

Ce 掺杂浓度对 Ce,Ca:Lu₃Al₅O₁₂ 陶瓷闪烁性能的影响

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摘 要: 以共沉淀纳米粉体为原料, 制备不同 Ce 掺杂浓度的 $x\%$ (摩尔分数) Ce_{0.15%Ca:Lu₃Al₅O₁₂} (Ce,Ca:LuAG, $x=0.1\sim0.5$) 闪烁陶瓷。在分析了 Ce,Ca:LuAG 陶瓷的相组成和微观结构的基础上, 研究了其闪烁特性与 Ce 浓度的关系, 包括 X 射线激发发射光谱、光致发光衰减、闪烁衰减、光产额及快分量、余辉。当 Ce 浓度超过 0.3% 时, 光致发光衰减的加速证实了浓度猝灭的发生。Ce,Ca:LuAG 陶瓷的 X 射线激发发射强度和光产额在 Ce 浓度为 0.3% 时达到最大值。随着 Ce 浓度的增加, 陶瓷的余辉水平逐渐降低。最后讨论了 Ce,Ca:LuAG 闪烁陶瓷的制备和性能优化的策略。

关键词: 铈; 钙; 铈铝石榴石陶瓷; 闪烁性能; 共沉淀法

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1 Introduction

Lutetium aluminum garnet (Lu₃Al₅O₁₂, LuAG) has been studied as a classical scintillation material for more than twenty years^[1-2]. LuAG has been fabricated in the form of single crystals^[3-4], optical ceramics^[5-6], thin films^[7-8] and other morphologies to meet different scintillation application demands. Cerium-doped LuAG (Ce:LuAG) continues to gain research attention because of its high density and high effective atomic number and excellent scintillation performance due to high light yield (LY), fast decay time, and radiation resistance^[9-11]. Due to the high preparation temperature of about 2 000 °C, a deteriorating Lu_{Al} antisite defect (AD) was evidenced in the Ce:LuAG single crystals grown from melt^[12]. The AD creates shallow electron traps retrapping charge carriers in transfer stage of scintillation mechanism which considerably slow down the scintillation response^[13]. Scintillation ceramics are sintered by powder metallurgy at temperatures several hundred degrees below the melting point, which results in nearly absent AD in the stoichiometric Ce:LuAG ceramics. Consequently, LuAG:Ce scintillation ceramics could show relatively faster scintillation response and higher LY compared to single crystals^[14-15].

Ceramic materials have played an important role in recent years in optical functional materials and have got comprehensive development^[16-18]. High density, fast decay, efficient scintillation and relatively low cost make Ce:LuAG ceramics a strong candidate for detection material in shashlik calorimeter for high-energy physics (HEP) experiments^[19]. For HEP experiments with high event rate, however, the slow scintillation component of Ce:LuAG ceramics leads to the pileup effect that needs to be diminished as much as possible^[20]. Divalent, optically inactive, ion co-doping has been shown to be a very effective strategy for suppressing slow scintillation component. According to the defect engineering theory, such ions can stabilize a part of cerium dopant into Ce⁴⁺, which competes for electrons in conduction band with other electron traps which accelerates scintillation response and lowers afterglow^[21]. In 2014, Liu *et al.*^[22] introduced Mg²⁺ into Ce:LuAG ceramics and obtained high LY of 21 900 ph·MeV⁻¹ at 1 μs shaping time. The fast to total intensity ratio, defined as the ratio of LY measured at 1 μs to that measured at 10 μs (LY_{1μs}/LY_{10μs}), was 79%, higher than that obtained from Ce,Mg:LuAG single crystal. In 2016^[9], after optimizing the Mg²⁺ doping concentration, the Ce,Mg:LuAG ceramics reached high LY of 25 000 ph·MeV⁻¹ at 1 μs shaping

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time. In addition to Mg^{2+} , also Ca^{2+} is another commonly used co-dopant to modify scintillation performance of Ce:LuAG ceramics. In 2019, Ma *et al.*^[23] fabricated Ce,Ca:LuAG ceramics with the LY of $24\,100\,\text{ph}\cdot\text{MeV}^{-1}$ at $1\,\mu\text{s}$ shaping time and the $\text{LY}_{1\mu\text{s}}/\text{LY}_{12\mu\text{s}}$ is 85.5%. In 2020^[20], the $\text{LY}_{0.2\mu\text{s}}/\text{LY}_{3\mu\text{s}}$ of Ce,Ca:LuAG ceramics reached 90%, which evidenced significant inhibition of the slow component and great potential of Ce,Ca:LuAG ceramics for HEP experiments. In 2022^[24], the Ca^{2+} doping concentration was optimized and the $\text{LY}_{0.5\mu\text{s}}/\text{LY}_{3\mu\text{s}}$ increased from 79% to 97%.

For all the above-mentioned cases, the ceramic preparation method was based on the solid-state reactive sintering method. In order to obtain higher homogeneity within microregions, Ce,Ca:LuAG ceramics were prepared by the coprecipitation method. Coprecipitation precursors enable homogeneous mixing of multiple metal elements at the atomic level to ensure the consistency of structure, composition and luminescence within the ceramics.

In this work, the Ce,Ca:LuAG ceramics with different Ce concentrations were prepared from the coprecipitation nano-powders. The effects of activator ion concentration on the decay behavior, LY at different shaping times and afterglow intensity of the Ce,Ca:LuAG ceramics were comprehensively analyzed.

