Luminescence and scintillation properties of Mg-codoped LuAG:Pr single crystals annealed in air

Jan Pejchal^{1*}, Maksym Buryi¹, Vladimir Babin¹, Petr Prusa^{1,2}, Alena Beitlerova¹, Jan Barta^{1,2}, Lubomir Havlak¹, Kei Kamada^{3,4}, Akira Yoshikawa^{3,4}, Valentin Laguta¹, Martin Nikl¹

¹*Institute of Physics AS CR, Cukrovarnicka 10, Prague 6, 16200, Czech Republic*

²*Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Brehova 7, Prague 1, 11519, Czech Republic*

³*Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan*

⁴*New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan*

*e-mail: pejchal@fzu.cz

Abstract

The influence of the Mg²⁺ codoping and annealing in the air on the scintillation and luminescence characteristics of Pr-doped lutetium-aluminum garnet crystals (LuAG) was studied to find a possible positive effect of Pr⁴⁺. The overall scintillation efficiency under X-ray excitation of the annealed Pr-doped samples decreased with increasing Mg concentration. This was explained by increased overlap of the Pr³⁺ 5d-4f emission with the charge-transfer (CT) absorption band of the Pr⁴⁺ ion stabilized by Mg²⁺. This absorption caused even greater decrease of the light yield, as the light is collected from the whole sample volume in the pulse-height spectrum measurement. Electron centers based on oxygen vacancies (F⁺ centers) which can have negative influence on scintillation mechanism were revealed by the electron paramagnetic resonance (EPR) experiments. The O⁻ hole center was detected as well and the temperature dependences of the EPR spectra showed that its thermal stability was decreased by Mg codoping. Negligible changes in the decay time of Pr³⁺ 5d-4f photoluminescence exclude the non-radiative energy transfer from relaxed 5d₁ excited state of Pr³⁺ towards CT absorption transition of Pr⁴⁺ and suggest that simple reabsorption of the emitted light takes place. Unlike for the Ce-doped analogues, promoting the Pr³⁺ luminescence center to the tetravalent state by divalent ion co-doping and air annealing did not improve scintillation properties of Pr-doped LuAG.

Keywords: Scintillation; Pr⁴⁺; luminescence; codoping; lutetium-aluminum garnet

1. Introduction

Inorganic scintillation single crystals have been employed in the ionizing radiation detection and related applications for several decades [1]. They are utilized in high-energy physics, environmental monitoring, geological survey and oil well logging or astronomy. Medical imaging and especially security scanning are the applications mostly stimulating the development of new scintillation materials due to increasing demands on their performance.

In several modern inorganic scintillators fast 5d-4f luminescence of Ce³⁺ has been employed to obtain the scintillation response of the order of several tens of ns with high efficiency (see [1] and references therein). Lutetium aluminum garnet (Lu₃Al₅O₁₂, LuAG) single crystal matrix appears as a very suitable host for the Ce³⁺ and other rare earth (RE) luminescence centers due to the Lu site where the RE³⁺ ion can be easily substituted, high density of 6.67 g/cm³, high effective atomic number and mechanical and chemical and thermal resistance [2]. The first systematic studies started almost 2 decades ago [3]. Besides favorable scintillation properties, one of the main demerits of this material was presence of slow components in the scintillation decay caused by retrapping of electrons at the traps related to Lu_{Al} intrinsic anti-site defects (AD) [4], generally present also in some other aluminum garnets due to high crystal growth temperature [5]. This phenomenon caused serious deterioration of the light yield and timing performance. However, it is well known that the flexibility of the garnet matrix allows incorporation of other elements [6] and therefore the lattice constants, band-gap and other parameters such as depth and trapping efficiency of the AD-related traps can be easily tuned. This approach led to development of new slow-component-free and highly efficient Ce-doped scintillator based on the Gd, Ga-admixed multicomponent garnet [7]. Another recent approach to improve the scintillation performance is employing Ce⁴⁺ stabilized with divalent ion (Mg²⁺, Ca²⁺) codoping in the scintillation mechanism [2, 8-10]. The Ce⁴⁺ can be regarded as Ce³⁺ with already captured hole, which is ready for an immediate capture of thermalized electron from the conduction band followed by forming the Ce³⁺ in an excited state. The stable Ce⁴⁺ center directly competes with shallow electron traps responsible for the slow decay components. The de-excitation of this temporary Ce³⁺ results in the usual Ce³⁺ emission which might show somewhat different emission characteristics regarding e.g. temperature stability [8, 11]. Finally, a nonradiative hole capture from a nearby defect or valence band leads to the Ce⁴⁺ center regeneration [12, 13]. This mechanism was reported to be responsible for improvement of scintillation properties of lutetium silicate crystals [8] and also LuAG:Ce optical

