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ABSTRACT

An investigation of the effects of Pr in $(Lu_{1-x}Pr_x)_3Al_5O_{12}$ (LuAG:Pr) ceramics was carried out by means of x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDX), and attenuated total reflection Fourier transform infrared spectroscopy (ATR FTIR) measurements coupled with luminescence measurements. It was found that the Pr concentration that maximizes luminescence emission depends on the thermal processing conditions. While the calcined LuAG:Pr powder showed maximum luminescence emission for Pr concentrations between 0.18 and 0.33 at.³, maximum emission of ceramic bodies sintered at 1500 °C for 20 h was obtained with Pr concentrations between 0.018 and 0.18 at.³. Further, for short sintering times up to about 3 h, luminescence emission intensity is maximum for Pr concentrations around 0.33 at.³. Longer sintering times lead to the formation of PrAlO₃ as a secondary phase, concomitant with a reduction of the intensity of luminescence emission.

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Optical Materia

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1. Introduction

 $(Lu_{1-x}Pr_x)_3Al_5O_{12}$ (LuAG:Pr) is a dense (6.7 g/cm³), fast and promising scintillator first reported in the mid-2000s [1-3] that is being considered for the next generation of positron emission tomography (PET) scanners. Luminescence activation by means of the incorporation of Pr³⁺ ions substituting for Lu³⁺ is essential in achieving the fast scintillation decay time of about 20 ns and the main emission band centered at 320 nm that closely matches maximum detection efficiency of photomultiplier tubes. The luminosity of this scintillator has been reported to be about 2-3 times that of BGO [2-6]. However, the relatively high difference in ionic radius between Lu³⁺ and Pr³⁺ of more than 13% limits the incorporation of Pr and leads to considerable inhomogeneity of the dopant in Czochralski-grown single crystals [3]. In these crystals, the maximum of the luminescence concentration quenching curve has been found to be between 0.2 and 0.3 at.% [3,7]. The Czochralski crystal growth method commonly involves slow growth rates and high temperatures that facilitate dopant segregation. On the other hand, the fabrication conditions of ceramic scintillators involve considerably lower synthesis times and temperatures and may

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allow for the incorporation and for the extension of concentration quenching to higher dopant concentrations. The investigation of LuAG:Pr ceramic scintillators is relatively recent [8–11], and has revealed that the use of sintering aids can enhance optical transparency but is detrimental to the light output [12,13]. Other works focused on the effects of Pr concentration on the luminescence and scintillation, though only a small number of concentrations were investigated in each work [9,10,14,15]. This work investigates the effects of the microstructure of LuAG:Pr ceramics fabricated with different Pr concentrations and under different sintering conditions towards obtaining brighter LuAG:Pr ceramic scintillators.

2. Experimental procedures

Powders of $(Lu_{1-x}Pr_x)_3Al_5O_{12}$ with different Pr concentrations, from x = 0.001 to x = 0.05, were obtained by a co-precipitation method. Lutetium nitrate was obtained by dissolving commercial Lu₂O₃ (99.995%, HEFA Rare Earth Canada Co.) in excess 70% nitric acid (Certified A.C.S., Spectrum, Gardena, CA) while stirring and heating. Aluminum nitrate (98%, Alfa Aesar, Ward Hall, MA) and praseodymium nitrate (99.9%, Acros Organics, NJ) were dissolved in ultrapure water at room temperature (RT) in a separate beaker and added drop-wise to the stirring lutetium nitrate solution after it cooled down to RT. The specific amount of Pr doping was determined through molar substitution of the Lu precursor up to 5 mol%. The mixed nitrate solution was added drop-wise to a 1:1 solution of

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ultrapure water and ammonium hydroxide (Certified A.C.S Plus, Fisher Scientific, Fair Lawn, NJ) towards the precipitation of LuAG:Pr. The precipitate was allowed to stir at room temperature for 1 h and then washed three times with ultrapure water and twice with ethanol before being dried at 60 °C overnight in vacuum. Since the precipitate was found not to be LuAG:Pr by means of X-ray diffraction (XRD) measurements, the precipitate was calcined in air and under oxygen flow at 1000 °C for 2 h in an alumina boat. Photoluminescence (PL) measurements revealed no difference in luminescence intensity between the samples calcined in air versus under oxygen flow, and calcination in air was adopted for the remaining of this work. Ceramic bodies were prepared by pressing about 0.25 g of powder into pellets at about 28 MPa and sintering them at 1500 °C in air for up to 20 h.

