Review

Development of LuAG-based scintillator crystals – A review

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Abstract

A review of research and development of Lu3Al5O12 (LuAG)-based single crystal scintillators is presented. Crystals of this type have been prepared by the micro-pulling down method at the initial stage of material screening and by Czochralski or Bridgman methods to obtain higher quality and larger size single crystals afterward. Several different activators, namely Ce3+, Pr3+, Yb3+ and Sc3+ have been reported in the literature and such doped LuAG single crystals have been extensively studied to understand a number of issues, including: the scintillation mechanism, underlying energy transfer and trapping processes including the nature and role of material defects involved in the scintillation process and their relation to manufacturing technology. Significant improvements in the understanding of aluminum garnet scintillators lead to the discovery of multicomponent garnet single crystal scintillators in 2011, which are described. These materials gave rise to new class of ultraefficient complex oxide scintillators, the light yield of which considerably exceeds the values achieved for the best Ce-doped orthosilicate scintillators.

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1. Introduction

Aluminum garnets are represented by chemical formula of RE$_3$Al$_5$O$_{12}$ (REAG), where rare earth cation RE = Y, Dy, Ho, Er, Tm, Yb and Lu or their combination. Provided that the average RE site ionic radius is sufficiently small, aluminum garnets can partially consist of RE$^{3+}$ elements that have a larger atomic number than Dy$^{3+}$ (e.g. Tb$^{3+}$ or Gd$^{3+}$). Single crystals of Y$_3$Al$_5$O$_{12}$ (YAG) were among the first oxide materials grown by the Czochralski technique during the 1960s [1], and the development of Nd-doped YAG was stimulated mainly by the application for solid state lasers [2]. However, soon the potential of Ce$^{3+}$−doped YAG single crystals for fast scintillators was realized [3]. An early study of the Ce$^{3+}$ and Pr$^{3+}$ photoluminescence decay kinetics in a YAG host [4] revealed the absence of nonradiative thermal quenching up to about 550 K and 250 K, respectively. Consequently, at room temperature (RT) the 5d-4f transition of Ce$^{3+}$ center can be exploited for fast and efficient scintillation in a YAG host, while for Pr-doped YAG the quantum efficiency of 5d-4f emission transition of Pr$^{3+}$ is about 0.6 due to 5d state partial thermal quenching. The first comprehensive description of YAG:Ce scintillator characteristics was reported by Moszynski et al. [5], who included this material among the high figure-of-merit oxide scintillators. Isostructural Lu$_3$Al$_5$O$_{12}$ (LuAG) has a higher density and effective atomic number ($\rho = 6.67$ g/cm$^3$, $Z_{\text{eff}} = 63$) than YAG ($\rho = 4.56$ g/cm$^3$, $Z_{\text{eff}} = 32.6$), which is advantageous in the case of hard X- and $\gamma$-ray detection. Nevertheless, by the mid 1990s Ce-doped LuAG was effectively demoted in favor of the analogous high density aluminum perovskite LuAlO$_3$:Ce (LuAP) [6] and thus corresponding research on garnets dwindled until the end of last century. However, triggered by industrial interest, systematic studies were reinvigorated around 2000 [7].

Growth of YAG or LuAG by the Czochralski technique is able to provide high quality single crystals, see an example in Fig. 1. Typical Czochralski growth involves either an iridium crucible in inert atmosphere (N$_2$) with small addition of oxygen [8], or a molybdenum crucible in a reducing (Ar + H$_2$) atmosphere [9]. Since isosctructural cubic garnet structures of YAG and LuAG form a solid solution, any intermediate mixed composition (i.e. $Y_xLu_{1-x}Al_5O_{12}$, for $0 < x < 3$) can be grown. The solidification points of mixed compositions range between 2010 °C (for LuAG) and 1930 °C (for YAG) [8]. The garnet structure exhibits very flexible cation substitution and such substitution was used to prepare materials with tailored lattice constants [10] and can, in principle, be used for the preparation of highly substituted crystals with a homogenous composition. However, at the same time, this readiness of solid solution formation in the garnet structure hints at the relative ease of intrinsic antisite defect formation. Indeed, theoretical studies have shown that the antisite defect, Y$_{Al}$, was found as the lowest formation. Antisite (octahedral Al) position, which was documented by luminescence studies of RE$^{3+}$ dopants predominantly substitute for the RE cation, but a small fraction can also be found at the antisite (octahedral Al) position, which was documented by luminescence studies of RE$^{3+}$ 4f−4f transitions by high resolution emission spectroscopy [13,14]. The segregation coefficient of Ce$^{3+}$ in YAG and especially in LuAG is relatively small (less than 0.1), which is an obstacle in obtaining a homogenous doping profile in large crystals.

Due to the high crystal field at the dodecahedral RE site, the 5d states of Ce$^{3+}$ are considerably split and shifted to a lower energy in garnet with respect to most other oxide hosts. The lowest 4f−5d absorption and emission bands peak around 450–460 nm and in the green–yellow part of the spectra, respectively. With the help of photoionization threshold and excited state absorption measurements [15] it was established that the lowest 5d$_1$ relaxed state is placed about 1.2 eV below the conduction band of YAG, which is enough to completely inhibit undesired ionization of the Ce$^{3+}$ relaxed excited state near RT. In LuAG, Ce$^{3+}$ emission is high energy shifted by about 0.1 eV with respect to YAG [7] pointing to a somewhat weaker crystalline field and/or covalent bonding at the Lu site.

This paper provides a survey of the technological development and achievements mainly on Ce and Pr-doped LuAG and their characteristics. Furthermore it describes the invention of Ga-admixed crystals, followed by the discovery of multicomponent garnet scintillators (e.g. (Gd, Lu)$_{2}$(Ga, Al)$_{5}$O$_{12}$:Ce). Physical understanding of the scintillation mechanism and typical defects that decrease the figure-of-
merit of these materials are described, as well as supporting atomic scale calculations. Finally, the application potential and future prospects of these scintillators are outlined.

2. Crystal growth, characterization and atomistic simulation

In this section, the most studied activators and compositions intended for fast scintillator applications will be described including theoretical aspects of defect formation in the garnet lattice.

2.1. Undoped and Ce-doped LuAG

2.1.1. Growth of single crystals

Undoped and Ce-doped LuAG single crystals were prepared by the Czochralski method in reducing \( \text{H}_2/\text{Ar} \) atmosphere which is suitable for dopant ions like \( \text{Ce}^{3+} \) or \( \text{Pr}^{3+} \) to stabilize their trivalent charge state. Furthermore, the host crystal properties can reflect the atmosphere used for the growth through color centers creation especially in UV region of spectra. To date, industrial scale crystals have been grown to a maximum diameter of 44 mm and length of up to 170 mm, see Fig. 2. Molybdenum crucible and a tungsten resistive heater were used in the reducing atmosphere. All starting materials were of
99.999% purity except for Ce oxide (99.99% purity). Nominally, Lu$^{3+}$ was substituted by Ce$^{3+}$ according to the formula of (Ce$_{0.01}$, Lu$_{0.99}$)$_3$Al$_5$O$_{12}$. Starting materials were pre-sintered at 1400 °C for 30 h. Typical rotation rate was 15 rpm and the pulling rate was 1.0 mm/h. An automated system, which monitors the weight of the crystal was applied to control the crystal diameter.

