A study of radiation effects on LuAG:Ce(Pr) co-activated with Ca

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A R T I C L E   I N F O

Article history:
Received 30 March 2015
Received in revised form 19 August 2015
Accepted 20 August 2015
Communicated by: Prof. A. Burger
Available online 29 August 2015

Keywords:
A1. Doping
A1. Radiation damage
B1. Rare-earth compounds
B2. Scintillator materials

A B S T R A C T

Single crystals of LuAG:Ce co-doped with Ca2+ were grown by the vertical Bridgman method and studied for optical properties, γ-irradiation induced absorption, scintillation light yield and decay. It is shown that addition of Ca2+ may efficiently limit the radiation induced absorption associated with presence of trace amounts of Yb. In bulk crystals with balanced Ca2+/Ce concentration the absorption induced in the emission range around 520 nm is less than 1 m–1, after the dose 1 kGy and 860 Gy/h dose rate. The light yield of LuAG:Ce upon co-doping with Ca2+ is preserved, while the fraction of the delayed recombination leading to slow scintillation components is decreased. The effects of Ca2+ were not favorable in Pr-doped LuAG studied so far. The absorption induced in the emission range around 300–400 nm range in the Ca-free LuAG:Pr, after the irradiation dose 1 kGy, is about 35 m–1, while it is above 100 m–1 in the Ca co-doped LuAG:Pr.

1. Introduction

Radiation stability of materials is governed by the combination of structural defects and electronic processes stimulated by radiation. It generally introduces additional absorption in the range of emission and also creates new relaxation channels of electronic excitations [1,2]. Scintillators based on lutetium-aluminum garnet (Lu3Al5O12, LuAG) doped with various rare-earths have the potential for application in high spatial-resolution imaging screens, medical imaging and high precision calorimeters in high energy physics [3–5]. In the latter case, a strong interest is emerging on garnet based scintillators shaped as fibers for next generation of calorimeters [6]. Due to high luminosities and collision rates involved in these applications, the crystals have to match several quality criteria, among which the radiation tolerance plays a critical role.

In this paper we shall consider LuAG single crystals with Ce3+ and Pr3+ ions. The two activators differ by their emission range and their decay time: the Ce3+ non-resolved two bands give rise to an emission maximum at 520 nm, while the Pr3+ emission is composed of two bands peaking at 320 and 370 nm. These materials satisfy the requirements for density (6.73 g/cm3) and effective atomic number (Zeff=62.9), timing and light yield performance (55 ns and 26,000 ph/MeV for Ce-doped [7] and 25 ns, 20,000 ph/MeV for Pr-doped [8] crystals). As for the radiation hardness, low-to-moderate performance has been reported based on a limited number of crystals studied so far. The γ-irradiation induced absorption in Czochralski LuAG:Pr at 320 nm was $\mu_{abs}=200$ m–1, after a dose 240 Gy [2]. The light yield degradation by 11% in LuAG:Pr, after 100 Gy, was reported in Ref. [9]. The absorption induced by γ-irradiation (with doses up to 10$^5$ Gy) in Bridgman LuAG:Ce and LuAG:Pr was studied in Ref. [10], after 1 kGy, the induced absorption in LuAG:Ce (at emission wavelength 535 nm) was 2 m–1, while in LuAG:Pr it was about 100 m–1 (at emission wavelength 320 nm). It has been shown [10] that the damage of transmission is mainly due to appearance of absorption bands peaking at 375 nm and 600 nm; the origin of these bands was assigned to trace amounts of Yb coming from raw oxides based on line locations, profiles and shifts with composition and supported by comparisons with crystals containing intentionally added Yb in the ppm level range. Ytterbium enters the lattice in the trivalent state substituting Lu3+ but, due to high electron affinity, it can easily acquire the 2+ valence state giving rise to absorptions at 375 nm and 600 nm (see Ref. [11] and references therein). The appearance of induced bands at similar locations was confirmed in γ-irradiated optical ceramics of LuAG:Pr [12] and LuAG:Ce [13] both prepared using 99.99% pure Lu2O3 oxide. In Ref. [12] trace amounts of Yb at 16.8 ppm level were found in the sample using Inductively Coupled Plasma Optical Emission Spectroscopy.

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http://dx.doi.org/10.1016/j.jcrysgro.2015.08.019
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Spectrometer. The origin of other types of color centers induced by γ-irradiation is associated with recharging of intrinsic lattice defects (oxygen vacancies with one or two trapped electrons) or other impurity defects. There may be some competition between Yb and different other types of traps in capturing charged particles depending on their relative amounts which are governed by growth conditions, activator concentration and purity of used oxides.

