Radiation hardness of LuAG:Ce and LuAG:Pr scintillator crystals

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Abstract

Single crystals of LuAG:Ce, LuAG:Pr and un-doped LuAG were grown by the vertical Bridgman method and studied for radiation hardness under gamma-rays with doses in the range 10–105 Gy (60Co). A wide absorption band peaking at around 600 nm springs up in all three types of crystals after the irradiations. The second band peaking at around 375 nm appears in both LuAG:Pr and un-doped LuAG. Compositional variations have been done to reveal the spectral behavior of induced color centers in more detail and to understand their origin. Similarities in behavior of Yb2+ centers in as-grown garnets are found, indicating that radiation induced color centers can be associated with residual trace amounts of Yb present in the raw materials. Un-doped LuAG and LuAG:Ce demonstrate moderate radiation hardness (the induced absorption coefficients being equal to 0.05–0.08 cm−1 for accumulated doses of 103–104 Gy), while LuAG:Pr is less radiation hard. The ways to improve the radiation hardness are discussed.

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1. Introduction

The interest around LuAG:Pr (Lu3Al5O12:Pr3+) and LuAG:Ce (Lu3Al5O12:Ce3+) garnets is rapidly increasing due to their excellent scintillation properties attractive for hard X-ray and gamma-ray detection in various applications. The reported light yield of LuAG:Pr is 16,000–20,000 ph/MeV, the fast decay time is 20–23 ns, and the energy resolution is 5–7% [1,2]; the light yield proportionality as a function of gamma-ray energy is superior, as compared to those of other dense scintillators with high Zeff [3]. This material has been already used for construction of a gamma camera for positron emission mammography [4] but has potential for electromagnetic calorimeter experiments too. The emission is due to the 5d–f transition of Pr3+ ion and lies in the range of 310–380 nm. The highest value of the light yield is attained in moderately doped single crystals containing 0.2–0.25 at% of Pr3+. LuAG:Ce was first reported in 1995 [5], however it appeared as not very much promising, since in comparison to several other known Lu-based compounds doped with Ce4+, its major characteristics (density, decay time and scintillation light yield) were lower. Studies on this material were however quite active during the last 10 years; in particular, it was shown that Ga co-doping leads to a strong increase of the light yield and to suppression of the slow scintillation components explained as due to a shift of the energy levels of shallow defects out of the forbidden gap [6]. The emission is due to the d–f transitions of Ce3+ with the maximum located at about 510 nm. Single crystals reported before 2010 were doped with only ~0.1 at% of Ce3+ and demonstrated light yields 10,000–12,500 ph/MeV. Our recent studies on Bridgman-grown crystals have shown that the light yield of LuAG:Ce can reach 26,000 ph/MeV (or comparable to that of LSO) if higher Ce concentrations are incorporated in optical quality crystals (the studied range was 0.1–0.55 at%) [7,8]. It was also shown that high Ce3+ concentrations could be accommodated in the lattice by larger extents of non-equivalent occupancies by Lu3+ for octahedral Al3+ sites (0.5–2.5 at% in un-doped LuAG [9–11] and up to about 5 at% in LuAG:Ce containing 0.7 at% of Ce3+ [8]). The obtained results have shown that LuAG:Ce can compete with presently used materials in a number of applications, including high energy calorimetry and medical imaging.

When considering the application potential of both of these scintillators several positive properties of the LuAG host should be also taken into account. It is a stable compound with very good mechanical and chemical stability and is non-hygrosopic; the melting point is lower than that of LSO; the production technology is well-developed using Cz, Bridgman or micro-pulling methods. The latter method provides a fabrication of shaped fibers suitable for construction of detectors consisting of arrays of different crystals and providing for high detection granularity [12].

The above mentioned applications of LuAG:Pr and LuAG:Ce assume satisfactory radiation hardness, since the light yield
dependence on the irradiation dose is among the major decisive parameters. More recently, discovery of the Higgs boson at CERN has shown the importance of crystal-based high precision calorimeters in fundamental physics. However scintillating crystals have to match several quality criteria, among which radiation hardness plays a critical role. In this context, garnet crystals doped either with Ce or Pr satisfy the stopping power, the timing performances, as well as the scintillation yield, but the radiation hardness has never been carefully studied.