2 Experimental procedure

Series of Ce,Ca:LuAG ceramics with the chemical composition of $(\text{Ce}_x\text{Ca}_{0.0015}\text{Lu}_{0.9985-x})_3\text{Al}_5\text{O}_{12}$; $x=0.1, 0.2, 0.3, 0.4, 0.5$ were prepared by coprecipitated nano-powders through vacuum pre-sintering and hot isostatic pressed (HIP) post-treatment. In the process of nano-powder preparation, the high purity Lu_2O_3 (99.995%), CeO_2 (99.999%), and CaCO_3 powders were dissolved in nitric acid solution, and the $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (AR) powders were dissolved in deionized water to obtain various nitrate solutions. The metal nitrate solutions were mixed and further diluted to a specific concentration. Ammonium hydrogen carbonate (AHC, 99%) was dissolved in de-ionized water as the precipitant solution and ammonium sulfate (99%) was added into the precipitant solution as the dispersant. The mixed metal nitrate solution was dripped into the AHC solution under mild agitation at room temperature (RT). The resulting suspension was aging for 1 h and then washed with deionized water and pure ethanol. The precursor was dried, sieved and calcined to obtain Ce,Ca:LuAG nano-powders with pure garnet phase. The powders were uniaxially dry-pressed into pellets at 20 MPa and then cold-isostatically pressed at 250 MPa. The green bodies were vacuum pre-sintered at $1\,825\,^\circ\text{C}$ for 10 h and then HIP at $1\,600\,^\circ\text{C}$ for 3 h under 176 MPa argon atmosphere. The fabricated Ce,Ca:LuAG ceramics were air annealed at $1\,450\,^\circ\text{C}$ for 10 h to remove oxygen vacancies introduced by sintering in the reducing atmosphere. The final Ce,Ca:LuAG ceramics were

polished on both sides to the thickness of 1 mm for characterization experiments.

The X-ray diffraction (XRD, D8 Advance, Bruker, Germany) was performed to determine the phase composition of prepared ceramics. The field emission scanning electron microscope (FESEM, SU-8220, Hitachi, Japan) was used to characterize the microstructure of the powders and thermally etched ceramic surfaces. The energy dispersive spectroscopy (EDS) was used to analyze the elemental composition of normal grain and secondary phase region in ceramics. The absorption spectra of the ceramics were measured by a UV-VIS-NIR spectrophotometer (Cary-5000, Varian, USA). The X-ray excited luminescence (XEL) spectra of ceramics were recorded by 5000M model of Horiba Jobin Yvon fluorometer using X-ray tube excitation (40 kV, 15 mA, Seifert GmbH) at RT. The photoluminescence (PL) decays were measured under the excitation wavelength (λ_{ex}) of 452 nm and the monitored emission wavelength (λ_{em}) of 510 nm using nanoLED (Horiba IBH Scotland) excitation at 5000M with TBX-04 photon counting detector. Scintillation decay curves were measured under excitation with ^{137}Cs γ -ray source using a Hamamatsu U7600 fast photomultiplier connected to a Tektronix TDS3052C digital oscilloscope. The LY and energy resolution (ER) under 662 keV γ -ray excitation at different shaping times were measured in the form of pulse-height spectra using hybrid photomultiplier (HPMT) DEP PPO 475B connected to a multichannel analyzer. Samples were optically coupled to HPMT photocathode by a silicon grease and wrapped in a reflecting Teflon tape. The afterglow signal at RT after X-ray irradiation cut-off was recorded by the above mentioned 5000M fluorometer.

3 Results and discussion

Figure 1(a) shows the XRD patterns of the Ce,Ca:LuAG ceramics with different Ce concentrations. The XRD patterns of all ceramic samples are in excellent agreement with the standard XRD pattern of LuAG (PDF 73-1368), indicating that the main body of the prepared ceramics is a LuAG garnet phase. However, according to the subsequent SEM results as shown in Fig. 2, a small amount of secondary phase was still found, suggesting that the content of secondary phase is less than the detection limit of the XRD diffractometer. The lattice parameters of Ce,Ca:LuAG ceramics with different Ce concentrations are shown in Fig. 2(b). Since Ce^{3+} (112 pm) has a larger ionic radius compared to Lu^{3+} (97.7 pm) in the dodecahedral lattice sites of garnet, the lattice parameter increases gradually with increasing doping concentration. The variation of the lattice parameters does not strictly follow Vegard's law, which may be due to presence of the secondary phase resulting in a slight change in the actual Ce doping concentration.

As can be seen in Fig. 2 for Ce,Ca:LuAG ceramics sintered at the same temperature, the grain size increases

significantly with increasing Ce concentration. For Ce,Ca:LuAG ceramics with increasing Ce concentration from 0.1% to 0.5%, the average grain sizes with more than 300 grains obtained using the linear intercept method are 1.9 ± 0.1 , 6.3 ± 0.4 , 6.6 ± 0.4 , 8.2 ± 0.7 μm and 13.8 ± 1.4 μm , respectively. The considerable increase of grain size indicates that the presence of Ce^{3+} can act as a sintering aid to accelerate the migration of grain boundaries during sintering of garnet ceramics. In addition to the irregular polygonal grains, a small amount of dark secondary phase was observed on the thermally etched surfaces of Ce,Ca:LuAG ceramics. It is worth stating that the presence of such secondary phases was observed in all ceramic samples with different Ce concentrations, so the formation of the secondary phase is independent of the doping concentration. The composition of the secondary phase was analyzed by EDS and the results are shown in Fig. 3. Compared to the normal grain region, the value of Lu/Al atom ratio in the secondary phase region deviates far from 3/5, which indicates that the primary cause of the secondary phase is the deviation of the actual local composition of the prepared ceramics from the design composition. This may be due to the fact that the precipitate formed by Lu^{3+} has a larger solubility product constant ($K_{\text{sp}}(\text{Lu}(\text{OH})_3) = 1.9 \times 10^{-24}$, $K_{\text{sp}}(\text{Al}(\text{OH})_3) = 1.3 \times 10^{-33}$) and is more difficult to precipitate completely compared to that of Al^{3+} , while the precipitate is also easily lost during the washing process after co-precipitation^[25]. In addition, the signals of Ce and Ca were not observed in the normal grain region due to the detection limit but were found in the secondary phase region, which indicates that the dopant ions are also enriched in this region while the Al-rich

secondary phase is formed, as well as the Ga impurities.