Several analytical techniques were used to characterize the microstructure of the samples. XRD measurements were carried out using a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation, transmission electron microscopy (TEM) with a Hitachi H9500 electron microscope operated at 300 kV, and scanning electron microscopy and energy dispersive x-ray spectroscopy (SEM/EDX) with a Hitachi S3400 electron microscope operated at 15 kV. The chemical composition was determined using Oxford software AZtec version 2.2, and results reported in this work correspond to the average of measurements at 3 different spots of the sample, with the error bars corresponding to the standard deviation of the results. Furthermore, attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR) in single reflection mode was carried out within the 400-4500 cm⁻¹ range using a Thermo-Scientific Nicolet 6700 FT-IR spectrometer equipped with a diamond crystal plate.

PL measurements were carried out using a Horiba Jobin-Yvon Fluorolog Tau 3 equipped with a 450 W Xe lamp and double monochromators both at excitation, set at 285 nm, and emission, carried out in the 295–500 nm range. The results were converted into spectra of intensity versus emitted photon energy to allow for deconvolution analysis using two Gaussian curves. The PL integrated intensity results reported in this work correspond to the average of measurements of up to 5 equivalent samples, with error bars corresponding to the standard deviation of the results of these measurements.

3. Results and discussion

TEM results revealed that grains of calcined powders are composed of several nanocrystals fused together, as illustrated in Fig. 1. The crystalline nature of the calcined powders is demonstrated by the presence lattice fringes as highlighted in the two insets. XRD results further confirmed the crystallinity of the powders and the lack of any amorphous phase. Diffractograms were matched with PDF card no. 01-073-1368, confirming the cubic garnet structure of the calcined powders, as shown in Fig. 2 for sample with x = 0.001. Moreover, detailed scans within $15^\circ \leq 2\theta \leq 35^\circ$ (not shown), where intense diffraction peaks of the possible secondary phases Pr_2O_3 and $PrAlO_3$ are located, revealed the absence of these secondary phases even for the x = 0.05 sample.

The chemical composition of the calcined powders was evaluated by SEM/EDX measurements, and a typical EDX spectrum is shown in Fig. 3a for x = 0.05. The inset highlights the Pr $L_{\alpha 1}+L_{\alpha 2}$, $L_{\beta 1}$, $L_{\beta 2}$, and $L_{\gamma 1}$ lines, from low to high energy, respectively. The x values correspond to the fraction of moles of the Pr precursor that substituted for the Lu precursor in the making of the powder, while the Pr concentration in at.% was obtained directly from the SEM/EDX measurements. The results showed a linear correlation between the x value and the actual Pr content (Fig. 3b), with the maximum value of x = 0.05 corresponding to 0.92 at.% of Pr



Fig. 1. TEM image of calcined $(Lu_{1-x}Pr_x)_3Al_5O_{12}$ powder with x = 0.0023. The insets are images at higher magnification of the corresponding selected areas, and highlight the crystallinity of the grain through the presence of crystalline fringes.



Fig. 2. XRD results of calcined $(Lu_{1-x}Pr_x)_3Al_5O_{12}$ powder with x=0.001, together with PDF card no. 01-073-1368 for $Lu_3Al_5O_{12}$.

incorporated in the sample. The EDX-determined at.% values are about 20% higher than the nominal at.% values calculated based on the x values. The actual Pr concentration in at.% of samples with x = 0.001 and x = 0.005 were determined based on the linear best fit of the data shown in Fig. 3b.

The incorporation of Pr into the LuAG atomic network was investigated by means of ATR FTIR measurements. Normalized spectra are shown in Fig. 4 for two Pr concentrations, 0.018 and 0.92 at.%, and show three overlapping bands between 600 and 900 cm⁻¹, and five overlapping bands between 400 and 600 cm⁻¹. These results are in agreement with previous reports on a variety of rare earth aluminum garnets [16–18]. The vibrational modes within 600–900 cm⁻¹ have been associated with the asymmetric stretching of the AlO₄ tetrahedra, the modes between 450 and 600 cm⁻¹ have been assigned to bending motions of the AlO₄ tetrahedra, while the vibrational mode at about 420 cm⁻¹ has been tentatively assigned to the translation of the octahedral cation [18].