ceramics, where Mg^{2+} was used as a sintering aid [9]. Another way to stabilize Ce in its tetravalent form in garnets is annealing in an oxidizing atmosphere [14]. The annealed crystals showed increased light yield and reduced proportion of the slow components in the scintillation decay. The suppression of the slow components is caused also by the reduction of concentration of deep traps related to oxygen vacancies.

Another suitable luminescence center is the Pr^{3+} ion. Some Pr-doped scintillators were briefly investigated in the past [15]. To obtain fast and high-energy-shifted 5d-4f emission of Pr^{3+} the crystal field of the host matrix should be strong enough to shift the lowest 5d-state well below the $^1\text{S}_0$ one to make the 5d-4f radiative transition possible. For details on these aspects of the Pr^{3+} luminescence, see for example [16]. High quality Pr-doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG:Pr) was announced as a fast and efficient scintillator [17,18] and an attempt of its application in positron emission mammography has been already made [19]. Analogous problems with the retrapping at AD's were observed [17]. Similar attempt of composition engineering using Gd and Ga admixture failed in the case of Pr-doped multicomponent garnets due to overlap of the Pr^{3+} 5d-4f emission with the $\text{Gd}^{3+} \text{ } ^8\text{S}_{7/2} \rightarrow ^6\text{P}_j$ transition and resulting energy back-transfer from the Pr^{3+} to the host [20]. There is a question if stabilizing Pr^{4+} by divalent ion codoping or annealing would improve the scintillation properties of garnet-based scintillators. Radiation hardness and some luminescence properties of Mg-codoped LuAG:Pr were studied recently and no positive influence was found mainly due to presence of Yb^{3+} and other impurities [21, 22]. However, systematic study of scintillation properties of Mg-codoped LuAG:Pr is still missing. Thus the aim of this work is to investigate absorption, luminescence and scintillation properties of Mg-codoped and annealed LuAG:Pr for different concentrations of Mg codopant.

2. Materials and Experimental Methods

The crystals were grown by micro-pulling-down method [23, 24] with radiofrequency inductive heating. An iridium crucible with a die of 3 mm in diameter was used. The growth was performed under N_2 (4N) atmosphere using $\langle 111 \rangle$ oriented LuAG single crystal as a seed. The pulling speed was around 0.07-0.1 mm/min. The starting materials were prepared by mixing 4N purity Lu_2O_3 , Al_2O_3 and Pr_6O_{11} powders. MgCO_3 of 4N purity was added to the mixture for the Mg-codoped samples.

The LuAG:Pr samples with Pr concentration of 0.2 atomic % were prepared. The Mg concentration was 0, 300 or 3000 atomic ppm. It is reasonable to suppose that Pr substitutes for Lu while Mg substitutes for Al, even though it can be incorporated in all the three kinds of sites available within the garnet structure [6]. Therefore the Pr concentration is given with respect to Lu, while the Mg concentration is given with respect to Al. Then

we can specify the hypothetical formula of the grown crystal as $\text{Lu}_{3(1-x)}\text{Pr}_{3x}\text{Al}_{5(1-y)}\text{Mg}_{5y}\text{O}_{12}$, where $x=0.002$ and $y=0, 0.0003$ and 0.003 . However, the atomic % or atomic ppm will be used for simplicity further in the text to specify the sample composition. One completely undoped crystal was also grown for comparison.

The crystal rods had diameter of 3 mm and were from 35 to 45 mm in length. 1 mm thick circular samples were cut from approximately 1 cm from the beginning (marked as START) and 1 cm from the end (marked as END) of the rod and mirror-polished for further optical characterization. The samples were annealed in air for 12 h at a temperature of 1200°C.