2.1.2. Optical, luminescence and scintillation characteristics

In Fig. 3, typical room temperature absorption spectra of Ce-doped YAG and LuAG single crystals are given. Intense allowed absorption transitions from the 4f ground state to the excited 5d levels are marked in the figure. A more intense crystal field in YAG causes a low energy shift of the 4f-5d$_1$ transition in YAG by nearly 12 nm and even larger separation between the 5d$_1$ and 5d$_2$ transition with respect to LuAG. Absorption spectra below 300 nm are frequently complex due to the overlap of Ce$^{3+}$-related absorption bands and various color and impurity related bands [16]. The onset of the absorption edge of undoped LuAG is at about 190–200 nm and temperature independent (due to defects) and temperature dependent (exciton origin) components have been identified [17].

In Fig. 4 the normalized excitation and emission spectra of Ce-doped YAG and LuAG are given at 80 K. At low temperature the doublet in the emission spectra (radiative transition 5d$_1$ → $^{2}F_{5/2}$, $^{2}F_{7/2}$ of Ce$^{3+}$) is well resolved and reflects the distance between the $^{2}F_{5/2}$ and $^{2}F_{7/2}$ 4f ground state levels of Ce$^{3+}$ of about 1800–2000 cm$^{-1}$. The peaks in the excitation spectra match the position of the 4f-5d$_1$ and -5d$_2$ absorption peaks in Fig. 3. As the higher 5d$_{3,4,5}$ states are in the conduction band, the excitation into these levels is rather inefficient due to the excited state ionization, and an additional effect can be due to overlap with mentioned color center absorption bands.

Early studies of LuAG:Ce [7,18] revealed a considerable percentage of slow, technologically unexploitable light in the scintillation response, which has been discussed in detail elsewhere [19]. While the steady-state scintillator efficiency (radioluminescence intensity) of both YAG:Ce and LuAG:Ce of high 5–6 N purity achieved up to 7–8 times higher value with respect to standard Bi$_4$Ge$_3$O$_{12}$ (BGO) scintillator – Fig. 5(A), their light yield using a few microsecond shaping time was considerably lower, namely for YAG:Ce up to 300% of BGO [5,6,20] and for LuAG:Ce, only about 150% of BGO [20]. This points to a considerable amount of “slow scintillation light”, especially in the latter compound. In fact, the competition between slow intrinsic emission around 300–350 nm and Ce$^{3+}$ luminescence is evident from radioluminescence spectra [18], Fig. 5(B). The retrapping of migrating electrons in shallow traps associated with cation antisite defects (AD) [21,22] during the transport stage of the scintillation mechanism was proposed as the main reason for slow scintillation in Ce-doped aluminum garnet scintillators [23]. Comparison of photoluminescence and scintillation decays of LuAG:Ce in Fig. 6 clearly demonstrates the slow decay phenomena in this material. While the dominant component has a decay time very similar to that of photoluminescence decay (55 ns), a slower decay process that can be fit by an exponential with a 600–1000 ns decay time is always

![Graph](image_url)

**Fig. 3.** Absorption spectra of Ce-doped YAG and LuAG hosts. Ce concentration in the samples is 0.03–0.04 wt%.

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**Fig. 4.** Excitation (em = 506 nm and 526 nm for LuAG and YAG host, respectively) and emission (ex = 340 and 335 nm for LuAG and YAG host, respectively) spectra at 80 K.

**Fig. 5.** Radioluminescence spectra (X-ray excitation, 35 kV), RT. (A) LuAG:Ce, YAG:Ce and BGO standard scintillator (x5). (B) Undoped and two Ce-doped LuAG crystals. Descriptions are in legends, all spectra are mutually comparable in an absolute way.
found. Moreover, the signal increase before the rising edge of the decay (marked by $I_S$ with respect to the true experimental background level given essentially by the detector electronic noise) points to the presence of very slow decay processes the time constant of which is comparable with the time interval between two subsequent excitation events (tens-to-hundreds of microseconds). The coefficient alpha, shown in Fig. 6, has been introduced for quantitative evaluation of these “superslow” decay components in scintillation decay [24] and more than 65% of the total intensity of scintillation is generated in these delayed recombination processes [18].

Spatially-correlated AD-Ce$_{Lu}$ pairs were found with the help of electron paramagnetic resonance experiments [25] and tunneling recombination between related electron and hole trapped at such pairs was proved within 10–100 K [23]. Based on these findings the tunneling recombination process was suggested to explain slower, submicrosecond decay component in the RT scintillation decay [26]. In fact, tunneling-driven recombination processes are characterized by the decay function $I(t) = (A + B \times t)^{-p}$, where $0.95 < p < 1.5$ [27] and such a dependence was confirmed in the scintillation decays measured with large dynamical resolution and extended time scale [28], see Fig. 6(B), where a straight line is clearly visible in $\log I(t) - \log t$ representation at longer times.
Thus, the antisite defects were found of fundamental importance in YAG and especially LuAG melt-grown crystals, Fig. 7, as they can trap excitons which gives rise to slow intrinsic UV emission in undoped crystals [29,30] and more importantly to shallow electron traps which are responsible for considerable intensity of slow decay components in scintillation response.

Since experimental results point at cation antisite defects as a predominant defect in the garnet system, and their detrimental influence on scintillator performance, it is worthwhile to complement the experimental studies already discussed with atomistic simulations. Some of us have pursued an atomistic simulation approach consisting of “defect screening” and “defect optimization” components. That is, in the first stage, we have used lattice statics calculations with empirical potentials or density functional theory calculations (though we have emphasized lattice statics for defect screening for efficiency purposes) to determine the types of defects likely present in the scintillator material. We then use similar theoretical techniques in a second stage, the goal of which is to reduce the effect of the defect, either by exchanging or removing the defect through doping (through “defect engineering”) or by removing the effect of the defect (through e.g. “band gap engineering”, which will be discussed later). For example, lattice statics calculations have been used to predict that cation antisite defect disorder is the lowest energy intrinsic defect process (i.e. only thermally created defects) in REAG [12]. Furthermore, the energy for the antisite reaction was predicted to neither vary between RE cations, nor
did the difference between the cation antisite reaction and the next lowest energy process (Schottky) vary with varying RE. Nevertheless, this type of study allows for a ranking of likely defects according to reaction energy.