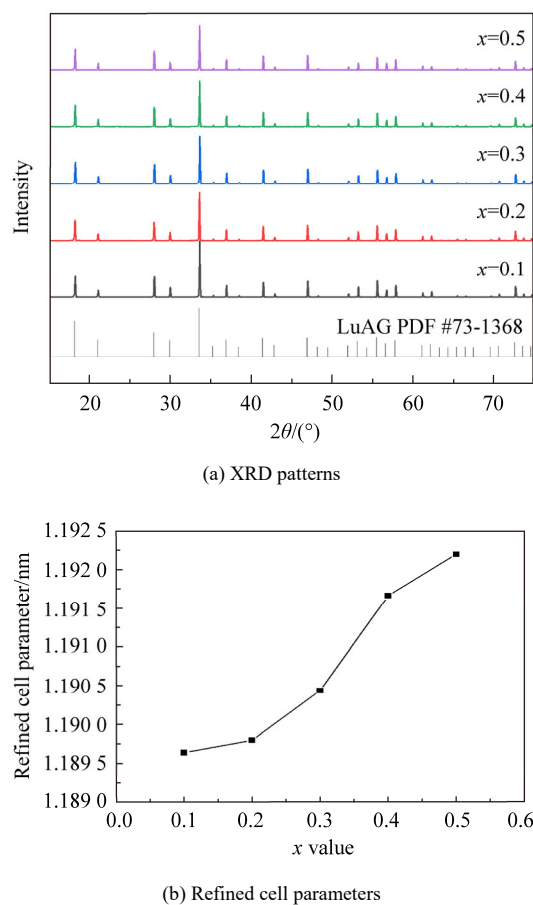


Fig. 1 XRD patterns and refined cell parameters of $x\%\text{Ce}$, $0.15\%\text{Ca}$:LuAG ceramics

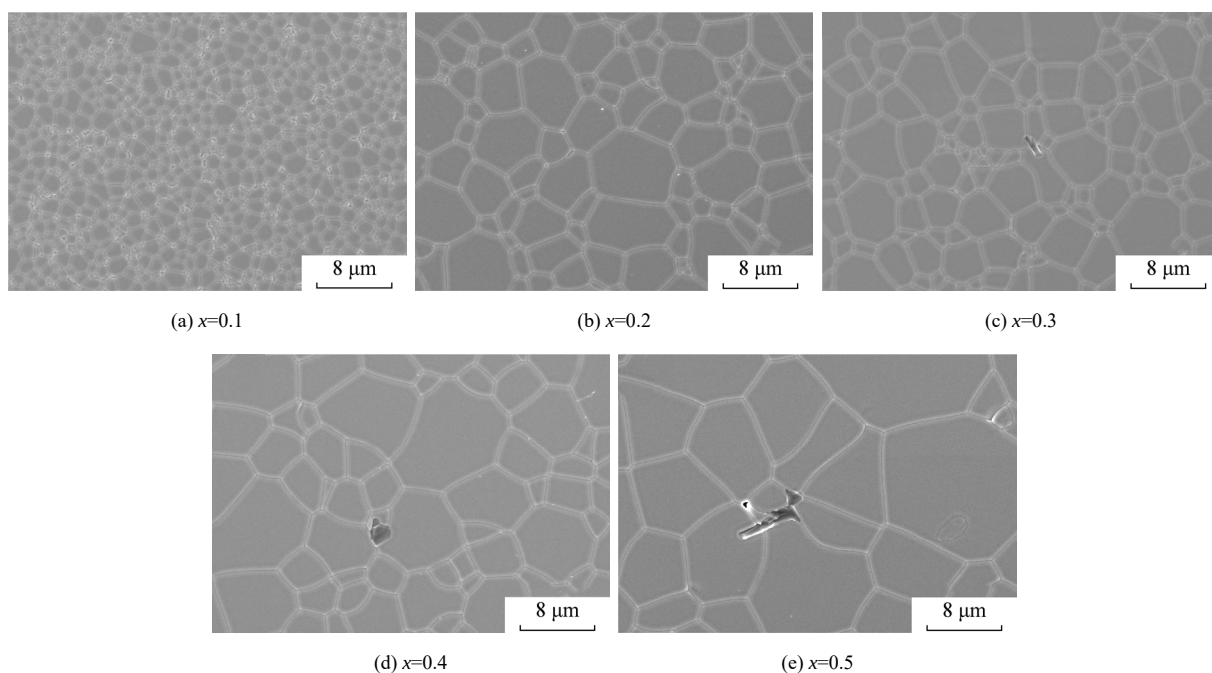


Fig. 2 SEM images for thermally etched surfaces of x at%Ce, $0.15\%\text{Ca}$:LuAG ceramics

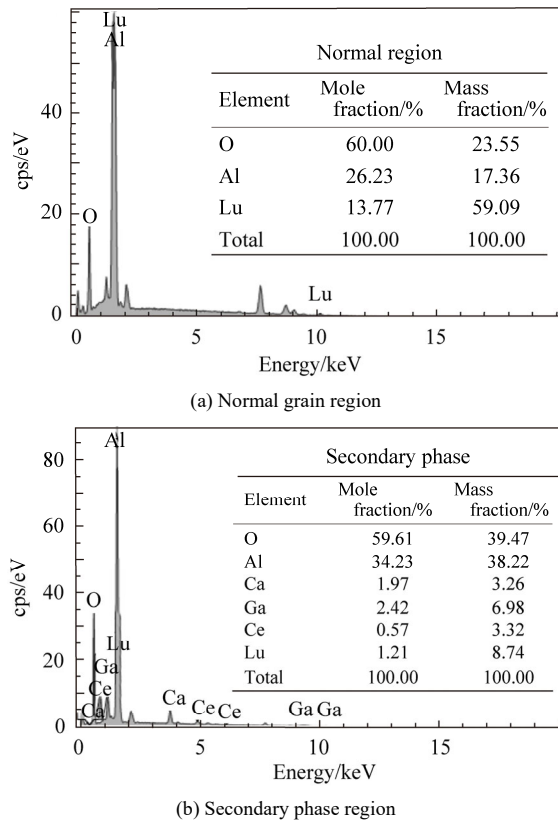
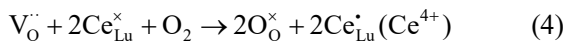
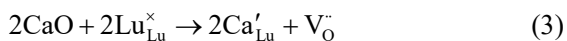
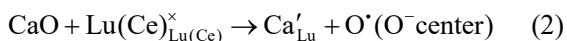
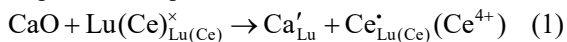