The phase purity of prepared crystals was examined by XRD analysis using the Rigaku MiniFlex 600 powder X-ray diffractometer equipped with Ni-filtered $\text{Cu-K}\alpha_{1,2}$ line and NaI:Tl scintillation detector. Prior to the measurement, a selected part of the prepared crystal was grinded into a fine powder in an agate mortar and its diffraction pattern was then measured in continuous mode between 10° and $80^\circ 2\theta$. The diffraction patterns recorded were fully consistent with the ICDD PDF-2 record 01-73-1368 ($\text{Lu}_3\text{Al}_5\text{O}_{12}$) and showed some evidence of slight preferred orientation due to the grinding of a single-crystalline material.

Luminescence measurements were performed by a modified spectrofluorometer (custom made 5000M model, Horiba Jobin Yvon) equipped with TBX-04 photon counting detector (IBH Scotland). A deuterium steady-state lamp was used for the excitation and emission spectra measurements. An X-ray tube operating at a voltage of 40 kV and 15 mA current with Mo anode (ISO-DEBYEFLEX 3003 Seifert GmbH.) was used as an excitation source for the radioluminescence (RL) measurements. All the spectra were corrected for experimental distortions. The hydrogen nanosecond flashlamp or pulsed nanoLED source (IBH Scotland) were used for the luminescence decay measurements using the methods of time correlated single photon counting. Exponential fits of the decays were obtained by performing the convolution of the considered function with the instrumental response and a least-square sum fitting procedure (SpectraSolve software package from Ames Photonics Inc.). For the light yield measurements, sample crystals were optically coupled with a hybrid photomultiplier (HPMT) DEP PPO 475B. Samples were coupled to the HPMT by silicon grease and wrapped in teflon tape used as a reflector (preliminary, BaSO_4 was used also for one sample, but the result was practically the same as for Teflon). The ^{137}Cs (661.6 keV) source was used for excitation and the amplifier shaping time was 6 μs . The scintillation decay kinetics was measured with a fast photomultiplier and Tektronix TDS3052C digital Phosphor Oscilloscope under ^{137}Cs excitation. Scintillation decay data were evaluated by SpectraSolve as well. All the optical and scintillation measurements were performed at room temperature (RT).

The electron paramagnetic resonance (EPR) spectra were measured using the commercial Bruker X-/Q-band E580 FT/CW ELEXSYS spectrometer at X-band (microwave frequency 9.5 GHz) within the temperature range 10-296 K using an Oxford Instruments ESR900 continuous flow cryostat. As a source of X-ray irradiation the same ISO-DEBYEFLEX 3003 X-Ray equipment mentioned above was used. The X-ray tube 55 kV voltage and 30 mA current were kept during the samples irradiation at liquid nitrogen temperature (LNT).

3. Results and discussion

The absorption spectra of the Pr-doped samples are compared with the undoped one in the figure 1. Only the START parts from each sample were chosen, as the spectra of the END parts did not show any significant differences. For the Pr-doped Mg-free sample, the curve gradually goes up above the baseline between 300-600 nm and one can notice prominent relatively sharp peaks related to Pr^{3+} 4f-5d₁ and 4f-5d₂ transitions that appear at 285 and 240 nm, respectively. This result corresponds to the observations in the literature (see [2] and references therein). The curve sharply increases below 200 nm which is most probably due to defect states modifying the band edge. For the sample codoped with 300 ppm Mg, the spectrum is very similar but the increase of the absorption between 300-600 nm is more pronounced. The absorption at the shortest wavelengths is significantly smaller. Concerning the sample codoped with 3000 ppm Mg, the absorption between 300-600 nm is very strong and obscures the features related to Pr^{3+} and band edge at the shorter wavelengths. The intensity of this absorption increases with increasing Mg concentration and it was ascribed to the charge-transfer (CT) transition of the Pr^{4+} ion, similarly as the analogous Ce^{4+} CT transition observed for Ce-doped scintillation materials codoped with divalent alkaline earth ions [8, 10-13]. As can be expected, annealing causes the oxidation of Pr to its tetravalent state while the Mg^{2+} codoping enhances its stability. The effect is especially prominent for the sample with 3000 ppm Mg, which follows from the charge compensation of the divalent Mg^{2+} by Pr^{4+} . It is not excluded that some Pr^{4+} ions are already present in the Mg-codoped samples before annealing. Comparative study of the properties before and after annealing is under way and will be published elsewhere, as some peculiarities in the luminescence behavior can be observed. Considering that the onset of the Pr^{4+} CT transition is situated around 600 nm and that the Ce^{4+} CT absorption for the Ce doped scintillators has an onset around 340 nm, the difference of the onset positions corresponds to some 1.5 eV, which exactly matches the difference between 4f ground state energies of Ce^{3+} and Pr^{3+} [25] and provides further support for the ascription of the smooth absorption band below 600 nm. It is worth noting that in the spectra for both Mg-doped samples that a new sharp peak at 213 nm emerges after annealing. Its origin is unknown but might be related to