A similar methodology of ranking defect reactions by their energy from atomistic simulation results has also been applied to study extrinsic defects (created through interaction with the environment) in REAG scintillators. The reader is directed to a previous paper for a more thorough description of intrinsic and extrinsic defects in REAG [31]. Here, we provide two brief examples of extrinsic processes that may influence the antisite defect concentration. First, we have used a combination of atomistic simulation and X-ray diffraction to confirm nonstoichiometry in YAG, see Fig. 8. In this study, in addition to ranking nonstoichiometry mechanisms by energy, we also compared the change in lattice volume associated with those defect mechanisms as calculated by atomistic simulations and as measured by careful X-ray diffraction experiments. What can be seen in Fig. 8 is that the lowest energy mechanisms for Al₂O₃ and Y₂O₃-excess are those that best match the experimental data for lattice parameter change [32]. The details of this study can be found elsewhere, but it is worth noting here that the Equations (1) and (6) in Ref. [32] referred here to in Fig. 8 correspond to nonstoichiometry mechanisms that involve cation antisites. Thus, not only can antisites be formed intrinsically, but also through slight deviations from stoichiometry.

Another example of using atomistic simulations for extrinsic defect screening in REAG is the charge compensation of aliovalent dopants. Specifically, we have performed atomistic simulations on the solution of Me²⁺ (ranging in ionic size from Mg²⁺–Ba²⁺) and Me⁴⁺ dopants (from Ti⁴⁺–Pb⁴⁺) in REAG [33], see Fig. 9. From the results of these calculations, we predict that Me²⁺ dopants reside on RE sites with oxygen vacancies as charge compensating defects, as well as cation antisites (for mass and site compensation). Thus, we have now shown that cation antisites can originate intrinsically and extrinsically via nonstoichiometry or aliovalent doping. As for Me⁴⁺ dopants (from Ti⁴⁺–Pb⁴⁺) in YAG, we predict that they reside on both RE and Al sites and are charge compensated by RE vacancies.

Attempts have been made to improve the synthesis of LuAG in order to improve the light yield and remove the slow components associated with antisite defects. For example, as was shown, the scintillation decay is dominated by the component of the same decay time value as in photoluminescence decay curve (55–60 ns), but intense slower components are evident which span to the tens-of-microseconds time scale. The light yield in the first generation of LuAG:Ce crystals was about 12 000 phot/MeV [20]. Recently, the Bridgman grown LuAG:Ce single crystals were reported

![Fig. 8. The variation in YAG lattice parameter with respect to deviation from stoichiometry, determined by either atomistic simulation or XRD. Each trend line refers to a specific mechanism for deviation from nonstoichiometry [32].]
Scatter-free crystals 14–18 mm in diameter and 60–80 mm in length were obtained with high doping levels of Ce$^{3+}$ up to 0.55 at%. An essential improvement of performance was demonstrated in samples containing >0.2 at% of Ce; the light yield measured in LuAG:Ce(0.55 at%) pixels of $2 \times 2 \times 8$ mm in a horizontal position was about 26 000 phot/MeV. Similar values of light yield for similarly shaped scintillation elements were obtained also for the latest generation of Czochralski grown crystals from CRYTUR Ltd. [36], which point to considerable improvement of manufacturing technology in recent years. Also a Czochralski-grown Y-admixed (Lu$_{1-x}$Y$_x$)$_3$Al$_5$O$_{12}$:Ce scintillator has been reported recently [36] which shows somewhat diminished content of slow decay processes in scintillation response at comparable LY as that of LuAG:Ce. Nevertheless, intense slow decay components do remain in these samples. Efforts to remove them via other means are discussed in Section 2.4.

2.2. Pr-doped LuAG

In this section the Pr$^{3+}$ doping in a LuAG host will be reported with a focus on the growth of single crystals and subsequent characterization.

![Fig. 9](image_url) The predicted extrinsic defects in RE$_3$Al$_5$O$_{12}$ associated with Me$^{2+}$ (bottom left) and Me$^{4+}$ (upper right) doping. Small and large gray atoms represent Al and RE lattice atoms respectively. Oxygen atoms are not shown [33].

![Fig. 10](image_url) Four inch diameter LuAG:Pr single crystal grown by Cz-method [45].
2.2.1. Growth of single crystals

In 2004–2005 we began a study of Pr-doped LuAG single crystals including a comparison of Pr-LuAG with the other Pr-doped materials [37]. For crystal growth, the micropulling-down crystal growth technology was used at Tohoku University [38] and Czochralski growth was applied soon after [39] to obtain larger high quality single crystals. At the industrial scale the Pr:LuAG single crystals grown by the Czochralski method using a radiofrequency heating system are as large as four inches in diameter. The rotation rate was 0.5–5 rpm and the growth rate was 0.9 mm/h. An automatic diameter control system by crystal weighing was applied to control growth parameters. Crystals were grown from an Ir crucible 180 mm in diameter and 180 mm in height. A mixture of Ar and N₂ atmosphere was used to prevent oxidization of the crucible. The seed crystal was [98] oriented Pr:LuAG. After the completion of growth, the grown crystal was taken off from the melt and was gradually cooled down to room temperature. As a result of optimization of growth conditions such as cone angle, rotation rate, positions of the radiofrequency coil and ceramic insulation design in the furnace, a crack-free 92 mm

![Graph A](image1.png)

**Fig. 11.** (A) Optical absorption (curve 1) and photoluminescence (curve 2, \(\lambda_{\text{exc}} = 285\) nm) spectra of micropulling-down-grown LuAG:Pr 0.1% at RT. In the inset the temperature dependences of the photoluminescence spectra integrals (\(\lambda_{\text{exc}} = 285\) nm) of CZ-grown LuAG:Pr 0.53% are displayed in the wavelength ranges shown in the legend. (B) Optical absorption (curve 1) and photoluminescence (curve 2, \(\lambda_{\text{exc}} = 290\) nm) spectra of the micropulling-down-grown YAG:Pr 0.1% sample at RT.

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A diameter Pr:LuAG single crystal with a length of 100 mm was grown with a nominal composition of (Pr\text{0.075} Lu\text{2.925})Al\text{5}O\text{12} \[45\] (see Fig. 10). Quantitative chemical analyzes of the grown crystals for the Pr content along the growth direction were performed by the electron probe micro-analysis (EPMA; JXA-8621MX, JEOL). The effective distribution coefficient value \( k_{\text{eff}} \) of Pr in LuAG was calculated of 0.066.

2.2.2. Optical, luminescence and scintillation characteristics

As the energy of 4f-5d transition of Pr\textsuperscript{3+} is high energy shifted by about 1.5 eV with respect to Ce\textsuperscript{3+} [40] these absorption and emission bands in LuAG are situated in the near ultraviolet region, see Fig. 11(A). Analogous to the Ce\textsuperscript{3+} center, there is small low energy shift of these transitions from LuAG to YAG, Fig. 11(B), so that the emission peak occurs at 308 nm and 318 nm in LuAG and YAG, respectively. By the evaluation of the energy difference between the absorption and emission maxima related to \(^{2}\text{H}_{4}\text{-5d}_{1}\) transition in Fig. 11 the Stokes shift of 0.34 eV and 0.41 eV is evaluated for Pr-doped LuAG and YAG, respectively. A somewhat smaller Stokes shift in LuAG results in remarkably higher temperature stability of Pr\textsuperscript{3+} center where the onset of temperature quenching is located above 500 K (inset of Fig. 11) [41], while it is at about 250 K in YAG [4,41]. Furthermore, the 4f-4f emissions starting from \(^{3}\text{P}_{0}\) and \(^{1}\text{D}_{2}\) states are also comparatively much less intense in LuAG at room temperature, Fig. 11.

