down) for 160 nm excitation of a LuAG:Pr<sup>3+</sup> ceramic with a Pr<sup>3+</sup> concentration of 1% (thickness of the tablets ~ 1.2 mm)

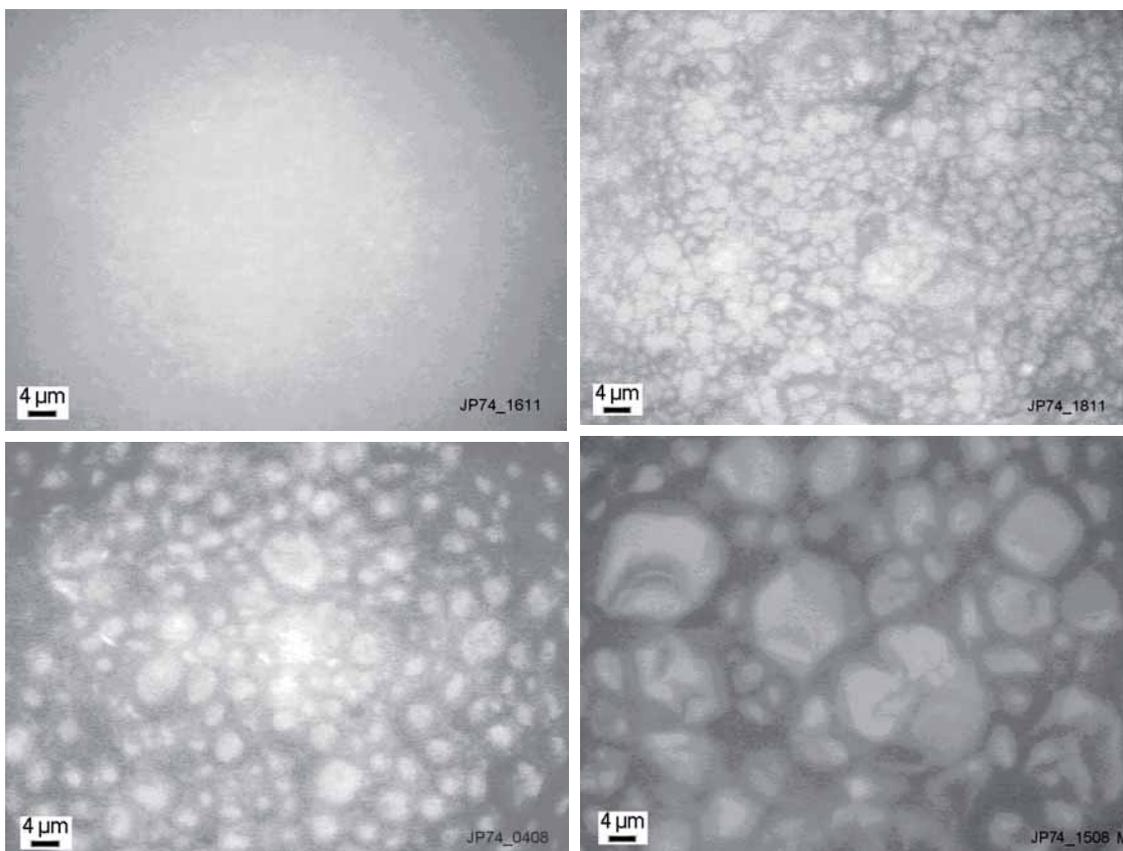


Fig. 6. Photographs of non-polished surface of a ceramic, firstly annealed at 1000°C in air for 12 h (top left) and subsequently annealed at 1650 °C in air for 12 h (top right) without a flux. Photographs of samples subsequently annealed at 1650°C in air for 48 h without a flux (bottom left) and with a  $MgSiO_3$  flux (bottom right). (magnification 1000x)

Finally, we investigated the luminescence of LuAG:Pr ceramics as function of time, since the rise and decay time of scintillators is of tremendous importance for many application areas. The decay curve of the 610 nm luminescence after excitation by 450 nm light is given in the following graph. The recorded intensity curve can be fitted by two exponential decay functions, whereby the decay constants are 42 and 108  $\mu\text{s}$  (fig. 7).

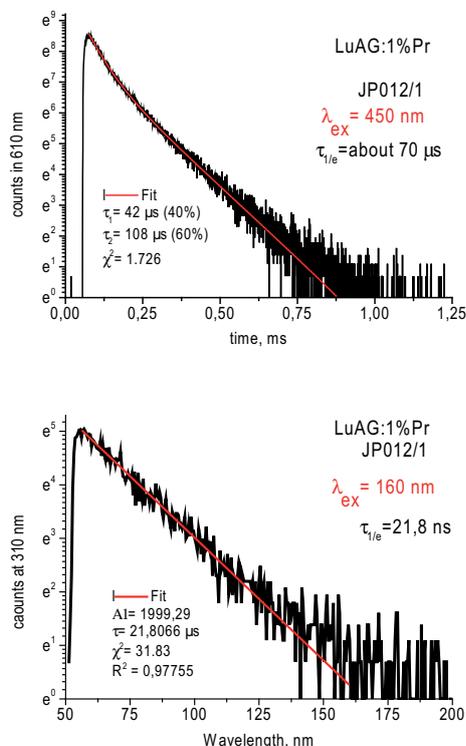


Fig. 7. Decay curves of a LuAG:Pr<sup>3+</sup> ceramic upon 450 nm excitation (up) and upon 160 nm excitation (down)

In contrast to that, results the excitation upon 160 nm in intense UV luminescence showing a mono exponential decay curve that can be fitted by a decay time constant of around 22 ns. This value is practically equal to the published data for single crystals [6-8].

## Conclusions

We have demonstrated that LuAG:Pr<sup>3+</sup> powders with a high quality can be made by sol-gel synthesis. The transformation into translucent ceramics can be done by standard ceramic processes; however, to achieve highly transparent ceramics a further optimisation of our process will be required. LuAG:Pr ceramics show mainly UV luminescence upon deep UV excitation, while excitation by a blue 450 nm LED results in green to red luminescence. The decay time of our LuAG:Pr ceramics upon 160 nm excitation is 22 ns, which is perfectly in line with the decay time of LuAG:Pr single crystals [9].

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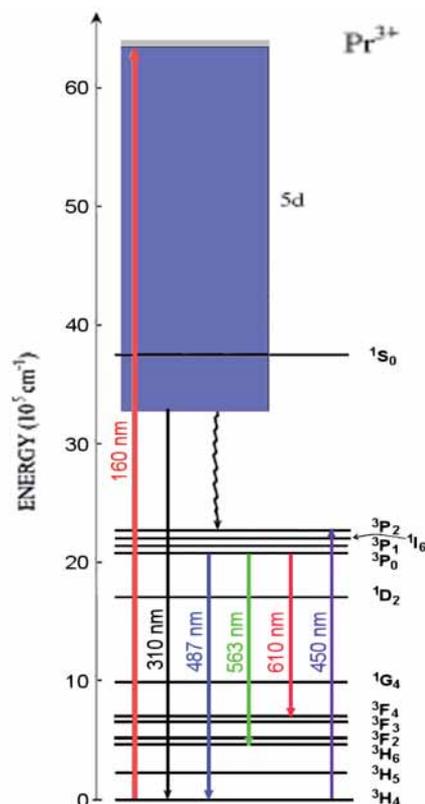


Fig. 8. Simplified energy level diagram of Pr<sup>3+</sup> in LuAG (Energy [in kJ] = Energy[in 10<sup>3</sup>cm<sup>-1</sup>]/83,57)

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