simultaneous occurrence of Pr^{4+} and Mg^{2+} , as the Pr^{4+} CT absorption is present also in the Mg-free sample where the 213 nm peak is missing. It is most probably not related to f-states of Pr^{3+} , as it is absent in the photoluminescence excitation spectra of Pr^{3+} emission (see below). In the undoped sample, the absorption at 250 nm may be related to the iron impurity, which can change valence from 2+ to 3+ during annealing [26].

The comparison of the RL spectra of the studied samples under X-ray excitation with that for the $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) commercially used reference scintillator is in the figure 2. They are dominated by the 5d-4f emission peak at 308 nm ($5d-^3\text{H}_4$) and a shoulder around 360 nm caused by transitions from the 5d state to the higher 4f levels ($^3\text{H}_{5,6}$, $^3\text{F}_{3,4}$). The shoulder at the short wavelength side of the 308 nm peak originates from host luminescence related to recombination of exciton at AD's. It is worth noting that its intensity is practically the same for both the Mg concentrations. Very weak 4f-4f transitions can be observed at longer wavelengths. The overall scintillation efficiency of all the samples is significantly higher than that of BGO scintillator and is slightly lower for the Mg-codoped samples. The cause can be an overlap of the Pr^{3+} 5d-4f emission peak with the broad absorption between 300-600 nm discussed above, which increases with increasing Mg concentration. Interestingly, the RL intensity for both Mg-codoped samples is practically the same. All the results shown here are again for the START parts. Only minimum differences were observed for the samples from the END parts.

The photoluminescence (PL) excitation spectrum of the 308 nm emission is shown in the figure 3a for the 300 ppm Mg Pr-doped LuAG sample (START). The dominant peaks at 280 and 235 nm corresponding to the 4f-5d transitions are already observed in the absorption spectra in the figure 1.

We guess that the slight shift to shorter wavelengths might be caused by an instrumental effect, as practically no changes can be observed for the 4f-5d peaks in the absorption spectra in the figure 1. The small peak below 200 nm is related to the defect states shaping the band edge. The 213 nm peak discussed above was not found at all, which again supports the idea that it is not related to Pr^{3+} ion. The same is valid for the excitation spectra of the other samples.

The comparison of the photoluminescence emission spectra for the same sample LuAG:Pr 0.2% Mg 300 ppm (START) under 200 nm and 285 nm excitation is in the figure 3b. Both spectra are again dominated by the Pr^{3+} 5d-4f luminescence and their shape is also comparable with the radioluminescence one (figure 2), but the host emission shoulder below 300 nm is obviously missing. For the spectrum excited under 200 nm (from valence band top to the defect levels near the bottom edge of the conduction band), the Pr^{3+} 4f-4f emission is quite apparent while it is almost missing in the spectrum excited under 285 nm. The pronounced 4f-4f emission can

be related to the simultaneous excitation of the Pr^{3+} ion and some defect state from which an energy leak to the other f-levels takes place. The assignment of the 4f-4f lines in the figure 3b was made according to [27].

It is worth mentioning that the shoulder related to the transitions from the 5d level to the higher 4f ones at 360 nm changes its relative intensity with respect to the dominant 5d-4f peak at 308 nm. It does not show any stable trend with the Mg concentration. Interestingly, the absorption of the F^+ center based on an oxygen vacancy in LuAG lies exactly in this spectral area [28]. Its creation might be modified by Mg codoping and annealing and it can influence the PL intensity in this region. Presence of an electron-like center (most probably the F^+ one) was proved by the EPR measurements below.