Due to the short-wavelength shift of the 5d-4f emission band of Pr\textsuperscript{3+} in LuAG, its radiative lifetime becomes much shorter compared to Ce-doped LuAG and the decay time of about 20 ns is measured in both photoluminescence and scintillation decays at room temperature [41]. The latter decay is affected by slower components in the same way and due to same reasons as in Ce\textsuperscript{3+} doped LuAG, see Fig. 12.

The measurements of other scintillation characteristics, namely the light yield, energy resolution and nonproportionality have been performed by several groups so far, see also Table 2 in Section 2.5. With respect to the Ce-doped LuAG, slightly inferior light yield value of 16 000–20 000 phot/MeV was reported [42–45], while the energy resolution shows better value down to 4.6% [42–46] and its non-proportionality was found the smallest among the high performance complex oxide scintillators [47]. It is worth noting that substantial room for improvement exists for the light yield of Pr-doped LuAG, where a theoretical limit of about 60 000 phot/MeV has been calculated from theoretical analysis regarding intrinsic performance limits of Ce, Pr and Eu doped scintillators [48]. An obvious area of improvement is the negative influence of slow scintillation decay components. Nevertheless, a desirable combination of fast decay time, high light yield and excellent energy resolution, together with

![Fig. 12. Normalized photoluminescence (ex = 280 nm, em = 320 nm) and scintillation (spectrally unresolved, ex = 511 keV, \(^{22}\text{Na}\) radioisotope) decays. Slower components in the latter are marked in the same way as in Fig. 6(A).](http://dx.doi.org/10.1016/j.pcrysgrow.2013.02.001)
high density, effective atomic number and favorable mechanical and chemical robustness of Pr:LuAG raised considerable interest in this material in scintillator community and became extensively tested in practical applications.

2.3. Other activators in LuAG

Single crystals of Yb-doped LuAG have been reported many times in recent literature regarding its possible use in solid state lasers [49]. An example of an industrial scale crystal grown by the Czochralski method from an Ir crucible under oxidizing (N\textsubscript{2}/O\textsubscript{2}) atmosphere is in Fig. 13. The charge transfer luminescence of Yb\textsuperscript{3+} became of interest due to the possible application of Yb-containing materials for scintillation detectors in neutrino physics experiments [50,51]. Its luminescence spectra and decay kinetics were briefly reviewed in many different host crystals including YAG [52]. This luminescence is characterized by a broad emission band in the UV–visible spectral region consisting of two subbands separated by about 10 000 cm\textsuperscript{-1} (equal to the separation of the 2\textsuperscript{F\textsubscript{7/2}} and 2\textsuperscript{F\textsubscript{5/2}} levels of Yb\textsuperscript{3+}). A large Stokes shift of 7000–17 000 cm\textsuperscript{-1} is typical as well, see Fig. 14(A). Fast decay with a radiative lifetime on the order of 100 ns is observed at sufficiently low temperatures since, in the case of the Yb\textsuperscript{3+} charge transfer transition, there is no inhibition due to parity or spin selection rules. The onset of luminescence quenching typically occurs at temperatures well below room temperature. That is why a very short decay time of about a few ns and low emission intensity are observed, for example, in YAG:Yb at 295 K [53]. In fact, though a radioluminescence intensity at RT of about 3–5% of that of BGO [54] and a photoluminescence decay time of about 1 ns, Fig. 14(B) [55] were reported, there is no report providing measurable value of light yield at RT which makes the practical application of this superfast scintillator improbable.

It has been already mentioned in the literature that doping by isovalent ions of sufficiently different radius at Lu (Y) or Al site in aluminum garnets will result in appearance of ultraviolet emission bands [30,56,57]. The nature of such bands is usually interpreted in terms of localized (trapped) excitons around such substitutional defects [30,58,59]. The scintillation characteristics of single crystal Sc-doped LuAG have been already reported in the literature [58], and the radioluminescence spectrum of 0.5%Sc-doped LuAG is shown in Fig. 15(A). The ultraviolet emission band shows a maximum at about 275 nm and an extended tail toward 400 nm can be interpreted as a residual intensity of the intrinsic undoped LuAG host emission in agreement with previous studies [58,59]. The 275 nm band is interpreted as a trapped exciton around the Sc-embedded site [58]. The excitation spectrum of the 275 nm emission closely follows that of the intrinsic 330 nm emission of undoped LuAG, see Fig. 15(A), which further supports such an interpretation. The scintillation decay reported in Fig. 15(B) is approximated by a two-exponential fit with decay times of about 5 ns and 1330 ns, where the latter component

![Fig. 13. Czochralski grown Yb-doped LuAG, φ 45 × 140 mm.](image-url)
contains more than 95% of the emitted scintillation light. Scintillation characteristics in the extended concentration range of Sc in \( \text{Lu}_3\text{Sc}_{x}\text{Al}_{5-x}\text{O}_{12} \), \( x = 0.001–2 \), were studied [58]: for \( x = 0.2–0.5 \) an optimum is found where the main scintillation decay time is within 610–760 ns and more than 92% of the total intensity is released in this component. A light yield value of 22 400–23 800 phot/MeV was measured in this Sc concentration range. Despite an encouraging light yield value the scintillation decay time is too long and cannot compete with Ce- or Pr-doped LuAG described above, so again, the practical prospective of this material system for a fast scintillator application is rather low.

2.4. Ce- and Pr-doped multicomponent garnet

Multicomponent garnets of the general chemical formula \( \text{RE}_3(\text{Al},\text{Ga})_5\text{O}_{12} \), where \( \text{RE} = \text{Gd, Y, Lu} \) or their mixture will be described in this Section. They differ from LuAG in the mixed occupancy of the dodecahedral RE site by multiple RE ions and that the octahedral and even possibly tetrahedral Al sites can contain both Al and Ga ions. Due to the presence of \( \text{Gd}^{3+} \) and \( \text{Ga}^{3+} \) cations, the forbidden gap shrinks and a composition of the bottom of the conduction band profoundly changes [60–62], although detailed and systematic band structure calculations have not yet been published.
2.4.1. Crystal growth by the micropulling-down method