Fig. 3. a) - EDX spectrum of calcined $(Lu_{1-x}Pr_x)_3Al_5O_{12}$ powder with x = 0.05. The inset highlights the presence of Pr $L_{x1}+L_{x2}$, $L_{\beta1}$, $L_{\beta2}$, and $L_{\gamma1}$ lines, from low to high energy, respectively. b) - Correlation between nominal doping x value with the average atomic concentration of Pr as determined by SEM/EDX measurements. The line corresponds to the linear best fit of the data.



Fig. 4. Partial ATR FTIR spectra of calcined powders with different Pr concentrations showing the asymmetric stretching modes of the AlO₄ tetrahedra from about 600 to 900 cm⁻¹, the bending motions of the AlO₄ tetrahedra from 450 to 600 cm⁻¹, and the translation of the octahedral cation at about 420 cm⁻¹.

In LuAG:Pr, Al is expected to occupy tetrahedral and octahedral sites, while Lu and Pr are expected to occupy dodecahedral sites. The average metal-oxygen distance increases from sites with tetrahedral to octahedral to dodecahedral coordination suggesting a progressive decrease in strength of the metal-oxygen bond [17]. Further, these structural units are interconnected in such way that the tetrahedra and the octahedra share edges with the dodecahedra. Since the expected ionic radii of Lu^{3+} and Pr^{3+} in an 8-coordination environment are 0.977 and 1.26 Å, respectively [19], the substitution of Pr³⁺ for Lu³⁺ should lead to an increase of the unit cell volume. This is supported by XRD measurements that show an increase of the lattice parameter from 11.903 to 11.917 Å for Pr concentrations from 0.018 to 0.92 at.%. The larger dodecahedra containing Pr distorts the interconnected tetrahedral and octahedral structural units ultimately lowering the frequency of their vibrational modes. This overall shift towards lower frequencies for higher Pr concentrations can be seen in Fig. 4 where the spectra of samples with 0.018 and 0.92 at.% were normalized to the intensity of the most intense peak. However, this effect is stronger in the smaller more tightly bonded tetrahedra than in the octahedra. Consequently, the higher frequency vibrational modes associated with the stretching of the AlO₄ tetrahedra shift more than the lower frequency modes associated with the bending of the tetrahedra, while the vibrational frequency related to the octahedra remains unchanged. This is shown explicitly in Fig. 5 for all of the vibrational modes as a function of the Pr concentration. In summary, the above discussion demonstrates that Pr is being incorporated into the atomic network of LuAG.

The calcined powders were mechanically pressed into pellets and the PL emission spectra of LuAG:Pr for several different Pr



Fig. 5. Peak position of the vibrational modes shown in Fig. 4 as a function of Pr concentration together with linear best fit of the experimental data. The same ordinate scale in all plots highlights the larger peak shift observed for modes at higher wave-numbers as the Pr concentration increases.

concentrations are shown in Fig. 6 as a function of the photon energy. Besides the narrow emission band at 2.55 eV (487 nm) ascribed to the $Pr^{3+3}P_0 \rightarrow {}^{3}H_4$ transition, the spectra are dominated by two overlapping bands centered at about 3.91 eV (320 nm) and 3.31 eV (370 nm). These bands have been assigned to the $5d \rightarrow 4f$ transition [20], and comparison between the spectra reveals a dependence of the luminescence intensity with the Pr concentration. This behavior is highlighted in Fig. 7 (triangles) where the integrated luminescence intensity is shown as a function of the actual Pr concentration determined by the SEM/EDX measurements. Maximum emission occurs for atomic concentrations between 0.18 and 0.33 at.%, in agreement with results obtained in single crystals [3,7]. Moreover, a systematic change of the relative intensity between the bands is also observed. The behavior of the integral intensity ratio, I_{320}/I_{370} , obtained by Gaussian deconvolution as a function of Pr concentration is shown in Fig. 8, while a typical result of the deconvolution is illustrated in Fig. 6 for the Pr concentration of 0.018 at.%. The dotted lines correspond to the Gaussian curves, and the dashed line to the resultant best fit. The intensity ratio shows a systematic decrease for higher Pr concentrations that has been attributed to the increasing self-absorption of Pr^{3+} ions [21].

The calcined powder pellets were sintered in air at 1500 °C for 20 h. PL measurements as a function of Pr concentration yielded spectra similar to those reported in Fig. 6 (and thus not shown) from which PL integrated intensity was extracted (Fig. 7; circles). Comparison between the results from calcined and 20 h.-sintered samples shows a considerable enhancement due to sintering together with a shift of the maximum from 0.18–0.33 at.% to lower Pr concentrations of 0.018-0.18 at.%. While similar behavior was reported in Ref. [9], the Pr concentration that maximizes luminescence of the sintered ceramics is somewhat lower than previously reported. This may be, in part, because of the small number of different concentrations investigated previously. In most previous works, only 3 or 4 different concentrations were investigated with most of them >1 at.% or mol% where Pr^{3+} emission is already significantly reduced, leaving few data points to determine the maximum of the relative PL intensity curve [10,14,15].