Another emission band emerged at 249 nm upon 200 nm excitation in the emission spectrum (figure 3b). This band can be related to an emission of some defect induced by annealing and stabilized by Mg^{2+} codopant. We should emphasize that this wavelength exactly corresponds with the emission of the low-temperature configuration of the AD- trapped exciton (TE) reported in [29]. It might be that this low-temperature trapped exciton configuration is stabilized by Mg co-doping. Note that the shape of this band might be further obscured by Pr^{3+} 4f-5d absorption bands at 245 and 280 nm. Due to this overlap an energy transfer from the defect levels to the 5d ones can take place, which can have an influence on the scintillation decay kinetics. As mentioned above, the intensity of the Pr^{3+} 4f-4f emission peaks in this spectrum are much more pronounced with respect to the spectrum under direct excitation at 285 nm. It seems that the levels related to the defect emitting at 249 nm can be responsible for the population of the Pr^{3+} 4f-levels. This effect is slightly more apparent also for the sample codoped with 3000 ppm Mg (not shown here).

The photoluminescence decay kinetics for the LuAG:Pr 0.2% Pr (START) under direct excitation to the 4f-5d₁ transition is in the figure 4 and is governed by a decay component with 21 ns decay time belonging to the 5d-4f Pr^{3+} emission. On the other hand, it seems that some slow component with a decay time around 200 ns emerges. Similar feature was observed for the other samples again. Concerning both of the Mg-codoped samples, the decay curve looked very similar and the leading decay time was shortened to around 19 ns. The decay curves under 200 nm excitation were very similar and followed the trends described for the direct excitation.

The observed very slight acceleration of the photoluminescence decay kinetics with increasing Mg concentration can be caused by a weak energy transfer from the excited Pr^{3+} 5d₁ state towards the Pr^{4+} CT state, as there is the spectral overlap of the 5d-4f emission with the CT absorption, see above. Similar effect was observed for the samples from the END part.

The emission spectrum under excitation into the unknown absorption sharp band at 213 nm discussed above is in the figure 5. It consists of the 5d-4f bands around 310 nm and the 4f-4f bands at longer wavelength, which are much more pronounced in this case. The 3P_0 - 3H_4 transition at 488 nm is quite apparent and was not observed in the previously discussed emission spectra. It is interesting to note that even though the 5d-4f emission is excited at 213 nm, it is not found in the excitation spectrum of this emission. The 213 nm wavelength exactly corresponds with the position of the 1S_0 state of Pr^{3+} . If this peak is ascribed to the transition to this level, it should be seen in the excitation spectra as well, as one could expect a nonradiative energy transfer from this level to the 5d one. However, this is not true (figure 3a). The decay kinetics of the Pr^{3+} 5d-4f emission under 213 nm excitation is very similar as that in the figure 4, just the leading decay time is the shortest observed in all the experiments with the value of 17 ns (not shown here). Further research is necessary to clarify the origin of the 213 nm peak.

The scintillation light yield was determined from the pulse-height spectra under 667 keV gamma ray excitation from ^{137}Cs source. The example of such a spectrum is in the figure 6, where the fitted curve for the LuAG:Pr 0.2% END sample is displayed. The full-absorption peak is clearly observed, but it interferes with Lu escape peak at slightly lower energy. However, peaks are separated enough and escape peak area is approximately 6 times smaller than area of full-absorption peak. Therefore, the measurement precision is not affected significantly by Lu escape peak.

The light yield values for all the samples including START and END parts are summarized in the Figure 7 (the 0 ppm concentration is indicated as 1 ppm to allow setting the logarithmic axis). A substantial decrease of the light yield with Mg codoping is observed for both parts of the Mg-codoped crystals. This decrease is the same for both START and END parts and seems to be independent on the Mg concentration similarly as radioluminescence intensities in the figure 2. On the other hand, the magnitude of the decrease of the light yield values for the samples with Mg 300 ppm and 3000 ppm with respect to the Mg-free one does not correspond to the decrease of the steady-state radioluminescence intensities (figure 2). This may be caused by much shorter penetration depth of X-ray excitation photons and reflection geometry used in RL measurement compared to all-the-volume excitation by 662 keV gamma photons and transmission geometry used in LY measurement. Slow components introduced by Mg-codoping or annealing through which the light is emitted outside the 6 μs shaping time window leading to the decrease of the light yield cannot be eventually excluded as well.