In a recent radiation hardness test short report [13], the light yield degradation of Pr:LuAG single crystal exposed to 100 Gy from $^{60}$Co was ($-11 \pm 3$)%. The influence of gamma-radiation on properties of LuAG:Ce single crystalline films is studied in [14]; along with some spectral shifts of absorption and emission lines associated with Ce$^{3+}$, decrease of the scintillation light by $\sim 50\%$ has been observed in films irradiated with doses up to $10^4$–$10^6$ Gy ($^{60}$Co).

In this work, we report the results of studies on radiation effects induced by gamma-rays ($^{60}$Co) in LuAG:Pr, LuAG:Ce and related crystals and observed as transmittance degradation in the UV–visible range. The role of residual Yb in decreasing the resistivity of crystals to radiation is revealed and analyzed in detail.

2. Experimental

Single crystals used in the present studies were grown by the vertical Bridgman method in Mo tubes 12–15 mm in diameter. Details of the method and of applied growth conditions can be found in [8,15,16]. The samples for radiation tests were selected from crystal sections free of light scattering inclusions or facets and controlled under polarized light (MPS-2 microscope). Besides LuAG:Ce and LuAG:Pr, a few other compositions doped or co-doped with Hf, Zr and Yb, as well as un-doped LuAG, YAG:Ce and LuYAG:Ce solid solutions were studied for comparison and supporting information. The concentration of Pr$^{3+}$ in LuAG:Pr ($4 \times 8 \times 17$ mm$^3$) was $0.18 \pm 0.05$ at%; the concentration of Ce$^{3+}$ in LuAG:Ce and solid solutions ($5 \times 5 \times 20$ mm$^3$) was $0.15 \pm 0.05$ at%.

Optically polished samples were irradiated by a $^{60}$Co gamma-ray ring-shaped source with 1.25 MeV photon energy and dose rate of 24 rad/s. The applied irradiation times were ranged from 1 min to 120 h for accumulated doses from $10$ to $10^5$ Gy respectively. The radiation damage was characterized by change in light transmittance in the UV–visible range measured longitudinally (Specord M40 spectrophotometer; 300 K).

3. Results and discussion

At the first stage LuAG:Ce, LuAG:Pr and un-doped LuAG were studied for transmittance variation as a function of the irradiation dose. The main feature observed in LuAG:Ce is appearance of a wide absorption band in the visible, the intensity of which increases with the dose (Fig. 1a). The maximum of the wide induced absorption band is at $\sim 610$ nm and saturation is seen at doses $10^4$–$10^5$ Gy. Note that the wide induced band peaking at $\sim 610$ nm coincides with the emission wavelength of Ce$^{3+}$ and should affect the scintillation light yield. Induced absorptions in LuAG:Ce in terms of difference absorption coefficients are shown

![Fig. 1. Transmission spectra before and after $^{60}$Co gamma-ray irradiations at different doses in (a) LuAG:Ce (l=20 mm) and (d) LuAG:Ce,Hf(30 ppm) (l=20 mm); (c) partial recovery of transmission in LuAG:Ce (l=20 mm); and (b) induced absorption coefficients for different irradiation doses.](image-url)
in Fig. 1b. The extent of partial recovery of the optical transmission for the sample kept in a box for 120 h is shown in Fig. 1c. In LuAG:Ce with 30 ppm of Hf (Fig. 1d) the degradation of transmission is larger, as compared to LuAG:Ce (1a).