A way to improve the radiation hardness of oxide-based scintillators is to introduce an excess charge in order to suppress some of the traps related to oxygen vacancies. This concept was successfully realized years ago in PbWO₄ by introducing trivalent lanthanides which substitute for divalent lead sites [14,15]. The same approach with a positive result was later applied to yttrium perovskite, YAlO₃, by introducing tetravalent Zr⁴⁺ [16], while it was not similarly efficient in the case of garnets [17–19]. As currently suggested [20,21], the charge compensation in garnets following tetravalent cation incorporation is the formation of cation vacancies, rather than a decrease of anion vacancy concentration. Following tetravalent cation incorporation is the formation of cation vacancies, rather than a decrease of anion vacancy concentration. An important requirement, when selecting the co-dopants to improve the radiation hardness of oxide-based scintillators is to introduce an excess charge in order to suppress some of the traps related to oxygen vacancies. This concept was successfully realized years ago in PbWO₄ by introducing trivalent lanthanides which substitute for divalent lead sites [14,15]. The same approach with a positive result was later applied to yttrium perovskite, YAlO₃, by introducing tetravalent Zr⁴⁺ [16], while it was not similarly efficient in the case of garnets [17–19]. As currently suggested [20,21], the charge compensation in garnets following tetravalent cation incorporation is the formation of cation vacancies, rather than a decrease of anion vacancy concentration.

Selection of co-dopants to improve the radiation hardness of Lu-based garnets is an open question and requires alternative concepts. An important requirement, when selecting the co-dopant, is conservation of a good balance between the radiation hardness and scintillation performance. Composition engineering to achieve these goals is the major aspect of many present studies. Unlike the previously applied methods aiming suppression of existing electron traps [14–16], it is suggested that the new trap centers (Ce⁵⁺) that could be created upon co-doping with divalent impurities [22,23] may efficiently compete in electron capture with Yb⁴⁺ and thus compensate its negative role, if present in noticeable amounts in raw materials. After proving on the first samples that there is no damage to scintillation performance, single crystals with Ce and Ca varied in a wide range of concentrations were grown. The strengths and limitations of co-doping with Ca were revealed. It is in particular shown that co-doping LuAG:Ce with Ca ions, if taken in balanced quantities, may efficiently limit Yb⁴⁺→Yb⁵⁺ reduction and decrease the radiation induced absorption in the Ce⁴⁺ emission range. At the same time the scintillation light yield is preserved, while the fraction of the delayed recombination leading to slow scintillation components is decreased.

It should be mentioned that co-doping of various Ce-activated materials with divalent impurities is presently an active research field aiming improvement of scintillation properties (see, e.g. [23–26] and references therein). The present studies therefore address directly the radiation tolerance of these newly developed materials.

3. Results and discussion

3.1. LuAG:Ce

Optical properties of crystals were examined in the UV–visible range. Fig. 1 shows the absorption spectra of as-grown LuAG:Ce and LuAG:Ce,Ca(50 ppm) samples. The bands at ~350 nm and ~450 nm are due to 4f-5d transitions of Ce⁴⁺. No additional absorption appears in the visible range upon co-doping with Ca thus conserving high transmission in the range of Ce⁴⁺ emission. Absorption in the UV is much stronger in the Ca co-doped crystal. Increase of absorption in the UV, as compared to crystals with no co-doping, was earlier observed in YAG:Ce,Ca [22], GGAG:Ce,Ca [24], LuAG:Ce,Mg [23, 25], LYSO:Ce,Ca(Mg) [26], LuAP:Ce,Ca [30]. The charge compensation in garnets following incorporation of divalent co-dopants is creation of oxygen vacancies [20,21]; in Ce-doped crystals they may favor formation of Ce⁴⁺ states for charge compensation [22,23,26]. Conversion of all Ce⁴⁺ to Ce⁴⁺ in as-grown YAG:Ce,Ca (evidenced by absence of 4f-5d absorption of Ce⁴⁺) and reconversion of some part of Ce⁴⁺ to Ce⁴⁺ upon reducing heat treatment was reported in Ref. [22]. The origin of the broad absorption band at 260 nm in LYSO:Ce,Ca(Mg) in Ref. [26] is ascribed to charge transfer band from the oxygen 2p orbitals of the valence band to the Ce⁴⁺ 4f orbitals (the estimated decrease of Ce⁴⁺ concentration in LYSO:Ce with Ca⁴⁺ is up to 35%, when 0.1 at% of Ca is added to the melt).

2. Experiment

Single crystals were grown by the vertical Bridgman method (or vertical directional crystallization) with resistive heating and using containers in the form of tubes 14–16 mm in diameter fabricated of vacuum melted pure Mo (details of the method can be found in Refs. [27,28]. High purity Lu₂O₃, Ce₂O₃, Pr₂O₃ (99.99%) and quality crystalline sapphire were used as starting materials; other oxides were of 99.9% purity. The concentrations of Ca and Ce (Pr) in melts were respectively 30–150 ppm (0.02–0.1 at%) and 0.5–1.0 at%.