Decay kinetics under the gamma-ray excitation for the LuAG:Pr0.2% Mg 0 ppm and Mg 3000 ppm (START) is shown in the figures 8a and 8b. Fitting the curves with the sum of exponentials was complicated

and often 4 or 5 components were necessary, which may be a consequence of the fact that the scintillation decay of the selected samples does not follow the usual exponential decay law. In the log-log scale (see figure 8) the course of the slower component following the fast exponential part is close to a straight line, which suggests that this part follows the inverse power law. Therefore the curves were fit with a sum of an exponential component and a power function according to the equation $I = A\exp(-t/\tau) + a(b+ct)^{-p}$, where A , a , b , c and p are constants, τ stands for the decay constant and t is time. The inverse power decay course was described in the past [31] and observed in the Ce-doped LuAG scintillators [32]. It was ascribed to the tunneling of the electrons from the AD-related shallow traps towards adjacent Ce^{3+} with a trapped hole (which is Ce^{4+}). The usual values of the parameter p range between 0.9-1.5. For more details about tunneling-related luminescence processes see for example [30] and also references therein. It is reasonable to assume that the same phenomenon takes place in the Pr-doped analogues.

In the curves for both the Mg-free and the Mg 3000 ppm samples the fast exponential component has a decay time of 21.6 ns and 21 ns respectively and is ascribed to the 5d-4f luminescence of the Pr^{3+} center in the crystals. The almost negligible shortening can be again related to the energy transfer from the Pr^{3+} excited 5d state to the Pr^{4+} CT one. The slower component described with the power function is due to the mentioned tunneling of the electrons to from the AD-related traps and the parameter p has values of 0.73 and 0.82 for the Mg-free and Mg 3000 ppm sample respectively. These values are slightly out of the range specified above, but it might be that there are other exponential components of small amplitude and substantially long decay time that may obscure the observed power decay kinetics. Taking into account that the value of p determines the slope of the power function in the log-log scale, it means that for the Mg-codoped sample the scintillation response is accelerated at the longer times when compared to the Mg-free sample.

Summarizing the influence of Mg codoping and annealing on luminescence and scintillation properties, we can state that it enhances the formation and stability of Pr^{4+} ion. This effect increases with increasing Mg concentration. The Pr^{4+} CT band is responsible for reabsorption of the 5d-4f emission coming from Pr^{3+} ions. The Pr^{3+} ions can be either regular ones or the temporary ones created in an alternative scintillation mechanism, which would be analogous with the mechanism taking part in LuAG:Ce codoped with divalent ions and which is described in the introduction and treated in [2, 8, 10, 11]. The nonradiative energy transfer from 5d₁ relaxed excited state of Pr^{3+} towards CT state of Pr^{4+} is probably responsible for very slight photoluminescence (and also scintillation) decay shortening. However, as this process is almost negligible, a simple reabsorption of the 5d-4f emission by the CT transition is supposed to be the dominant process which leads to decrease of RL intensity

and scintillation light yield for the Mg-codoped samples. Further studies are needed to explain the observed independence of this effect on Mg concentration. The decrease of the RL intensity upon Mg codoping is much smaller than the decrease of the scintillation light yield. It can be tentatively explained by different excitation energies and experiment geometries as mentioned above. Moreover, an introduction of very slow components by Mg-codoping, through which most of the scintillation light is emitted outside the corresponding time window in the light yield measurement cannot be excluded as well.

The selected samples were studied by EPR before and after X-ray irradiation at approximately 77 K. The samples were LuAG:Pr0.2% START and END, LuAG:Pr 0.2%, Mg 300 ppm START and END, and LuAG:Pr 0.2%, Mg 3000 ppm START and END. The EPR spectra measured at 40K prior to an X-ray irradiation contained mostly resonance lines coming from Yb^{3+} ions, see for example the spectrum for the LuAG:Pr 0.2% START in the figure 9a. The Yb^{3+} was already described in LuAG [33] and in our samples it is obviously present as an accidental impurity. Moreover, there is also a number of lines of unknown origin (Figure 9a) which could not be properly identified due to their low intensities. No Pr^{4+} resonance lines were found in the spectra at all. The Pr^{4+} spectral lines would be easy identified due to pronounced hyperfine structure produced by ^{141}Pr nucleus having 100% natural abundance and the nuclear spin 5/2. Therefore, either their position is out of the EPR spectrometer magnetic field range or the concentration of these ions is too low to be detectable. When the samples were exposed to the X-ray irradiation at liquid nitrogen temperature, new lines emerged in the spectra in the 3300-3450 G magnetic field range (see Figure 9b,c), near g factor 2.