Ce and Pr doped \((\text{Gd,Y,Lu})_2(\text{Al,Ga})_5\text{O}_{12}\) crystals were grown by the micropulling-down (\(\mu\)-PD) method with a radiofrequency heating system. The \(\mu\)-PD method is a fast and economic tool to prepare single crystal systems \([63,64]\) and to optimize the growth technology. This efficiency makes the \(\mu\)-PD method advantageous in comparison to conventional Czochralski or Bridgman growth methods and has been successfully used to investigate many oxide and halide single crystals. In the case of melt growth of gallium containing garnet by the Czochralski method, internal strains and inclusions are induced into the grown crystals because of gallium oxide evaporation during the growth process. Consequently, scintillation performance is degraded \([65]\). On the other hand, this problem is less serious in the \(\mu\)-PD method that has uniaxial melt flow in the capillary and the growth process is much faster \([63,64]\). A stoichiometric mixture of 4 N CeO\(_2\), Pr\(_6\)O\(_{11}\), Gd\(_2\)O\(_3\), Y\(_2\)O\(_3\), Lu\(_2\)O\(_3\), \(\beta\)-Ga\(_2\)O\(_3\) and \(\alpha\)-Al\(_2\)O\(_3\) powders (High Purity Chemicals Co.) was used as starting material. More specifically, the Lu\(^{3+}\), Y\(^{3+}\) and Gd\(^{3+}\) sites were substituted by Ce\(^{3+}\) or Pr\(^{3+}\) according to the formula of \((\text{Ce}_z, (\text{Lu,Y,Gd})_{1-z})_3\text{(Ga}_x\text{Al}_{1-x})_5\text{O}_{12}\). The \(z\) was 0.002 and additionally 3 mol% of \(\beta\)-Ga\(_2\)O\(_3\) was added to compensate ignition loss. Typical pulling rates were 0.05–0.07 mm/min and the diameter was around 3 mm. The seed crystals

Fig. 15. (A) Radioluminescence spectrum of 0.5%Sc-doped LuAG in absolute comparison with standard BGO scintillator sample. RT, excitation by X-ray tube, 40 kV, 15 mA. Excitation spectra of intrinsic luminescence of undoped LuAG (em = 330 nm) and that of Sc-related one (em = 275 nm). (B) 10 Spectrally unresolved scintillation decay of 0.5%Sc-doped LuAG at RT. Excitation by \(\text{\(^{22}\)Na}\) radioisotope (511 keV). The fit by solid line is the convolution of instrumental response and the function \(l(t)\) in the figure.

2.4.1. Crystal growth by the micropulling-down method

Ce and Pr doped \((\text{Gd,Y,Lu})_2(\text{Al,Ga})_5\text{O}_{12}\) crystals were grown by the micropulling-down (\(\mu\)-PD) method with a radiofrequency heating system. The \(\mu\)-PD method is a fast and economic tool to prepare single crystal systems \([63,64]\) and to optimize the growth technology. This efficiency makes the \(\mu\)-PD method advantageous in comparison to conventional Czochralski or Bridgman growth methods and has been successfully used to investigate many oxide and halide single crystals. In the case of melt growth of gallium containing garnet by the Czochralski method, internal strains and inclusions are induced into the grown crystals because of gallium oxide evaporation during the growth process. Consequently, scintillation performance is degraded \([65]\). On the other hand, this problem is less serious in the \(\mu\)-PD method that has uniaxial melt flow in the capillary and the growth process is much faster \([63,64]\). A stoichiometric mixture of 4 N CeO\(_2\), Pr\(_6\)O\(_{11}\), Gd\(_2\)O\(_3\), Y\(_2\)O\(_3\), Lu\(_2\)O\(_3\), \(\beta\)-Ga\(_2\)O\(_3\) and \(\alpha\)-Al\(_2\)O\(_3\) powders (High Purity Chemicals Co.) was used as starting material. More specifically, the Lu\(^{3+}\), Y\(^{3+}\) and Gd\(^{3+}\) sites were substituted by Ce\(^{3+}\) or Pr\(^{3+}\) according to the formula of \((\text{Ce}_z, (\text{Lu,Y,Gd})_{1-z})_3\text{(Ga}_x\text{Al}_{1-x})_5\text{O}_{12}\). The \(z\) was 0.002 and additionally 3 mol% of \(\beta\)-Ga\(_2\)O\(_3\) was added to compensate ignition loss. Typical pulling rates were 0.05–0.07 mm/min and the diameter was around 3 mm. The seed crystals

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were $<111>$ oriented undoped YAG crystals. Crystals were grown from an Ir crucible under N$_2$ atmosphere with 2% of O$_2$ added to prevent evaporation of gallium oxide. Example photographs are shown in Fig. 16. The grown crystals were transparent with 2–3 mm in diameter and 10–30 mm in length. Some of them looked slightly cloudy because of the rough surface caused by gallium oxide evaporation or thermal etching. However, the inner part of all the crystals was perfectly transparent. Plates of $\phi$ 3 mm × 1 mm were cut and polished for the purposes of the absorption and luminescence spectra measurement. The composition distribution in grown crystals was monitored by the EPMA. For example, the effective segregation coefficient of Ce ions in a Ce0.2% Lu$_2$Gd$_3$Ga$_2$Al$_3$O$_{12}$ crystal showed $k_{\text{eff}} = 0.407$. This value is one order larger than that of Czochralski grown Ce doped garnet single crystals [3,6,7], and therefore, a more favorable segregation coefficient is one of the advantages of the $\mu$-PD method.

2.4.2. Optical, luminescence and scintillation characteristics

Due to the above mentioned problem with decelerated energy transfer to Ce$^{3+}$ and Pr$^{3+}$ emission centers in a LuAG host because of shallow electron traps in the material, there has been an intense effort to discover a feasible technological method to diminish these negative effects. The gallium admixed LuAG composition has paved the way: with increasing Ga concentration the intensity of TSL glow curves below RT dramatically decreased and scintillation response was noticeably accelerated [66]. A tentative explanation was based on the hypothesis that Ga-admixture lowers the bottom of conduction band in which the shallow electron traps become gradually buried [67], see Fig. 17. This hypothesis was later confirmed through a combination of DFT calculations of the Ga-admixed aluminum garnet band structure and several optical experiments [62]. Rather than employ doping to reduce the concentration of deleterious antisite defects (as is done in so-called “defect engineering”), in this case dopants have been introduced for the purpose of altering the electronic structure (“band-gap engineering”). That is, Ga-doping does not reduce the concentration of antisite defects, but rather removes the trapping effect. Although this combined experimental-theoretical approach was shown to be successful for Ga-doped LuAG, it is likely that a similar defect screening and optimization approach is generally applicable to complex oxide scintillators.
ponent garnets are yet to be done. A stoichiometric mixture of 4 N CeO$_2$, Gd$_2$O$_3$, α-Ga$_2$O$_3$, and z-Al$_2$O$_3$ powders (High Purity Chemicals Co.) was used as starting material. Nominally, the Gd$^{3+}$ site was substituted by Ce$^{3+}$ according to the formula of Ce$_{0.03}$Gd$_{2.97}$Ga$_3$O$_{12}$. Ce:GAGG single crystals were grown by the Czochralski method using a radiofrequency heating system. The rotation rate was 4–12 rpm and the growth rate was 1.0 mm/h. An automatic diameter control system using crystal weighing was applied to control the growth parameters. The crystal growth was performed from a 100 mm ⌀ iridium crucible under Ar + 2% of O$_2$ atmosphere to prevent evaporation of gallium oxide. The seed was a [98] oriented GAGG.