Fig. 3 EDS and the calculated elemental composition of normal grain region and secondary phase region

Figure 4 shows the absorption spectra of the Ce,Ca:LuAG ceramics with different Ce concentrations. The amplitudes of $4f \rightarrow 5d_1$ transition at 447 nm and the $4f \rightarrow 5d_2$ transition at 345 nm of Ce^{3+} increase with the starting content of Ce^{3+} which evidences its entering into the garnet lattice. When the Ce concentration is higher than 0.3%, the absorption peaks at 447 nm flatten which is an experimental artifact due to penetrating material luminescence into the detection part of the device. All ceramic samples have strong absorption below 350 nm, which is due to the charge transfer (CT) absorption band induced by Ce^{4+} in the garnet lattice^[22,26]. The formation of these stabilized Ce^{4+} centers is attributed to the charge compensation effect caused by the introduction of Ca^{2+} codopant. The reactions that occur during the introduction of Ca^{2+} into the garnet lattice and the oxygen annealing process can be expressed by the following defect equilibrium equations:



The PL decay curves of the $5d_1 \rightarrow 4f$ emission of Ce^{3+} (510 nm) under the 452 nm excitation were measured at RT and are shown in Fig. 5. The solid lines in Fig. 5 are convolution of the instrumental response

with the two-exponential fit of the experimental data. The fit functions $I(t)$ are also shown in the figures. For all Ce,Ca:LuAG ceramics with different Ce concentrations, the fast component intensity in PL decay, calculated as $I(t) = (A_1 \times \tau_1) / (A_1 \times \tau_1 + A_2 \times \tau_2)$, accounts for more than 95%. The origin of weak slow component is not clear, it may be due to the delayed luminescence caused by closely spaced defects around Ce^{3+} centers. The main decay time shows acceleration when the Ce concentration is higher than 0.3%. The introduction of divalent ions (Me^{2+}) will induce the stabilization of Ce^{4+} fast scintillation centers and create the $(Ce^{4+} - Me^{2+})$ pairs, which leads to optical quenching and shortening of PL decay time, as has been demonstrated in single crystals and thin films^[27–28]. In this work, the formation of closely spaced $(Ce^{4+} - Ca^{2+})$ pairs could be increased with an increase of Ce concentration, resulting in the PL decay acceleration^[29].

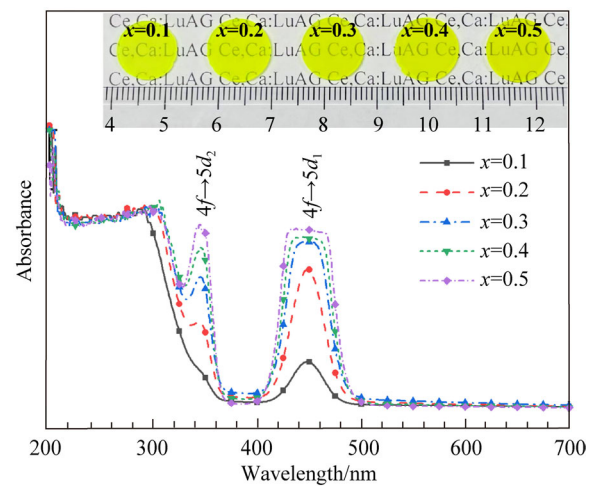


Fig. 4 Photograph and absorption spectra of $x\%Ce, 0.15\%Ca:LuAG$ ceramics

The scintillation decays of the Ce,Ca:LuAG ceramics under γ -excitation are presented in Fig. 6 approximated by the two-exponential fit. Unlike the PL decays, the fast scintillation decay time of Ce,Ca:LuAG ceramics tends to increase with increasing Ce concentration. The tendency of scintillation decay to become slower can be seen more clearly from the decrease in the fast scintillation component and the increase in the time required for the decay intensity to reach 1/e of the starting intensity. Scintillation decay can reflect the delay in the whole process of energy conversion, carrier transport and luminescence during scintillation. Therefore, the difference between scintillation decay and PL decay indicates that the increase in Ce concentration causes a delay in transport stage. Since the amount of Ca^{2+} introduced into the ceramic samples is fixed, the proportion of induced Ce^{4+} decreases with increasing total Ce concentration, and the competition in accelerating scintillation process becomes progressively

weaker, resulting in a slight slowing of scintillation decay.