The results of similar studies performed with LuAG:Pr are given in Fig. 2. In addition to the induced band at 602.4 nm, another one appears at 374.8 nm Fig. 2a and b). Note that in LuAG:Ce the range between 300 and 400 nm is obscured by the f–d absorption band of Ce³⁺. As seen from Fig. 2a (curve 1), the band at around 375 nm is present in the as-grown crystal as well. The emission of Pr³⁺ covers the 300–400 nm range; therefore high transmission in this range is important to avoid self-absorption. A partial recovery of the optical transmission (after 120 h) is also shown in Fig. 2a. Saturation of both the bands upon irradiation is observed at doses near 10⁵ Gy (Fig. 2c). The damage of transparency at 374.8 nm however proceeds in a quite different way, since other types of color centers (not considered in this article) may interfere in this range. It should be also noted that the reverse processes of slight decrease of the induced absorption have been seen at higher doses (not shown in the figures) in both Ce- and Pr-doped crystals.

The bands at ~375 and ~600 nm are induced in un-doped LuAG and LuAG:Hf as well (Fig. 3); the difference absorption coefficients are much larger in LuAG:Hf (Fig. 3b).

Comparison of the induced absorption in the studied crystals (Figs. 1–3) shows a similar qualitative behavior. Un-doped LuAG and LuAG:Ce exhibit satisfactory radiation hardness (the induced absorption coefficients at 600 nm for 10⁴–10⁵ Gy doses have comparable values in the range 0.05–0.08 cm⁻¹). The induced absorption in the studied LuAG:Pr crystal is by a factor of 10 higher and needs additional studies. Simultaneous increase of induced band intensities at around 375 and 600 nm with the dose suggests that centers of the same type are responsible for their origin. Similar studies performed with YAG:Ce garnet (7 × 7 × 15 mm³) have not revealed any noticeable induced absorption in the visible range (even for the 10⁵ Gy dose) and confirm high radiation stability of this scintillator. The contrasting behavior between Lu- and Y-based garnets can be attributed to different levels of residual impurities present in the corresponding raw materials used for crystal growth. Traces of Yb (≥ 2 ppm) are usually mentioned in the quality certificates of high purity Lu₂O₃, while Yb is usually not mentioned for Y₂O₃ oxide of the same overall purity, possibly due to its low quantity.

The f–f absorption lines of Yb³⁺ located in the 0.9–1 μm range are quite weak and narrow to be readily seen at low concentrations; however, Yb³⁺ ions have been seen in ESR spectra of LuAG grown from 5N Lu₂O₃ [17]. In contrast to Yb³⁺, high intensities and large shifts of spectral lines with interatomic distances in the lattice are characteristics to Yb²⁺ ions. Appearance of two wide absorption bands stable for sufficiently long time periods at 300 K has been observed in gamma-irradiated YAG:Yb and attributed to Yb²⁺ [18]. A small amount of Yb²⁺ ions is stabilized in YAG:Yb, when grown under a reducing atmosphere [19,20]. The amount of Yb²⁺ in YAG:Yb or LuAG:Yb could be significantly increased by quadrivalent co-doping [20]. The two absorption bands in YAG:Yb attributed to Yb²⁺ (4f⁶→4f⁴–5d transitions) are located at around 395 and 650 nm, while in LuAG:Yb they are shifted to shorter wavelengths (~375 and ~600 nm). The inter-configuration transitions depend on the destabilization energy of the 5d state associated with the spherically-symmetric component of the crystal field which, in turn,
is responsible for the character of spectral line shifts of $\text{Yb}^{2+}$ ions upon change of one of the host cations in the lattice. Spectral line shifts, when compared in different rare-earth aluminum garnets, depend on the unit cell ($a_0$) variation; increasing $a_0$ leads to a slight divergence and shift of absorption bands to longer wavelengths [20].

Fig. 4 shows absorption in as-grown LuAG:Yb,Zr; a quadrivalent co-doping (by $\text{Zr}^{4+}$) was done to stabilize high concentrations of $\text{Yb}^{2+}$. The spectrum exhibits absorption bands located at 371.5 and 600 nm and associated with $\text{Yb}^{2+}$; the induced absorption bands in gamma-ray irradiated crystals (Figs. 1–3) have similar profiles and spectral locations.