The Ga-admixture, however, shows the opposite tendencies for the shift of the bottom of conduction band and for the 5d$_1$ level of Pr$^{3+}$ or Ce$^{3+}$ center. Unfortunately, while the former shows a down energy shift with Ga concentration $[61,62]$, the opposite is true for the 5d$_1$ state of the dopant $[63,68,69]$ so that unwanted 5d$_1$ excited state ionization occurs and light yield is decreasing $[70]$. That was why the improved light yield in Lu$_2$Ga$_5$Al$_{12-x}$O$_{12}$:Ce was observed for low values of $x = 1$ only $[71]$. It is known, however, that the admixture of larger RE cations such as Gd$^{3+}$ or La$^{3+}$ causes the down-energy shift of 5d$_1$ level and was studied both in white LED phosphors based on aluminum–gallium garnets $[68,69]$ and in scintillation ceramics based on aluminum $[72,73]$ and aluminum–gallium $[74–76]$ compositions where in the latter the simultaneous admixture of Gd and Ga into the YAG structure leads to considerable LY increase in Ce:$(Gd,Y)_3(Al,Ga)_5O_{12}$ optical ceramics with respect to Ce:YAG. The balanced Ga and Ga content in the multicomponent garnet $(Gd,RE)_2(Ga,Al)_5O_{12}$, RE = Lu, Y thus appears a critical parameter to tune the scintillation performance. Very recent combinatorial studies of Ce-doped $(Gd,Lu)_2(Ga,Al)_5O_{12}$ $[77]$ and $(Gd,Y)_2(Ga,Al)_5O_{12}$ $[78]$ single crystals have systematically mapped the compositional dependence of luminescence characteristics and scintillation performance as well as provided physical explanations. The dependence of absorption spectra, position of radioluminescence maxima and Stokes shift on the composition of $(Gd,Y)_3(Ga,Al)_5O_{12}$ hosts is shown in Figs. 18 and 19. It has been shown that there is a relatively narrow composition range for Gd-rich and Ga-intermediate compositions where light yield value is enormously increased up to almost 50 000 phot/MeV due to diminished trapping effect and yet negligible Ce$^{3+}$ 5d$_1$ excited state ionization at RT, Table 1.

Interestingly, the Pr-doped multicomponent garnet hosts of the same composition have shown, however, much worse scintillation performance $[79]$ which must be related to the positioning of Pr$^{3+}$ ground and excited state levels within the forbidden gap, the energy transfer to and from the Pr$^{3+}$ emission center and the eventual d-f intracenter transition in the excited Pr$^{3+}$ center. The most recent study $[80]$ indicates an unwanted energy transfer depleting the 5d$_1$ state of Pr$^{3+}$ center due to the resonance of 5d$_1$-$^3$H$_4$ emission transition of Pr$^{3+}$ and $^8S_7/2$-$^5P_0$ absorption transition of Gd$^{3+}$ within 300–311 nm which can be responsible for the deterioration of scintillation performance. However, systematic studies and explanations of such a discrepancy between the Ce and Pr-doped multicomponent garnets are yet to be done.

2.4.3. Single crystal growth of Ce:Gd$_3$Al$_2$Ga$_3$O$_{12}$(GAGG) by Cz method

Based on the above described combinatorial studies $[77,78]$, the Ce:Gd$_3$Al$_2$Ga$_3$O$_{12}$(GAGG) composition appeared the most attractive composition from the point view of light yield, decay time, density and the absence of intrinsic radioactivity. Czochralski growth was applied soon after the study by micropulling-down growth to obtain high quality single crystals.

A stoichiometric mixture of 4 N CeO$_2$, Gd$_2$O$_3$, β-Ga$_2$O$_3$ and α-Al$_2$O$_3$ powders (High Purity Chemicals Co.) was used as starting material. Nominally, the Gd$^{3+}$ site was substituted by Ce$^{3+}$ according to the formula of Ce$_{0.03}$Gd$_{2.97}$Ga$_3$Al$_2$O$_{12}$. Ce:GAGG single crystals were grown by the Czochralski method using a radiofrequency heating system. The rotation rate was 4–12 rpm and the growth rate was 1.0 mm/h. An automatic diameter control system using crystal weighing was applied to control the growth parameters. The crystal growth was performed from a 100 mm ⌀ iridium crucible under Ar + 2% of O$_2$ atmosphere to prevent evaporation of gallium oxide. The seed was a [98] oriented GAGG.

Fig. 17. Schematic of the band structure of undoped LuAG (left-hand side), with a band gap of >7 eV and an antisite trap depth of 0.29 eV, compared to the proposed band shift due to Ga doping (right-hand side), where the antisite defect is no longer in the forbidden gap, but rather is enveloped by the CB.
Fig. 18. Absorption spectra of Gd$_2$Y$_{1-x}$Al$_{5-x}$Ga$_x$O$_{12}$:Ce single crystals. In the inset, the position of 4f-5d$_1$ absorption maxima of Ce$^{3+}$ center are provided for all the sample set, see also Ref. [78].

Fig. 19. (A) The positions of radioluminescence maxima (5d$_1$-4f transition of Ce$^{3+}$); (B) Stokes shifts for all the material compositions, see also Ref. [78].
crystal. After the growth was completed, the crystal was removed from the melt and gradually cooled to room temperature. Growth conditions such as the cone angle, rotation rate, and heat insulation design were optimized for obtaining crack-free Ce:GAGG crystals with a diameter of 2 inches and with uniform light yield along the entire crystal. The effective distribution coefficient $k_{\text{eff}}$ of Ce was 0.083.

A representative Ce1%:GAGG single crystal of 190 mm length is shown in Fig. 20. The density of CeGAGG is 6.63 g/cm$^3$. The light yield value was measured of about 46 000 phot/MeV. Energy resolution was 4.9%@662 keV for the 5 × 5 × 1 mm size sample [81].