The XEL spectra of the Ce,Ca:LuAG ceramics with different Ce concentrations are shown in Fig. 7. The main emission band with a double-peak shape of the Ce,Ca:LuAG ceramics can be observed in a 450–700 nm range, corresponding to the $5d_1 \rightarrow 4f$ emission of Ce^{3+} . The XEL intensity of the Ce,Ca:LuAG ceramics firstly increases with the Ce concentration reaching the maximum at $x=0.3$ and then decreases. There are some faint emission peaks at 311, 381, 685 nm and 702 nm, which may be caused by the trace rare-earth impurities

from the raw materials. Local details of the normalized XEL spectra in the 480–580 nm range can be seen in Fig. 7(b): the redshift of the main emission peak was observed with increasing Ce concentration. Since the Ce-activated garnet emission and absorption bands partially overlap, higher Ce concentrations cause enhanced reabsorption which leads to the emission redshift. In addition, possible distorted ambient of Ce^{3+} can induce larger crystal field splitting and the lowest $5d_1$ state shifts to a lower energy causing a redshift in Ce^{3+} emission^[30]. Fig. 7(c) presents the integral scintillation efficiency of Ce,Ca:LuAG

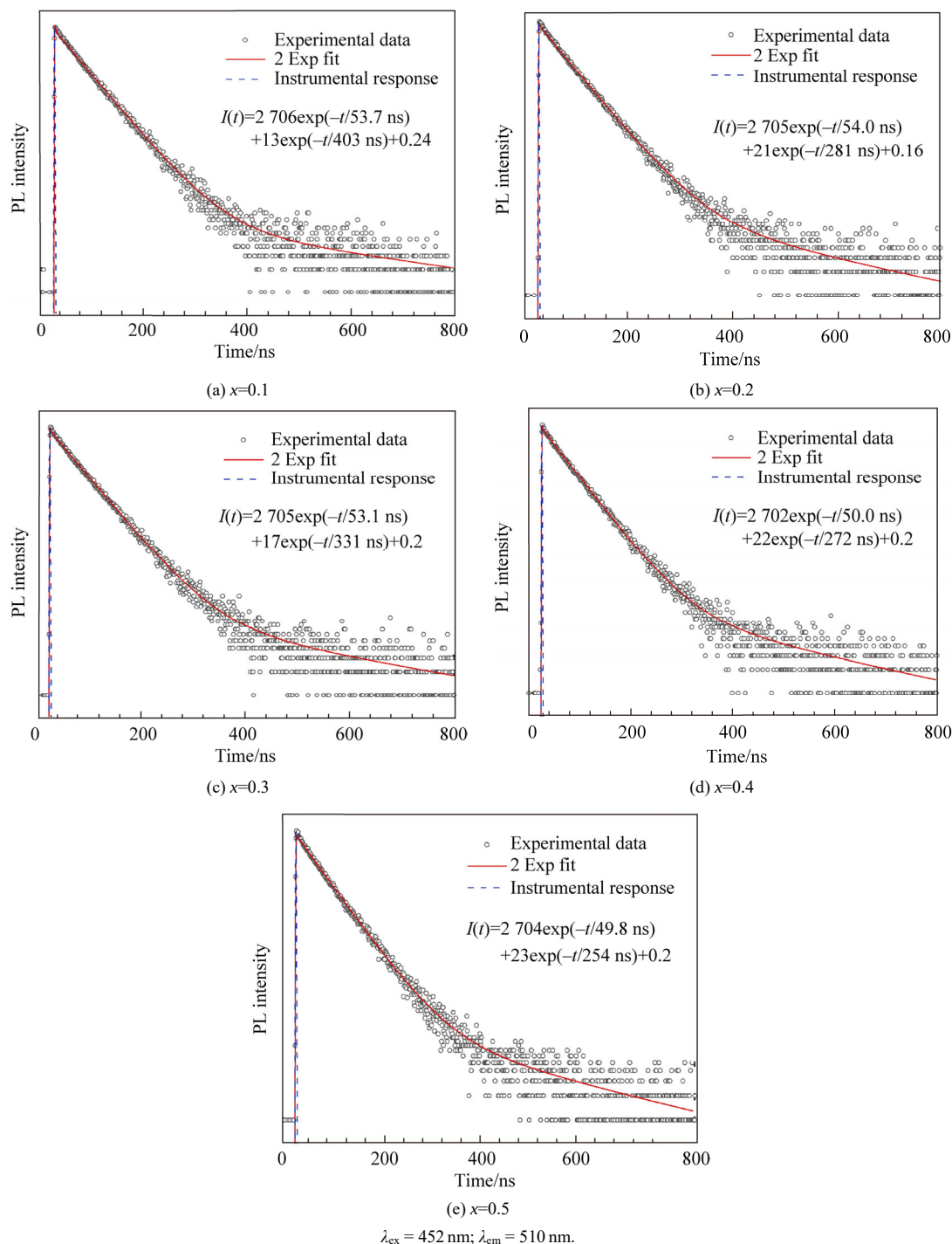


Fig. 5 PL decay curves and their approximations by $I(t)$ functions of $x\%\text{Ce}, 0.15\%\text{Ca:LuAG}$ ceramics