The evolution of the PL integrated intensity of 3 representative Pr concentrations, 0.091, 0.33, and 0.92 at.%, is shown in Fig. 9 for several sintering times. It can be seen that short sintering times, up



Fig. 6. PL spectra as a function of the emitted photon energy for calcined powders with different Pr at.%. The deconvolution of the spectrum of sample with Pr concentration of 0.018 at.% is also shown. The dotted lines correspond to the individual contribution of each emission band, and the dashed line to the best fit of the experimental data.



Fig. 7. PL integrated intensity of calcined powders and ceramics sintered for 20 h. The lines are guides to eye, only.



Fig. 8. Relative integral intensity ratio of the two PL emission bands as a function of Pr concentration. The line is a guide to the eye, only.

to about 3 h, are advantageous to maximize luminescence emission and that longer sintering times are detrimental to luminescence output, for all concentrations investigated.

In order to understand these changes, microstructural characterization was carried out as a function of sintering time. XRD measurements are illustrated in Fig. 10 where a selected region of the diffractogram of the 0.92 at.% Pr doped ceramic treated for 20 h is shown. All diffraction peaks were assigned to LuAG, according to PDF card no. 01-073-1368, with the exception of the small peak at $2\theta = 23.84^{\circ}$, that besides a small shift towards higher 2θ values $(\Delta(2\theta) = 0.11^{\circ})$, was assigned to PrAlO₃ (101) in agreement with PDF card no. 00-058-0796 (where $2\theta_{(101)} = 23.73^{\circ}$). The relative diffraction intensity of PrAlO₃ peaks as obtained from this PDF card is also shown in the figure as the bar plot at the bottom. The contribution of the PrAlO₃ (200), (002) and (121) diffraction peaks located between $2\theta = 33^{\circ}$ and 34° to the LuAG (420) peak is highlighted in the right inset through the asymmetry of the diffraction peak. The contribution of these peaks at the high-angle side of the LuAG (420) diffraction peak is in agreement with the shift of the PrAlO₃ (101) peak towards higher angles, as discussed



Fig. 9. PL integrated intensity of ceramics with representative Pr concentrations of 0.091, 0.33, and 0.92 at% sintered for different times up to 20 h. The lines are guides to the eye, only.



Fig. 10. XRD results of LuAG ceramic with Pr concentration of 0.92 at.% sintered for 20 h, together with PDF card no. 00-058-0796 for PrAlO₃. The left inset shows the temporal evolution of the diffraction peak attributed to PrAlO₃ (101) due to sintering. The right inset shows the asymmetry of LuAG (420) diffraction peak due to the contribution of PrAlO₃ (200), (002) and (121) diffraction peaks. The dotted line is a guide to the eye only.

above. The overall shift of the PrAlO₃ diffraction peaks towards higher angles suggests the secondary phase to be distorted under compression. The evolution of the intensity of the PrAlO₃ (101) peak as a function of sintering time is illustrated in the left inset. These results reveal the progressive formation of the PrAlO₃ secondary phase that becomes detectable for sintering times ≥ 5 h. This is supported by a previous work where the segregation of rare earth dopants in sintered ceramics was observed [22], as well as by the fact that the presence of PrAlO₃ has been suggested as a subproduct of the growth of LuAG:Pr single crystals by the Czochralski method [3]. The formation of the PrAlO₃ phase is related to the diffusion of Pr, being a function of Pr. Further, the onset for the $4f \rightarrow 5d$ absorption of PrAlO₃ is at about 250 nm [23] and thus

4. Conclusions

In this work, an investigation of the effects of the microstructure of LuAG:Pr ceramics fabricated with different Pr concentrations and under different sintering conditions on the luminescence was carried out. It shows that the Pr concentration that maximizes luminescence emission depends on the thermal processing conditions. For a sintering temperature of 1500 °C and a sintering time up to about 3 h, the Pr concentration that maximizes luminescence is around 0.33 at.%. Longer sintering times lead to the formation of PrAlO₃ as a secondary phase, concomitant with a reduction of the intensity of luminescence emission.

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