### Table 1

<table>
<thead>
<tr>
<th>Host composition</th>
<th>L.Y. (photon/MeV)</th>
<th>1st decay time (ns)</th>
<th>2nd decay time (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$_3$Al$_2$Ga$_4$O$_12$</td>
<td>15 895</td>
<td>316 (100%)</td>
<td>–</td>
</tr>
<tr>
<td>Gd$_3$Al$_2$Ga$_3$O$_12$</td>
<td>45 931</td>
<td>221 (100%)</td>
<td>–</td>
</tr>
<tr>
<td>Gd$_3$Al$_2$Ga$_2$O$_12$</td>
<td>42 217</td>
<td>52.8 (73%)</td>
<td>282 (27%)</td>
</tr>
<tr>
<td>Gd$_3$Al$_2$ Ga$_1$O$_12$</td>
<td>17 912</td>
<td>42.2 (34%)</td>
<td>90.5 (66%)</td>
</tr>
<tr>
<td>Gd$_3$Al$_2$Ga$_3$O$_12$</td>
<td>0</td>
<td>*N.M.</td>
<td>*N.M.</td>
</tr>
<tr>
<td>Lu$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>6410</td>
<td>*N.M.</td>
<td>*N.M.</td>
</tr>
<tr>
<td>Lu$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>3633</td>
<td>*N.M.</td>
<td>*N.M.</td>
</tr>
<tr>
<td>Lu$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>30 627</td>
<td>75.7 (38%)</td>
<td>326 (62%)</td>
</tr>
<tr>
<td>Lu$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>18 166</td>
<td>50.7 (65%)</td>
<td>298 (35%)</td>
</tr>
<tr>
<td>Lu$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>14 000</td>
<td>177 ns (100%)</td>
<td>–</td>
</tr>
<tr>
<td>Y$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>16 600</td>
<td>88.0 (76%)</td>
<td>388 (24%)</td>
</tr>
<tr>
<td>Y$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>25 700</td>
<td>78.4 (64%)</td>
<td>254 (36%)</td>
</tr>
<tr>
<td>Y$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>44 000</td>
<td>56.9 (66%)</td>
<td>236 (34%)</td>
</tr>
<tr>
<td>Y$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>37 800</td>
<td>41.4 (54%)</td>
<td>125 (46%)</td>
</tr>
<tr>
<td>Y$_1$Gd$_2$Ga$_3$Al$_2$O$_12$</td>
<td>0</td>
<td>*N.M.</td>
<td>*N.M.</td>
</tr>
</tbody>
</table>

*N.M. not measurable.

2.5. Comparison of scintillation characteristics and performance

Essential luminescence and scintillation characteristics of all compositions described in Section 2 are summarized in Table 2 below. Related references are cited and also our unpublished data have been provided to consider the most reliable values.

It is worth mentioning that all the spectra shapes and light yield values were spectrally corrected to remove experimental distortions due to photodetector contributions to the spectral sensitivity and to correctly compare to materials emitting in different spectral regions. To measure the relative scintillation efficiency, all the radioluminescence measurements were carefully made with the same sample sizes, equivalent geometries and other experimental conditions to enable absolute comparison of the

Fig. 20. Ce1%:GAGG single crystal with a diameter of 2 inches grown by the Cz method.
spectra of a standard BGO scintillator and the studied materials. Relative scintillation efficiency is obtained as an integral of the measured spectra and evaluates relative efficiency of the scintillation process regardless of the duration of the scintillation response. On the contrary, light yield value was determined for carefully wrapped samples, and the measurement of classical pulse–height spectra was employed under 662 keV ($^{137}$Cs) or 511 keV ($^{22}$Na) gamma–photon excitation. The shaping times in detection electronics were typically in the range of 1–3 μs. Energy resolution values can be degraded due to the escape peak of Lu which can broaden the low energy side of the photopeak depending on the shape and volume of the sample [36,86]. In scintillation decay measurements, the restricted time scale of the measurement (few microseconds) results in seemingly higher relative intensity of the fastest decay component, while only the measurement with high dynamic resolution made within a few tens of microseconds time window reveals more precisely slower decay components and provides realistic (lower) relative intensities of fast components, see e.g. Refs. [43,83,85] and Fig. 6(B).

3. Applications

Research and development of scintillating materials during the last two decades has been triggered mainly by modern medical imaging methods using X-ray sources or radioisotopes. A thorough overview of medical imaging principles, techniques and devices can be found in Refs. [90,91]. Positron emission tomography (PET) is the most sophisticated imaging technique used today. PET allows visualization of intriguing processes, organ functioning or malformed tissue in human or animal bodies which can be labeled by positron emitting radioisotopes [91,92]. When time-of-flight (TOF) information from the coincidence detection events is evaluated in so called TOF–PET, the entire measurement sequence can be made shorter or isotope dose smaller which is highly beneficial so that this principle and its technical application is nowadays of great interest [93,94]. The field of homeland security applications is rapidly developing after the events of September 11th, 2001. Namely, there is the demand for so-called radiation portal monitor systems to be applied e.g. at country borders, sea ports etc. They must be able to rapidly detect localized sources of radiation with a very high detection probability and low false-alarm rate, while screening all of the traffic without impeding the flow of commerce [95]. Revealing illicit traffic of nuclear weapons, special nuclear material, and radiation dispersal device materials is of the utmost importance. Environmental applications are of increasing importance, e.g. radon detection or ambient monitoring for trace radioisotope occurrence at large areas e.g. after nuclear accidents as has recently happened in Fukushima, Japan, or for homeland security purposes. Finally, usage of scintillation detectors in the science-oriented applications, e.g. in accelerator facilities, and in hi-tech devices, e.g. detectors in electron microscopes, is also very important field which requires often specially tailored material systems.

In applications requiring low background counts, LuAG-based scintillators might be limited due to their intrinsic radioactivity given by the 2.59% natural abundance of $^{176}$Lu radioactive isotope (half-life

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Table 2
Survey of luminescence and scintillation parameters of LuAG-based scintillators. LuYAG stands for $(\text{Lu}_{1-x}\text{Y}_x)\text{Al}_5\text{O}_{12}$, $x = 0.05–0.1$ and GAGG for Gd$_3$Al$_5$Ga$_3$O$_{12}$ compositions.

<table>
<thead>
<tr>
<th>Crystal formula abbrev.</th>
<th>Emission maximum (nm)</th>
<th>Scintillation efficiency (% BGO)</th>
<th>Light yield (phot/MeV)</th>
<th>Energy res.@662 keV (%)</th>
<th>Main decay time/comp. Intensity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped LuAG</td>
<td>300–330</td>
<td>300–400</td>
<td>2700–3500</td>
<td>n.r.</td>
<td>1400–3000 ns/n.r.</td>
<td>[29,82]</td>
</tr>
<tr>
<td>LuAG:Ce</td>
<td>510–520</td>
<td>600–800</td>
<td>18 000–26 000</td>
<td>5.5–7</td>
<td>55–65 ns/20–40%</td>
<td>[18,26,34–36,83], [36]</td>
</tr>
<tr>
<td>LuYAG:Ce</td>
<td>510–530</td>
<td>700–900</td>
<td>19 000–22 000</td>
<td>5–7</td>
<td>60–70 ns/20–40%</td>
<td>[77,81,84]</td>
</tr>
<tr>
<td>GAGG:Ce</td>
<td>530–540</td>
<td>550–600</td>
<td>46 000–51 000</td>
<td>4.9–5.5</td>
<td>88 ns/90%</td>
<td>[41,43,45,46,85,86]</td>
</tr>
<tr>
<td>LuAG:Pr</td>
<td>310</td>
<td>550–650</td>
<td>16 000–20 000</td>
<td>4.6–6.5</td>
<td>20–22 ns/17–60%</td>
<td>[36,87]</td>
</tr>
<tr>
<td>LuYAG:Pr</td>
<td>310</td>
<td>450–500</td>
<td>15 000–24 500</td>
<td>4.7–7.0</td>
<td>19–22 ns/n.r.</td>
<td>[79]</td>
</tr>
<tr>
<td>GAGG:Pr</td>
<td>315–320</td>
<td>n.r.</td>
<td>4500</td>
<td>n.r.</td>
<td>8 + 214 ns/4 + 94%</td>
<td>[58,88,89]</td>
</tr>
<tr>
<td>LuAG:Sc</td>
<td>270–280</td>
<td>600–700</td>
<td>22 500</td>
<td>7</td>
<td>600 ns/90%</td>
<td>[54,55]</td>
</tr>
<tr>
<td>LuAG:Yb</td>
<td>335–340</td>
<td>3–5</td>
<td>n.r.</td>
<td>n.r.</td>
<td>1 ns/n.r.</td>
<td></td>
</tr>
</tbody>
</table>