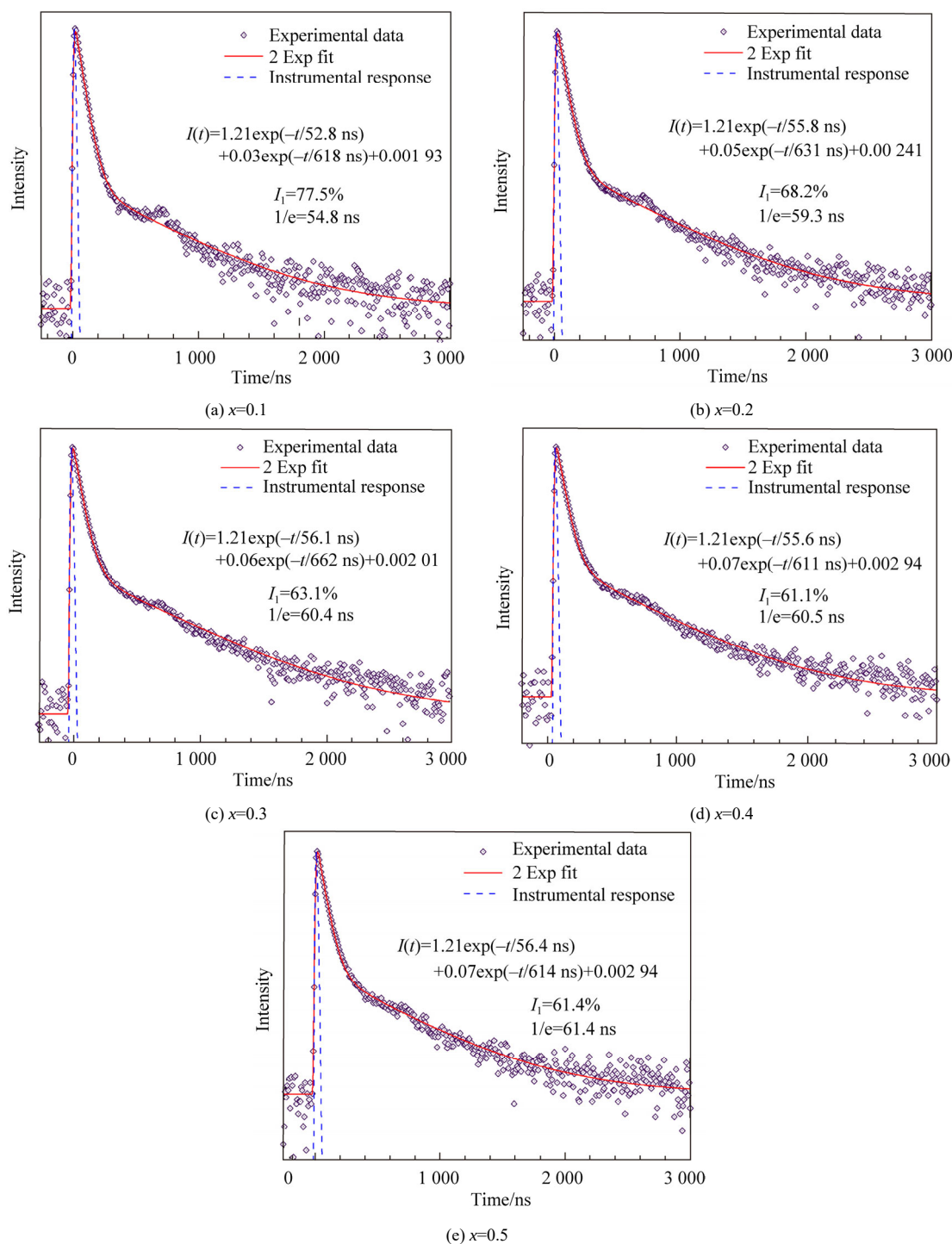


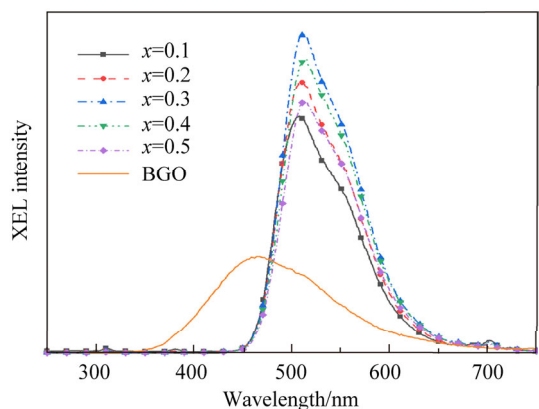
Fig. 6 Scintillation decay curves of $x\%\text{Ce}, 0.15\%\text{Ca}:\text{LuAG}$ ceramics under the ^{137}Cs excitation source

ceramics defined here as an integral intensity of the XEL spectrum (450–650 nm) compared to that of the XEL spectrum (350–750 nm) of a BGO crystal, as measured under the same experimental conditions. The integral scintillation efficiency of the $\text{Ce,Ca}:\text{LuAG}$ ceramics is 146%–190% of a BGO crystal.

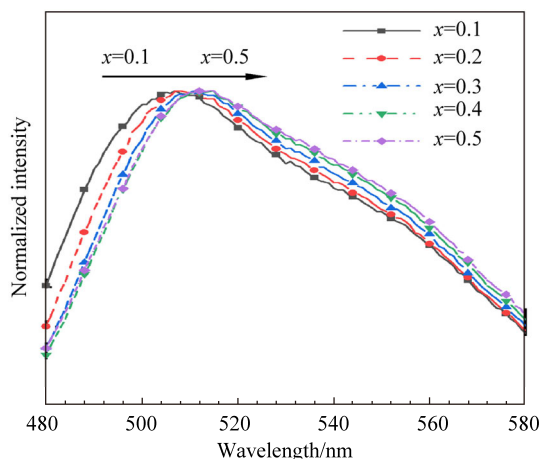
LY is technically more important to evaluate scintillation performance in view of applications. The LY values at different shaping times from 0.5 to 10 μs were measured under ^{137}Cs γ -excitation, as shown in Fig. 8.

The variation of the LY and the integral scintillation efficiency obtained from XEL have a similar pattern, both rising and then falling with the increase of Ce concentration, also the best energy resolution (ER) is obtained at $x=0.3$. It is worth noting that when $x=0.1$, the magnitude of the increase in LY is the smallest as the shaping time increases, which implies a high content of fast scintillation component. To reflect this more intuitively, the ratio of LY at 0.5 μs and 3 μs shaping time is defined as the fast-to-slow component ratio and is

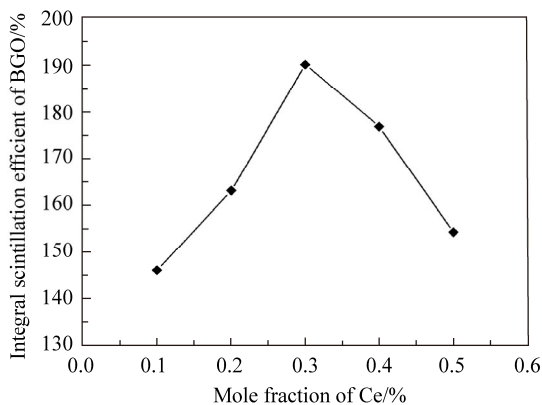
presented in Table 1. The increase in LY with increasing Ce concentration is attributed to the greater number of luminescent centers, but the decrease in $LY_{0.5\ \mu s}/LY_{3.0\ \mu s}$ ratio is due to the fact that 0.15%Ca co-doping is not sufficient to provide enough Ce^{4+} . This reminds us that high throughput analysis is necessary when more than one dopant ion is present, *e.g.* for orthogonal experiments.