The resonance line marked as 1 in Figure 9b,c was ascribed to the g -factor value $g \approx 2.026$ whereas the spectral position of the line marked as 2 is characterized by the $g \approx 1.949$. The g -factor value for the first one is common for the hole-like centers, namely O^- defects [34-40], since it is a bit higher than 2.0023, which is the value for a free electron. Remarkably, the position of the line 1 is almost independent on the orientation of the external magnetic field with respect to the $\langle 100 \rangle$ crystallographic direction. The g factor of the paramagnetic center responsible for this line is thus almost isotropic. In principle, the O^- defects show very small or no anisotropy of the g factor, especially in cubic lattices [13, 34-40]. The line 1 could be then ascribed to the O^- defect. The presence of O^- defect further supports the existence of the alternative scintillation mechanism similar to the Mg-codoped LuAG:Ce [2, 10, 11]. It involves the O^- center which releases a hole to regenerate the tetravalent luminescence ion in the final stage of the mechanism.

The line 2, which is observed only in the crystal with the highest Mg concentration, shows the isotropy of the g factor as well. Most probably, it belongs to the electron captured at an oxygen vacancy forming an F^+

center, since such centers similarly to the O^- ones show no or weak anisotropy of the g factor, see for example [34, 41]. The intensity of this line does not change after heating of a sample up to RT and holding on at this temperature for 1 day (see Figure 9b). Prompt heating of the sample up to approximately 420-450 K makes no effect as well. However, after keeping the sample for four days at RT, the center completely disappeared. F^+ centers can be very stable [40, 41] surviving annealing even at the temperatures much higher than RT [40]. Moreover, it is possible that even after annealing in air not all the oxygen vacancies and related defects were removed in the Pr 0.2% Mg 3000 ppm (START) sample. It might be that the local lack of charge due to divalent Mg^{2+} codopant embedded at a trivalent site can stabilize the oxygen vacancies. Such an effect is expected to be significant especially in the samples with high Mg concentration, which is the case of this studied sample. However, such defects responsible for the line 2 were not detected in the END counterpart. Taking into account small or no differences in the luminescence and scintillation characteristics of both parts, such an observation is hard to explain so far and further study is necessary to clarify this discrepancy.

Due to similarity of the spectra measured in Pr0.2% START and END samples, the spectrum measured for the END sample was not shown in Figure 9c.

It was found from the temperature dependences of the EPR signal that the O^- defects in the Pr only doped samples and those the Pr,Mg co-doped have different thermal stability, which was observed from measurements of the dependence of the intensity of the line 1 (Figure 9 b,c) on temperature for the LuAG:Pr0.2% START and END samples together with the Pr0.2% Mg 300 ppm START and Pr0.2% Mg 3000 ppm START. The corresponding dependences are shown in the figure 10 together with the fitted curves.

In this experiment the spectra were measured always at the reference temperature of 40 K but the sample was quickly heated up to the chosen temperature T_h and then promptly cooled down to the reference temperature, each time increasing T_h with the step of 10-15 K.

The Pr 0.2% START and END samples showed roughly the same temperature dependences of the O^- EPR intensity (Figure 10). With Mg codoping the stability of the O^- center decreased and seems again almost independent on the Mg concentration as the dependences for the 300 ppm or 3000 ppm Mg^{2+} sample are quite similar especially at the highest temperatures.

The dependences shown in figure 10 have been fitted with the calculated curves according to the expressions 1 and 2 presented below. Each of them describes the hole trap kinetics (first order – Eq. 1, and second order – Eq. 2, respectively) which were adapted for the aims of the above described heating method mentioned in [42].

$$I_{i+1} = I_i \exp\left(-f_{01} t \exp\left(-\frac{E_{t1}}{k_B T_i}\right)\right), \quad i = 0, 1, \dots, m, \quad (1)$$

$$I_{i+1} = \frac{I_i}{1 + \frac{I_i f_{02}}{P} \exp\left(-\frac{E_{t2}}{k_B T_i}\right)}, \quad i = 0, 1, \dots, m, \quad (2)$$

Here the EPR intensity I_i [43], is proportional to the trapped holes concentration remaining after each heating cycle i ; P is the coefficient which depends on the whole amount of traps in the crystal, and transition coefficients [42]. E_{t1} and E_{t2} , f_{01} and f_{02} are the trap depths and frequency factors for the first or second order kinetics, respectively. The parameters determined from the fit are: $E_{t1} = 0.338 \pm 0.005$ eV, $f_{01} = (1 \pm 0.5) \times 10^8$ s⁻¹; $E_{t2} = 0.105 \pm 0.005$ eV, $f_{02} = (1 \pm 0.5) \times 10^1$ s⁻¹.