Crystallization processes were carried out at rates 1–1.3 mm/h under an enclosed Ar/H₂ atmosphere and using seed crystals oriented along the < 100 > axis. Single crystals 60–80 mm long were obtained and controlled for macroscopic defects under polarized light (MPS-2 microscope). Bulk samples of rectangular shape (4 x 4 x 15 mm³ and larger) polished on all sides and plates (0.5–5 mm thick) were fabricated. The concentration of Ce⁴⁺ was measured by optical absorption methods [29].

Optical transmittance was measured at 300 K in the range 200–800 nm using Specord M40 spectrophotometer. ⁶⁰Co gamma-ray ring shaped source with a 1.25 MeV photon energy and 860 Gy/h dose rate was used in irradiation tests. The radiation induced damage was characterized by the change in light transmittance in the UV-visible range and given in units of induced absorption coefficient $\mu_{\text{abs}}(m^{-1})=1/([\ln T]/\lambda)$, where $\lambda$ is the sample length, $T_o$ and $T$ are the transmission before and after irradiation.

Scintillation light yield and decay measurements were performed under ¹³⁷Cs (662 keV) excitation using a Photonis XP2020Q photomultiplier (PMT). The samples of $7 \times 7 \times 2$ mm³ size polished on the two large faces were measured in the vertical position; they were wrapped in Teflon and optically coupled to the PMT with optical grease (one of the 2 x 7 mm² faces was put in contact with the PMT window). The light yield was corrected by the PMT’s spectral response and the decays were integrated during 12 μs.

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![Fig. 1. Absorption in as-grown LuAG:Ce and LuAG:Ce,Ca; emission of Ce⁴⁺ is given by a dot curve, inset shows the difference absorption spectrum.](image-url)
It should be noted that CaO doping in small amounts (10^{-2}–10^{-3} wt%) is commonly applied in the technology of rare-earth gallium garnets (see, e.g. [31] and references therein) to compensate the traces of tetravalent impurities (Si,Zr) which otherwise lead to creation of cation vacancies and screw growth behavior. MgO is used as sintering aids in the technology of LuAG:Ce(Pr) ceramics and improves the transmittance [12,25].

The ionic radius of Ca^{2+} is by ~14% larger than of Lu^{3+} (respectively 1.12 Å and 0.977 Å in 8-fold coordination) suggesting that Ca^{2+} ions occupy dodecahedral positions (c-sites). No degradation in optical quality was noticed in LuAG:Ce,Ca for the Ca concentration range taken in this study.

As mentioned, co-doping with Ca^{2+} was performed to evaluate whether the new trap centers (Ce^{4+}) would efficiently compete with Yb^{3+} or other traps in electron capture in the course of irradiation. Fig. 2 shows radiation induced changes in LuAG:Ce,Ca crystal (4 × 4 × 21 mm^3): transmission before and after irradiation (Fig. 2a) and radiation induced absorption (μ_{ind}), after the dose 1 kGy (Fig. 2b). The induced absorption coefficients are 0.3 m⁻¹ at 520 nm and 1 m⁻¹ at 600 nm. For comparison, μ_{ind} for a typical LuAG:Ce without co-dopant is also given in Fig. 2b. It should be noted that the lowest μ_{ind} values measured so far in bulk (up to 8 × 8 × 40 mm^3) LuAG:Ce crystals without co-dopants and with nearly the same Ce content were 1.45 m⁻¹ (at 520 nm) and 1.4 m⁻¹ (at 600 nm); in most of studied LuAG:Ce samples they were in the 2–3 m⁻¹ range. Small or no indication of induced absorption at 600 nm in LuAG:Ce,Ca (Fig. 2b, curve 1) implies that Ce^{4+}, as electron traps, efficiently compete with Yb^{3+}, so that the recombination processes proceed rather on Ce, than on Yb or on oxygen defects.

Measurements on several series of Ca-doped samples have shown that μ_{ind} strongly depends on the Ce/Ca ratio. Intense absorption bands appear at λ > 500 nm in crystals with high Ca concentrations relative to Ce. Ce, at% (Fig. 3a) shows the damage of transmission in LuAG:Ce,Ca(100 ppm) series after 1 kGy. The corresponding μ_{ind} values measured at 620 nm gradually decrease with increasing the Ce concentration, Fig. 3b. A similar tendency was observed in crystals with other Ce and Ca amounts. Ca^{2+} ions favor, for charge compensation, Ce^{4+} states, however, the charge compensation may proceed via creation of oxygen vacancies as well; the concentration of the latter will increase with Ca concentration. The competing centers in LuAG:Ce,Ca for electron trapping are oxygen vacancies, Yb^{3+} and Ce^{4+}. If the Ce/Ca ratio is high enough, the trapping of electrons proceeds mainly on Ce^{4+}, while in the case of smaller ratios, the trapping of electrons proceeds also on other defects giving rise to absorption bands shown in Fig. 3a. The origin of these bands may be associated with F-type or O⁻ centers and requires additional studies. Comparison among different crystal compositions in respect to the radiation tolerance has shown that in crystals co-doped with 100 ppm of Ca, μ_{ind} is ≤ 1 m⁻¹, when Ce > 0.12 at%; for Ca=50 ppm, μ_{ind} is ≤ 1 m⁻¹, when Ce > 0.05 at%.