(a) XEL spectra



(b) Normalized XEL spectra at the range of 480–580 nm



(c) Integral scintillation efficiency

Fig. 7 XEL spectra of $x\%Ce,0.15\%Ca:LuAG$ ceramics and integral scintillation efficiency of the Ce,Ca:LuAG ceramics with respect to a BGO crystal

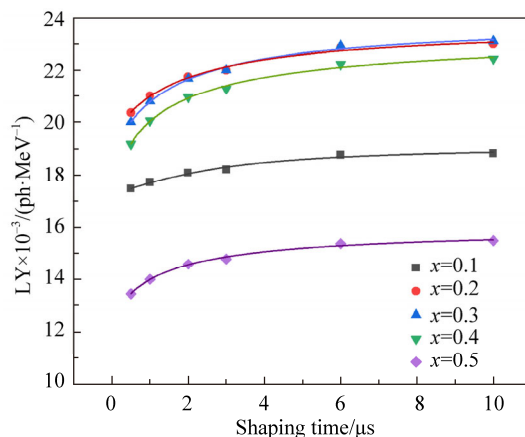


Fig. 8 LY of $x\%Ce,0.15\%Ca:LuAG$ ceramics at different shaping times

Table 1 Light yield (LY) values and energy resolutions (ERs) of $x\%Ce,0.15\%Ca:LuAG$ ceramics at different shaping times and the values of $LY_{0.5\ \mu s}/LY_{3.0\ \mu s}$ ratio

x	0.5 μs shaping time		3 μs shaping time		$LY_{0.5\ \mu s}/LY_{3.0\ \mu s}/\%$
	LY/(ph·MeV ⁻¹)	ER/%	LY/(ph·MeV ⁻¹)	ER/%	
0.1	17 500	13.3	18 200	15.0	96.2
0.2	20 400	13.1	22 000	13.9	92.7
0.3	20 000	12.0	22 000	13.5	90.9
0.4	19 200	13.3	21 300	15.5	90.1
0.5	13 400	19.8	14 800	21.4	90.5

The normalized afterglow intensity after continuous X-ray irradiation is shown in Fig. 9. The afterglow intensity monotonically decreases with the Ce concentration. When the activator ion concentration is higher, its ability to capture migrating charge carriers increases and successfully competes with any electron traps, which results in a lower afterglow intensity. The Ce,Mg:LuAG samples with high Ce concentration show lower thermoluminescence (TSL) intensity, which also indicates that the concentration of electron traps is reduced by Ce concentration^[31].

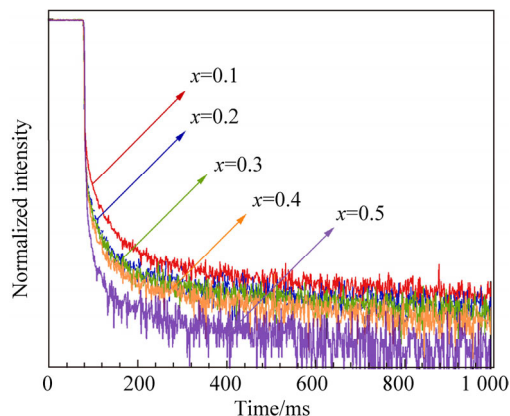


Fig. 9 Afterglow profile after continuous X-ray irradiation for $x\%Ce,0.15\%Ca:LuAG$ ceramics

4 Conclusions

Ce,Ca:LuAG scintillation ceramics with different Ce concentrations were prepared by coprecipitation nano-powders combined with vacuum pre-sintering and HIP post-treatment. Due to the loss of lutetium during coprecipitation and washing, a small amount of Al-rich secondary phase exists in the ceramics, which can be avoided by component design in the future ceramic preparation. The PL decay time of Ce,Ca:LuAG ceramics is nearly constant at $x=0.1-0.3$, while higher Ce concentrations lead to accelerated decay, which is explained by quenching caused by closely spaced Ce—Ca pairs. The scintillation decay under γ -excitation shows a slight slowing down with increasing Ce concentration, which is explained by the gradual decrease of the proportion of Ce^{4+} in total ($\text{Ce}^{3+}+\text{Ce}^{4+}$) content due to fixed amount of Ca codoping. The XEL intensity and LY of the ceramics both rise and then decrease with increasing Ce concentration showing maximum at $x=0.3$, the decrease in luminescence efficiency is consistent with the quenching revealed by PL decay. By measuring the LY values at different shaping times, it was found that the Ce,Ca:LuAG ceramics with $x=0.3$ had the best performance in terms of LY and ER under γ -excitation. However, when considering the percentage of the fast component in the whole scintillation response, represented by $\text{LY}_{0.5\text{ }\mu\text{s}}/\text{LY}_{3.0\text{ }\mu\text{s}}$, ceramic samples with lower Ce concentrations performed better, reminding us to consider the effect of the combination of two co-doped ions. Ce,Ca:LuAG ceramics have low afterglow level under X-ray excitation and show a lower afterglow intensity for higher Ce concentration samples which is due to stronger competition ability of cerium centers for charge carrier capture.