The dependence in the Pr-only doped samples shows a very unusual course since it does not obey either of the kinetics separately but the combination of them. However, the second-order kinetics (Eq. 2) prevails. The f_{02} value obtained from fit does not have much physical sense since the frequency factor is mostly found within 10^6 - 10^{12} s⁻¹ range [36, 41, 44, 45]. The calculated trap depth E_{t2} is very big and considering the O⁻ to be a shallow trap, most probably we deal with some kind of thermally-assisted tunneling described for the Ce-doped analogue in [30].

As mentioned above, the Mg codoping significantly decreases the stability of the centers and the kinetics becomes the first order one (Eq. 1) with the usual values of the trap depth and frequency factor.

When compared with the other observations [34-36, 45], the relatively high thermal stability of the holes (see Figure 10) in all the samples suggests that the holes must be stabilized by some imperfection nearby which can be further modified by Mg codoping. Correlated thermoluminescence experiments would bring deeper insight in the above described processes, but they will be published in the forthcoming more detailed comparative study of both the annealed and as-grown samples.

Conclusions

This study focuses on the influence of Mg codoping and annealing on luminescence and scintillation properties. Both Mg codoping and annealing lead to promotion of Pr to its tetravalent state and moreover the Mg codopant enhances its stability, which increases with increasing Mg concentration. The Pr⁴⁺ CT band is

responsible for absorption of the 5d-4f emission coming from Pr^{3+} ions. A very slight photoluminescence (and also scintillation) decay acceleration may be caused by an almost negligible nonradiative energy transfer from the $\text{Pr}^{3+} 5d_1$ level to the Pr^{4+} CT state. As this process is not significant, it means that the absorption by the CT state is responsible for the decrease of RL intensity and scintillation light yield for the Mg-codoped samples. Further studies are needed to explain the observed independence of this effect on Mg concentration. The decrease of the RL intensity upon Mg codoping is much smaller than the decrease of the scintillation light yield which can be tentatively explained by different excitation energies and geometries of radioluminescence and light yield measurements. This would imply that the absorption by the Pr^{4+} CT state might be hampered in thin films and thus positive effects of divalent ion codoping can be expected for Pr-doped garnet scintillators, which have faster response when compared to the Ce-doped counterparts.

The scintillation decay curves are composed of a fast component related to Pr^{3+} emission and a slower component described by a power function, which indicates a tunneling recombination process from the traps related to the anti-site defects. This was already observed in the Ce-doped analogues and therefore such an interpretation is plausible.

The EPR spectra measurements revealed presence of $\text{O}^\cdot$ centers in all the samples, which further supports the existence of the alternative scintillation mechanism in the Mg-codoped crystals. It involves the $\text{O}^\cdot$ center which releases a hole to regenerate the tetravalent luminescence ion in the final stage of the mechanism. The temperature dependence of the EPR spectra showed that Mg codoping significantly decreases the stability of this center. The EPR experiments revealed also presence of centers based on oxygen vacancies, most probably F^+ centers, which are stable above room temperature. They were observed only in the crystal with the highest Mg concentration which would mean that in this case Mg on a trivalent site stabilizes the oxygen vacancies due to charge compensation and makes them resistant to annealing in air.

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Figure 1. Absorption spectra of the START parts of the annealed LuAG:Pr0.2% samples with 0, 300 and 3000 ppm of Mg codopant

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Figure 10. Dependence of the O' line EPR intensity on heating temperature T_h measured for the Pr0.2% START and END samples and Pr0.2% Mg 300 ppm START and Pr0.2% Mg 3000 ppm START samples at fixed temperature $T = 40$ K. Solid lines are the calculated dependences.

Fig 1

Fig 2

Intensity (arb. units)

Fig 3b

LuAG:Pr 0.2%, Mg 300ppm START

Fig 4

LuAG:Pr 0.2% START
Ex=281 nm, Em=308 nm

Fig 5

LuAG:Pr 0.2%, Mg 3000 ppm

Fig 6

LuAG-Pr0.2% END ^{137}Cs

Fig 7

Light yield (photoelectrons)

Fig 8a

Fig 8b

Fig 9

Fig 10