3.2. LuAG:Pr

Absorption induced in LuAG:Pr in the range of Pr^{3+} emission (at 300–400 nm) is much stronger than that in LuAG:Ce (at

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**Fig. 2.** (a) Transmission in as-grown and γ-irradiated LuAG:Ce,Ca crystal (1 kGy); (b) μ_{ind} at λ > 500 nm in LuAG:Ce,Ca (curve 1) and in LuAG:Ce without co-dopant (curve 2).

**Fig. 3.** (a) Transmission in as-grown LuAG:Ce,Ca(100 ppm) (1), and γ-irradiated LuAG:Ce,Ca(100 ppm) crystals with Ce=0.05% (2), Ce=0.035% (3) and Ce=0.03% (4) (l=5 mm); (b) variation of μ_{ind} at 620 nm with Ce concentration.
Scintillation yields were carried out on LuAG:Ce crystals with Ca$^{2+}$ co-dopant, as well as without co-dopant. The results of light yield measurements under $^{137}$Cs (662 keV) are summarized in Table 1.

The relatively low light yield measured on $7 \times 7 \times 2$ mm$^3$ plates is due to their shape leading to different terms of light collection (a significant part of the light escapes from the side surfaces), as compared in the case of pixels [7]. In addition, the Ce content in these samples is far from optimum. Some variation of the pulsed height spectrum shape (width of the photopeak) with variation of the integration time gate has been observed in Ca-free samples. It suggests a variability of the slow component fraction which might be due to in-homogeneities in defect distribution in crystals. No meaningful variations of the light yield were observed between Ce-doped and Ca co-doped crystals.

The results of decay measurements are given in Fig. 6. Decays were fitted by a three exponential function. Decay times were constrained to those values for all other samples. Nevertheless, this restriction does not deteriorate fit’s residual. The obtained time constants and component weights are given in Table 2. The evolution of the fast/slow component ratio with Ce concentration in Ca-free and Ca co-doped LuAG:Ce crystals is given in Fig. 7.

By increasing the Ce concentration the weight of the fast component in Ca-free samples clearly increases, while the slow

![Fig. 4](image1.png)

![Fig. 5](image2.png)
components decrease. This was expected, since an increase in the number of recombination centers related to Ce reduces the probability for charge carriers to be trapped on other centers; the ratio between components becomes closer to intrinsic Ce decay. In comparison to Ca-free crystals, the slow component in Ca co-doped crystals is by one order of magnitude lower giving evidence of a noticeable reduction of traps (mainly oxygen vacancies) or of other centers (Yb\(^{3+}\), oxygen vacancies or other impurity centers). As a result, the measured radiation induced absorption at the peak emission wavelength of Ce\(^{3+}\) (520 nm), after 1 kGy, is much less than 1 m\(^{-1}\). Selection of balanced Ce/Ca ratios is however important to avoid formation of other types of color centers giving rise to absorption in the red-infrared; the results specify the corresponding concentration ranges. The results may have importance for optimization of several other scintillation materials containing additional divalent impurities which is presently an active research field. Co-doping of LuAG:Pr with Ca (and Sc) in the studied few compositions gave no positive result. The \(\gamma\)-induced absorption in the range 300–400 nm, after 1 kGy, in a low-concentrated LuAG:Pr(0.09%) was about 35 m\(^{-1}\), while in LuAG:Pr,Ca and LuAG:Pr,Sc it was above 100 m\(^{-1}\).

It is shown that the light yield of LuAG:Ce co-doped with Ca, as compared to Ca-free crystals, is preserved, while the magnitude of slow scintillation components is decreased by one order due to suppression of the trapping function of oxygen related traps. The obtained results give ground that further optimization of the composition by introducing other divalent impurities or of their combinations may further improve both the radiation resistance and scintillation performance of garnet crystals.

### Acknowledgments

The research leading to these results has received funding from the European Union Seventh Framework Program (FP7/2007–2013) under Grant Agreement no. 295025. It has been conducted in the frame of the Crystal Clear Collaboration and in the scope of the International Associated Laboratory (CNRS–France & SCS–Armenia) IRMAS.

### References