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Effect of Ce Doping Concentration on Scintillation Performance of Ce,Ca:Lu₃Al₅O₁₂ Ceramics

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Extended Abstract

Introduction Lutetium aluminum garnet (Lu₃Al₅O₁₂, LuAG) is investigated as a classical scintillation material. LuAG can be fabricated in the form of single crystals, optical ceramics, thin films and other morphologies to meet different scintillation application demands. Cerium-doped LuAG (Ce:LuAG) ceramics can be used as a promising candidate for detection material in shashlik calorimeter for high-energy physics (HEP) experiments due to their high density, fast decay, efficient scintillation and relatively low cost. For HEP experiments with a high event rate, however, a slow scintillation component of Ce:LuAG ceramics leads to a pileup effect that needs to be diminished as much as possible. Divalent, optically inactive, Ca²⁺ co-doping is an effective strategy for suppressing slow scintillation component according to the defect engineering theory. In addition, the coprecipitated nano-powder can be also used as a raw material of ceramics, and improving the consistency of structure, composition and luminescence within the ceramics is also an important strategy to optimize the performance of Ce:LuAG scintillation ceramics. In this paper, Ce,Ca:LuAG ceramics with different Ce concentrations were prepared with the coprecipitation nano-powders. The effect of activator ion concentration on the decay behavior, light yield (LY) at different shaping times and afterglow intensity of Ce,Ca:LuAG ceramics were investigated.

Methods A series of Ce,Ca:LuAG ceramics with the chemical composition of (Ce_xCa_{0.0015}Lu_{0.9985-x%})₃Al₅O₁₂; $x=0.1, 0.2, 0.3, 0.4, 0.5$ were prepared with coprecipitated nano-powders through vacuum pre-sintering and hot isostatic pressed (HIP) post-treatment. In the process of nano-powder preparation, high purity Lu₂O₃ (99.995%), CeO₂ (99.999%), and CaCO₃ powders were dissolved in nitric acid solution, and Al(NO₃)₃·9H₂O (AR) powders were dissolved in deionized water to obtain various nitrate solutions. The metal nitrate solutions were mixed and further diluted to a specific concentration. Ammonium hydrogen carbonate (AHC, 99%) was dissolved in de-ionized water as a precipitant solution, and ammonium sulfate (99%) was added into the precipitant solution as a dispersant. The mixed metal nitrate solution was dripped into the AHC solution under mild agitation at room temperature (RT). The resulting suspension was aged for 1 h and then washed with deionized water and ethanol. The precursor was dried, sieved and calcined to obtain Ce,Ca:LuAG nano-powders with a pure garnet phase. The powders were uniaxially dry-pressed into pellets at 20 MPa and then cold-isostatically pressed at 250 MPa. The green bodies were vacuum pre-sintered at 1 825 °C for 10 h, and then HIP in argon atmosphere under 176 MPa at 1 600 °C for 3 h. The fabricated Ce,Ca:LuAG ceramics were annealed in air at 1 450 °C for 10 h to remove oxygen vacancies introduced via sintering in a reducing atmosphere. The final Ce,Ca:LuAG ceramics were polished on the both sides to the thickness of 1 mm for the coming characterization.

Results and discussion The XRD patterns of all the ceramic samples are in reasonable agreement with the standard XRD patterns of LuAG (PDF 73-1368), indicating that the main phase of the prepared ceramics is a LuAG garnet phase. The lattice parameters of Ce,Ca:LuAG ceramics with different Ce concentrations increase gradually with increasing doping concentration. The presence of Ce³⁺ can act as a sintering aid to accelerate the migration of grain boundaries during sintering of garnet ceramics and increase the

average grain size. The absorption spectra of Ce,Ca:LuAG ceramics indicate that the amplitudes of $4f \rightarrow 5d_1$ transition at 447 nm and the $4f \rightarrow 5d_2$ transition at 345 nm of Ce^{3+} increase with the starting content of Ce^{3+} that evidences its entering into the garnet lattice. An intense absorption below 350 nm is due to the charge transfer absorption band induced by Ce^{4+} in the garnet lattice. The photoluminescence decay curves of the $5d_1 \rightarrow 4f$ emission of Ce^{3+} (510 nm) under the 452 nm excitation show that the fast component intensity I_1 of all Ce,Ca:LuAG ceramics is $> 95\%$. The main decay time shows an acceleration at the Ce concentration of $> 0.3\%$ because the formation of closely spaced ($Ce^{4+}-Ca^{2+}$) pairs can increase with the increase of Ce concentration. The scintillation decay under γ -excitation slightly slows down with increasing Ce concentration, since the proportion of induced Ce^{4+} decreases with increasing total Ce concentration, and the competition in accelerating scintillation process becomes progressively weaker. The X-ray excited luminescence (XEL) intensity of the Ce,Ca:LuAG ceramics firstly increases and then decreases with the Ce concentration, reaching the maximum value as $x=0.3$. The integral scintillation efficiency of Ce,Ca:LuAG ceramics is 146%–190% of a BGO crystal. The variation of the LY and the integral scintillation efficiency obtained from XEL have a similar pattern, *i.e.*, increasing and then decreasing with the increase of Ce concentration. The optimum energy resolution (ER) is obtained as $x=0.3$. The normalized afterglow intensity after continuous X-ray irradiation monotonically decreases with the Ce concentration due to the more intense competition ability of cerium centers for charge carrier capture.

Conclusions Ce,Ca:LuAG scintillation ceramics with different Ce concentrations were prepared with coprecipitation nano-powders *via* vacuum pre-sintering and HIP post-treatment. A small amount of Al-rich secondary phase existed in the ceramics due to the loss of lutetium during coprecipitation and washing, which could be avoided by component design in the future ceramic preparation. At the Ce concentration of 0.3%, Ce,Ca:LuAG ceramic had the optimum XEL integral efficiency, LY and ER. This study demonstrated that Ce doping concentration had a certain effect on the PL decay, scintillation decay and afterglow of Ce,Ca:LuAG ceramics, providing a guidance for the subsequent selection of doping concentration in practical applications.

Keywords cerium; calcium; lutetium aluminum garnet ceramics; scintillation performance; coprecipitation method