n.r. = not reported.
3.78 × 10^{10} \text{ years}), which results in about 300 background counts per-second per each cm^3 of the material. On the contrary, Ce:GAGG is expected to be promising scintillator not only for PET, but also for SPECT or gamma camera medical imaging [90] and other applications because of its excellent combination of very high light yield, good energy resolution, high density and no intrinsic radioactivity. As an example, the applications of Pr:LuAG for medical imaging and Ce:LuAG in X-ray microradiography are described below.

3.1. Development of positron emission mammography (PEM) using Pr:LuAG scintillator

Breast cancer is one of the most frequent causes of death among female cancer patients of the age within 30–50 years. If breast cancer is discovered at the early stage (tumor size less than 1 cm), the probability of a successful cure is significantly higher. Therefore, there is an urgent need to develop a system to detect the breast cancer at the early stage with high efficiency. An example of an advanced technique is the Positron Emission Mammograph (PEM). A typical approach uses conventional X-ray mammography, however, its specificity is rather low, typically 30% [96]. PET using \(^{18}\)F-fluorodeoxyglucose is an effective method of cancer detection [97]. Therefore, the whole body PETs are often used for breast cancer detection. However, as it is located near the lungs, breathing and related body movement decrease the capability of detection of small tumors (less than 1 cm in diameter). Thus, the development of PEM scanners, which would be intentionally designed for breast cancer detection has been proposed. The PEM has the same mechanism as PET, where two 511 keV annihilation gamma-rays are detected in coincidence by two gamma cameras at opposite sides, and resulting data allow for a reconstruction of the image of the tumor. In recent years, PEMs, including LBNL-PEM [98], Planar type PEM [99], Clear-PEM [100], and PEM/PET [101] have been under intensive development by several research groups.

Recently, some of us developed a PEM using a Pr:LuAG scintillator, Fig. 21, owing to its attractive properties such as light yield of approximately 20 000 phot/MeV, decay time around 20 ns and the energy resolution of 4.6% [42–45]. The Pr:LuAG-PEM is equipped with four layers of 20 × 64 pixelated arrays for each side. The Pr:LuAG pixel size is 2.1 × 2.1 × 15 mm^3 and the BaSO_4 was used as a reflector. In total, 20 × 64 × 8 = 10 240 Pr:LuAG pixels were used. Scintillator arrays were optically coupled with three H8500 photomultipliers and weighted summing amplifiers where the signals were summed with the linear weights according to the position of the rows and columns of the anodes. The spatial resolution of 1.1 mm using a \(^{22}\)Na point source and 4.8 mm by \(^{18}\)F hotspot image using a breast

![Pr:LuAG array](image1)

![PSPMTs](image2)

![weighted summing amplifiers](image3)

![Read out LSIs](image4)

**Fig. 21.** Detector components (left), the full-scaled Pr:LuAG-PEM (center) and \(^{18}\)F hotspot image using a breast phantom. From top left to bottom, Pr:LuAG array, H8500-03 PSPMTs, and weighted summing amplifiers, respectively, see also Ref. [102].

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phantom were achieved in the Pr:LuAG-PEM [102]. The Pr:LuAG-PEM is now in clinical test stage and will be commercially available from Furukawa Co.

3.2. High resolution low energy X-ray microradiography

X-ray microradiography is a non-destructive technique that has received much attention in recent years [103–108]. Low energy X-ray radiation passes through an inspected sample and a high position resolution detector, based on a scintillator and an optical device, which is used to detect the transmitted X-rays. It is a contrast imaging technology which utilizes the difference in X-ray absorption by different materials. The sketch of the set-up developed in CRYTUR Ltd. is in Fig. 22(a): the high-resolution X-ray camera consists of a high sensitivity digital CCD detector and a thin LuAG:Ce scintillator imaging screen (b) [107,108]. The scintillator screen must be thin enough (5–20 μm) to avoid blurring of the image [103,105]. The CCD camera uses a sensor with the dimensions of 24 × 36 mm², and 11 Mpixels (4008 × 2672). A Peltier thermoregulation system is used for cooling and temperature stabilization. The CCD pixel size is 9 μm thus, using the optical system magnification 1:1, the CCD limits

Fig. 22. The sketch of X-ray radiography experiment (a), LuAG:Ce thin plate glued on glass support (b) and X-ray radiography of a spider (c) [99].
the X-ray resolution to about 10 μm, and using the optical system with a 10-times magnification the system can reach 1 μm resolution in X-rays. The maximum resolution is limited by the screen thickness and numerical aperture of the objective. The objective is focused on the plane inside the scintillator where the absorption image has the best contrast. Sufficient contrast can be achieved even in the case of radiography of small biological objects, e.g. spider in Fig. 22(c), and achieved 2D-resolution is of about 1 μm [108].

4. Conclusions, future work and prospects

Research and development of LuAG based scintillators within the last decade has been described including the recent discovery of new class of ultraefficient scintillators based on multicomponent garnets. Undoubtedly, Ce and Pr-doped LuAG have found their position in the family of high density, fast and efficient complex oxide scintillators, together with aluminum perovskite and orthosilicate materials. High quality and large size crystals of Ce and Pr-doped LuAG are commercially available from several industrial enterprises and are extensively tested for various practical applications. The recent discovery of Ce-doped multicomponent garnets with a balanced Gd and Ga admixture into LuAG or YAG host gave rise to new class of ultraefficient scintillators: the Gd₃Ga₃Al₂O₁₂:Ce composition has been realized already as 2-inch size single crystal using Czochralski method and with a light yield of 46 000photon/MeV and energy resolution of 4.9%@662 keV is clearly superior to the best Ce-doped orthosilicate scintillators on the market. Nevertheless, to achieve deep understanding of the energy transfer process and scintillation mechanism in this group of new materials an extensive experimental and theoretical effort and systematic studies will be yet required and further material optimization and parameter improvement is far from complete.

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