A single crystal of LuAG:Ce intentionally co-doped with 30 ppm of Yb was studied next for additional supporting information. Fig. 5 shows transmission in as-grown and gamma-irradiated samples. The initial spectrum shows no strong evidence of absorption near 600 nm, while after irradiation to $10^3$ Gy dose it acquires the same features, as observed in irradiated LuAG:Ce (Fig. 1a), but with much higher induced band intensity; in addition, appearance of the second band peaking at about 375 nm is now clearly visible. The next figure (Fig. 6) shows that the induced absorption band located at $\sim 600$ nm in LuAG:Ce shifts to longer wavelengths in solid solutions ($\text{ Lu}_{1-x}\text{Y}_x\text{Al}_3\text{O}_{12}$:Ce, for which $a_0$ parameter increases with $Y$ content. The peak wavelength of the induced absorption band shifts to $\sim 645$ nm for $x=0.6$, in qualitative agreement with the shift of $\text{Yb}^{2+}$ associated absorption lines observed in rare-earth aluminum garnets as a function of $a_0$ [20].

To summarize, radiation induced bands in the studied crystals and those in as-grown Yb-doped garnets (in which a part of Yb is stabilized as $\text{Yb}^{2+}$) are very similar in terms of line locations, profiles and spectral shifts with the composition. These observations give ground to suggest that the radiation induced bands in LuAG, LuAG:Pr and LuAG:Ce are associated with $\text{Yb}^{2+}$ ions.

It should be noted that similar profiles of transmittance degradation at $\sim 600$ nm have been recorded in gamma-ray irradiated LuAG:Ce ceramics [21] and can be thus assigned to $\text{Yb}^{2+}$ ions; for the YAG:Ce ceramics a weak induced band is seen at around 650 nm, the location of which coincides with that of $\text{Yb}^{2+}$ in YAG:Yb. It should be also mentioned that, due to a lower preparation temperature, the non-equivalent substitutions $\text{Lu}_4\text{Al}_3$ (Lu on octahedral Al sites) are almost absent in ceramics; therefore the observed induced absorption cannot be ascribed to defects arising from such substitutions.
Slow recovery of transmission has been observed in all studied crystals (two examples shown in Figs. 1 and 2) but proceeds much faster if the samples are exposed to sunlight. The observed behavior differs from that of garnets with as-grown Yb$^{3+}$ centers, which are stable in time, evidencing that charge compensation mechanisms in the two cases are dissimilar. Weakly bound electrons are involved in formation of gamma-ray induced color centers associated with Yb$^{3+}$ (e.g., those in near-by defect centers) which can easily abandon the center. In HF-containing crystals the charge compensation of induced centers is accomplished in part by HF$^{+}$ ions; therefore the induced absorption coefficients are much larger and the recovery is incomplete and proceeds slower.

4. Conclusions

The effects of gamma-ray irradiation upon optical transmittance of LuAG single crystals both un-doped and doped with Ce$^{3+}$ and Pr$^{3+}$ have been documented. Un-doped LuAG and LuAG:Ce demonstrate moderate radiation hardness, when exposed to gamma-rays ($^{60}$Co; $10^4$–$10^5$ Gy), while the radiation hardness of LuAG:Pr is much weaker. Degradation of transmittance begins for accumulated doses above $10^2$–$10^3$ rad and is due to appearance of intense and wide absorption bands peaking at around $375$ and $600$ nm. Characterization of crystals differing in composition is done in terms of line locations, profiles and spectral shifts of the induced absorption bands. The obtained results give ground to suggest that residual Yb present in the raw Lu$_2$O$_3$ oxide in ppm levels and incorporated in crystals as Yb$^{3+}$ transforms under irradiation to Yb$^{2+}$, giving rise to the observed induced absorption bands. An additional purification of lutetium oxide (and possibly of cerium and praseodymium oxides as well) from Yb may provide for a substantial increase of the radiation resistivity of LuAG:Ce and LuAG:Pr scintillators. Co-doping studied so far did not improve the radiation hardness and played even a negative role. For deeper understanding of these materials, the next steps will include thermal annealing in different media, as well as identification of other types of color centers which may contribute to the observed transmission degradation. The results suggest that the role of Yb should be studied in other types of Lu-based scintillators as well.

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